

On the way to molecular optical switches: A solid-state NMR study of *trans*-cinnamic acids

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Isa Alexandra Queiroz da Fonseca

**On the way to molecular optical switches:
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Imagination is more important than knowledge, for knowledge is limited, whereas imagination embraces the whole world.

Albert Einstein

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Symbols and abbreviations

AFM	atomic force microscopy
B_0	static magnetic field vector
B_1	radio frequency field
CPMAS	cross polarization under magic angle spinning
CSA	chemical shift anisotropy
d	dipolar coupling constant
$\mathbf{D}$	dipolar coupling tensor
DD	heteronuclear dipolar decoupling
DQ	double quantum
GB	gigabytes
GIAO	gauge-including atomic orbitals
$\mathbf{H}$	Hamilton operator
$\hbar$	Planck's constant divided by 2π
$\mathbf{I}$	spin operator
$\mathbf{I}^I$	spin operator of spin I
$\mathbf{I}^S$	spin operator of spin S
JMAK	Johnson-Mehl-Avrami-Kolmogorov
k	rate constant
n	Avrami exponent
NMR	nuclear magnetic resonance
$\mathbf{P}$	coupling tensor
r	internuclear distance
rf	radio frequency
r_{HH}	hydrogen-hydrogen distance
SGU	signal generating unit
SQ	single quantum
T_1	longitudinal relaxation time
TB	terabytes

TMS	tetramethylsilane
UV	ultraviolet
UV-VIS	ultraviolet-visible
V	volume
Δ	anisotropy parameter
Δ_{red}	reduced anisotropy
$\delta_{11}, \delta_{22}, \delta_{33}$	principle values of the chemical shift tensor
δ_{iso}	isotropic chemical shift
γ	gyromagnetic ratio
γ_i	gyromagnetic ratio of spin i
γ_j	gyromagnetic ratio of spin j
η	asymmetry parameter
μ_0	magnetic permeability on vacuum
ν	frequency
ν_{ref}	frequency of the reference
θ_r	angle between sample rotation axis and applied field
σ	chemical shielding tensor
σ_{iso}	isotropic value of the chemical shielding tensor
ω_0	NMR frequency in angular units
ω_{iso}	isotropic frequency in angular units
ω_{rf}	frequency of the radio frequency carrier

1. Introduction

Since the antiquity until the modern days the storage of information has been vital in our society. Requirements have increased enormously within the last century and are predicted to continue increasing in size of storage memory and with that carrying an associated demand of decrease in the volume of the storage system. Research and industrial efforts of miniaturization in the digital technology have reached the microarchitecture level, as seen for example, in the new 45 nm chip from Intel [Int]. Exclusively in our homes, with computers, digital photos, movies, TV, digital music, etc., the amount of digital information grew from gigabytes (GB) to terabytes (TB) from the early 1990's until today and will be petabytes within the next 30 years. In 1995 Notebook PC's had 20 GB of memory capacity and the TB seemed impossible to obtain [Str]. The list of requirements continues to increase, to name a few examples, there are office archives, hospital records, legal information, historical archives, inventories in libraries, museums, data acquisition archives in research, along with many others, that will need even more memory space.

Among the leading technologies for data storage are the optical systems as CD's, DVD's and Blu-ray DVD's. Growing interest has come to the field of molecular optical storage systems [Kaw, Ike]. For example in molecular electronics, individual molecules (molecular switches) can replace in electronic circuits the function of semiconductor based devices [Cal]. Because molecules are a thousand times smaller than their equivalent parts in the semiconductor technology, the storage devices can become a thousand times smaller for the same capacity. Another example, in the step of miniaturization, is the 2-photon-3D technology, where organic molecules are used as optical switches for writing, reading, and rewriting of information in a three-dimensional fashion within a disk, on the terabyte scale thereby exploiting the volume instead of the area of a material for data storage [Lia, Dvo, Cal2]. The switch between two forms of a molecule is optically activated and each form can be assigned to 0 and 1 in the computer code for the storage of information [Lia, Dvo]. With dimensions of a single molecule (nm size scale) molecular electronics redefines the ultimate limit of miniaturization.

The design of materials for molecular switches is an essential step in the miniaturization of optical data storage systems. Materials which are good candidates for optical molecular storage systems are those where two stable modifications of a molecule can be obtained. Examples considered at the present are those of materials that can undergo cis-trans isomerizations, such as azobenzenes or stilbenes [Fer]; photocyclizations, such as the fulgides [Yok], diarylalkenes [Iri], or spiropyrans [Ber]; or keto-enol tautomerizations, such as salicylideneaniline [Fer1]. A review of these systems has been given by Feringa [Fer1, Fer2].

By molecular engineering it is possible to shape organic compounds into the desired structures. For example, asymmetric synthesis in solid crystals, cascade reactions, and reactions between components in co-crystals are possible [Atk1 and references therein]. By making small changes in the structure, physical properties can be adjusted and fundamental issues studied. While many systems are investigated currently, most of the basics of reaction are not fully understood.

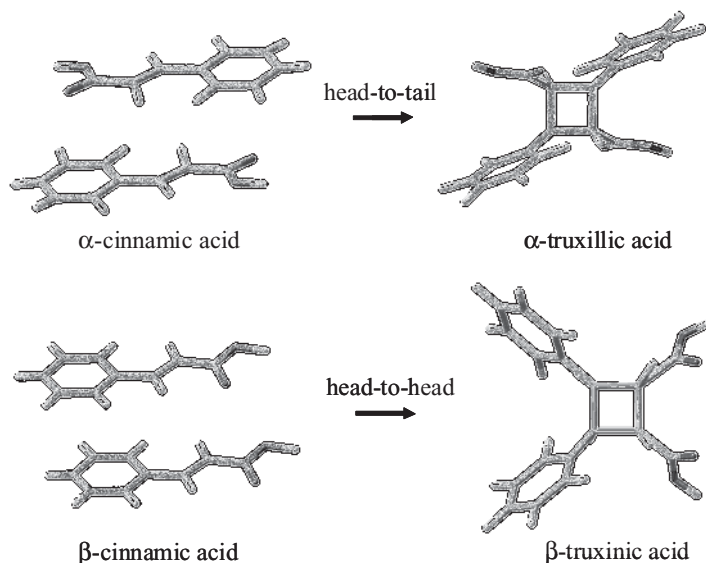
In solid-state reactions the crystal structure of the solid reactant usually determines the course of the reaction and the stereochemistry of the products. This has been a field of intense study in organic chemistry and one of the most widely investigated solid-state reactions over the past 40 years is the [2+2] photodimerization [Ram, Tan1, Coh1, Coh2, Sch1]. A classical example of a solid-state stereoselective reaction is the [2+2] photodimerization of *trans*-cinnamic acid, which is investigated in the current work by solid-state NMR methods. Cohen and co-workers [Coh1] observed that *trans*-cinnamic acid crystallizes in three different polymorphs α , β , and γ , where the first two follow the topochemical principle [Her1] and undergo a photodimerization under UV irradiation, and the third one is photo-inactive. The topochemical principle states that two molecules with parallel double bonds should have an intermolecular double bond distance of less than 4.2 Å in order for the photoreaction to occur. This photoreaction should involve a minimum amount of molecular displacement and therefore stereoselective photoproducts are obtained according to the orientation of the reacting molecules in the crystal. As a result, the photoproduct of the head-to-tail α -cinnamic acid polymorph is the centrosymmetric α -truxillic acid dimer, whereas the photoproduct of the head-to-head β -cinnamic acid polymorph is the mirror-symmetric β -truxinic acid dimer (for an illustration see Scheme 1.1).

The optically activated and stereoselective reaction of *trans*-cinnamic acid makes it a potential candidate for an optical switch material in data storage. The study presented

here focuses on the [2+2] photodimerization of *trans*-cinnamic acid as a model system for optical storage materials. However, the physical rules that determine and influence this reaction still need a thorough investigation. *Trans*-cinnamic acid, being a small and relatively simple molecule, is therefore also a good model to improve the understanding of solid-state reactions in general. Other interesting applications of cinnamic acid can be found in the literature. Cinnamic acid and its photodimer have been proposed as crack-healing agents in polymers [Chun] as well as reversible cross-linkers in side-chains of shape-memory polymers [Len].

Several techniques have been used in the past to study the [2+2] photodimerization of *trans*-cinnamic acid such as X-ray diffraction [Enk], atomic force microscopy (AFM) [Kau], and vibrational spectroscopy [All]. However, these techniques all suffer from some limitations. Atomic force microscopy is sensitive to surfaces and provides no information on the bulk structures. In vibrational spectroscopy studies, infrared and Raman techniques are used complementary and often require the use of single crystals. Finally, in X-ray diffraction studies, it has been observed that the X-ray irradiation can initiate the [2 + 2] cycloaddition [Ohb]. For the purpose of this work, solid-state nuclear magnetic resonance (NMR) is therefore the most suitable. It is an element-selective, non-invasive spectroscopic technique that yields bulk information and can be applied to powders or single crystals as well as partially or fully amorphous materials. Especially, it has been demonstrated to be an efficient method for the differentiation of polymorphs [Rip, Har2, Smi, Har4] as well as reactants and products in solid-state reactions [Sch2, Har1]. Furthermore, the rich variety of solid-state NMR techniques provides structural information ranging from orientational changes of groups within one molecule and intermolecular proximities to the accurate determination of atomic positions, especially for hydrogen positions. In this way, solid-state NMR spectroscopy provides, by itself, the possibility to extract a manifold of information regarding these solid-state reactions.

In this work, the influence of polymorphism and aromatic substitution on the photoreaction of cinnamic acid is studied. For this purpose several cinnamic acid samples have been chosen, starting with the two photoactive cinnamic acid polymorphs, α and β . Then, within the α -polymorphs *o*-methoxy and *o*-ethoxy cinnamic acids are investigated to study the effect of aromatic substitution on the *ortho* position with increasing substituent chain length and size. Finally, within the β -polymorphs *o*-, *m*- and *p*-bromo substituted cinnamic acids are studied to determine the effect of substitution in the different *ortho*, *meta* and *para* aromatic positions on the photoreaction.



Scheme 1.1 – Photodimerization reaction of α - and β -cinnamic acid to α -truxillic and β -truxinic acid, respectively.

This thesis is organized in six chapters. Chapter 2 gives a theoretical background for the current study, where the basics of solid-state NMR of relevance within the scope of this work are reviewed. The nuclear spin interactions are described and insight into the techniques used in the course of this study are provided, such as the theory of cross polarization under magic angle spinning, the 2D PASS [Dix, Ant] experiment for analysis of the chemical shift anisotropy tensors, and the 2D BABA experiment [Feil] where double-quantum single-quantum correlations allow structural analysis. A brief introduction to the theoretical chemical shift calculations performed is given, followed by the theory of the kinetics of phase changes. In chapter 3, the [2+2] photodimerization reaction of the two photoactive *trans*-cinnamic acid polymorphs, α and β , is studied and compared using ^{13}C solid-state NMR spectroscopic techniques with the aid of theoretical calculations of NMR parameters. The kinetics of the reaction is monitored in a straightforward way by means of ^{13}C cross polarization spectra under magic angle spinning (CPMAS) and a model, which relates the reaction constants to the dimensionality of the growth, is used. Moreover, ^{13}C chemical shift anisotropy (CSA) tensors have been determined using the 2D PASS sequence [Dix, Ant] to get an insight into the relative orientations of carbon atoms, which

is sensitive to molecular conformational changes during the reaction [Har2, Smi]. A detailed structural analysis of the photosystems is done using ^1H NMR spectroscopy, where correlations between atoms of adjacent molecules are studied. In chapters 4 and 5 the techniques employed for the study of unsubstituted cinnamic acid are used to study the α -cinnamic acid derivatives and the β -cinnamic acid derivatives, respectively. Finally, general conclusions about the influence of polymorphism and aromatic substitution are summarized in chapter 6, which also includes an outlook on the possibilities to use solid-state NMR for this field of research.

2. Theoretical background

In this chapter, a brief introduction to the NMR theory necessary to understand the experiments performed in this study is presented. More detailed descriptions of the NMR theory can be found in several textbooks [Blü1, Lev, Sli, Abr, Ern, Meh, Due]. The nuclear spin interactions of relevance in the solid-state NMR for spin- $\frac{1}{2}$ nuclei are reviewed, followed by the description of the experimental techniques used during this work. A brief description of the calculations, performed with the commercial program Gaussian, is given and finally, the theory of the kinetics of phase changes is introduced.

2.1 Anisotropic nuclear spin interactions

In order to describe the nuclear spin interaction a quantum mechanical approach is necessary. An important quantity that describes these interactions is the Hamilton operator ($\mathbf{H}$). The eigenvalues of the Hamilton operator determine the nuclear energy levels and the transition frequencies between them. The analysis of these transitions is essential for NMR spectroscopy. The Hamilton operator is part of the Schrödinger equation, which determines the evolution of the wave function of a nuclear spin with time [Blü1].

There are two contributions for the nuclear spin interactions, the external and the internal interactions. The external interactions are those with external magnetic fields, the Zeeman interaction ($\mathbf{H}_Z$) and the interaction with the radio frequency field ($\mathbf{H}_{rf}$). The internal interactions are those with internal fields, the chemical shift ($\mathbf{H}_\sigma$), the dipole-dipole coupling ($\mathbf{H}_D$), the quadrupole interaction ($\mathbf{H}_Q$) for spins with a spin quantum number $I > \frac{1}{2}$, and the indirect coupling ($\mathbf{H}_J$), also known as J -coupling. The last two interactions are not relevant for the study presented here and will not be further discussed. The total Hamiltonian describing the system is the sum of each individual interaction.

$$\mathbf{H} = \mathbf{H}_Z + \mathbf{H}_Q + \mathbf{H}_{rf} + \mathbf{H}_D + \mathbf{H}_\sigma + \mathbf{H}_J \quad (4)$$

500 MHz	250 kHz	100 kHz	50 kHz	1 kHz	10 Hz	($^1\text{H}/^2\text{H}$)
500 MHz	–	100 kHz	30 kHz	25 kHz	150 Hz	(^{13}C)

The frequencies under each operator indicate the typical size of the interaction for ^1H (including ^2H for $\mathbf{H}_Q$) and ^{13}C , respectively.

The Zeeman interaction

The Zeeman interaction is the largest interaction and defines the nuclear polarization

$$\mathbf{H}_Z = -\gamma \mathbf{I} \mathbf{B}_0. \quad (5)$$

Where γ is the gyromagnetic ratio and the coupling tensor between the spin vector operator $\mathbf{I}$ and the applied magnetic field $\mathbf{B}_0$ is the unity matrix (therefore omitted from the equation). $\mathbf{B}_0$ is by convention oriented along the z -direction of the laboratory frame. From the Zeeman interaction there is a splitting of energy levels, whose difference determines the NMR frequency ω_b .

$$\Delta E = \hbar \omega_b = 2\pi \hbar \nu_0, \quad (6)$$

where $\hbar$ is the Planck's constant divided by 2π .

The Zeeman interaction is the dominant interaction in a spin system at high magnetic fields. The effects of other spin interactions can be treated using perturbation theory. The other interactions are treated as a perturbation on the spin system and added to the Zeeman interaction to obtain the total Hamilton operator, simplified by the secular approximation [Ern, Abr].

The interaction with the radio frequency field

The radio frequency field B_1 is an oscillating field, much smaller than B_0 and applied along the x - (or y -) axis of the laboratory frame, which excites nuclear transitions giving rise to the NMR signal. It has the same general form as the Zeeman interaction

$$\mathbf{H}_{rf} = -\gamma \mathbf{I} \mathbf{B}_1. \quad (7)$$

It is useful to imagine this field as the sum of two rotating components in the xy -plane, at the same frequency, but in opposite directions [Lev]. The component rotating in the same sense as the Larmor frequency is called the resonant component of the radio frequency (rf) field. The component rotating in the opposite sense is non-resonant and can be shown to have almost no influence on the motion of the spins, so it is neglected. The Hamilton operator can then be rewritten as

$$\mathbf{H}_{\text{rf}} = -\frac{1}{2} \gamma \mathcal{B}_{\text{rf}} [\cos(\omega_{\text{rf}} t + \phi) I_x + \sin(\omega_{\text{rf}} t + \phi) I_y]. \quad (8)$$

where ω_{rf} is the frequency of the rf pulse and ϕ its phase.

The applied field $\mathbf{B}_1$ should be strong enough so that the $\mathbf{H}_{\text{rf}}$ dominates all other interactions apart from the Zeeman interaction. The pulses applied should be short enough to excite the whole spectrum of frequencies. However, probe arcing may take place at high pulse powers, so that care must be taken, especially in solid-state experiments, which often require high pulse powers for long periods of time.

The external interactions, namely the interaction with the rf field opens up many possibilities to manipulate the spinsystem through the delays and phases of the applied pulses. This demonstrates the great potential of (solid-state) NMR to study materials. On the other hand, the internal interactions carry structural information about these materials and those interactions of relevance in solid-state NMR and within the scope of this work, the chemical shielding and the dipole-dipole coupling, are treated below.

The chemical shift and chemical shift anisotropy

The electrons that surround the nucleus in the external magnetic field create a secondary field, which contributes to the total field felt at the nucleus. This is called the shielding interaction. This shielding of the external applied field by the surrounding electrons of a nucleus changes the resonance frequency of the nucleus and originates the chemical shift observed in the NMR spectrum. The resulting local field is given by

$$\mathbf{B} = (\mathbf{1} - \boldsymbol{\sigma}) \mathbf{B}_0 \quad (9)$$

where $\boldsymbol{\sigma}$ is the shielding tensor. The Hamilton is given by

$$\mathbf{H}_{\sigma} = -\gamma \mathbf{I} \boldsymbol{\sigma} \mathbf{B}_0 \quad (10)$$

The electron distribution around a nucleus is in general not spherically symmetric, so the size of the shielding depends on the orientation of the molecule in the applied field $\mathbf{B}_0$. To represent this dependence, the shielding tensor $\boldsymbol{\sigma}$ (as the other coupling tensors in the nuclear spin interactions) is described by a second rank tensor. This tensor, $\mathbf{P}$ can be separated into an isotropic part $\mathbf{P}^{(0)}$, an antisymmetric part $\mathbf{P}^{(1)}$, and a traceless symmetric part $\mathbf{P}^{(2)}$ [Blü1]. In the principal axes system XYZ of the symmetric part of the coupling tensor, $\mathbf{P}$ can be written as

$$\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} + \mathbf{P}^{(2)} = \sigma_{iso} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 & P_{XY} & P_{XZ} \\ -P_{XY} & 0 & P_{YZ} \\ -P_{XZ} & -P_{YZ} & 0 \end{bmatrix} + \frac{2}{3} \Delta \begin{bmatrix} -\frac{1}{2}(1+\eta) & 0 & 0 \\ 0 & -\frac{1}{2}(1-\eta) & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (11)$$

The orientation of the principal axes frame is determined by the electronic structure of the molecule that contains the corresponding nucleus and is fixed with respect to the molecule [Due]. Then, if the orientation of the molecule changes so does the orientation of the shielding tensor. The three principal values of the shielding tensor can be expressed by the isotropic value σ_{iso} , the anisotropy Δ , and the asymmetry η , as follows

$$\sigma_{iso} = \frac{1}{3}(P_{XX} + P_{YY} + P_{ZZ}) = \frac{1}{3} \text{Tr}\{\mathbf{P}\} \quad (12)$$

$$\Delta = \left[P_{ZZ} - \frac{P_{XX} + P_{YY}}{2} \right] \quad (13)$$

$$\eta = \frac{P_{YY} - P_{ZZ}}{P_{ZZ} - \sigma_{iso}} \quad (14)$$

during this work, the tensor values will be analyzed in terms of asymmetry and reduced anisotropy, which is given by

$$\Delta_{red} = P_{ZZ} - \sigma_{iso} \quad (15)$$

and $P_{ZZ} \geq P_{XX} \geq P_{YY}$.

To describe the shielding tensor in a frame other than the principal axes frame of the tensor, as the laboratory frame, a rotation is necessary. If the direction of $\mathbf{B}_0$ in the shielding tensor principal axes frame is described by the polar angles (θ, ϕ) [Due], then the contribution of the chemical shielding to the NMR frequency is

$$\omega_{cs}(\theta, \phi) = -\omega_0 \sigma_{iso} - \frac{1}{2} \omega_0 \Delta \{3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi\} \quad (16)$$

where $-\omega_0 \sigma_{iso} = \omega_{iso}$ is the isotropic chemical shift frequency relative to the bare nucleus.

In a powder sample all the molecular orientations are present, i. e. all the values of θ and ϕ are possible, so each molecular orientation will contribute to the spectrum with a different chemical shift. The spectrum obtained is called a powder spectrum and will cover a range of frequencies corresponding to the different orientations of the shielding tensor regarding the direction of the magnetic field. The powder spectrum will be broad, because all the different frequency lines overlap, and will reflect the symmetry of the tensor at the nucleus.

The total spectral frequency is the Larmor frequency plus the chemical shift contribution. However, the NMR frequency of the free nuclei cannot be measured directly and a reference substance is used. The chemical shift is then defined as δ_{iso}

$$\delta_{\text{iso}} = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \quad (17)$$

where ν is the frequency of the signal of interest and ν_{ref} the one of the reference. The principal values of the chemical shift tensor obtained are not in the principal axis frame of the tensor, and are now designated δ_{11} , δ_{22} , and δ_{33} , where $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. The isotropic chemical shift, the anisotropy, reduced anisotropy and asymmetry are defined in an analogous way to the shielding anisotropy and asymmetry in equations (10) to (13).

The dipole-dipole interaction

The dipole-dipole coupling describes the through-space interaction between nuclear spins. Each nuclear spin generates a magnetic field looping around in the surrounding space, according to the direction of the spin magnetic moment [Lev]. A second spin interacts with this magnetic field through the intervening space, without involving the electron clouds. The dipole-dipole coupling can be intermolecular or intramolecular. The Hamilton operator for the coupling between two spins is given by

$$\mathbf{H}_D = \frac{-\mu_0 \gamma_I \gamma_S}{4\pi} \mathbf{I}^I \mathbf{D} \mathbf{I}^S \quad (18)$$

Where $\mathbf{I}^I$ and $\mathbf{I}^S$ are the spin vector operators of the coupling nuclei I and S . $\mathbf{D}$ is the dipolar coupling tensor, with principal values $-d/2$, $-d/2$, $+d$ where d is given by

$$d = \hbar \left(\frac{\mu_0}{4\pi} \right) \frac{1}{r^3} \gamma_I \gamma_S \quad (19)$$

and is known as the dipolar coupling constant. r is the distance between the two spins I and S and because of the inverse cubic relation to the dipolar coupling this interaction is very sensitive to determine distances of spins. $\mathbf{D}$ describes how the field due to spin I varies with orientation of the I - S internuclear vector in the applied field, $\mathbf{B}_0$ [Due]. The dipolar coupling tensor is traceless, so it has no isotropic component. Therefore, upon molecular motion, in solution, the dipolar coupling is averaged to zero and has no effect in the NMR spectrum. In the solid-state however, the dipolar coupling is a source of broadening and its dependence on the distance can be exploited to obtain information on the structural geometry of the molecules as well as internuclear distances.

In a sample containing many spins, each pair of spins is coupled. There are two cases of dipolar coupling, the homonuclear dipolar coupling where the species I and S are the same, and the heteronuclear dipolar coupling where I and S are different. The Hamilton operator expressed in polar coordinates in the homonuclear case is given by

$$\mathbf{H}_D^{\text{homo}} = -d \frac{1}{2} (3 \cos^2 \theta - 1) [3 I_z S_z - \mathbf{I}' \cdot \mathbf{I}^S] \quad (20)$$

and in the heteronuclear case is

$$\mathbf{H}_D^{\text{hetero}} = -d (3 \cos^2 \theta - 1) I_z S_z \quad (21)$$

where θ is the angle between the internuclear vector and the applied field.

2.2 Experimental Techniques

In solid-state NMR, one frequently deals with powder samples (as in this work), which usually consist of many crystals in random orientations. The previously discussed nuclear spin interactions depend on orientation and are therefore anisotropic, which results in broad NMR spectra where different chemical sites are often unresolved. Whereas the study of the interactions may reveal important information the low resolution often hinders all the potential information from being obtained.

Solid-state NMR techniques have been developed to achieve high-resolution spectra and still obtain the desired information. Here, some of these techniques are described, which were used during the course of this work.

2.2.1 Magic angle spinning

Magic angle spinning is used to remove the effects of the angular dependent part of the anisotropic interactions, $(3 \cos^2 \theta - 1)$. In solution spectra, the effects of chemical shift anisotropy and dipolar-coupling are rarely observed because of the rapid molecular tumbling. The angle θ describing the orientation of the shielding/dipolar tensor with respect to the applied field is rapidly averaged over all possible values. Magic angle spinning achieves the same results for solids.

By spinning the sample about an axis at θ_R with the applied field, the angle θ describing the orientation of the interaction tensor fixed in a molecule within the sample,

varies with time as the molecule rotates with the sample [Due]. The average of $(3\cos^2 \theta - 1)$ is, given in this case by

$$\langle 3\cos^2 \theta - 1 \rangle = \frac{1}{2} (3\cos^2 \theta_R - 1) (3\cos^2 \beta - 1) \quad (22)$$

where β defines the angle between the principle z-axis of the shielding tensor and the sample rotation axis. The angle β is fixed for a given nucleus in a rigid solid, θ can take all possible values in a powder samples and θ_R is under the control of the experiment. If θ_R is set to 54.74° , the magic angle, then $(3\cos^2 \theta_R - 1) = 0$ and so the average $\langle 3\cos^2 \theta - 1 \rangle$ is also zero. The anisotropy of the interactions is averaged to zero provided that the spinning rate is fast enough on the NMR time scale, i. e. faster than the anisotropy of the interaction. Magic angle spinning will then remove the effects of chemical shift anisotropy, the heteronuclear dipolar-coupling and to a limited amount the homonuclear dipolar coupling (at very high spinning speeds).

2.2.2 Cross polarization under magic angle spinning

Cross polarization is used to enhance the signals of low abundance spins, such as ^{13}C , by transferring polarization from abundant nuclei, usually ^1H . The direct observation of nuclei that, as ^{13}C , possess low γ and low natural abundance has the drawback of a low polarization and a poor signal-to-noise ratio. Furthermore, relaxation to the equilibrium magnetization (with the time constant T_1) of such nuclei is usually very long because the strong homonuclear dipolar interactions that contribute to relaxation are mostly absent. Therefore, the acquisition of a spectrum can become very time consuming.

For the polarization to flow from abundant highly polarized nuclei, I , to the nuclei with lower polarization, S , contact between the two spins must take place. This can be achieved through the Hartmann-Hahn condition. The cross polarization is a double-resonance experiment (see Fig. 2.1) in a doubly rotating frame, i. e. the I spins are in a frame in which all the magnetic fields due to I -pulses appear static, and the S spins are in a frame where the fields due to S -pulses also appear static. Transverse magnetization of the spins I is generated by a 90° pulse at the frequency ω_{rf} . Then, another pulse (contact pulse) at ω_{rf} but with a phase shift of 90° is applied to lock the magnetization along the field B_{1I} due to this pulse, the spin-locking field. Simultaneously, another radio frequency field B_{1S}

is applied to the S spins, at ω_{rfS} . If now the magnitudes of B_{1I} and B_{1S} are matched by the Hartmann-Hahn condition

$$\gamma_S B_{1S} = \gamma_I B_{1I} \quad (23)$$

each spin species precesses with the same frequency $\omega_1 = -\gamma B_1$ around the axis of its radio frequency field and in its own rotating frame. The polarization can then be transferred from the initially polarized I spins to the S spins. Finally the S spins are detected while decoupling from the abundant I spins, which otherwise would be a source of broadening. Decoupling from spins of the own species is not necessary due to the low natural abundance of the S spins. The acquisition rate is determined by the relaxation time T_1 of the I nuclei, which is generally much smaller than that of the S nuclei.

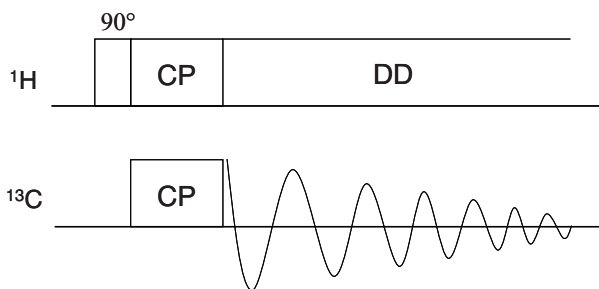


Figure 2.1 – Illustration of the cross polarization experiment. The polarization is transferred from the abundant ^1H spins to the ^{13}C spins. DD denotes heteronuclear dipolar decoupling.

The CPMAS experiment can be used selectively by changing the contact pulse time. For short contact times, only the strongly coupled nuclei are polarized, whereas for long contact times also the weakly coupled ones are polarized. This is often used for assignment purposes where a combination of CP, short CP experiments and other spectral editing techniques can be used in a complementary way [Ope, Bur, Wu1, Wu2, San].

2.2.3 Multidimensional NMR spectroscopy

Multidimensional NMR arises when the properties of a molecular system cannot be fully characterized by a conventional one-dimensional NMR experiment [Ern], as for example

overlapping of resonances in powder samples. In this case, resolution can be achieved by introducing a second frequency axis representing a different interaction of spins, which will allow disentanglement of the spectra and correlations to be visualized [Meh].

Figure 2.2 illustrates the general form of a two dimensional NMR experiment. There are three time periods (or sometimes four) in the experiment. In the preparation period, the magnetization is prepared appropriately for the properties, to be detected. Subsequently, the magnetization is allowed to evolve during the period t_1 (also called the indirect dimension) under a specific Hamilton. Following, an optional mixing period (fourth time period) can be used to prepare the magnetization for the final detection period t_2 (the direct dimension). The preparation period (and mixing period) depends on the spectrum desired. By acquiring the individual signal responses for different values of t_1 , under the influence of the active Hamilton operator, a 2D-free induction decay is obtained. By performing a Fourier transform in both dimensions t_1 and t_2 , a 2D spectrum is produced which correlates the interactions detected in the indirect dimension t_1 with the interactions detected in the direct dimension t_2 .

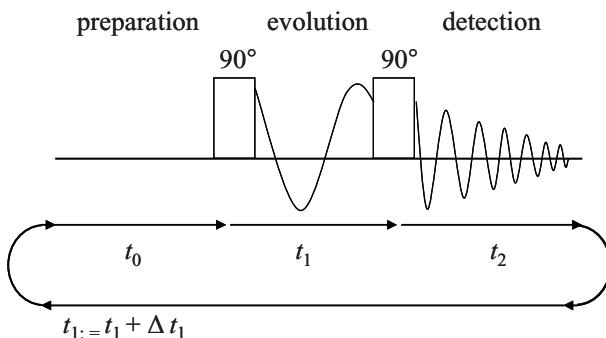


Figure 2.2 – General scheme of a two-dimensional NMR pulse sequence (adapted from [Blü2]).

2.2.4 2D PASS

Chemical shift anisotropy information can be directly obtained from a static powder spectrum. However when multiple sites are present, the broad individual powder patterns

often overlap. As discussed before magic angle spinning allows resolution by averaging out the anisotropy of the chemical shift, but therefore precludes CSA studies. Nevertheless, the chemical shift anisotropy is only completely averaged out when the magic angle spinning rate is higher than the chemical shift anisotropy. Lower spinning rates give rise to a set of spinning sidebands at multiples of the spinning speed apart from the isotropic chemical shift. Analysis of the spinning sideband pattern can give information about the chemical shift tensor and thus about molecular orientation. However, a large number of spinning sidebands is necessary for this study and in a one-dimensional experiment, enough resolution between sidebands of different chemical sites is often difficult to achieve.

A two-dimensional experiment has been proposed, where separation of sidebands by order is obtained, the 2D-PASS (Phase Adjusted Spinning Sidebands) [Dix, Ant]. The 2D-PASS pulse sequence is illustrated in Fig. 2.3. Initial excitation of transverse magnetization is obtained by a 90° pulse or via cross polarization from ^1H and followed by five 180° pulses (t_1 period). The timings between pulses, on the t_1 period, are varied in a systematic way and the signal is recorded in the t_2 period. The result is that after successive t_1 increments the phase of each order of sideband is shifted by an amount dependent only on the sideband order. Subsequent Fourier Transformation in both dimensions yields the 2D spectrum, where spinning sidebands are separated by order in the indirect dimension.

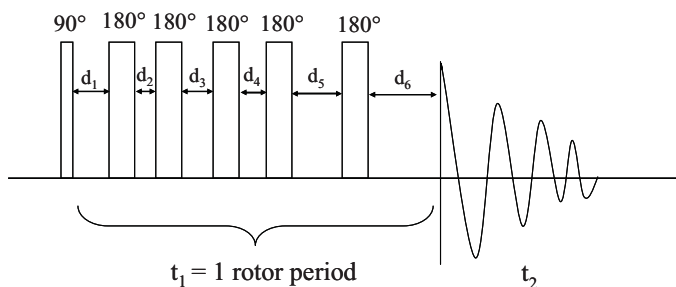


Figure 2.3 – Illustration of the 2D PASS experiment. The positions of the five 180° pulses are changed between successive t_1 increments of the two-dimensional experiment.

The 2D PASS, originally developed by Dixon [Dix], was used in this work with the modification of Levitt and coworkers [Ant] containing 5 π -pulses together with cogwheel phase cycling [Ivc]. Because of the long recycle delays, cogwheel phase cycling is ultimately important for our system since it reduces the phase cycle from 243 to just 11

phases. The results were analyzed using the software package HBA [HBA], which performs the analysis of spinning sideband intensities using the Herzfeld-Berger method [Her2]. This is a graphical method where each sideband has a contour map that reflects the anisotropy and asymmetry of the interaction. Plotting the contours for each sideband and finding their common intersection gives the principal values of the chemical shift tensor. The individual sidebands, obtained from the 2D-PASS spectrum, can be fit and their intensities used as the input for the calculation in HBA.

2.2.5 2D BABA

In coupled spins, only energy transitions that change the quantum number, m , of the spin by ± 1 are directly observable. They correspond to transverse magnetization and are called single-quantum coherences. In this case, one of the interacting spins changes its orientation in the magnetic field by absorption or stimulated emission of one rf quantum. The absorption or stimulated emission of more than one rf quantum leads to multiple-quantum coherences (zero-quantum and double-quantum) that cannot be directly observed, but indirectly by multi-dimensional NMR [Blü2].

The dipolar coupling interaction, being dependent of the distance between the coupled spins, can provide information on internuclear distances and geometry and conformation of molecules. However, for obtaining chemical shift resolution the linebroadening caused by the dipolar coupling needs to be removed, which is mostly done by magic-angle spinning (MAS). The dipolar couplings can be investigated with double-quantum (DQ) filtered experiments, as the excitation efficiency for DQ coherence depends on the strength of the dipolar coupling. Pulse sequences have been developed, which can reintroduce the dipolar coupling under MAS by combining DQ filters with recoupling sequences. In this work, the 2D-BABA pulse sequence [Fei] used to study ^1H couplings, is now introduced.

Figure 2.4 a) shows the general scheme for recording a two-dimensional multiple-quantum spectrum. Under fast MAS the excitation and reconversion sequences can be identical and are usually applied to z -magnetization [Fei]. The laboratory-frame pulse sequences for excitation/reconversion of multiple-quantum coherences are composed of 90° radiofrequency pulses as exemplified in Fig. 2.4 b). The pulses in the middle of the pulse sequence and in between different cycles are back-to-back (BABA). The timing of

the back-to-back sequence is set for full synchronization to the sample rotation for generating a pure DQ Hamilton, which leads to its maximum strength.

The two-dimensional spectrum obtained establishes dipolar connectivities. In the DQ dimension, resonances are present at the sum of the single-quantum (SQ) frequencies of the two involved nuclei. The diagonal peaks indicate couplings between spins with the same chemical shift, for example spins (AA) with a single peak at frequencies ($2\omega_A$, ω_A) in the F_1 and F_2 dimension, respectively. The intensity due to DQ coherences between two peaks with different SQ chemical shifts (spins A and B) is split, in the SQ dimension, between a pair of cross-peaks symmetrically arranged on each side of the diagonal, at frequencies ($\omega_A + \omega_B$, ω_A) and ($\omega_A + \omega_B$, ω_B). The intensity of each peak is proportional to the number of spin-pairs giving rise to the DQ coherence and to the dipolar coupling strength.

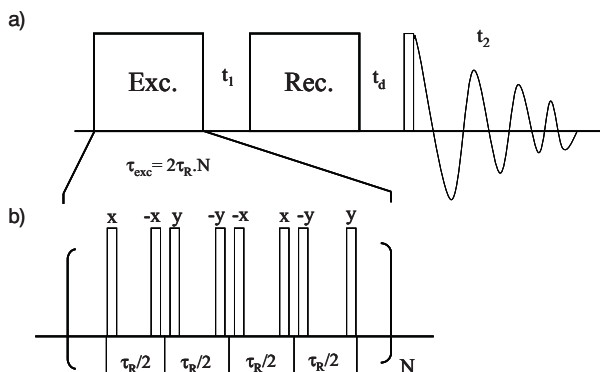


Figure 2.4 – a) General scheme of multiple quantum 2D spectroscopy. During the multiple-quantum excitation and reconversion periods the rotor-synchronized pulse sequences are applied. The excitation part is phase cycled in 90° steps to provide a double quantum filter, whereas the reconversion period is 90° phase shifted from the excitation sequence but without phase cycling. The delay after the reconversion part is included for the dephasing of spurious transverse magnetization. b) Back-to-back pulse sequence acting of multiple of two rotor periods ($2\tau_R$). Other variants of the back-to-back sequence can be found in the original publication [Fei].

In this work, a variation of the 2D BABA, with only four pulses over one rotor period, was used. This results in the observation of only the strongest couplings with a reduced broadening of the lines, providing a better resolution between signals. Semi-quantitative information about proximities can be obtained from the rotor-synchronized 2D

experiment by studying the relative intensities of double-quantum cross peaks. In a non-rotor synchronized variation of this experiment [Gra2], spinning sidebands are observed. The sideband patterns can be simulated and the dipolar coupling constant obtained, thus enabling a quantitative determination of the internuclear distance between an isolated coupled spin pair.

2.3 Chemical shift calculations

The NMR theoretical calculations were performed using the Gaussian simulation software package [Gau1]. It is not the purpose of this work to develop the methods for theoretical calculation of NMR parameters, but to use the existing methods as a tool for the elucidation of experimental data. Therefore, only a brief introduction to the procedure used in the current study will be given.

The Gaussian software package allows the calculation of molecular structures and properties based on quantum chemistry methods. Within this study two types of calculations were performed using density functional theory methods, geometry optimisation and calculation of NMR parameters. The geometry optimisations are carried out based on an energy minimization algorithm leading to the most probable molecular structure. These were performed using the B3LYP functional [Bec, Lee] and an appropriate basis set for geometry calculations, 6-311G(2df, 2p) [Mar]. The chemical shift calculations were done using the GIAO method [Dit1, Wol], with the B3LYP functional and the cc-PVDZ [Tho] basis set, which is suited for the calculation of NMR parameters. The spectra were referenced to tetramethylsilane calculated at the same level of theory. Several basis sets were tested (with increasing sizes) during this work, for both geometry optimization and NMR calculation, until a convergence of values was found that efficiently modelled the experimental data.

2.4 Kinetics of phase changes

The development of a new phase within a mother phase involves the birth of the phase and its subsequent expansion. The former process is called nucleation and the later growth [Man]. Nucleation can be homogeneous where the nuclei (seeds of the new phase) appear

randomly in a given volume, or heterogeneous where the nuclei form at preferred sites, for example, structural inhomogeneities such as surfaces and grain boundaries.

In a homogeneous reaction, the probability of any small region transforming in a given time interval is the same in all parts of the untransformed volume. The volume transforming will be proportional to the volume remaining untransformed at a given interval, and this leads to a first order rate process. If the total volume is V and the volume, which has transformed from α to β at any time is V^β , then:

$$\frac{dV^\beta}{dt} = k(V - V^\beta) \quad (24)$$

or

$$\frac{V^\beta}{V} = 1 - e^{-kt} \quad (25)$$

The constant k is called the rate constant. The rate of the transformation decreases continuously with time, as represented in Fig. 2.5 [Chr].

Considering now the nucleation and subsequent growth, the individual nuclei are formed at a time $t = \tau$, which is called the induction period. Then, when the transformed region has the same composition as the mother region (without diffusion) the growth of the transformed region takes place as a linear function of time until the transformed regions impinge upon each other and the growth rate starts to decrease with time (see Fig. 2.6). Linear growth is an interface controlled process, so that the rate of volume change is proportional to the surface area of the growing centre. In diffusion controlled processes the growth follows a parabolic growth law dependent of the diffusion rates [Man]. As this does not apply to the systems studied in this work, only linear growth rates will be discussed.

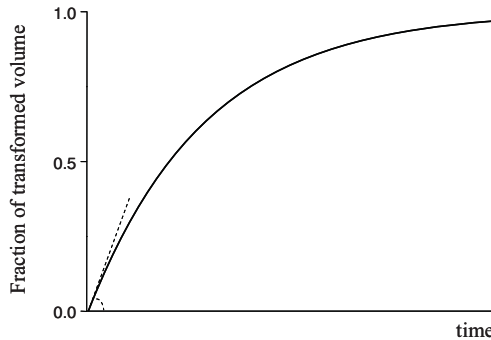


Fig. 2.5. Reaction curve for a homogeneous transformation. The slope of the curve gives the rate of the transformation, which decreases continuously with time.

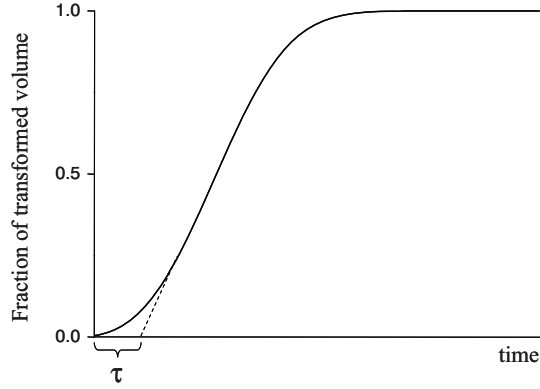


Fig. 2.6. Reaction curve for a transformation involving nucleation and growth of nuclei. τ is the induction period for formation of nuclei. The dashed line represent the case when the nuclei are initially present, so the initial sigmoidal part of the curve is not observed.

The description of the kinetics of phase transformations, where the mutual impingement of growing centres is taken into account was first given by Johnson, Mehl, Avrami and Kolmogorov, using the general equation [Joh, Avr1, Avr2, Avr3, Kol]

$$X(t) = 1 - e^{-kt^n} \quad (26)$$

where $X(t)$ is the transformed volume fraction as a function of time; k is called the rate constant of the reaction and includes nucleation, temperature, shape, and volume dependent terms; and n , also known as the Avrami exponent, is the reaction order and describes the dimensionality and mechanism of the growth of the new phase.

The model can be applied to three-dimensional linear growth (sphere), using simplifying assumptions, where the nucleation is homogenous, with constant rate from $t = 0$, and growth of particles terminates at their points of mutual contact, but continues normally elsewhere. In this case the Avrami exponent is $n = 4$. In the case of a two-dimensional linear growth, i. e. for a disk of fixed thickness, growing radially, $n = 3$. Finally, for one-dimensional linear growth in the shape of a rod $n = 2$. However, nucleation may not be homogenous and have a constant nucleation rate, but instead be heterogeneous with a specific rate throughout the reaction or there could even be an initially fixed number of nuclei present. Then, in the case of three-dimensional growth the values of n range between 3 and 4, covering all cases in which the nucleation rate is a decreasing function of time, up to the limit when it is constant. In the extreme cases, when there is an initially fixed number of nuclei $n = 3$, and when not all the nuclei are present at $t = 0$, but they are

formed at a constant rate throughout the reaction, $n = 4$. In an analogous way, for two-dimensional growth, $2 \leq n \leq 3$ and for one-dimensional growth, $1 \leq n \leq 2$. An Avrami exponent of $n = 1$ gives the kinetics curve an equivalent shape to that of a first-order homogeneous reaction, and all other possibilities give sigmoidal curves.

Several models can be used to describe kinetics in the solid-state (see [Kha] and references therein). The JMAK model, was however, the best fit for the data obtained in this work. Furthermore this model carries a phenomenological description, which has been successfully applied on an extensive number of systems [Kön, Sin, Ran, Min]. A detailed description of this model can also be found in textbooks [Chr, Man, Bol].

3. Unsubstituted *trans*-cinnamic acid polymorphs: α - and β -cinnamic acid and their photoreaction products

Cohen, Schmidt and Sonntag have investigated the photodimerization reaction of the two photoactive polymorphs of cinnamic acid, α and β , and established their reaction following the topochemical principle [Coh1, Coh2, Sch1]. Since then, several other studies have been carried out regarding the monitoring of this reaction, the polymorphism and stereoselectivity of these compounds [Enk, Abd, Atk2, Kau]. The reaction kinetics of α -cinnamic acid has been studied recently with vibration spectroscopy [Atk3] and solid-state NMR [Ber1]. The crystal structures with atom positions of α -cinnamic acid [Enk, Wie], β -cinnamic acid [Abd] and of α -truxillic acid [Abd] have been solved. For the β -reaction product this is still lacking.

Following the experimental section, section 3.2 is dedicated to the study of the α - and β -cinnamic acid polymorphs and the effects of polymorphism in the photodimerization reaction of *trans*-cinnamic acid using ^{13}C NMR spectroscopy. The kinetic behaviour of β -cinnamic acid is studied and compared to that of α -cinnamic acid. Differences are explained in terms of distances between reacting double bonds and orientational changes of side-groups upon photoreaction. These orientational changes are investigated by a comparison of chemical shift anisotropy tensors of the atoms before and after photoreaction.

In section 3.3 a more detailed structural analysis of the photosystems is done using ^1H NMR spectroscopy together with double-quantum excitation where connectivities and correlations between atoms of adjacent molecules are studied. The isotropic chemical shift of the carboxyl acid proton of reactant and product are compared and related to the oxygen-oxygen distance as deduced from the crystal structure. From double-quantum correlation spectra, connectivities and peak intensities of cross peaks are obtained and compared to results from SIMPSON [Bak1] simulations. Since the protons are all strongly

dipolar coupled, the multiple proton-proton distances taken from the crystal structures are related to the relative peak intensities of the correlation peaks.

3.1 Experimental Section

Commercial 97% *trans*-cinnamic acid (Aldrich) was used for the crystallization of both α - and β -polymorphs. The α -polymorph was recrystallized from a hot toluene solution by slow cooling [Kau]. For the preparation of the β -polymorph the procedure of Ref. [Abd] was adopted. A solution of 1.5 g of cinnamic acid in 25 mL of ether was prepared and divided among 5 test tubes. Then, in each tube 5 mL petroleum ether at $\sim 0^\circ\text{C}$ was poured very slowly along the wall assuring two separate layers, one of the ether solution (at the bottom of the tube) and another of petroleum ether. This process was carried out inside a freezer at -20°C to ensure minimal displacement of the tubes hindering mixture of the two liquids. The crystallization of β -cinnamic acid started between the two layers as diffusion took place and after one day the β -cinnamic acid needles were carefully removed from the tube. Crystals of α -cinnamic acid (square plates) also formed and deposited at the bottom of the tube. The amount of α -crystals increased significantly with time after approximately 24 hours, as reported in the literature [Abd]. The β -cinnamic acid crystallites are small, in the order of 100 μm . The α -cinnamic acid crystallites on the other hand can easily be prepared in mm size.

The preparation of the reaction products of α - and β -cinnamic acids, i. e. α -truxillic acid and β -truxinic acid, respectively, was carried out as follows. The UV irradiation was generated by an OSRAM Ultravitalux lamp under water-cooling (wavelengths above 280 nm) for consecutive irradiation periods of 10 minutes, with agitation of the powders between each consecutive period until (almost) full conversion was reached. Each respective reaction product was separated from (residual) cinnamic acid by extraction with ether, where the reaction product is the insoluble fraction [Sto].

For the photoreaction kinetics experiments an amount of approximately 50 mg of β -cinnamic acid crystals was evenly distributed in a thin layer and placed under the focus of a 150 W xenon arc lamp (Thermo Oriel). The lamp is equipped with a dichroic mirror to transmit wavelengths between 280 and 400 nm. Since the longer (infrared) wavelengths

were blocked from the sample, the sample temperature could be maintained at room temperature ($21^{\circ}\text{C} \pm 2^{\circ}\text{C}$) without additional cooling. The samples were irradiated for consecutive periods of 10 minutes of broadband light, with agitation of the powders between each consecutive period. The irradiance was measured with a Scientech power meter to be $3\text{--}4\text{ mW/cm}^2$. The irradiation of the samples was performed in the Washington University of St. Louis, USA, since the collaborators of this project have the adequate equipment.

The NMR experiments on the UV irradiated samples for the photoreaction kinetics studies were obtained using a 4 mm triple resonance magic angle spinning (MAS) probe from Varian, and data were recorded using a Tecmag Apollo spectrometer (Washington University, St. Louis). Resonance frequencies were 294.35 and 74.028 MHz for ^1H and ^{13}C , respectively. The ^1H $\pi/2$ pulse length was $2.5\text{ }\mu\text{s}$, the contact time 1 ms. A spinning speed of 4.8 kHz was chosen to avoid overlapping of signals with spinning sidebands. The spectra were acquired with a recycle delay of 1200 seconds, 5 times the longitudinal relaxation time (T_1) of the reactant, in order to quantitatively compare the relative ratios of the reactant and photoproduct signals. Furthermore, the contact time used was observed to be long enough for the relative ratios between vinyl and cyclobutane signal to be constant, providing a quantitative analysis of the CPMAS spectra. All the other NMR experiments were performed on a Bruker Avance DSX 500 spectrometer with frequencies of 500.46 and 125.84 MHz for ^1H and ^{13}C , respectively. The experiments were carried out using a 4 mm MAS probe head. For the CPMAS experiments an 8 kHz spinning speed was chosen to avoid overlap of signals with spinning sidebands. The ^1H $\pi/2$ pulse length was $2.5\text{ }\mu\text{s}$, and the contact time was set to 1 ms. Temperature dependent spectra were acquired from room temperature ($\sim 298.5\text{ K}$) up to 350 K in 10-degree intervals with a 20 minute temperature stabilization period. Each spectrum was acquired with 64 scans. The 2D PASS [Dix, Ant] experiments were performed at a spinning speed of 1.5 kHz, in order to have several spinning sidebands to improve accuracy of the analysis performed using the Herzfeld-Berger method [Her2] and the HBA software [HBA] (see 2.2.2 for more details). The recycle delays for the different samples were 400 s for α -cinnamic acid, 200 s for α -truxillic acid 160 for β -cinnamic acid, and 30 seconds for the β -truxinic acid, respectively. All spectra were referenced to tetramethylsilane (TMS) using glycine as secondary reference.

The NMR theoretical calculations were performed using the Gaussian commercial program [Gau1]. In all the simulations, the atom positions were taken from the available

X-ray crystal structures. The geometry optimizations were performed using density functional theory with the B3LYP functional [Bec, Lee] and a 6-311G(2df, 2p) basis set [Mar]. At first, geometry optimizations were done only for the protons i. e. keeping all the other atom positions fixed, since the position of light atoms such as hydrogen are not accurately determined by X-ray techniques. In some cases, after relaxing the proton positions the forces on the backbone are still large so that a relaxation of the whole structure, i. e. a further optimizing of all the atom positions, yields better results. The full optimization will yield the minimum energy conformation of a free molecule, as in the gas phase, which can be different from the solid one, since packing effects and hydrogen bonding is not accounted for. Whereas this method was successful in the case of the cinnamic acids, for α -truxillic acid this procedure could not be adopted. The full geometry optimization of the non-centrosymmetric photodimer yielded a centrosymmetric photodimer, which is the most stable conformation (polymorph) when no neighbor molecules are present. In fact, this is what is observed in the solution state spectrum of α -truxillic acid indicating a centrosymmetric photodimer. The chemical shift calculations were done using the GIAO method [Dit1, Wol] with the B3LYP functional and a cc-PVDZ basis set [Tho] (for more information see 2.3).

The ^1H experiments were performed on the Bruker Avance DSX 500 spectrometer with the exception of the 2D BABA spectra of the photoproducts α -truxillic and β -truxinic acid that were obtained on a Bruker Avance 750 spectrometer. The ^1H MAS spectra were done with a 2.5 mm MAS probe at a spinning speed of 30 kHz. To remove signal contributions from the probe background, the technique from Chen et al. [Che] was employed. The ^1H $\pi/2$ pulse length was 1.7 and 1.6 μs at the two magnetic field strengths, respectively. Referencing was done using TMS as external reference at 0 ppm. For the double-quantum experiments the simple back-to-back (BABA) sequence with the minimum of 4 pulses for excitation and reconversion was employed [Som, Fei1, Fei2] (for more details see 2.2.5). With this procedure, only the strongest coupled protons within approximately 0.4 nm distance should give rise to double quantum signals [Sch3]. To obtain 2D pure-absorptive spectra, the TPPI scheme [Dro] was employed. Based on the available crystal structures of α -cinnamic acid [Enk], β -cinnamic acid [Abd], and the stable conformation of α -truxillic acid [Abd], the proton distances with respect to a central carboxyl proton were evaluated using the Diamond crystal structure program [Dia] and converted using SIMMOL [Bak2] into the *spinsys*-part of a SIMPSON [Bak1] input file. Simulations were performed using the measurement parameters with increasing number of

coupled next-nearest hydrogens, the limitation being the calculation time. It should be mentioned that a metastable modification of α -truxillic acid exists [Enk, Abd] which can be prepared using irradiation wavelengths to which α -cinnamic acid has low absorption (tail-irradiation). In this study, however, this procedure was not followed.

3.2 ^{13}C CPMAS spectroscopy

3.2.1 Identification of polymorphs

Trans-cinnamic acid crystallizes in two different photoactive polymorphs, α and β , that undergo a photodimerization under UV irradiation. This photoreaction should involve a minimum amount of molecular displacement (as discussed in Chapter 1) and therefore stereoselective photoproducts are obtained according to the orientation of the reacting molecules in the crystal. As a result, the photoproduct of the head-to-tail α -cinnamic acid polymorph is the centrosymmetric α -truxillic acid dimer, whereas the photoproduct of the head-to-head β -cinnamic acid polymorph is the mirror-symmetric β -truxinic acid dimer, as illustrated in Scheme 1.1.

Figure 3.1 shows the comparison between the ^{13}C CPMAS spectra of the two cinnamic acid polymorphs, α and β . The assignments (Tab. 3.1) for the α -polymorph were already carried out in the literature [Ber1] and are also manifested by theoretical chemical shift calculations done in this work (Tab. 3.1). For the β -polymorph, the assignments were performed in correlation to those of the α -polymorph and are also documented by corresponding Gaussian simulations (Tab. 3.1). Comparing the spectra of the two polymorphs, it can be seen that the vinyl and aromatic signals of the β -polymorph are shifted to lower values, with the exception of the ipso carbon (non-protonated aromatic), whereas the carboxyl carbon has a lower chemical shift value in the α -polymorph. The differences observed in the spectra originate from the different solid-state packing of the polymorphs, where intramolecular distances are slightly different and from the fact that the α -cinnamic acid polymorph adopts an antiplanar conformation, whereas the β -polymorph a synplanar conformation (see Scheme 3.1). This is confirmed by the chemical shift simulations, where only one molecule was used, so there are no influences of neighbouring

molecules or solid-state packing effects, and the obtained spectra for both polymorphs differ. Furthermore simulations including 2 and 3 molecules showed negligible differences. The Gaussian simulations performed are in good agreement, within less than 2 ppm, with the experimental observations apart from the carboxyl carbon, since the carboxyl group participates in a hydrogen bond which is not taken into account in the simulation.

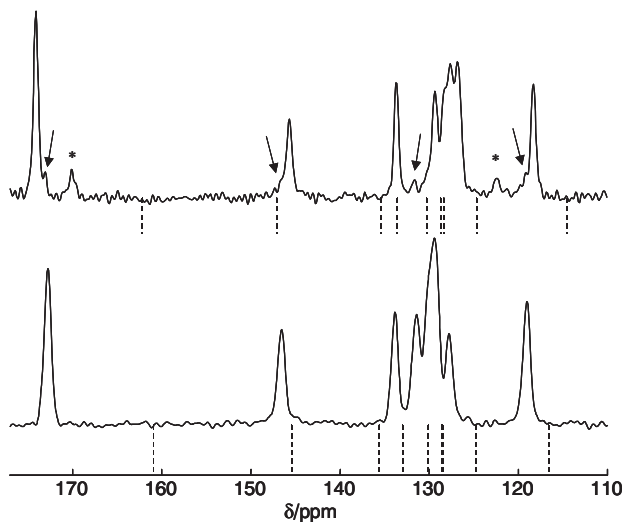
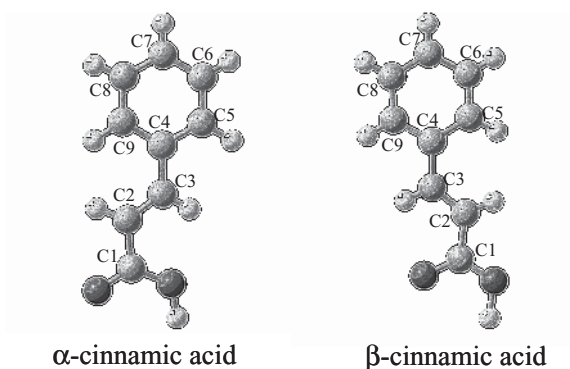


Figure 3.1 – ^{13}C CPMAS spectra of α -cinnamic acid (bottom) and β -cinnamic acid (top). Spinning sidebands are indicated by asterisks; arrows indicate residual α -cinnamic acid. The dashed vertical lines represent the results of the Gaussian simulations.



Scheme 3.1 – Numbering scheme of α - and β -cinnamic acid.

Table 3.1 – Resonance assignments for α -cinnamic and β -cinnamic acid, together with values obtained from Gaussian calculations. Numbering from Scheme 3.1.

Sample	Assignment	δ [ppm]	δ [ppm] theoretical
α -cinnamic acid	C1	173	161
	C2	147	145
	C3	119	117
	C4	134	136
	C5	131	133
	C6, C7, C8	129	128, 129, 130
	C9	127	125
β -cinnamic acid	C1	174	162
	C2	146	147
	C3	118	114
	C4	134	135
	C5	127	125
	C6, C7, C8, C9	128, 129	128, 130, 129, 134

The β -cinnamic acid spectrum contains small peaks that correspond to residual α -cinnamic acid (indicated by arrows in Fig. 3.1). This small contribution of the α -polymorph arises from the synthesis procedure of the β -cinnamic acid where it is very complicated to differentiate small α -crystal plates or cubes from β -crystal needles and the fact that the α -modification is the thermodynamically more stable polymorph (the transformation of β -cinnamic acid into the stable α -cinnamic acid is discussed below).

Conversion of β - to α -cinnamic acid polymorph

It is known that the β -polymorph of cinnamic acid is metastable and converts to the α -polymorph at about 45° C [Coh2], which led to confusions regarding the origin of different photoproducts (see Ref. [Coh2] and references therein). Interestingly, a sample of β -cinnamic acid stored at room temperature in the dark was measured 6 months after its preparation and showed full conversion into α -cinnamic acid, as confirmed by its ^{13}C CPMAS spectrum (cf. Fig. 3.1). This indicates that β -to- α conversion also proceeds at temperatures below 45° C. Temperature dependent ^{13}C CPMAS measurements were performed in order to follow this conversion experimentally. The temperature dependent spectra are shown in Fig. 3.2 where the relative intensities of the carboxyl signals of α - and β -cinnamic acid are taken to deduce the degree of conversion. The shifting of the β -polymorph signals into α -polymorph ones can be easily observed with increasing

temperature. The transformed amount is observed to be relatively stable but slowly increasing until 340 K (at room temperature there is already some amount of α present, as discussed above), from where it starts to increase rapidly. Additionally, a slight broadening of the peaks is observed (even at temperatures below 340 K), probably because of loss of crystallinity. A spectrum of the sample heated up to 350 K was then recorded at room temperature showing a spectrum fully converted to α -cinnamic acid. The observation that transformation of β - into α -cinnamic acid takes place even below 340 K may have consequences on the spectra measured under MAS, since this will induce some heating of the samples and it might be quite complicated to obtain pure β -cinnamic acid spectra. This effect could be aggravated at higher spinning speeds and long measurement times, where there is more time for conversion to take place.

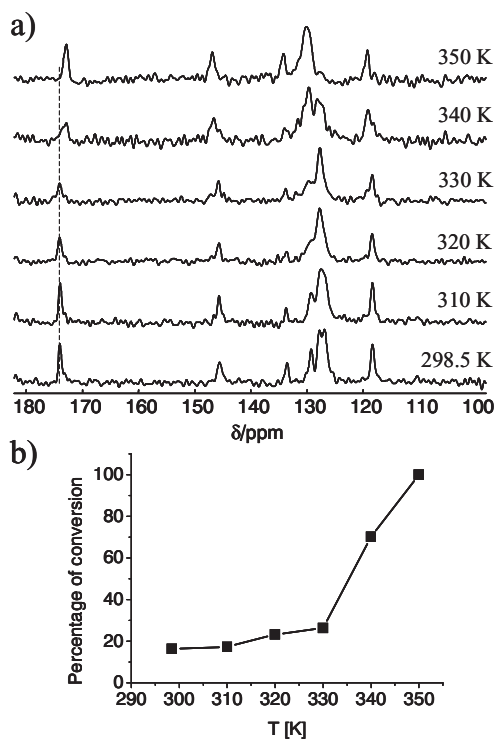
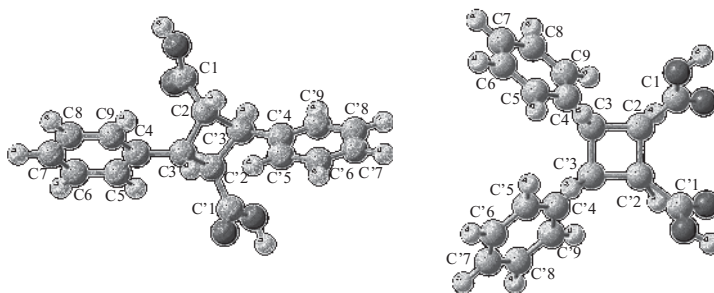


Figure 3.2. a) ^{13}C CPMAS spectra of β -cinnamic acid as a function of temperature. The dashed line indicates the shifting of the carboxyl peak as conversion from β -to- α cinnamic acid takes place. b) Percentage of conversion to α -cinnamic acid calculated from the intensity ratios of the carboxyl signals of α - and β -cinnamic acid.

3.2.2 Photoreaction products

The ^{13}C CPMAS spectra of the photoproducts of α - and β -cinnamic acid shown in Fig. 3.3, i. e., α -truxillic and β -truxinic acid, display distinct differences in the aromatic region as well as in the resolved photoproduct cyclobutane peaks. Based on Scheme 1.1, the photoproducts of the head-to-tail α -cinnamic acid and head-to-head β -cinnamic acid are expected to exhibit inversion symmetry in the case of the α -truxillic acid dimer and mirror-symmetry in the case of the β -truxinic acid dimer. In both cases, two signals for the cyclobutane ring carbons would result together with one signal each for the adjacent carboxyl and ipso-carbon. However, the truxinic and truxillic acid ^{13}C spectra exhibit three and four cyclobutane signals for β -truxinic and α -truxillic acid, respectively, as well as two carboxyl and two ipso-carbon signals each (for α -truxillic acid the second ipso-carbon signal is visible as a shoulder only), thereby indicating loss of the magnetic equivalence of these carbons probably due to loss of symmetry. The observed three cyclobutane signals for β -truxinic acid account for four signals that partially overlap, as evidenced by the 1:2:1 signal ratio, in contrast to the four truxillic acid cyclobutane signals that are of almost equal intensity.



Scheme 3.2 – Numbering scheme of α -truxillic acid (left) and β -truxinic acid (right).

The assignment of the photoproducts spectra is summarized in Tab. 3.2 (numbering from Scheme 3.2). Simulations have been performed only for the α -truxillic acid, since the crystal structure of the β -truxinic acid is not yet solved. The simulation results are in good agreement with the experimental data (3 ppm in average), yielding four cyclobutane ring signals and two carboxyl and ipso carbon signals. The chemical shifts of the carboxyl carbons are the ones which show the biggest difference with respect to the experimental

data, which is expected. The successful simulation of the non-centroymmetric structure allows the assignment of all resonances, as well as of the corresponding theoretical chemical shift anisotropy tensors, which will be discussed below.

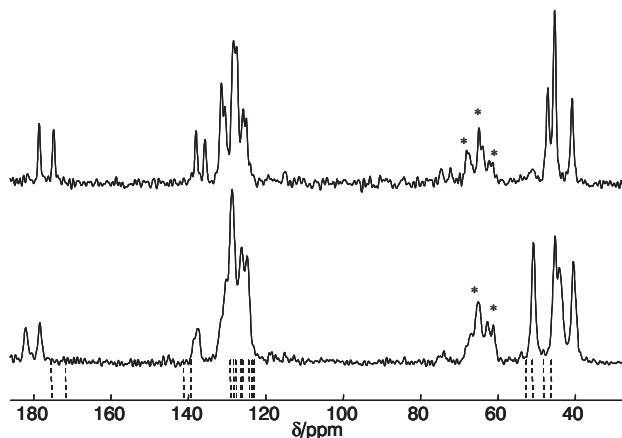


Figure 3.3 – ^{13}C CPMAS spectra of α -truxillic (bottom) and β -truxinic acid (top). The dashed vertical lines represent the results of the Gaussian calculations.

Table 3.2 – Resonance assignments for α -truxillic and β -truxinic acid together with values obtained from Gaussian calculations. Numbering from Scheme 3.2.

Sample	Assignment	δ [ppm]	δ [ppm] theoretical
α -truxillic acid	C1	182	175
	C'1	178	172
	C2	40	46
	C'2	44	52
	C'3	45	48
	C3	51	51
	C4	137	139
	C'4	138	141
	C7-9, C5-6 C'7 C'9	125, 126	123, 124, 126
	C'6 C'8	129	128
	C'5	130	129
β -truxinic acid	C1	175	
	C'1	179	
	C2	41	
	C'2 C3	45	
	C'3	47	
	C4	136	
	C'4	138	
	C5-C9 C'5-C'9	125, 128, 131	

3.2.2 Kinetics of photoreaction

During the [2+2] photoreaction of cinnamic acid, the vinyl bond is broken by UV radiation to form the cyclobutane ring between two cinnamic acid molecules (Scheme 1.1). For the photoreaction kinetics studies, samples were irradiated with UV light and their ^{13}C spectra analyzed individually. The corresponding ^{13}C CPMAS spectra as a function of irradiation time can be seen in Fig. 3.4 for β -cinnamic acid, for the α -polymorph, the kinetics investigation has already been published [Ber1]. The decrease of vinyl signal intensity and built-up of cyclobutane signal intensity can be followed as the reaction takes place. The degree of conversion was obtained from the ratio between the integrated areas of vinyl and cyclobutane carbon signals. The resulting kinetics curve is shown in Figure 3.5. As for the α -polymorph [Ber1], the Johnson–Mehl–Avrami–Kolmogorov (JMAK) [Joh, Avr1, Avr2, Avr3, Kol] theory has been used for the description of the kinetics of phase transformation (see section 2.4 for a more detailed description).

The kinetics curve of α -cinnamic acid [Ber1] showed the typical sigmoidal behaviour with an Avrami exponent of $n = 1.66$ indicative of a heterogeneous one-dimensional linear growth with a decreasing nucleation rate. The fit parameters for the β -polymorph $k = 0.007 \pm 0.001 \text{ min}^{-1}$ and $n = 0.87 \pm 0.07$ are considerably smaller than for the α -polymorph ($k = 0.019 \text{ min}^{-1}$, $n = 1.66$) [Ber1]. An Avrami exponent of $n \approx 1$ is indicative of a heterogeneous one-dimensional linear growth but with an initially fixed number of nuclei present. The nuclei already present before irradiation may have been induced by exposure to UV radiation from natural light already during the crystallization of β -cinnamic acid. The kinetics curve does not show the typical sigmoidal behaviour but a shape similar to a homogeneous first order reaction rate (see Fig. 3.5 and 2.1). A comparison of the fit function for α and β photoreaction curves can be seen in Fig. 3.6.

Questions arise as to why the photoreaction kinetics of the two polymorphs is so different. The α -conformation seems to be more favourable for photoreaction. One factor that could be of influence is the size of the crystals used for irradiation. The α -cinnamic acid crystals consisted of laths varying between 1–2 mm in their biggest dimension (high aspect ratio), whereas the crystals of β -cinnamic acid were much smaller, consisting of needles of less than 500 μm . Interestingly, vibrational studies in *o*-methoxy cinnamic acid have revealed that bigger crystals react slower than bigger ones [Atk3]. However, this is

not reflected in the case of α - and β -cinnamic acid, since the β polymorph is the one reacting slower even with much smaller crystal sizes.

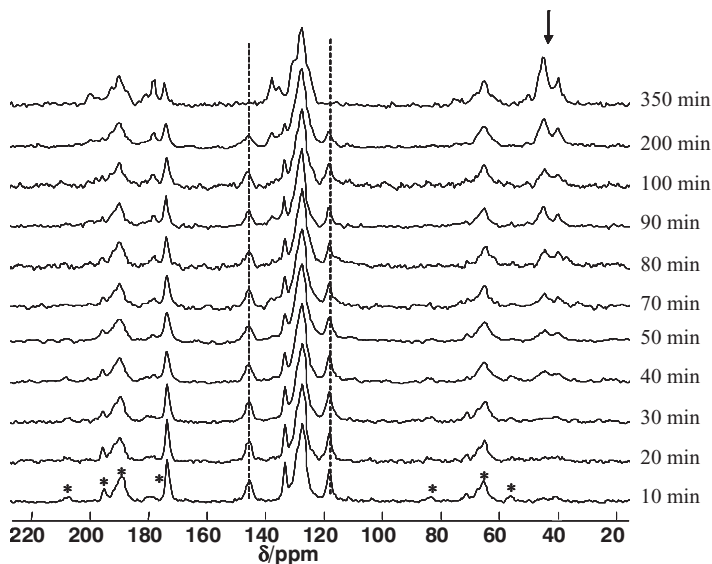


Figure 3.4 – Stack plot of the ^{13}C CPMAS spectra of the irradiated samples of β -cinnamic acid with varying total irradiation time. The degree of conversion was calculated based on the intensity of the vinyl and cyclobutane carbon signals. The dashed lines mark the vinyl positions, and the arrow indicates the cyclobutane peaks. To avoid confusion, spinning sidebands are marked with asterisks only for the first spectrum.

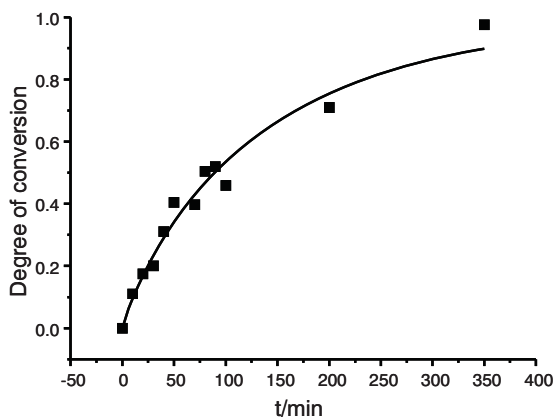


Fig 3.5 – Photodimerization kinetics of β -cinnamic acid converting into β -truxinic acid. The curve is the fit using the Johnson-Mehl-Avrami-Kolmogorov model with $k = 0.007 \pm 0.001 \text{ min}^{-1}$ and $n = 0.87 \pm 0.11$.

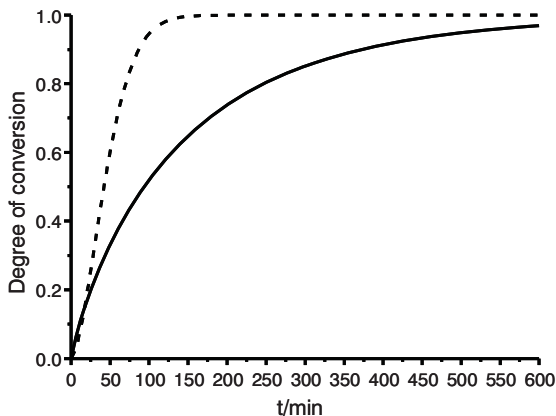


Figure 3.6 – Comparison between the fit functions of the photoreaction kinetics of β -cinnamic acid (solid curve) and α -cinnamic acid (dashed curve).

Another factor that could influence the kinetics of the photoreaction is the distance between the vinyl carbons of the two reacting cinnamic acid molecules, which is bigger in the case of β -cinnamic acid (4.015 Å [Abd]) compared to α -cinnamic acid (3.591 Å [Enk]). Therefore, larger movements of atoms adjacent to the reaction centre could be necessary for the photoreaction to take place. For example, if these reorientations were more severe in one of the cases it could lead to a slower reaction rate.

3.2.3 Chemical shift anisotropy

To get information about these orientational changes upon photoreaction the chemical shift anisotropy (CSA) tensors have been measured using 2D PASS [Dix, Ant, Ivc] and analyzed with the HBA software [HBA] (see section 2.2.2 for more details). The resulting 2D PASS spectra of α -cinnamic acid and α -truxillic acid are shown in Figs. 3.7 and 3.8, and those of β -cinnamic acid and β -truxillic acid in Figs. 3.10 and 3.11, respectively, along with the projection of the isotropic spectrum. The resulting principal values of the chemical shift tensor as well as the reduced anisotropy and asymmetry are given in Tabs. 3.3 to 3.6 for the four samples, along with the corresponding theoretical CSA values, in the appendix. For better comparison between reactants and photoproducts, the principle values of the

chemical shift tensor for the aromatic carbons are plotted in Fig. 3.9 for the α -system and Fig. 3.12 for the β -system.

Due to the reaction of the two carbon-carbon double bonds, the participating carbons change their hybridization from sp^2 to sp^3 . The CSA tensors of the vinyl and cyclobutane carbons are therefore expected to differ considerably as is also observed. Therefore, these values cannot be used to obtain information regarding reorientational changes and will not be discussed any further.

The carbon atoms next to the reaction center, i. e. the carboxyl carbon (C1) and the non-protonated (ipso) carbon (C4), both have higher isotropic chemical shift values for the photoproduct, since the neighboring nucleus changes its hybridization from sp^2 to sp^3 [Hes]. For the α polymorph this is due to a change of the δ_{11} principal tensor element, which is more pronounced for the carboxyl carbon (C1). The other tensor values remain more or less constant. For the β -polymorph, the situation is more complex. For the carboxyl carbon (C1) the biggest changes are again for the δ_{11} component, but also rather big variations are present for the δ_{22} component and happen in the opposite direction as for the δ_{11} component. For the ipso carbon (C4) the changes are even more pronounced for the δ_{22} and δ_{33} principal tensor values. Furthermore, for both carbons two signals are present for the photoproduct which we assign to the fact that the cyclobutane ring is non-planar (as already mentioned above). Nevertheless, the principal tensor elements are quite similar for both sites.

For the remaining aromatic carbon signals of the α -system C5-C9, the situation is clearer as can be seen in Fig. 3.9. The differences for the principal tensor values are minor for carbons C6-C8 and more pronounced for carbons C5 and C9. The latter are the ones closest to the reaction center (apart from the ipso carbon). This therefore gives an indication for the reorientations that take place during the photoreaction and its effects on the principal CSA tensor elements. Again, this effect is stronger for the β -polymorph (see Fig. 3.12) taking into account the fact that a differentiation of carbons C5 and C6 in the photoproduct cannot be done.

To summarize the observations regarding the changes in the principal CSA tensor elements between reactant and product, it is found that there are changes to the isotropic shifts for the carbons next to the reaction center which mainly originate from changes in the δ_{11} principal tensor value. More important however is the fact that for the aromatic carbons in *ortho* position the changes to the principal tensor elements are the largest

compared to the other aromatic carbons. This is even more pronounced for the β - than the α -polymorph.

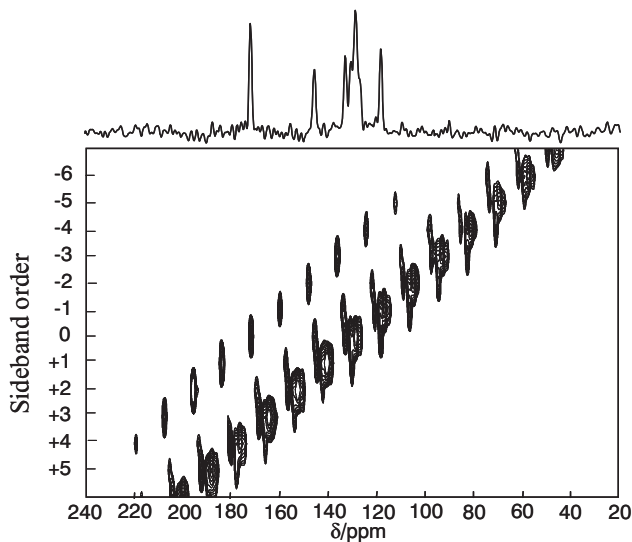


Fig. 3.7 – Bottom: 2D PASS spectrum of α -cinnamic acid, MAS rate 1.5 kHz. Top: slice representing only the isotropic signals.

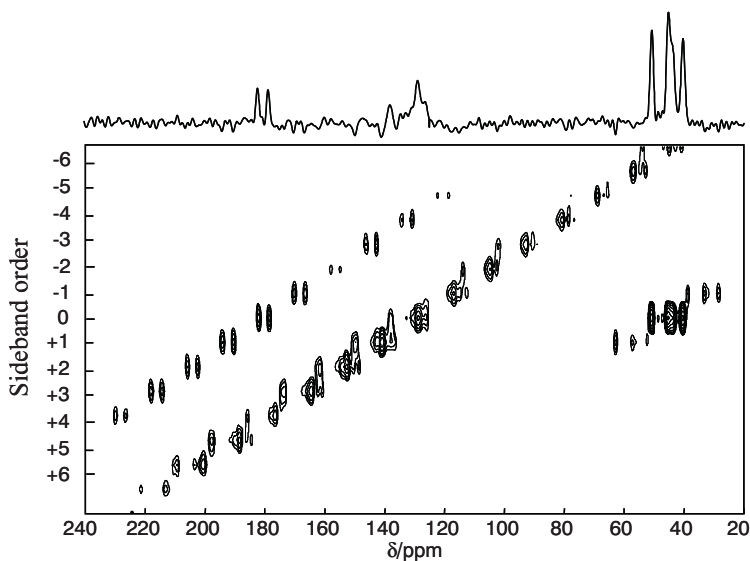


Fig. 3.8 – Bottom: 2D PASS spectrum of α -truxillic acid, MAS rate 1.5 kHz. Top: slice representing only the isotropic signals.

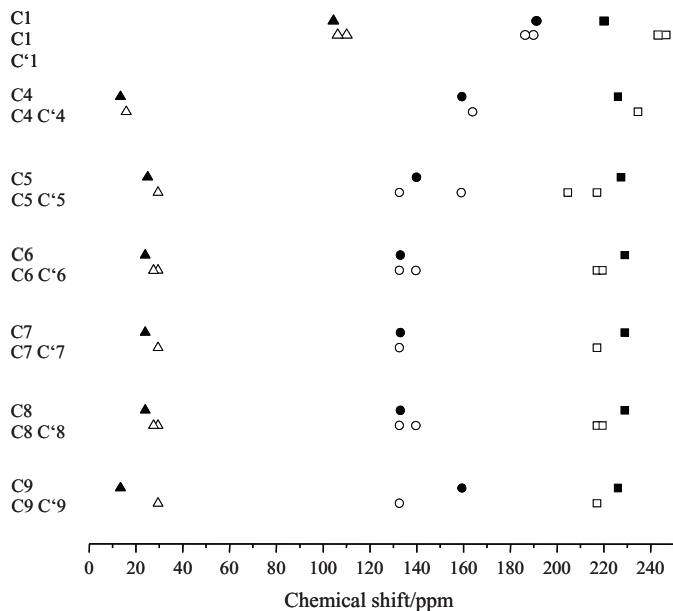


Figure 3.9 – Comparison of the principal components of the chemical shift tensor between α -cinnamic acid and α -truxillic acid. Filled symbols refer to cinnamic acid and open symbols to truxinic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

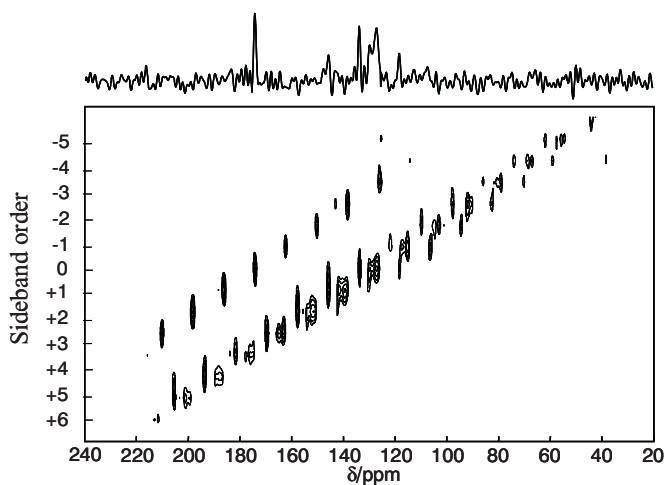


Fig. 3.10 – Bottom: 2D PASS spectrum of β -cinnamic acid, MAS rate 1.5 kHz. Top: slice representing only the isotropic signals.

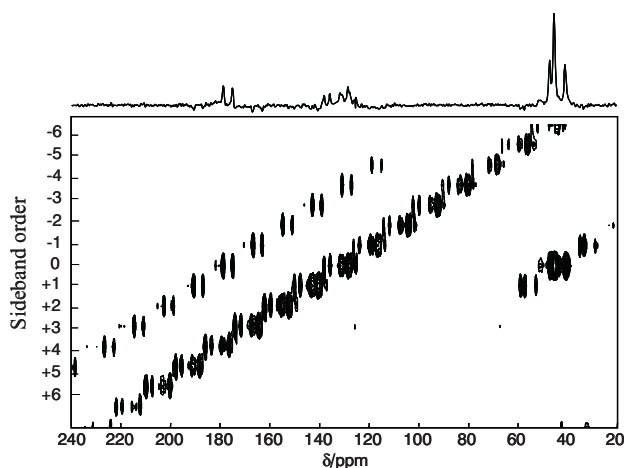


Fig. 3.11 – Bottom: 2D PASS spectrum of β -truxinic acid, MAS rate 1.5 kHz. Top: slice representing only the isotropic signals.

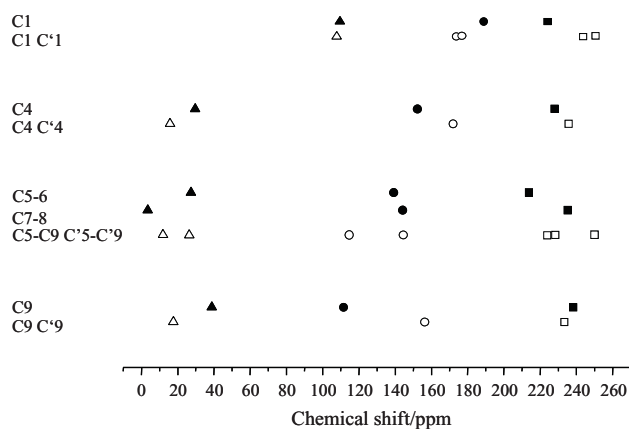


Figure 3.12 – Comparison of the principal components of the chemical shift tensor between β -cinnamic acid and β -truxillic acid. Filled symbols refer to cinnamic acid and open symbols to truxinic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

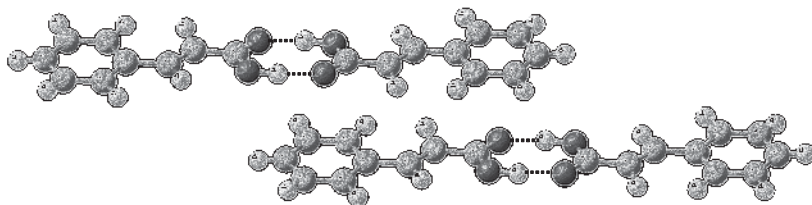
In the light of these results, the differences between the photoreaction kinetics of both systems are proposed to be explained as following: there is a higher distance between two reacting molecules of β -cinnamic acid, which requires a more pronounced reorientation of atoms upon photoreaction. This requires higher (activation) energy so that the photoreaction is slower compared to the α -polymorph.

3.3 ^1H high-speed MAS

Hydrogen bonding is an important structure directing principle and also plays a major role in biology and catalysis with regard to reaction processes. The determination of hydrogen bonds and their strength via X-ray diffraction techniques is limited due to the small mass of the hydrogen. Neutron scattering techniques are superior in this case but not widely applicable because of the need for large single-crystals and also the respective measurement facility. On the other hand, solid-state NMR has become an important tool for studying hydrogen bonding because of the high sensitivity of ^1H and the fact that it is the direct approach to look at the proton position. Solid-state NMR can also be thought of as being complementary to X-ray diffraction studies for an exact localization of proton positions within the crystal [Bro1].

The dipolar coupling between two spins is inversely dependent on the cubic distance between them, and is therefore an important parameter that can be directly obtained from NMR studies. However, limitations are the strong homonuclear ^1H - ^1H dipolar couplings from neighboring protons which also lead to a strong broadening of the spectral lines (as discussed in Chapter 2). Multiple pulse narrowing techniques have therefore been applied in recent years. Nowadays, with the available high MAS speeds, fairly well resolved ^1H spectra can be obtained and directly interpreted in terms of hydrogen bond strength. It has been realized already in the 1980's that there is a correlation of the ^1H isotropic chemical shift and the oxygen-oxygen distance along the hydrogen bond [Ber2, Sch4, Har3, Per, Bru], which enables a classification into strong and weak hydrogen bonds. The oxygen-oxygen distance in this case can be accurately determined with X-ray diffraction.

Two cinnamic acid molecules form within the crystal structure a dimer by hydrogen bonding using the two carboxyl acid functional groups, as illustrated in Scheme 3.3. This is also known from many other organic carboxyl acids. In the photodimerization process of cinnamic acid, a study of the contribution of hydrogen bonds with regard to their structure directing effects and the intermolecular orientation in the crystal structure could reveal some influence on the photodimerization kinetics. In the particular case of β -truxinic acid the crystal structure is not determined, so this type of analysis is a way to elucidate information on its structure.



Scheme 3.3 – Hydrogen bonding (dashed lines) in α -cinnamic acid.

3.3.1 ^1H chemical shift and intermolecular distances

Resolved carboxyl proton signals in the cinnamic acid system are visible separated from the aromatic (and other) proton signals starting at a spinning speed of about 15 kHz (at a magnetic field strength of 11.7 T). Figure 3.13 shows the isotropic part of the ^1H MAS spectra of α - and β -cinnamic acid and their corresponding photodimers at a spinning speed of 30 kHz. The corresponding peak positions are summarized in Tab. 3.7, the fit was done using the dmfit-Program [Mas] (that does not account for the number of protons present but only for the distinguishable signals in the spectrum).

Not all functional groups are resolved due to the strong homonuclear dipolar couplings. Nevertheless the carboxylic acid proton is well enough separated from the rest of the signals to enable a clear assignment and to resolve main connectivities (see below). For the cinnamic acids, aromatic and vinyl proton signals are strongly overlapping because they have similar isotropic chemical shifts, which is known for many organic compounds. In the case of the photodimers, the protons at the cyclobutane ring are visible as shoulders next to the aromatic signals. Because of the photodimerization the sp^2 -hybridized vinyl carbons transform into sp^3 -hybridized carbons and with that there is a shift of the proton signals to smaller ppm values. However, the shift is not large enough to yield separate signals.

For β -truxinic acid, small signal intensities of the carboxyl proton of α -truxillic acid are visible as a shoulder. This arises from the synthesis procedure of the β -cinnamic acid and the fact that the α modification is the thermodynamically more stable polymorph, as discussed above. Therefore, in the photoirradiation process the α -cinnamic acid crystals form α -truxillic acid as a side product. Based on the ^1H spectrum, we estimate the amount of the α -polymorph to be about 16%. In the 2D BABA spectra shown below the signals of

the carboxyl protons are clearly separated from those of the β main compound so that this is of no further consequence for the present discussion. In the β -cinnamic acid spectrum small amounts of α -cinnamic acid cannot be distinguished due to the similar chemical shifts. Nevertheless, the β -cinnamic acid was produced very carefully and the ^1H spectrum measured with a freshly prepared sample to minimize the amount of α -cinnamic acid that originates from the β -to- α conversion with time (although this process is slow at room temperature, as seen previously).

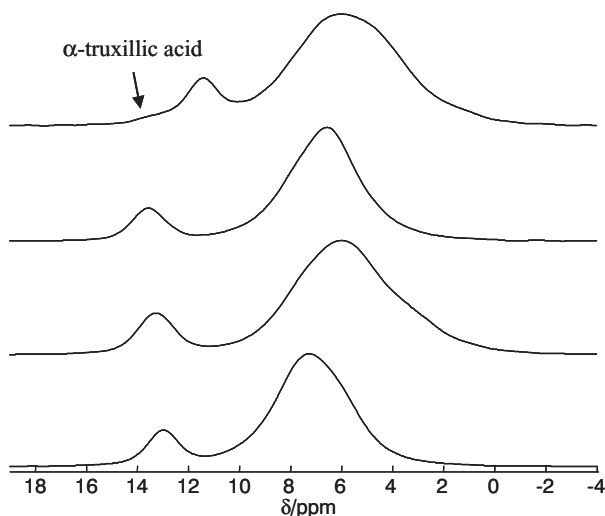


Figure 3.13 – ^1H MAS spectra at a spinning speed of 30 kHz showing the isotropic region only. Sample declaration from bottom to top: α -cinnamic acid, α -truxillic acid, β -cinnamic acid, and β -truxinic acid. The dashed line indicates the shift of the carboxyl signal before and after photoirradiation for the α -polymorph.

Table 3.7 – ^1H chemical shifts in the cinnamic acid photosystem.

Sample	^1H Chemical shift [ppm]		
	COOH	H^1_{Arom}	$\text{H}^2_{\text{Cyclo}}$
α -cinnamic acid	12.94	7.16	-
α -truxillic acid	13.25	6.19	3.22
β -cinnamic acid	13.52	6.70	-
β -truxinic acid	11.4	6.92	4.89

1: including vinyl protons for cinnamic acids

2: only visible as a shoulder

Interestingly, along with the photodimerization, there is also shift of the carboxyl proton signal. This can be interpreted in terms of a stronger hydrogen bond if the shift is to higher ppm values as for α -truxillic acid or weaker hydrogen bond as in the case of β -truxinic acid. The basis for this conclusions was derived by a theoretical calculation of Ditchfield in 1976 [Dit2] on the magnetic shielding of the water molecule and of water dimers. Later this was adapted for carboxyl acid dimers by Berglund and Vaughan [Ber2] for carboxyl acid dimers and verified experimentally using multiple-pulse narrowing techniques to resolve different proton sites. There is a clear correlation of the isotropic chemical shift and the oxygen-oxygen distance taken from the crystal structure data, which has been used in several studies [Sch4, Har3, Per, Bru]. To demonstrate this relationship selected literature data including the results obtained within this thesis are summarized in Fig. 3.14.

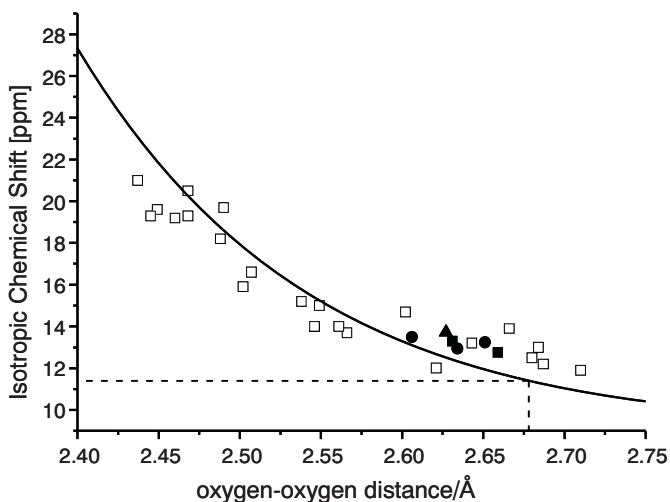


Figure 3.14 – Plot of ^1H isotropic chemical shift versus oxygen-oxygen distance along the hydrogen bond as taken from published crystal structure data for carboxyl acid dimers. The solid line corresponds to the theoretical calculation from Ref. [Dit2] corrected according to Ref. [Ber2]. Open squares indicate values taken from literature data [Ber2], filled circles indicate the data on the α -, β -cinnamic and α -truxillic acids. For β -truxinic acid, the estimated oxygen-oxygen distance is indicated by the dashed line. The filled squares indicate data from the α -cinnamic acid derivatives and the filled triangle from β -*o*-bromocinnamic acid (discussed in the next chapters).

The experimental data show a fairly good correlation with the theoretical curve. For the cinnamic acid system, the experimental results from this study also fit reasonably well. In the crystal structure data, α -truxillic acid has a slightly longer oxygen-oxygen distance compared to α -cinnamic acid in opposition to our prediction from the ^1H MAS spectrum. Nevertheless, the values of both samples are still close to the theoretical curve. Since for the β -truxinic acid no crystal structure data exists, the predicted oxygen-oxygen distance based on the isotropic ^1H chemical shift is 267.8 pm. The difference in the ^1H isotropic chemical shift of the β system are larger than in the α system, so a slightly bigger distance would be expected for β -truxinic acid. However, the theoretical curve starts to be rather flat at these values, and furthermore, all the cinnamic acid data points are above the theoretical curve. Taking this into account, the distances obtained are most probably underestimated, with an uncertainty that could go up to 5 pm.

Since the theoretical calculation concerns magnetic shielding in water molecules, it did not take into account effects of aromatic ring currents (see e. g. [Gom]), i. e., the fact that relatively strong isotropic chemical shift differences can occur when protons are in definite positions with respect to the aromatic ring. This can certainly play a role in the cinnamic acid system as can be visualized from Scheme 1.1. The aromatic rings and the carboxyl acid overlap more strongly in the α -polymorph where the experimental data fit reasonably well to the theoretical curve. However, the scheme only displays the relative orientations of two phenyl rings within one molecule for the photodimer or between the two reacting molecules and not between different molecules in the crystal packing. Especially, in the β system, $\pi - \pi$ stacking effects could be present in the crystal lattice that can have large effects on chemical shifts [Bro2, Bro3].

3.3.2 ^1H - ^1H correlation experiments

The 2D BABA correlation spectra of the four compounds are shown in Figs. 3.15 to 3.18. In this presentation, correlation peaks in the F1-dimension (the double quantum dimension) of two peaks with frequencies ω_a and ω_b in the F2-dimension will show up at a value of $\omega_a + \omega_b$ (as discussed in section 2.2.5). Some directly observable correlations are indicated by the dashed lines. It should be kept in mind that also signals along the diagonal only occur with this double-quantum technique if two protons with identical chemical shift are in

close connection to each other. This is clearly fulfilled in the case of hydrogen bonded carboxyl acid dimer protons.

Although not all expected cross peaks are fully resolved, the respective ones for the carboxyl proton are clearly visible. For the β -truxinic acid, the separation of carboxyl proton signals originating from the α -truxillic acid byproduct is evident. Other than for the carboxyl proton correlations, correlation peaks between aromatic and vinyl respective cyclobutane proton signals are not resolved because of strong signal overlap within the small frequency range. The resolution for the photoproducts in terms of line widths is improved because they were obtained at the higher magnetic field. However, the effect is not very pronounced taking into account the 50% higher magnetic field strength. Due to the isotropic shift difference of cyclobutane and aromatic proton signals there is also a larger spread of frequencies that contribute to the better resolution. This can be seen especially for the β -truxinic acid where a correlation peak from the carboxyl acid proton to a cyclobutane proton is observed. The 2D spectra give a qualitative picture of correlation peaks. To get more quantitative information a more detailed look will be taken at the relative intensities of the carboxyl acid correlation peaks.

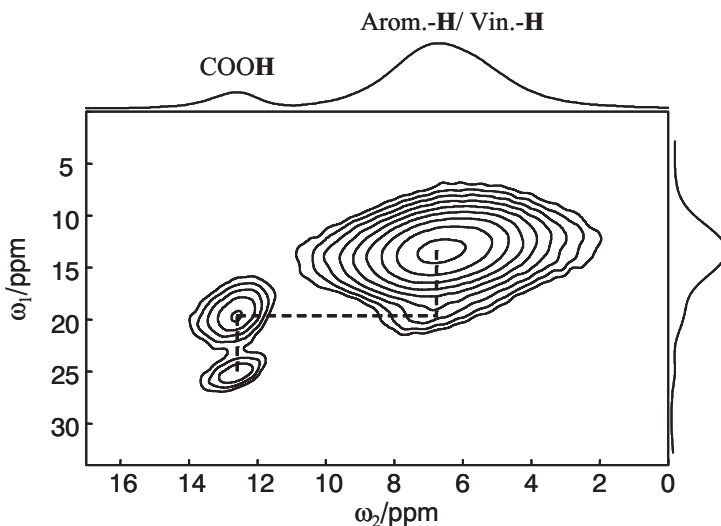


Fig. 3.15 – 2D BABA spectra of α -cinnamic acid at 30 kHz MAS. General correlation peaks are indicated by dashed lines.

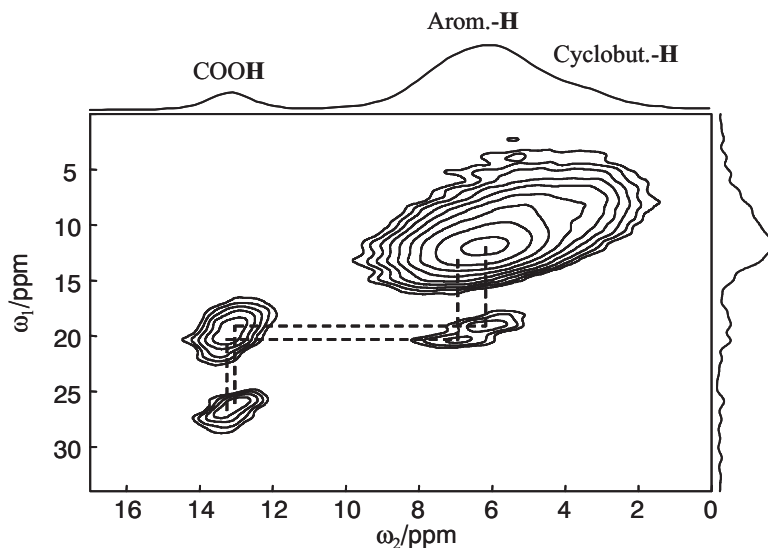


Fig. 3.16 – 2D BABA spectra of α -truxillic acid at 30 kHz MAS. General correlation peaks are indicated by dashed lines.

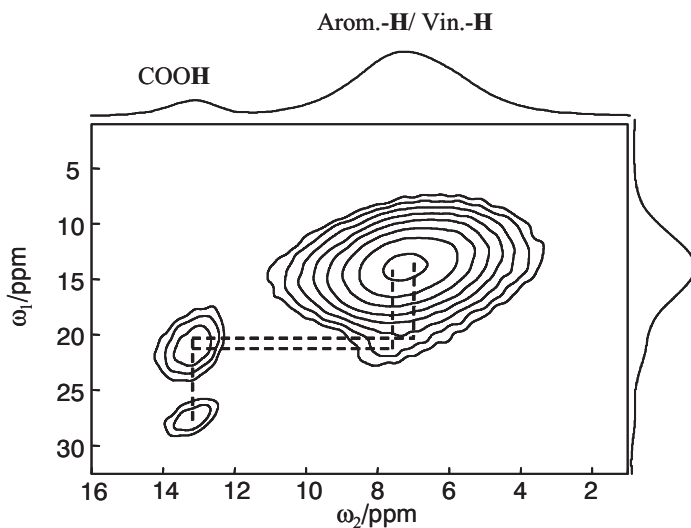


Fig. 3.17 – 2D BABA spectra of β -cinnamic acid at 30 kHz MAS. General correlation peaks are indicated by dashed lines.

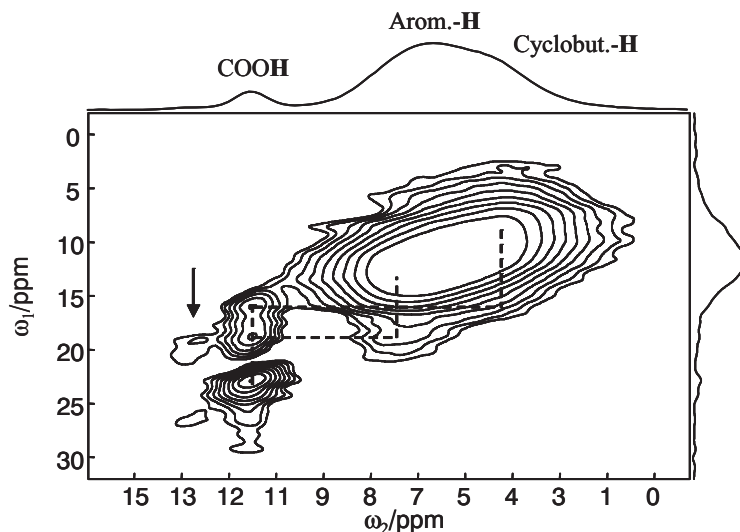


Fig. 3.18 – 2D BABA spectra of β -truxinic acid at 30 kHz MAS. General correlation peaks are indicated by dashed lines. The arrow points at the carboxyl proton correlation peaks of the α -truxillic acid byproduct.

Quantitative analysis of multiple quantum data can be complicated. Possibilities for the quantitative deduction of the homonuclear dipolar coupling have been done by using non rotor-synchronized t_1 -increments and fitting the double quantum sideband intensities (see e. g. Ref. [Bro1] and references therein). Alternatively, varying the number of rotor periods for excitation and reconversion has been used and the resulting buildup curves fitted [Ber3, Gra1]. For the latter, a sample for referencing with a known proton-proton dipolar coupling is needed. However, because of the long relaxation times of the different compounds studied here, these two possibilities are very time consuming and could not be realized in this case. As an alternative, a semi-quantitative analysis that analyzes the relative peak intensities of the different cross peaks is presented.

The different F1-projections shown in Fig. 3.19 for the four samples only represent those signals along the carboxyl protons in the F2-dimension. For the β -truxinic acid, only the projections corresponding to the β carboxyl acid signal is shown. For the α samples the aromatic-carboxyl cross peak has a higher intensity than the carboxyl-carboxyl cross peak. This is also the case for the β -cinnamic acid whereas for the β -truxinic acid the carboxyl-carboxyl cross peak is clearly the dominating peak. From Scheme 1.1 and the overall orientation of carboxyl and aromatic groups in the crystal structures, it is expected that the

α -polymorphs have a relatively strong intermolecular coupling between carboxyl acid protons of one molecule to aromatic protons of an adjacent molecule due to the head-to-tail arrangement. For the β -polymorphs the head-to-head arrangement in the crystal structure would result in stronger intermolecular couplings between carboxyl-carboxyl and aromatic-aromatic groups. This is evident for the β photodimer but surprisingly not for the reactant. Fitting the experimental F1-projections yields for α -cinnamic acid 1:2.29, for α -truxillic acid 1:1.95, for β -cinnamic acid 1:2.09, and for β -truxinic acid 1:0.98 for the ratio of carboxyl-to-other protons, respectively. In fact, the 2D BABA of β -cinnamic acid is comparable to the one of α -cinnamic, as are the relative intensities of F1-projections (Fig. 3.19). It as been discussed above that the metastable β -polymorph converts into the α -polymorph at a fast rate at elevated temperatures and that at high-spinning speeds and long measurement times this could be of consequence. These observations and the relative ratios of the F1-projections values will be used for the analysis discussed below.

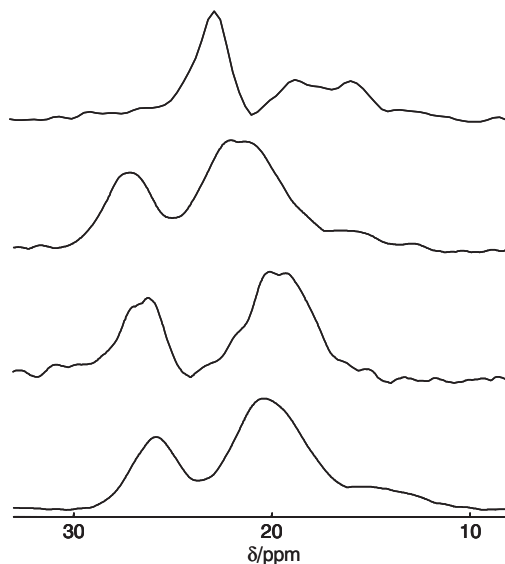


Figure 3.19 – F1-projections of the 2D BABA spectra corresponding to the carboxyl proton signal in F2. Notification of samples from bottom to top: α -cinnamic acid; α -truxillic acid; β -cinnamic acid; β -truxinic acid.

In principle, simulations using the SIMPSON program [Bak1] can match the relative signal intensities correctly. However, the large number of protons at short

distances usually prevents an accurate simulation due to the strongly increasing calculation times. To demonstrate the effects of taking into account increasing number of next-nearest coupled spins, the *spinsys*-section of the SIMPSON input file (presented in the A.2.1 of the Appendix) containing the relative orientations of the closest spins was obtained using SIMMOL [Bak2] together with the DIAMOND software program [Dia] according to the published crystal structure data for α -cinnamic and truxillic acid as well as for β -cinnamic acid. The limitation of the simulation lies furthermore in the available computation time which increases dramatically by adding another spin since every additional spin doubles the spin density matrix dimension. To demonstrate the changes in relative intensities of carboxyl and aromatic connection peaks, Fig. 3.20 shows exemplified simulated F1-projections with increasing number of coupled protons for up to five protons coupled to the central carboxyl proton. The most strongly coupled spin is usually the other carboxyl proton along the hydrogen bonded dimer. Therefore, the carboxyl-carboxyl cross peak intensity is normalized in all simulations. Of importance is the fact that for the α -cinnamic acid the shortest distance to the carboxyl proton is from a proton of the aromatic ring. Therefore, the two-spin simulation was scaled with respect to the three-spin simulation for the aromatic peak intensity. Overall, for the maximum number of spins simulated, proton-proton distances of up to less than 350 pm were taken into account which only includes one next-nearest carboxyl proton.

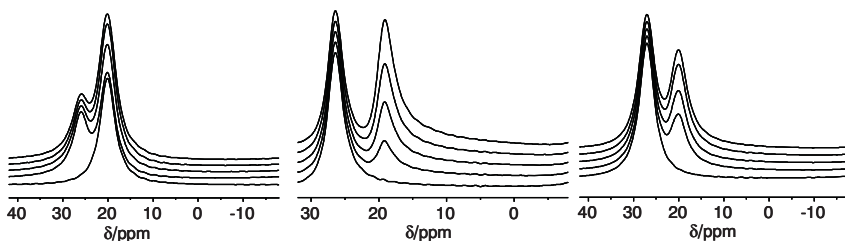


Figure 3.20 – SIMPSON simulations of the F1-projections of the 2D BABA spectra for the carboxyl proton signal using different numbers of coupled spins. From bottom to top in every simulation one more next-nearest proton is taken into account. Intensities are scaled for the carboxyl-carboxyl cross peak. Left: α -cinnamic acid, middle: α -truxillic acid, right: β -cinnamic acid.

It can be seen that with increasing number of spins, the intensity of the carboxyl-aromatic cross peak continuously increases relative to the carboxyl-carboxyl cross peak. For α -cinnamic acid, the intensity of the aromatic cross peak is much more intense than for

the carboxyl one, and for α -truxillic acid they are almost at equal intensities for the largest spin system. For β -cinnamic acid, the peak intensity for the carboxyl peak is always more intense than the aromatic peak as expected from the considerations mentioned above regarding the head-to-head arrangement. However, the in this way obtained relative intensities in comparison of the three samples do not reflect the experimental data. Therefore, a different approach follows the definition of moments [Van], where the second moment is directly related to the sum of all homonuclear dipolar couplings. From the respective distances in the crystal structures, the individual proton-proton homonuclear dipolar couplings are obtained and summed up for selected distances up to 5 nm with respect to a central carboxyl proton. This was done separately for couplings from the carboxyl proton to other carboxyl protons and to all other protons. For the latter, the differentiation between different proton species was not done, since they are not separated in the F1-projections. From this, the theoretical relative ratios are calculated which are summarized in Fig. 3.21 for the three samples with known crystal structure and selected distances.

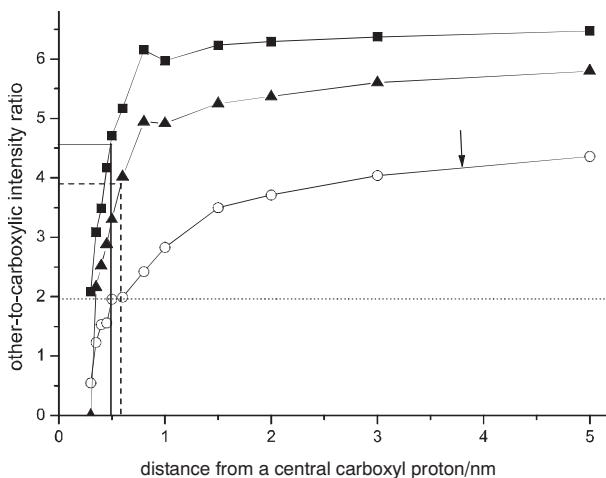


Figure 3.21 – Intensity ratio of all other protons relative to the carboxyl protons coupled to a central carboxyl proton as a function of distance as obtained from the crystal structure. Solid squares: α -cinnamic acid; solid triangles: α -truxillic acid; open circles: β -cinnamic acid. The solid and dashed lines represent the experimental intensity ratios of α -cinnamic and α -truxillic acid, respectively, multiplied by a factor of two. The arrow corresponds to the measured value for β -cinnamic acid and the dotted line represents the experimental intensity ratio for β -truxillic acid.

The general trend is an increase of the other-to-carboxyl intensity ratio which levels off at above 4 nm. Due to the higher number of aromatic, vinyl, and cyclobutane protons with regard to only one carboxyl proton per molecule, this increase is certainly expected. At larger distances the relative preference of carboxyl protons to each other due to the hydrogen bonding and with that resulting higher dipolar couplings does not play an important role any more. For small distances, there are some sudden jumps within the curve since only few protons are involved in the calculation and it makes a large difference if one or two carboxyl protons are taken into account.

Although this procedure is only semi-quantitative, it can be observed that for α -cinnamic and truxillic acid the experimentally observed intensity ratios fit to this calculation reasonably well, i. e. protons up to about 0.5 to 0.6 nm contribute to the cross peak intensity. At this distance, SIMPSON simulations would have to take more than 20 proton spins into consideration. Due to the fact that the intensity of the aromatic-carboxyl cross peak in the 2D BABA spectra is distributed to two signals from which only one is selected in the F1-projection in opposition to the carboxyl-carboxyl cross peak, a factor of two is introduced for the primer peak to adapt to the calculated ratios from the crystal structures.

For the β -cinnamic acid, a correlation with the experimentally obtained intensity ratio fits to the calculated curve at distances of about 4 nm. This, however, cannot be correct and is contradictory to the results on the α -polymorphs. In fact, the intensity ratio fits exactly the curve of α -cinnamic acid and in the same range of values. This indicates that transformation from β - to α -cinnamic acid occurs at this high-spinning speeds (which can induce heating [Bru2]) and over the long period of the measurement (over 24 hours). In the case of the ^1H spectrum the measurement time is so short (2 minutes) that the transformation did not take place at an observable amount. The β -truxinic acid is expected to have a related structure to β -cinnamic acid because of the topochemical principle, which assumes that only small changes occur to the structure and the orientation of atoms. In fact, a much smaller intensity ratio is observed experimentally, as expected from the head-to-head arrangement, and this value crosses the calculated curve for β -cinnamic acid in the same range of distances of the α -polymorphs.

3.4 Conclusions

The distinction between the two photoactive *trans*-cinnamic acid polymorphs, as well as their photoproducts was successfully carried out using ^{13}C solid-state NMR spectra and theoretical calculations. The transformation of β -cinnamic acid into α -cinnamic acid was observed to occur even at room temperature on the contrary to what was initially proposed in the literature. However, temperature dependent measurements showed that high temperature increases the speed of this transformation. The photoreaction of β -cinnamic acid was explained based on the JMAK model, where the growth of initially present nuclei proceeded one-dimensionally through the crystal. The photoreaction of β -cinnamic acid was observed to take place at a slower rate than that of α -cinnamic acid. One of the possibilities for slower reaction, besides intermolecular distances, and which could be tested by NMR are reorientational changes to functional groups measured via comparative CSA tensor analysis of the two polymorphs before and after photoreaction. The photodimerization of β -cinnamic acid requires a more severe reorientation of groups (mainly identified by the aromatic carbon atoms C5 and C9) near the reaction center, probably due to a higher distance between the reacting molecules, which slows down the reaction rate. The crystal size, which is reported in the literature to have an influence in the photodimerization rate (slower reaction rate for bigger crystals [Atk3]) did not seem to have a strong effect, if any, in this case.

High magic angle spinning speeds enabled partial resolution in ^1H spectra of the strongly coupled organic acid dimer systems. The comparison of the ^1H isotropic chemical shift of the carboxyl protons (which form a hydrogen bond between two dimers) between the cinnamic acids and their photoproducts, allowed a relative evaluation of the hydrogen bond strengths. Furthermore, the ^1H isotropic chemical shift was correlated to the oxygen-oxygen distance available from crystal structure data. This allowed an estimation of the oxygen-oxygen distances between two molecules, namely in the case of β -truxinic acid where the crystal structure is not known. Additionally, the ^1H - ^1H dipolar coupling could be efficiently employed to determine connectivities in these acid dimers using double-quantum excitation techniques such as back-to-back, which represent intra- and intermolecular proton-proton couplings. SIMPSON simulations are in principle possible for theoretically mapping these connectivity experiments. However, in these strongly

coupled systems, the needed computation time is too high since the spin system to be taken into account is too large to efficiently model the experiments. Nevertheless, it is already indicated that the difference between a head-to-tail and a head-to-head arrangement should be, as expected, reflected in the relative intensities of the F1-projections of the 2D BABA spectrum. This however, was not observed for β -cinnamic acid. A different approach related to the sum of dipolar couplings was presented and found to be suited to reflect the relative peak intensities in the double quantum dimension for α -cinnamic and truxillic acid, but again not for β -cinnamic acid. For the α -system it was found that proton-proton distances of up to 0.5 to 0.6 nm contribute to the double quantum intensities. Overall, the values obtained for β -cinnamic indicate transformation to α -cinnamic acid at high spinning speeds, which is a consequence of temperature increase with spinning speed.

4. α -*trans* cinnamic acid derivatives: *o*-methoxy and *o*-ethoxy cinnamic acid and their photoreaction products

In the previous chapter the influence of polymorphism on the photoreaction of *trans*-cinnamic acid was studied. Now the photoreaction studies are extended to cinnamic acid derivatives in order to elucidate general rules that influence the topochemical reactions in the photodimerization of cinnamic acid. For this, several derivatives are studied in this chapter dealing with different α and in the next chapter with different β polymorphs.

This chapter is dedicated to study the influence of aromatic substitution on the photoreaction of α -cinnamic acid derivatives, when the size of the substituent is varied at a particular position (in this case the *ortho* position). For this purpose, two derivatives with known crystal structures were chosen, α -*o*-methoxy cinnamic acid [Atk1] and α -*o*-ethoxy cinnamic acid [Fer]. In section 4.2, the kinetic behaviour of both samples is studied and compared with the one of unsubstituted α -cinnamic acid. An interpretation of the differences observed is carried out based on crystal sizes, UV absorption, and orientational changes of the groups near the reaction center. As in Chapter 3, these changes are investigated by comparing chemical shift anisotropy tensors of the samples before and after photoreaction. Section 4.3 is dedicated to the structural analysis of the photosystems using ^1H NMR spectroscopy and double quantum-coherence excitation, where connectivities and correlations between atoms of adjacent molecules are studied in the same fashion as in Chapter 3.

4.1 Experimental Section

Commercial 98% *trans*-*o*-methoxy-cinnamic acid (Aldrich) was used for the crystallization of α -*o*-methoxy-cinnamic acid from a solution in methanol (henceforth *o*-methoxy

cinnamic acid for simplicity). *trans*-*o*-ethoxy-cinnamic acid (98%, Alpha Aesar) was crystallized in the α -polymorph from a hot solution in ethyl acetate (henceforth *o*-ethoxy cinnamic acid for simplicity) [Coh2]. The *o*-methoxy cinnamic acid crystals were small, with < 500 μm size. The *o*-ethoxy cinnamic acid crystallized in thin laths of various sizes, from which crystals between 1 and 2 mm size were selected using mesh sieves. The UV-Vis absorption spectra of *o*-methoxy and *o*-ethoxy cinnamic acids were taken on a Cary UV-Vis spectrometer with 0.1 nm resolution. The samples were melted between two quartz plates, where a thin film was obtained by the application of pressure during cooling and subsequent crystallization.

The preparation of the photoproducts, i. e. *o*-methoxy and *o*-ethoxy truxillic acid, was carried out under broad-band UV irradiation using an OSRAM Ultravitalux lamp under water-cooling for consecutive irradiation periods of 10 minutes, with agitation of the powders between each consecutive period. The reaction product of *o*-ethoxy cinnamic acid was separated from cinnamic acid using ethanol, where the reaction product is the insoluble fraction [Str2]. For the *o*-methoxy cinnamic acid no solvent was found to dissolve only one of the components, i. e. reactant or photoproduct. Nevertheless, the measured *o*-methoxy truxillic samples did not show reactant signals, so the conversion is considered to be completed.

For the photoreaction kinetics the samples were irradiated with the same procedure and equipment as described for β -cinnamic acid (see section 3.1). The NMR experiments on the UV irradiated samples for the photoreaction kinetics studies were performed on a Bruker Avance DSX 500 spectrometer with a 4 mm MAS probe head (for more details see section 3.1). For the *o*-methoxy samples a spinning speed of 5.5 kHz was chosen, whereas for the *o*-ethoxy samples the spinning speed was 4.7 kHz. The spinning speeds were chosen to avoid overlapping of signals with spinning sidebands. The ^1H $\pi/2$ pulse length was 2.5 μs and the contact time 1 ms. The chemical shift anisotropy tensor studies were performed at a spinning speed of 1.5 kHz at the Bruker Avance DSX 500 for the *o*-methoxy and at a Bruker Avance 400 for the *o*-ethoxy system (see Chapters 2 and 3.1 for details on pulse sequence and data processing). The ^{13}C CPMAS spectra of *o*-ethoxy cinnamic acid and its photoproduct were also obtained at the Bruker Avance DSX 400 spectrometer. The recycle delays used are as follows: 20 seconds for the *o*-methoxy cinnamic acid, 10 seconds for the *o*-methoxy truxillic, 50 seconds for *o*-ethoxy cinnamic acid and 30 seconds for the *o*-ethoxy truxillic acid. All the spectra were referenced to TMS

using glycine as a secondary reference. The ^1H measurements were done as described in section 3.1.

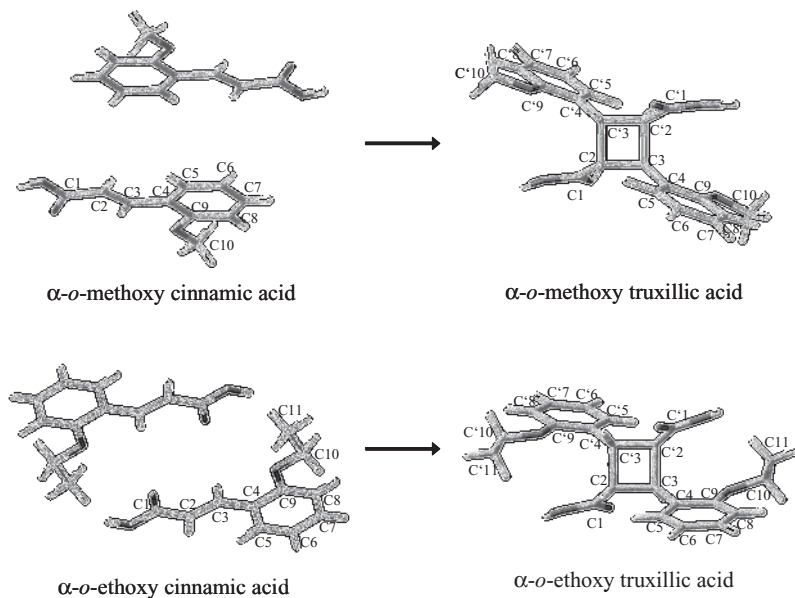
The NMR theoretical calculations were performed using the Gaussian commercial package [Gau1] as described in section 3.1. In all the simulations, the atom positions were taken from the X-ray crystal structures. The X-ray structures were available for *o*-methoxy cinnamic acid [Atk1] and *o*-ethoxy cinnamic acid [Fer], but not for any of the photoproducts.

4.2 ^{13}C CPMAS spectroscopy

4.2.1 Characterization of the derivatives

Scheme 4.1 illustrates the photodimerization of *o*-methoxy and *o*-ethoxy cinnamic acid, where the numbering scheme is the one used in the Gaussian calculations and in the assignment of the spectra. Figure 4.1 shows the comparison between the ^{13}C CPMAS spectra of the *o*-methoxy cinnamic acid and its photoproduct. The assignment of the spectra can be seen in Tab. 4.1. The assignments were carried out based on the theoretical calculations, on the comparison to solution spectra available in the Spectral Database of Organic compounds [SDBS], and by spectral editing techniques. For example, dephasing spectra of the *o*-methoxy system are shown in Fig. 4.2, where the ipso carbon, the methyl carbon and the one attached to the methoxy group as well as the carboxyl carbon, could be clearly assigned. Short contact time CPMAS experiment was also performed and confirmed these assignments.

The spectra of *o*-methoxy cinnamic acid and *o*-methoxy truxillic acid show several differences. As expected, the vinyl signals are no longer present in the reaction product, instead two cyclobutane signals are observed. Unlike in the case of α - and β -cinnamic acid only two cyclobutane signals are present (instead of four) indicating a centrosymmetric photoproduct. The carboxyl and the ipso carbon signals are shifted to higher ppm values (4 and 9 ppm shift difference, respectively). All the other aromatic signals, that were well separated in the cinnamic acid are now grouped together and shifted to slightly lower ppm values. Furthermore, two methyl carbon resonances are observed in the photoproduct. The reason for this is unclear.



Scheme 4.1 – Photoreaction scheme of *o*-methoxy (top) and *o*-ethoxy (bottom) cinnamic acid.

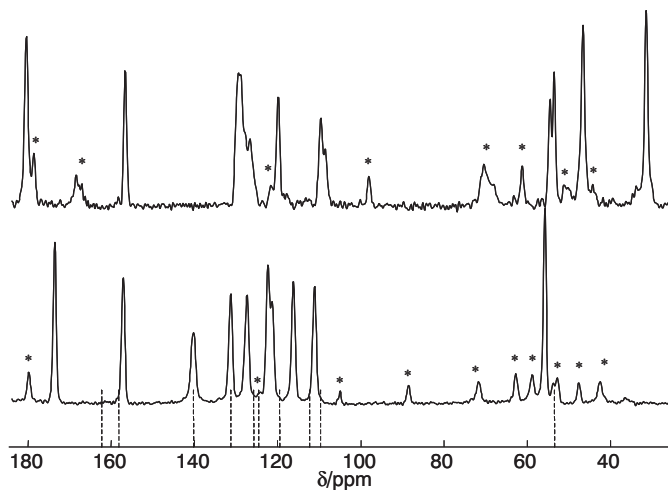


Figure 4.1 – ^{13}C CPMAS spectra of *o*-methoxy cinnamic acid (bottom) and *o*-methoxy truxillic acid (top). Asterisks mark spinning sidebands. The dashed vertical lines represent the results of the Gaussian calculations.

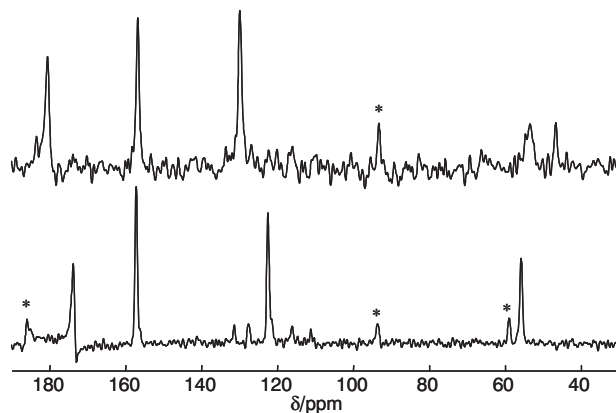


Figure 4.2 – ^{13}C CPMAS dephasing spectra of *o*-methoxy cinnamic acid (bottom) and *o*-methoxy truxillic acid (top). Asterisks mark spinning sidebands. The protonated carbon signals still present and the slight phase distortion for the peak at 174 ppm are due to partial inefficiency of the dephasing experiment.

Table 4.1 – Resonance assignments for *o*-methoxy cinnamic and truxillic acid together with values obtained from Gaussian calculations. Numbering from Scheme 4.1.

Sample	Assignment	$\delta[\text{ppm}]$	$\delta[\text{ppm}]$ theoretical
<i>o</i> -methoxy-cinnamic acid	C1	174	162
	C2	116	113
	C3	140	140
	C4	122	125
	C5	127	126
	C6	121	120
	C7	131	131
	C8	111	110
	C9	157	158
	C10	56	54
<i>o</i> -methoxy-truxillic acid	C1 C'1	180	
	C2 C'2, C3 C'3	31, 47	
	C4 C'4	129	
	C5-C8 C'5-C'8	129, 127, 120, 109	
	C9 C'9	157	
	C10 C'10	55, 54	

Figure 4.3 shows the comparison between the ^{13}C CPMAS spectra of *o*-ethoxy cinnamic acid and its photoproduct. Interestingly, only one cyclobutane signal is observed in the photoproduct spectrum. This one signal is most probably comprised of two overlapping resonances, as expected from a centrosymmetric photodimer. As for *o*-

methoxy cinnamic acid, also the carboxyl and the ipso carbons are shifted to higher ppm values (3 and 9 ppm shift difference, respectively). All the other aromatic signals are shifted to slightly lower ppm values. Additionally, the oxymethylene carbon signal shifts to a slightly lower value.

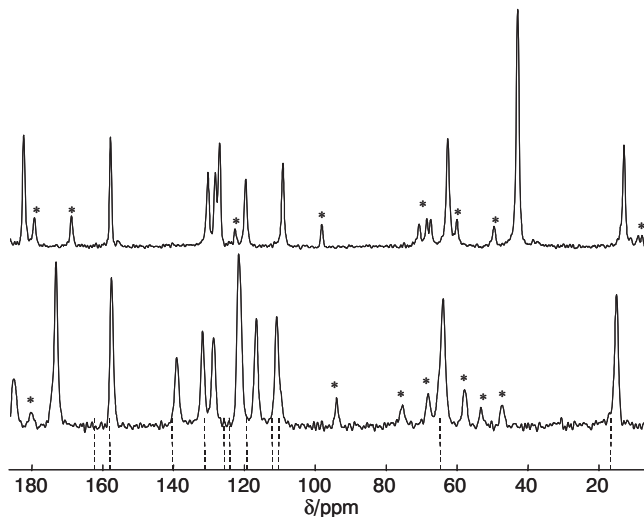


Figure 4.3 – ^{13}C CPMAS spectra of *o*-ethoxy cinnamic acid (bottom) and *o*-ethoxy truxillic acid (top). Spinning sidebands are marked by asterisks. The dashed vertical lines represent the results of the Gaussian calculations.

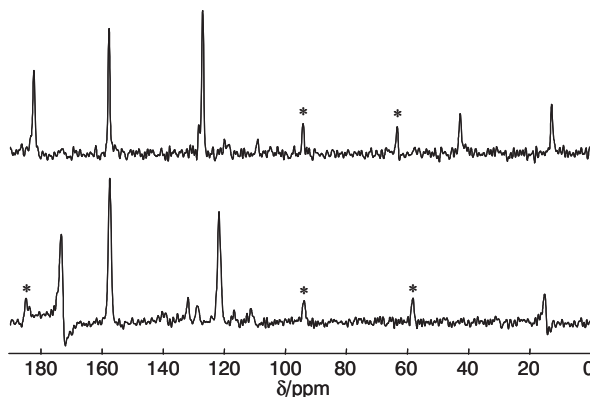


Figure 4.4 – ^{13}C CPMAS dephasing spectra of *o*-ethoxy cinnamic acid (bottom) and *o*-ethoxy truxillic acid (top). Asterisks mark spinning sidebands. The protonated carbon signals still present and the slight phase distortion for the peak at 173 ppm are due to partial inefficiency of the dephasing experiment.

Table 4.2 – Resonance assignments for *o*-ethoxy cinnamic acid together with values obtained from Gaussian calculations. Numbering from Scheme 4.1.

Sample	Assignment	δ [ppm]	δ [ppm] theoretical
<i>o</i> -ethoxy-cinnamic acid	C1	173	163
	C2	117	112
	C3	139	141
	C4	122	124
	C5	129	126
	C6	121	120
	C7	132	131
	C8	111	111
	C9	157	158
	C10	64	65
	C11	15	17
<i>o</i> -ethoxy-truxillic acid	C1 C'1	182	
	C2 C'2 C3 C'3	43	
	C4 C'4	127	
	C5-C8 C'5-C'8	130, 128, 120, 109	
	C9 C'9	158	
	C10 C'10	63	
	C11 C'11	13	

The performed Gaussian simulations agree well with the experimental observations (see Tabs. 4.1 and 4.2), on average within less than 2 ppm, apart from the carboxyl carbon (hydrogen bond is not simulated as discussed in 3.2.1). Along with the isotropic chemical shift calculation, the CSA tensors have also been simulated and will be compared with the experimentally obtained values below.

4.2.2 Kinetics of photoreaction

For studying the kinetics of the photoreaction of both *o*-methoxy and *o*-ethoxy cinnamic acid, samples were irradiated and their ^{13}C CPMAS spectra measured (Figs. 4.5 and 4.7). The degree of conversion was obtained from the ratio between the integrated areas of vinyl and cyclobutane carbon signals and is plotted versus time to obtain the kinetics curves shown in Figs. 4.6 and 4.8. As for the α - and β -cinnamic acid, the JMAK model [Joh, Avr1, Avr2, Avr3, Kol] was used to fit the curves and extract the parameters n and k . For the kinetics curve of *o*-methoxy cinnamic acid $n = 0.98 \pm 0.11$ and $k = 0.008 \pm 0.001 \text{ min}^{-1}$.

A value of $n \approx 1$ is indicative of a heterogenous one-dimensional linear growth with an initially fixed number of nuclei present. As discussed for β -cinnamic acid, exposure to UV radiation from natural light may have induced nucleation already during the crystallization of β -cinnamic acid. The curve of *o*-ethoxy cinnamic acid has a sigmoidal behaviour as also observed for α -cinnamic acid, with fit parameters $n = 2.22 \pm 0.11$ and $k = 0.0193 \pm 0.0003 \text{ min}^{-1}$, indicative of a heterogeneous two-dimensional growth, with a decreasing nucleation rate ($2 \leq n \leq 3$). However, for α -cinnamic acid the Avrami exponent indicated a heterogeneous one-dimensional growth, with a decreasing nucleation rate ($1 \leq n \leq 2$).

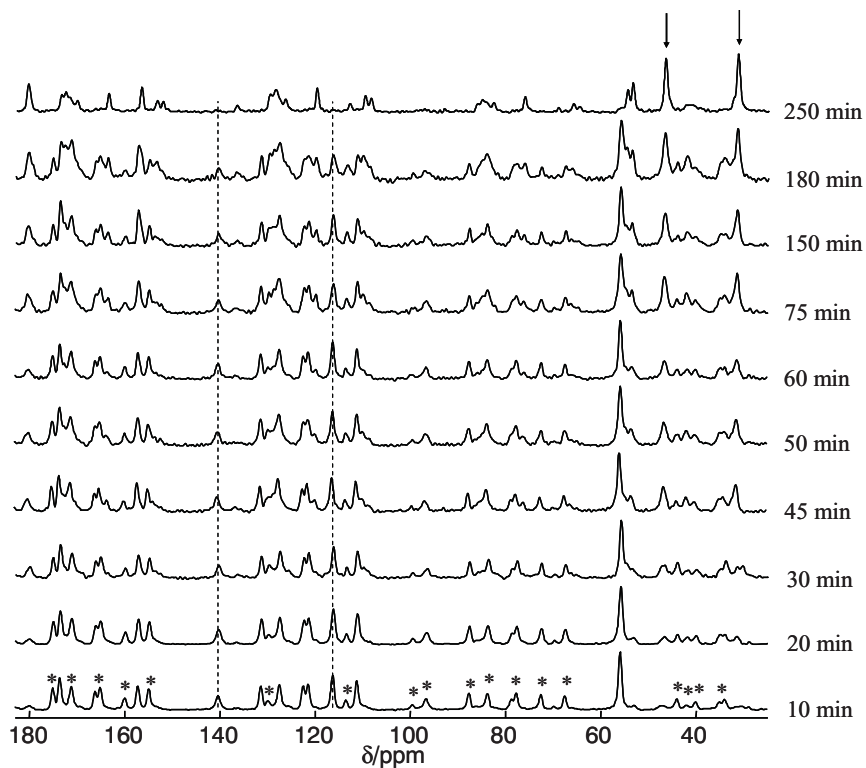


Figure 4.5 – ^{13}C CPMAS spectra of the irradiated samples of *o*-methoxy cinnamic acid used to calculate the kinetic curve. The total irradiation time is indicated on the right. The dashed lines mark the vinyl positions and the arrows indicate the cyclobutane peaks. To avoid confusion, spinning sidebands are marked with asterisks only for the first spectrum.

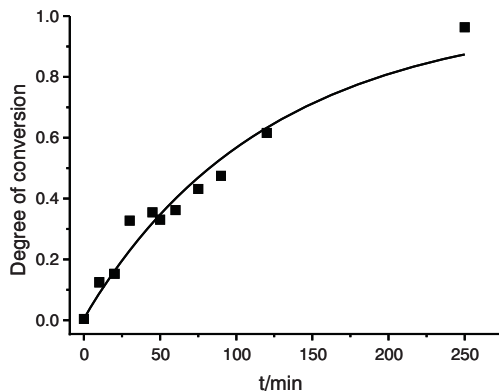


Figure 4.6 – Photodimerization kinetics of *o*-methoxy cinnamic acid converting into *o*-methoxy truxillic acid. The curve is the fit using the Johnson-Mehl-Avrami-Kolmogorov model with $k = 0.008 \pm 0.001 \text{ min}^{-1}$ and $n = 0.98 \pm 0.11$.

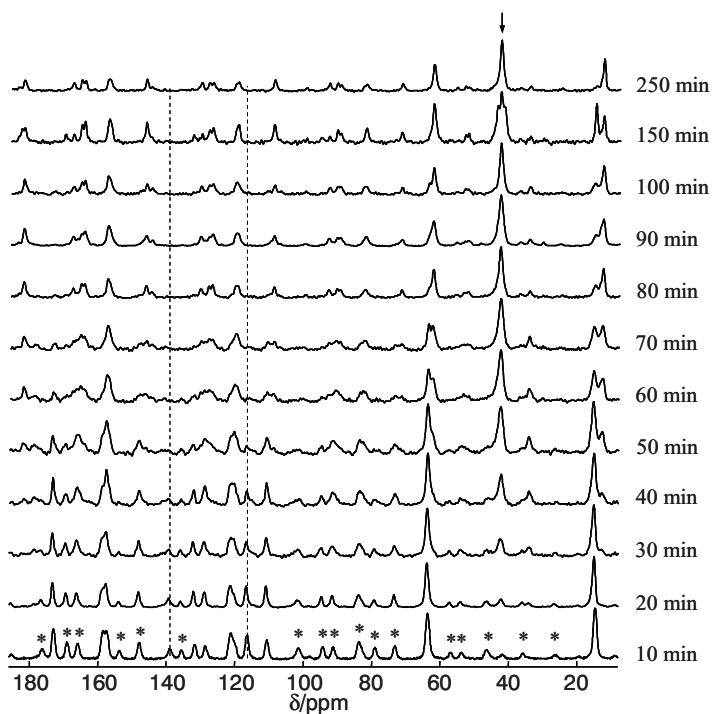


Fig 4.7 – ^{13}C CPMAS spectra of the irradiated samples of *o*-ethoxy cinnamic acid used to calculate the kinetics curve. The total irradiation time is indicated on the right. The dashed lines mark the vinyl positions and the arrow indicates the cyclobutane peak. To avoid confusion, spinning sidebands are marked with asterisks only for the first spectrum.

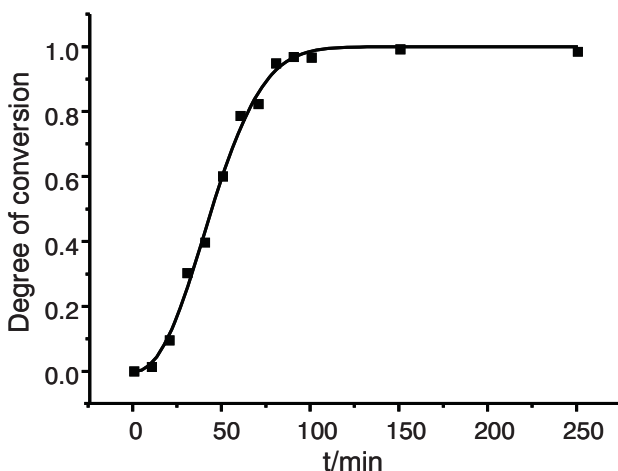


Fig 4.8 – Photodimerization kinetics of *o*-ethoxy cinnamic acid converting into *o*-ethoxy truxillic acid. The curve is the fit using the Johnson-Mehl-Avrami-Kolmogorov model with $k = 0.0193 \pm 0.0003 \text{ min}^{-1}$ and $n = 2.22 \pm 0.11$.

For comparison, the fit functions of α -cinnamic acid, *o*-methoxy, and *o*-ethoxy cinnamic acid kinetics curves are plotted together in Fig. 4.9. It can be observed that α -cinnamic and *o*-ethoxy cinnamic acids react considerably faster than *o*-methoxy cinnamic acid. The *o*-ethoxy has initially a lower conversion amount than the α -cinnamic acid, but since the growth is two-dimensional for *o*-ethoxy and one-dimensional for α -cinnamic acid, at around 50 minutes of irradiation *o*-ethoxy overcomes α -cinnamic acid and reaches 100% of conversion faster. The *o*-methoxy cinnamic acid has at low irradiation times a higher converted amount, which quickly decreases when compared to the other two. For *o*-methoxy cinnamic acid the nuclei are initially present and growth can readily begin, while for the other two there is first a nucleation time later followed by growth.

Such a big difference between the *o*-ethoxy and *o*-methoxy cinnamic acid kinetic behaviour is unexpected, considering the fact that the two molecules are quite similar. However, the ethoxy sidechain is already quite large and even the crystal structures exhibit different unit cells ($a = 7.17$, $b = 17.69$, $c = 8.10$ and $V = 908 \text{ \AA}^3$ for *o*-methoxy cinnamic acid; $a = 6.70$, $b = 8.68$, $c = 10.02$ and $V = 500 \text{ \AA}^3$ for *o*-ethoxy cinnamic acid) and space groups ($P2_1/a$ for *o*-methoxy cinnamic acid and $P\bar{1}$ for *o*-ethoxy cinnamic acid). Furthermore, the distance between the vinyl carbons, C2 and C3, of two parallel molecules of *o*-ethoxy cinnamic acid ($\sim 4.5 \text{ \AA}$) is higher than *o*-methoxy cinnamic acid ($\sim 4.1 \text{ \AA}$),

which would indicate an easier photoreaction for *o*-methoxy cinnamic acid. The 4.5 Å distance observed for *o*-ethoxy cinnamic acid is above the accepted in the topochemical principle (4.2 Å). However, photoreaction has been observed to occur at distances higher than 4.2 Å (see [Kau] and references therein). Moreover, the *o*-methoxy cinnamic acid crystals are light brown in color, whereas the *o*-ethoxy ones are transparent. There could be a difference in the UV absorption of the derivatives also in the UV range that could influence the kinetics behaviour. To investigate this, solid-state UV absorption spectra of these two samples were acquired and are shown in Fig. 4.10. No major differences in absorption of UV radiation between the derivatives are observed apart from the absorption maximum, which originates from the differences in thickness between the measured films. This indicates that the reason for the different kinetic behavior is not related with differences in UV absorption between the two samples.

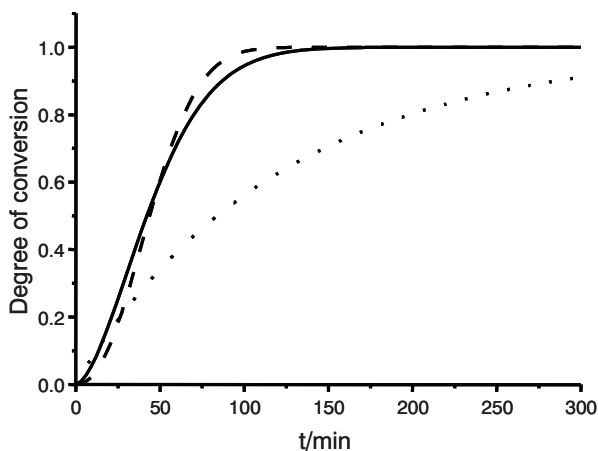


Figure 4.9- Comparison between the fit functions of the photoreaction kinetics of α -cinnamic acid (solid curve), *o*-methoxy (dotted curve), and *o*-ethoxy cinnamic acid (dashed curve).

Another issue is the size of the crystals used for irradiation. The *o*-ethoxy cinnamic acid crystals consisted of laths varying between 1-2 mm in their biggest dimension (high aspect ratio) similar to α -cinnamic acid, whereas the crystals of *o*-methoxy cinnamic acid were much smaller, less than 500 μm . Interestingly, vibrational studies in *o*-methoxy cinnamic acid have revealed that bigger crystals react slower than smaller ones [Atk3].

However, whereas in that study single crystals were investigated, in this investigation a distribution of crystallite sizes within a given range is used and the results do not indicate the same dependence (further discussion in the next chapter). Other factors may as well contribute to the observed differences, such as the reorientation of functional groups near the reaction center, as observed in the case of the α - and β -cinnamic acid polymorphs. This fact will be discussed below by studying the CSA tensors.

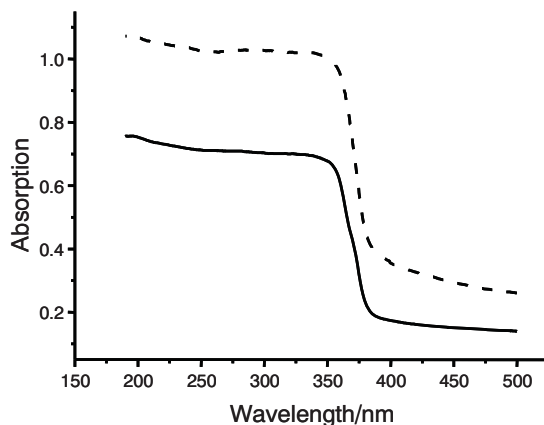


Figure 4.10- Comparison between UV solid-state spectra of *o*-methoxy (solid curve) and *o*-ethoxy cinnamic acids (dashed curve).

4.2.3 Chemical shift anisotropy

As discussed above, upon photoreaction changes in orientation of substituents near the reaction center take place (see e. g. Scheme 4.1), which could help explain the different reaction kinetics of the two polymorphs. To get information about these orientational changes the chemical shift anisotropy tensors have been analyzed using the 2D PASS sequence [Dix, Ant, Ivc] and the HBA software [HBA] (see section 2.2.4 for a more detailed description). The resulting 2D spectra along with the projection of the isotropic spectrum of *o*-methoxy cinnamic acid and its photoproduct are shown in Figs. 4.11 and 4.12. The resulting principal values of the chemical shift tensor as well as the reduced anisotropy and asymmetry are given in Tabs. 4.3 and 4.4 of the appendix for *o*-methoxy

cinnamic acid and its photoproduct, respectively. The theoretical CSA values for *o*-methoxy cinnamic acid obtained from the Gaussian calculation are also included in Tab. 4.3. The theoretically obtained values agree well with the experimentally obtained ones, apart from the carboxyl carbon.

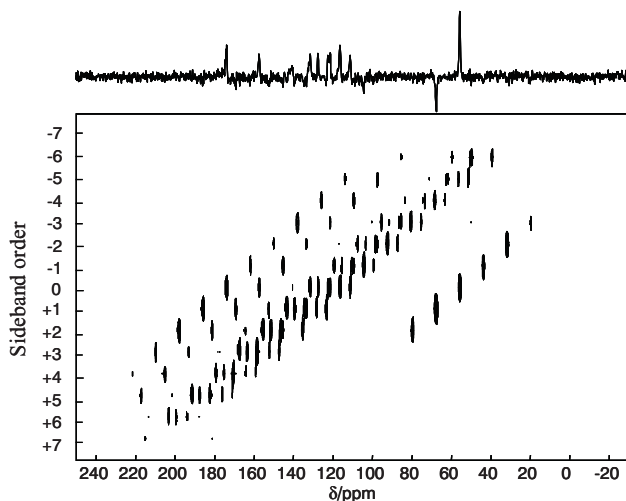


Figure 4.11 – 2D PASS of *o*-methoxy cinnamic acid.

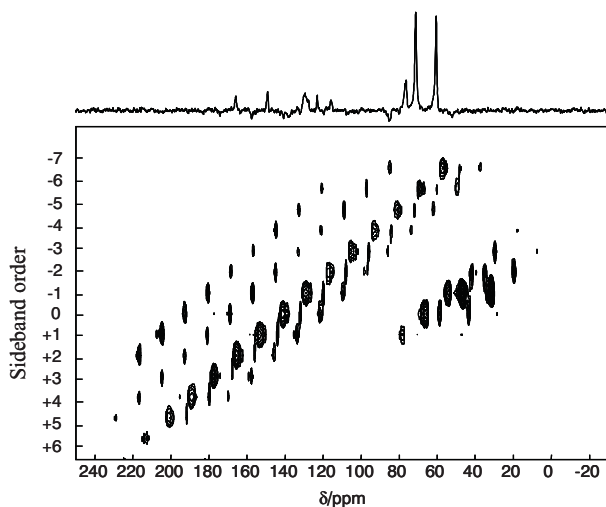


Figure 4.12 – 2D PASS of *o*-methoxy truxillic acid.

As discussed in the previous chapter, the CSA tensors of the vinyl and cyclobutane carbons will not be analyzed, as they take part in the reaction and will give no information on orientation changes. Then, one should analyze the CSA tensors of the carboxyl and aromatic groups. To facilitate the comparison, the CSA principal components of the carboxyl and aromatic carbons before and after photoreaction are plotted together in Fig. 4.13 for the *o*-methoxy system. The biggest changes upon photoreaction are observed for carbons C5-8 mainly due to changes in δ_{22} and δ_{33} . Since the photoproduct resonances for protonated aromatic carbons are not resolved, the CSA tensor values are analyzed in terms of the overall changes. The ipso carbon (C4) obtains a rather big change in isotropic chemical shift (7 ppm), which origins almost exclusively from the δ_{33} component. The carboxyl carbon experiences a big shift in isotropic values due mainly to δ_{22} . C9 exhibits smaller changes probably due to the more mobile methyl group. This gives an indication for the reorientations that take place during the photoreaction and its effects on the principal CSA tensor elements.

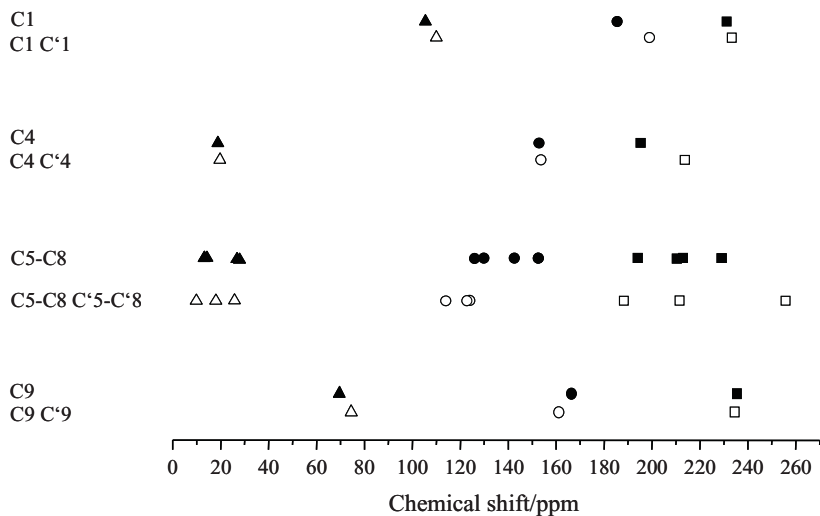


Figure 4.13 – Comparison of chemical shift tensor values between *o*-methoxy cinnamic acid and *o*-methoxy truxillic acid. Filled symbols refer to cinnamic acid and open symbols to truxillic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

For *o*-ethoxy cinnamic acid, the resulting 2D spectra along with the projection of the isotropic spectrum are shown in Figs. 4.14 and 4.15. The lack of phase distortions observed in comparison to the *o*-methoxy case is due to the fact that these experiments were done on a Bruker Avance 400 spectrometer with a later version of the hardware, especially the signal generating unit (SGU) which is lacking in the Bruker Avance 500 spectrometer. The resulting principal values of the chemical shift tensor as well as the reduced anisotropy and asymmetry are given in Tabs. 4.5 and 4.6 of the appendix for *o*-ethoxy cinnamic acid and its photoproduct, respectively. The theoretical CSA values for *o*-ethoxy cinnamic acid obtained from the Gaussian simulation are also indicated in Tab. 4.6 and the values agree well with the experimentally obtained ones, with the exception of the carboxyl carbon.

Figure 4.16 shows a comparison between the CSA principal components of the carboxyl and aromatic carbons before and after photoreaction for the *o*-ethoxy system. The carboxyl carbon (C1) signal changes considerably in chemical shift due changes in δ_{11} and δ_{22} . The non-protonated aromatic carbons, C4 and C9 exhibit minor changes in CSA tensor values. All the other aromatic carbons are not resolved for the photoproduct so a comparison is done considering an average of all. The changes observed are also not very pronounced. In comparison to the *o*-methoxy cinnamic acid the differences observed here are smaller.

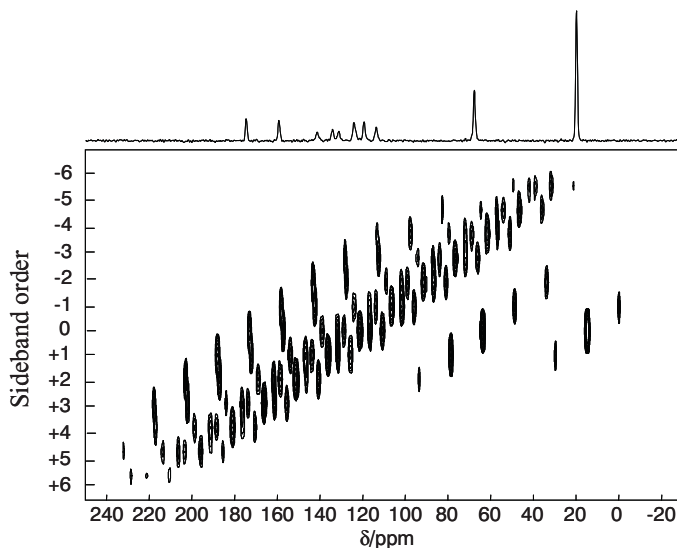


Figure 4.14 – 2D PASS of *o*-ethoxy cinnamic acid.

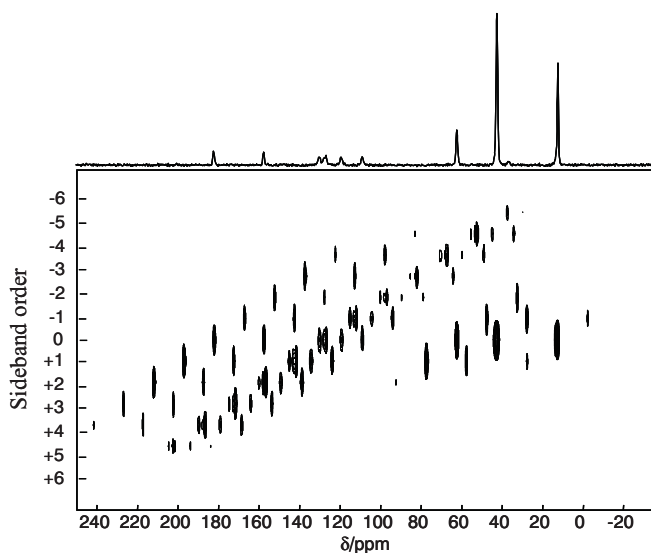


Figure 4.15 – 2D PASS of *o*-ethoxy truxillic acid.

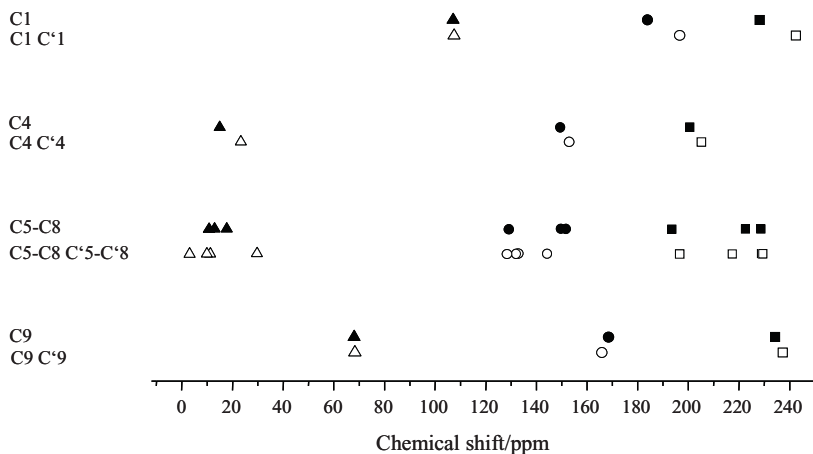


Figure 4.16 – Comparison of chemical shift tensor values between *o*-ethoxy cinnamic acid and *o*-ethoxy truxillic acid. Filled symbols refer to cinnamic acid and open symbols to truxillic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

Overall, more pronounced changes in the principal values of the CSA tensor and hence in orientation are observed in the photoreaction of *o*-methoxy cinnamic acid, which could contribute to the lower reaction rate when compared to *o*-ethoxy cinnamic acid. The

differences are however small in comparison to the big differences in kinetic behaviour. Nevertheless, it seems that substitution in *ortho*-position has remarkable effects on the photoreaction of α -cinnamic acids. This does not appear to be proportional to the size of substituent by itself, considering the case of unsubstituted α -cinnamic acid, which reacts faster than *o*-methoxy cinnamic acid but slower than *o*-ethoxy cinnamic acid.

4.3 ^1H High-speed MAS

4.3.1 ^1H chemical shift and intermolecular distances

Figure 4.17 shows the isotropic part of the ^1H MAS spectra of *o*-methoxy and *o*-ethoxy cinnamic acid and their corresponding photodimers at a spinning speed of 30 kHz. The corresponding peak positions are summarized in Tab. 4.7. The assignment of overlapping signals was done by fitting using the dmfit-Program [Mas].

As previously seen in Chapter 3, not all functional groups are resolved due to the strong homonuclear dipolar couplings. Nevertheless the carboxyl acid proton is well enough separated from the rest of the signals to enable a clear assignment and to resolve main connectivities (see below). Even though the aromatic and vinyl proton signals are strongly overlapping due to their similar isotropic chemical shifts, a deconvolution between the two signals was partially possible (see fits in Fig. 4.17), where the vinyl signal on the right side of the aromatic signals could be resolved (the other vinyl signal is on the left side of the aromatic one). In the case of the photodimers, the protons at the cyclobutane ring are better separated from the aromatic signals, although there is still some overlapping. Furthermore, an additional signal at low ppm values is observed, which corresponds to the protons of the methoxy group in the case of *o*-methoxy cinnamic acid and its photoproduct, and to the methyl protons of ethoxy group of the *o*-ethoxy system. The OCH_2 protons (oxymethylene) of the ethoxy group have typically chemical shift values between 3 and 4 ppm, which is quite similar to the shifts of the cyclobutane ring signals. However deconvolution of OCH_2 from vinyl protons was possible (see fits in Fig. 4.15).

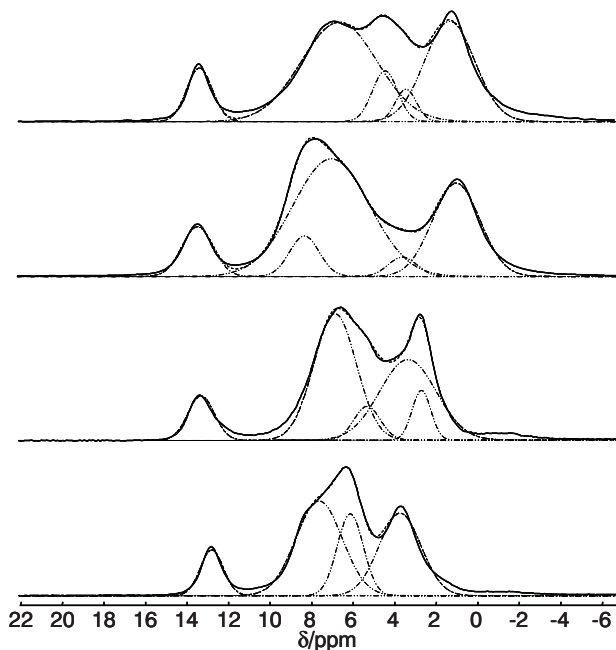


Figure 4.17 – ^1H MAS spectra at a spinning speed of 30 kHz showing the isotropic region only. Notification of samples from bottom to top: *o*-methoxy cinnamic acid; *o*-methoxy truxillic acid; *o*-ethoxy cinnamic acid; *o*-ethoxy truxillic acid. The dashed line corresponds to the fit and the dash-dot lines to the deconvolution in different peaks

Table 4.7 – ^1H chemical shifts in the *o*-methoxy and *o*-ethoxy cinnamic acid photosystems.

Sample	^1H Chemical shift				
	COOH	H _{arom}	H _{vinyl}	H _{cyclo}	H _{methoxy/ethoxy}
<i>o</i> -methoxy cinnamic acid	12.71	7.54, 6.04	-	-	3.65
<i>o</i> -methoxy truxillic acid	13.17	6.54	-	3.13 ³ , 5.20 ⁴	2.59
<i>o</i> -ethoxy cinnamic acid	13.28	8.11, 6.80	-	-	3.35 ¹ , 0.75 ²
<i>o</i> -ethoxy truxillic acid	13.20	6.41	-	4.18	3.17 ¹ , 1.02 ²

¹OCH₂ protons of the ethoxy group

²methyl protons

³carboxyl side; ⁴phenyl side

As observed in α - and β -cinnamic acid, along with the photodimerization there is also a shift of the carboxyl proton signal. In the case of *o*-methoxy truxillic acid the

carboxyl proton chemical shift increases, whereas in the case of *o*-ethoxy truxillic acid the change in chemical shift is negligible. As discussed in the previous chapter, this can be interpreted in terms of a stronger hydrogen bond if the chemical shift is at higher ppm-values as for *o*-methoxy truxillic acid or in the case of *o*-ethoxy truxillic acid it remains the same. Interestingly, for the photoproducts the chemical shifts of the carboxyl protons are identical. The correlation between the isotropic chemical shift and the oxygen-oxygen distance was already discussed in Chapter 3 and the isotropic chemical shifts of several compounds (data taken from literature [Ber2]), including the α -cinnamic acid derivatives are plotted versus oxygen-oxygen distance along the hydrogen bond are plotted in Fig. 3.14. For the cinnamic acid samples deviations from the theoretical curve are observed. Therefore, a prediction of oxygen-oxygen distances based on the ^1H isotropic chemical shift according to the theoretical curve is not straightforward. Nevertheless, for the *o*-methoxy and *o*-ethoxy truxillic acids no crystal structure data exists, but the oxygen-oxygen distance is expected to fall within the same range of values (above the curve) as the other cinnamic acids and photoproducts, based on the isotropic ^1H chemical shifts observed. In the following section more information on the relative orientation of functional groups and proton-proton through-space connectivities is obtained by applying double-quantum excitation techniques.

4.3.2 ^1H - ^1H correlation experiments

The 2D BABA correlation spectra of *o*-methoxy cinnamic acid and its photoproduct are shown in Figs. 4.18 and 4.19, respectively. Some directly observable correlations are indicated by the dashed lines. In *o*-methoxy cinnamic acid, the cross peaks between the carboxyl proton and the aromatic/vinyl protons are clearly visible. Since the aromatic and vinyl signals are not fully resolved, only one rather broad set of cross peaks is observed for the correlation with the carboxyl protons. Furthermore, connectivities between the carboxyl and methoxy protons are also observed. In the case of *o*-methoxy truxillic acid cross peaks between the carboxyl proton and the all the other protons are observed, however at maximum intensity with the aromatic protons. There is not enough resolution to distinguish between the correlations of the carboxyl protons to aromatic and cyclobutane protons, due to the small chemical shift range. Moreover, cross peaks between the aromatic and the methoxy protons are also present.

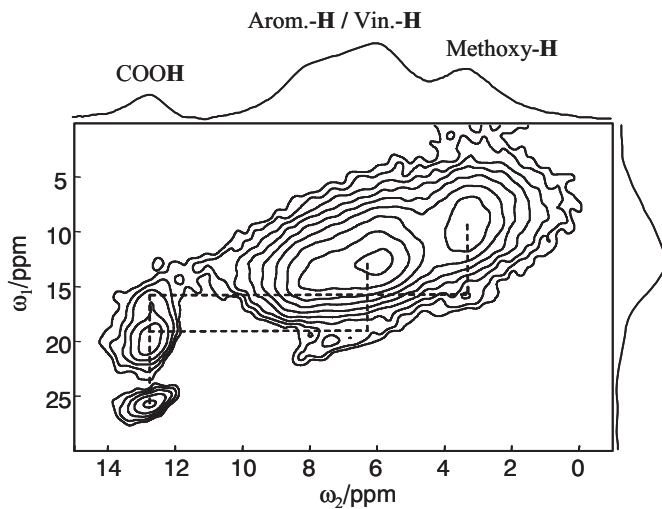


Figure 4.18 – 2D BABA of *o*-methoxy cinnamic acid. General correlation peaks are indicated by dashed lines.

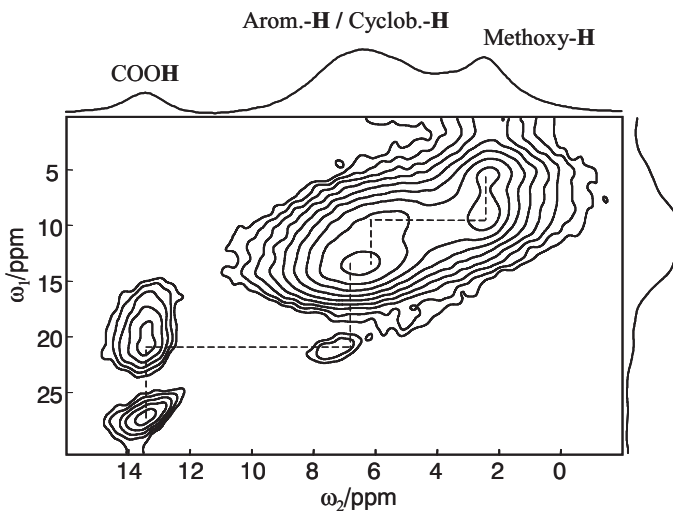


Figure 4.19 – 2D BABA of *o*-methoxy truxillic acid. General correlation peaks are indicated by dashed lines.

The 2D BABA correlation spectra of *o*-ethoxy cinnamic acid and its photoproduct are shown in Figs. 4.20 and 4.21, respectively, where correlations are indicated by the dashed lines. In *o*-ethoxy cinnamic acid, the cross peaks between the carboxyl proton and the aromatics are clearly visible and slightly better resolved than for the *o*-methoxy spectra because of the larger chemical shift range. As for the oxymethylene protons, at their chemical shifts no crosspeaks are observed to the carboxyl protons, but instead to the aromatic/vinyl protons and methyl protons of the methoxy group. In the case of *o*-ethoxy truxillic acid cross peaks between the carboxyl and the aromatic protons are resolved. Between all the other protons couplings are resolved but probably present considering the broadness of peaks in the diagonal region.

The 2D spectra give a qualitative picture of correlation peaks, which indicate through space connectivities and help in identifying the solid-state packing of these structures, when the crystal structure is not known. However, even at 30 kHz spinning speed the resolution is not sufficient to unambiguously assign intra- and intermolecular distances of functional groups.

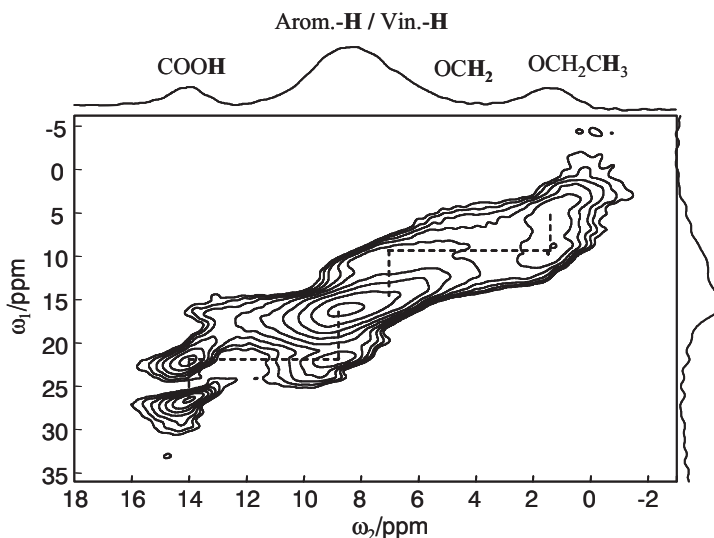


Figure 4.20 – 2D BABA of *o*-ethoxy cinnamic acid. General correlation peaks are indicated by dashed lines.

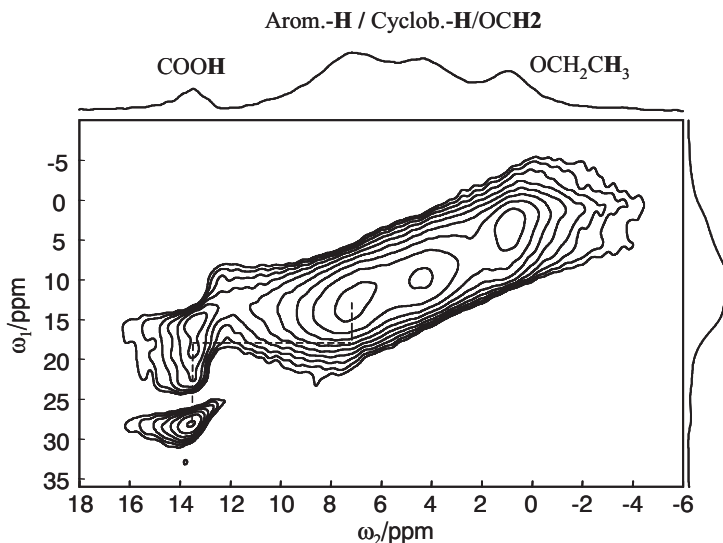


Figure 4.21 – 2D BABA of *o*-ethoxy truxillic acid. General correlation peaks are indicated by dashed lines.

Spinning sideband patterns

The quantitative deduction of the homonuclear dipolar couplings can be done by using non rotor-synchronized t_1 -increments. However, because of the long relaxation times of most compounds in our study, this is very time consuming so that it could not be realized (as discussed in Chapter 3). Since the *o*-methoxy samples have much shorter relaxation times, the 2D BABA version with non rotor-synchronized t_1 -increments was tested. The F1-projection of only the carboxyl proton region is shown in Figs. 4.22 and 4.23 for *o*-methoxy cinnamic acid and truxillic acid, respectively. The SIMPSON program [Bak1] was used to simulate this experiment using the simplest approach of a two spin-system, varying the dipolar coupling constant until a good match with the experimental results was found and from that the H-H distances are determined (see A.2.2 of the Appendix for more details on the simulation). The simulations of the F1-projections are included in Figs. 4.22 and 4.23. The spinning sideband intensities at the same distance to the origin are not symmetric, therefore the simulated spectra had to be arbitrarily calibrated with one of the first order spinning sidebands (the highest in intensity was chosen). Then a match between first and third-order spinning sidebands was done by varying the dipolar coupling value. A

drawback is that the third order spinning sideband has very low intensity, which increases the uncertainty of the dipolar coupling value obtained. The result obtained for the H-H distance, $r_{\text{HH}} = 242$ pm (with $D = 8.5$ kHz) for *o*-methoxy cinnamic acid is identical to the distance determined by neutron diffraction techniques [Atk1]. Another drawback in the simulation is the fact that the simulation does not give even order spinning sideband intensity. Even-order spinning sideband intensity arises from multiple spin effects in a pure two-spin system no even-order sidebands would be present. Taking into account more spins would also lead to even-order sideband intensity at the expense of long calculation times. Nevertheless, the analysis shows that a good assignment of the carboxyl acid dimer proton-proton distance is possible. The uncertainty in dipolar coupling might still be rather big, but due to the inverse cubic dependence of dipolar coupling to distance, an error of 1 kHz in dipolar coupling would in this case lead to an error in distance of only ± 10 pm. This means that ^1H double quantum techniques yield very accurate ^1H - ^1H distances even when the error bars for the dipolar coupling are big.

The same study was performed for the *o*-methoxy truxillic acid, where the ^1H - ^1H distance between two carboxyl acid groups is not known. The determined distance is $r_{\text{HH}} = 233$ pm for a dipolar coupling value of 9.5 kHz. The distance is slightly smaller than that of *o*-methoxy cinnamic acid and this is in accordance with the ^1H chemical shifts as discussed above.

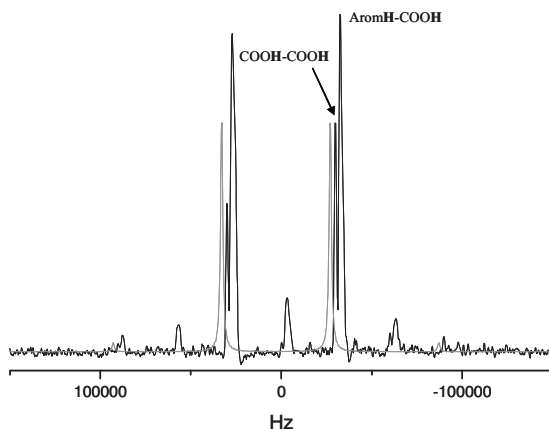


Figure 4.22 ^{-1}H 2D BABA F1 projection of the carboxyl protons of *o*-methoxy cinnamic acid (in black), acquired using t_1 increments of $1\ \mu\text{s}$ at a spinning speed of 30 kHz MAS. Simulated spectra (in grey and shifted to the left to allow a better comparison) using the simulation program SIMPSON, with a dipolar coupling of 8.5 kHz; this corresponds to a distance of $r_{\text{HH}} = 242$ pm.

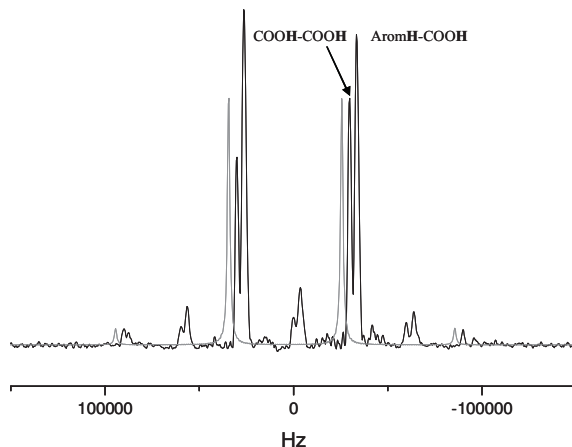


Figure 4.23 ^1H 2D BABA F1-projection of the carboxyl proton for *o*-methoxy truxillic acid (in black), acquired using t_1 increments of 1 μs at 30 kHz MAS. Simulated spectra (in grey and shifted to the left to allow a better comparison) using the simulation program SIMPSON, with a dipolar coupling of 9.5 kHz. $r_{\text{HH}} = 233$ pm.

The much longer longitudinal relaxation times (T_1) of the other derivatives and of α - and β -cinnamic acid do not allow performing these experiments with respect to available measurement time. Therefore, the semi-quantitative approach as already presented in Chapter 3 using the relative peak intensities of the different cross peaks of the rotor-synchronized 2D BABA will be studied.

The different F1-projections shown in Fig. 4.24 for the four samples only represent the signals along the carboxyl protons in the F2-dimension. Fitting the experimental F1-projections yields a carboxyl-to-other protons ratio for *o*-methoxy cinnamic acid of 1:1.85, for *o*-methoxy truxillic acid 1:2.22, for *o*-ethoxy cinnamic acid 1:1.40, and for *o*-ethoxy truxillic acid 1:2.06. The carboxyl-to-other protons intensity includes the aromatic and vinyl protons for the cinnamic acids. The differentiation between proton species was not done, since they are not well separated in the F1-projections. The relative intensities of the carboxyl-to-other protons are lower for the *o*-methoxy than for *o*-ethoxy samples, indicating closer through-space distances for the aromatics with respect to the carboxyl protons. The sum of proton-proton homonuclear dipolar couplings up to 5 nm separately for carboxyl-carboxyl and carboxyl-other protons was calculated with respect to a central carboxyl proton (as done in 3.3.2). The relative ratios obtained in this way from the

available crystal structures for *o*-methoxy and *o*-ethoxy cinnamic acid are represented in Fig. 4.25. The general trend (discussed in more detail in 3.3.2) is an increase of the other-to-carboxyl intensity ratio which levels off at above 4 nm. Although this procedure is only semi-quantitative, it can be observed that for *o*-ethoxy and *o*-methoxy cinnamic acid protons up to about 0.4 to 0.5 nm contribute to the cross peak intensity.

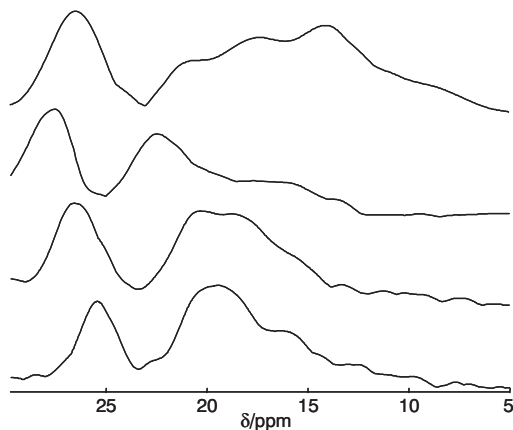


Figure 4.24 – F1-projections of the 2D BABA spectra corresponding to the carboxyl proton signal in F2. Notification of samples from bottom to top: *o*-methoxy cinnamic acid; *o*-methoxy truxillic acid; *o*-ethoxy cinnamic acid; *o*-ethoxy truxillic acid.

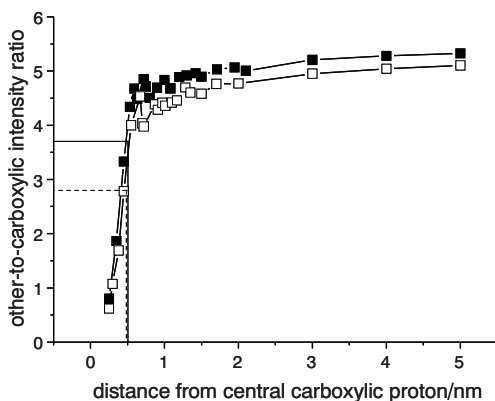


Figure 4.25 – Intensity ratio of aromatic and vinyl (other) protons relative to the carboxyl protons coupled to a central carboxyl proton as a function of distance as obtained from the crystal structure. Solid squares: *o*-methoxy cinnamic acid; open squares: *o*-ethoxy cinnamic acid. The solid and dashed lines represent the experimental intensity ratios of *o*-methoxy cinnamic and *o*-ethoxy cinnamic acid, respectively, multiplied by a factor of two.

4.4 Conclusions

The distinction between the two α -cinnamic acid derivatives, as well as their photoproducts was successfully carried out using ^{13}C solid-state NMR spectra with the support of theoretical calculations. The photoreaction process of these derivatives was explained based on the JMAK model, where in the case of *o*-methoxy cinnamic acid the growth, starting from initially present nuclei, proceeded one-dimensionally through the crystal. As for the *o*-ethoxy cinnamic acid the reaction took place two-dimensionally through the crystal with a decreasing nucleation rate. The photoreaction rate was observed to be faster for the *o*-ethoxy cinnamic acid than for the *o*-methoxy cinnamic acid. This is proposed to be explained by a combination of two effects, the different internuclear distances between reacting molecules and reorientations necessary upon photoreaction. Although not very pronounced, the photodimerization of *o*-methoxy cinnamic acid requires more reorientation of groups near the reaction centre as the photodimerization of *o*-ethoxy cinnamic acid. Interestingly, the distance between two reacting molecules is smaller for *o*-methoxy cinnamic acid, which could be expected to facilitate this photoreaction in detriment of the one of *o*-ethoxy cinnamic acid, as had already been observed in the case of the α - and β -polymorph of unsubstituted cinnamic acid. Nevertheless, if smaller distances between two reacting molecules are favorable for the photoreaction of unsubstituted α -cinnamic acid, the advantage of shorter intermolecular distance could vanish once the phenyl ring is substituted by a larger side chain. The reorientation necessary for photoreaction may increase due to repulsions from neighboring molecules. Then, bigger intermolecular distances may allow the photoreaction to be faster as observed in the comparison between *o*-methoxy and *o*-ethoxy cinnamic acid. The crystal size is reported in the literature to have an influence on the photodimerization rate, where the reaction should be slower for bigger crystals. However, the observations in this study do not reflect that. In fact, already in the previous chapter it had been observed that the β -polymorph has the slowest reaction rate even with much smaller crystals. Therefore, if present, this effect is not dominant in the case of the *o*-methoxy and *o*-ethoxy cinnamic acid photoreaction. Overall, it can be concluded that substitution in the *ortho*-position has remarkable effects on the photodimerization of α -cinnamic acid, which does not appear to be proportional to the size of the substituent by itself.

High magic angle spinning speeds enabled partial resolution in ^1H spectra of the strongly coupled organic acid dimer systems. The ^1H isotropic chemical shift of the carboxyl groups, which form hydrogen bonds between two dimers, was qualitatively correlated to the hydrogen bond strength and the oxygen-oxygen distance. However, the theoretical prediction of the oxygen-oxygen distance was observed to underestimate the distances for cinnamic acids of known crystal structures, so that an accurate determination was not possible. Additionally, the ^1H - ^1H dipolar coupling can efficiently be employed to determine connectivities in these acid dimers using double quantum excitation techniques such as back-to-back, which represent intra- and intermolecular proton-proton couplings. The non-rotorsynchronized 2D BABA experiment allowed the determination of the hydrogen-hydrogen distance between to hydrogen bonded *o*-methoxy cinnamic and truxillic acid molecules. This experiment yields good results, even with a 10% uncertainty in the determination of the dipolar coupling constant the distance is determined within ± 10 pm. However, as it is a very time consuming experiment it could only be employed to samples with short longitudinal relaxation times (T_1). Another semi-quantitative approach was followed, using the relative peak intensities of the different cross peaks of the rotor-synchronized 2D BABA, where the sum of dipolar couplings was presented and found to be suited to reflect the relative peak intensities in the double quantum dimension. Overall, these experiments revealed important structural information on these photosystems, as predictions for (inter-)molecular arrangements where X-ray crystals structures were not known, and hydrogen-hydrogen distances that can not be accurately determined by X-ray diffraction.

5. β -*trans*-cinnamic acid derivatives: *o*-, *m*-, *p*-bromo cinnamic acid and their photoreaction products

The first studies on β -bromo-cinnamic acid date back to 1886, when they were first obtained with several other studies following its synthesis [Sud and references therein]. Interestingly, when investigating the synthesis of β -*trans*-bromo cinnamic acid and β -*cis*-bromocinnamic acid from the reaction between phenylpropionic acid and hydrogen bromide, as done in 1886, Sudborough and Thompson observed that the exposure of β -*cis*-bromocinnamic acid to sunlight for several weeks induced a transformation to β -*trans*-bromo cinnamic acid [Sud] These conclusions were taken, at the time, from a complex study of solubilities in different solvents and changes in melting points of the samples and the photodimerization of cinnamic acid went unnoticed. Since then, studies on the photodimerization reaction of bromo cinnamic acids have been reported including the kinetics of photoreaction [Ahn, Jen, Kan1, Kan2]. Unlike in our observations, the photoreaction not always yielded 100% conversion. For example, the photodimerization of *p*-bromo cinnamic acid has been reported to take place only up to 80% conversion as determined from IR [Sav].

This chapter is dedicated to the study of the β -cinnamic acid derivatives, β -*o*-, *m*- and *p*-bromo cinnamic acid and their photoreaction. In particular, the influence of aromatic substitution effects on the photoreaction of the β -cinnamic acid polymorph is discussed. For this purpose, the kinetics behaviour of the three samples is studied and compared with the one of unsubstituted β -cinnamic acid. An interpretation of the differences observed is carried out based on crystal sizes, UV absorption and orientational changes of functional groups near to the reaction centre, as seen in the two previous chapters. Then, a more detailed structural analysis of the photosystems is done using ^1H NMR spectroscopy and ^1H - ^1H double quantum correlations, where connectivities and intra- and intermolecular distances are studied, again following the structure of the previous chapters.

5.1 Experimental Section

Commercial *trans*-*o*-bromo-, *m*-, and *p*-cinnamic acid (Aldrich, 95%, 98% and 98% respectively) were used for the crystallization of the corresponding β -polymorphs. The *ortho* and *para* derivatives were crystallized from a hot solution of diluted ethanol (ethanol+water), and the *meta* derivative from a hot solution of 99% acetic acid [Coh2]. The different derivatives exhibit different crystal shapes and sizes. The *o*-bromo cinnamic acid crystallizes in colourless thin laths with variable size. A selection of crystals from 1-2 mm size was made using mesh sieves. However, due to the aspect ratio of the crystals (thin laths) there was still a distribution of crystals sizes. The *m*-bromo cinnamic acid crystallizes in semi-transparent cubic crystals, which were also selected to have 1-2 mm in size. Finally, the *p*-bromo cinnamic acid crystallizes in small white needles with sizes of less than 500 μm , which did not require sieving. The UV-Vis absorption spectra were taken using the same procedure and equipment as in Chapter 4 (see 4.1).

The photoproducts of β -*o*-, *m*- and *p*-bromo cinnamic acid, i. e. β -*o*-, *m*- and *p*-bromo truxinic acid, were obtained after exposure of the cinnamic acids to broad-band UV irradiation. This was performed using an OSRAM Ultravitalux lamp under water-cooling for consecutive irradiation periods of 10 minutes, with agitation of the powders between each consecutive period. The reaction product *o*-bromo truxinic acid was separated from cinnamic acid with ether, and the *m*- and *p*-truxinic acid were separated from the reactant using toluene, the reaction products being the insoluble fraction in all three cases [Coh2]. The photoproduct samples were then evacuated for several days to extract the remains of solvent.

For the photoreaction kinetics the samples were irradiated with the same procedure and equipment as β -cinnamic acid (see section 3.1). The NMR experiments were performed on a Bruker Avance DSX 500 spectrometer with a 4 mm MAS probe head (more details in 3.1). For the kinetics studies, for all the irradiated samples a spinning speed of 8 kHz was chosen to avoid overlap of signals with spinning sidebands and the recycle delays ($5 \times T_1$) of the respective cinnamic acids before irradiation were 1200 seconds for the *o*-bromo samples, 600 seconds for the *m*-bromo samples, and 1000 seconds for the *p*-bromo samples. The ^1H $\pi/2$ pulse length was 2.5 μs and the contact time 1 ms. The chemical shift anisotropy tensors studies were performed at a spinning speed of 1.5 kHz at the Bruker Avance DSX (see section 2.2.3 and 3.1 for details on the pulse sequence

and data processing). All the spectra were referenced to TMS using glycine as secondary reference. The ^1H measurements were done as described in section 3.1.

The NMR theoretical calculations were performed using the Gaussian commercial program [Gau1] as described in 3.1. In the simulations, the atom positions were taken from the X-ray crystal structures for *o*-bromo cinnamic acid [Jen], *m*-bromo cinnamic acid [Kan1] and *m*-bromo truxinic acid [Kan2]. For *p*-bromo cinnamic acid there is no published X-ray crystal structure, so the simulation was done starting from a *m*-bromo cinnamic acid molecule modified in Gview [Gau2] to a *p*-bromo cinnamic acid molecule. Then, a complete geometry optimization was performed, i. e., all atom positions were optimized before the NMR calculation was done.

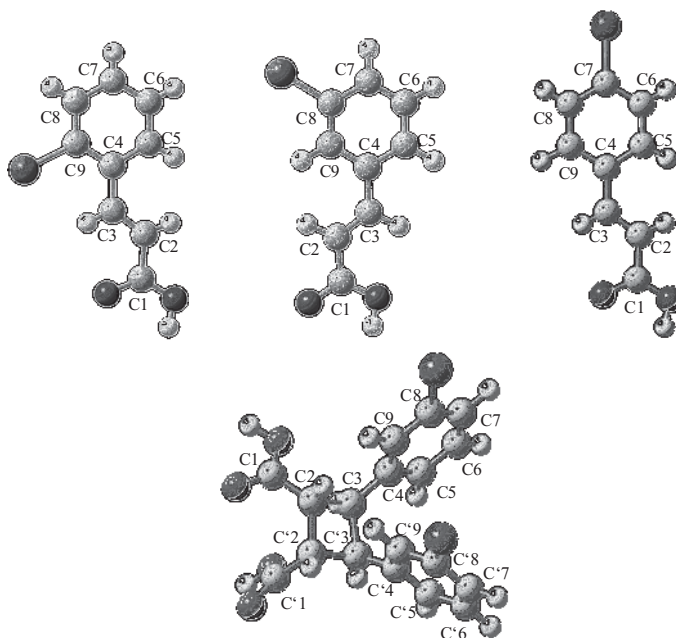
5.2 ^{13}C Spectra

5.2.1 Characterization of the derivatives

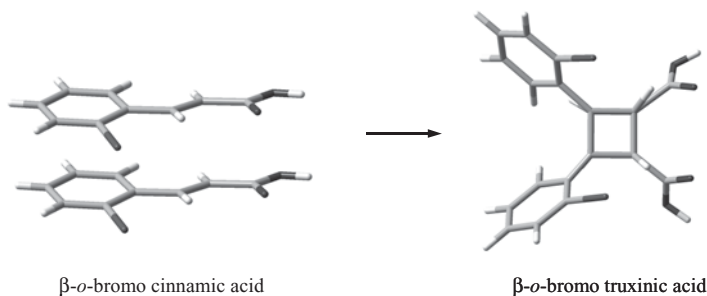
Scheme 5.1 shows the structure of *o*-, *m*- and *p*-bromo cinnamic acid and *m*-bromo truxinic acid, and the numbering used in the Gaussian simulations and in the assignment of the spectra. The ^{13}C CPMAS spectra of the reactants and their photoproducts are compared in Figs. 5.1, 5.3, and 5.5, respectively. The spectra were assigned based on spectral editing techniques, the theoretical calculations performed, and with comparison to the solution spectra available in the Spectral Database of Organic compounds [SDBS] (see Tabs. 5.1 to 5.3). The dephasing spectra performed are shown in Figs. 5.2, 5.4 and 5.6 where the ipso and carboxyl carbons could be clearly assigned. Short contact time CPMAS experiment was also performed and confirmed these assignments. The carbon attached to the bromine atom is very broad because bromine is a quadrupolar nucleus and quite difficult to identify even in the dephasing experiments. The assignment of this carbon is further discussed below.

Scheme 5.2 illustrates the photoreaction dimerization of *o*-bromo cinnamic acid. Comparing the *o*-bromo cinnamic acid and *o*-bromo truxinic acid spectra (Fig. 5.1), it is observed that the vinyl signals are no longer present in the photoproduct as expected but

instead three resolved cyclobutane ring signals. These three resolved signals correspond in fact to four cyclobutane signals that partially overlap and together with the two carboxyl and ipso signals observed each are indicative of a non-centrosymmetric photoproduct, as seen for α - and β -cinnamic acids in Chapter 3. All the other aromatic signals are shifted to slightly higher values. The calculated chemical shifts are in good agreement with the experimental ones, with an average difference of less than 2 ppm, except for the carboxyl signal (as discussed in the preceding chapters). The photoproduct spectrum shows residual solvent peaks (ethanol), which are believed to have been included in the crystal structure, since they remained even after several days of evacuation of the sample, furthermore, the peaks are slightly shifted compared to the pure solvent. In fact, it has been observed that β -cinnamic acids often incorporate solvent molecules in their crystal structure [Kau2]. In this case, the solvent peaks are well separated from the truxinic acid ones, so that they have no influence in the experiments performed.



Scheme 5.1 – Top: *o*-bromo cinnamic acid (left), *m*-bromo cinnamic acid (middle) and *p*-bromo cinnamic acid (right) together with carbon numbering. Bottom: *m*-bromo cinnamic acid together with carbon numbering used in the Gaussian calculations (equivalent for *o*- and *p*-bromo truxinic acids).



Scheme 5.2 – Photoreaction scheme of *o*-bromo cinnamic acid.

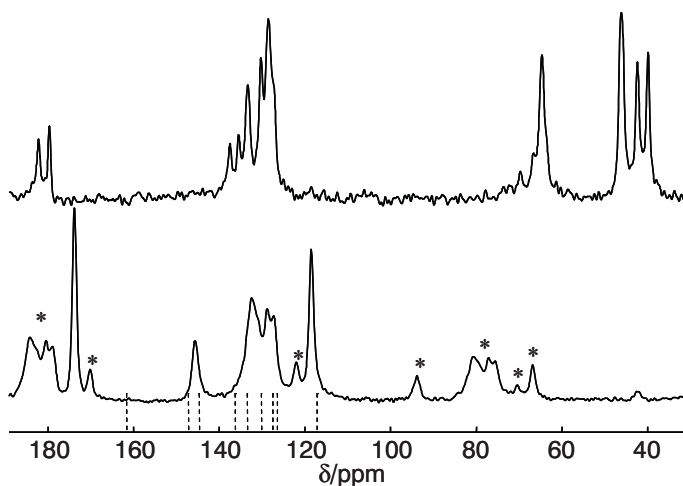


Figure 5.1 – ^{13}C CPMAS spectra of *o*-bromo cinnamic acid (bottom) and *o*-bromo truxinic acid (top). The dashed vertical lines represent the results of the Gaussian calculations. Asterisks mark spinning sidebands and the arrow indicates a residual solvent peak.

For the *meta* substituted photosystem, the ^{13}C CPMAS spectra shown in Fig. 5.3 also exhibit three resolved cyclobutane ring signals (four cyclobutane signals that partially overlap) and two carboxyl signals, which indicate a non-centrosymmetric photoproduct. Only one ipso signal is observed in the photoproduct, but the theoretical calculations indicate two ipso signals of similar chemical shifts, which probably overlap in the experimental spectrum. All the other aromatic signals are shifted to lower ppm values. The broad aromatic signal at 127 ppm corresponds to the carbon attached to the bromine atom.

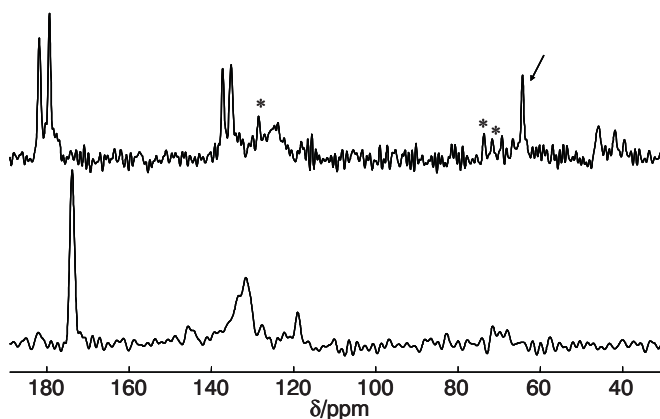


Figure 5.2 – ^{13}C CPMAS dephasing spectra and *o*-bromo truxinic acid (top). Asterisks mark spinning sidebands and the arrow indicates a residual solvent peak. Signals of protonated carbons are still present due to partial inefficiency of the dephasing experiment.

Table 5.1 – Resonance assignments for *o*-bromo cinnamic and truxinic acid together with the values obtained from the Gaussian calculations. Numbering from Scheme 5.1

Sample	Assignment	$\delta[\text{ppm}]$	$\delta[\text{ppm}]$ theoretical
<i>o</i> -bromo cinnamic acid	C1	174	162
	C2	118	117
	C3	146	145
	C4	131	136
	C5	129	128
	C6	127	126
	C7-8	132	130-133
	C9	Not resolved	147
<i>o</i> -bromo truxinic acid	C1 C'1	182, 180	
	C2 C'2 C3 C'3	46, 42, 40	
	C4 C'4	137, 135	
	C5-C8 C'5-C'8	133, 130, 128	
	C9 C'9	124 (dephasing)	

In the case of the *o*- and *p*-bromo photosystems this peak is not resolved from the other aromatic signals but dephasing experiments in combination with short contact time CPMAS experiments revealed the peak to be between 122 and 128 ppm, when present (see assignment Tabs.). In the solution spectra, this signal is present at about 120 ppm [SDBS]. The results of the theoretical calculation however give much higher chemical shift values for this resonance, due to the fact that bromine is a much bigger atom than carbon or

proton and the much higher number of electrons probably require bigger basis sets for a more accurate calculation.

In the photoproduct spectrum, a small peak corresponding to residual solvent (toluene) is observed. Other toluene peaks in the aromatic region could not be identified, since they overlap with sample signals. Another small intensity peak at about 20 ppm was also present, which is not within the scale of Fig. 5.3. Given that all the photoproduct samples were evacuated for several days in order to remove all the solvent present, it is most probable that the solvent is included in the crystal structure of *m*-bromo truxinic acid. In fact, the reported X-ray structure of *m*-bromo truxinic acid, used in theoretical calculations, included a molecule of the solvent acetic acid. Since the solvent used here is toluene, the acid molecule was not included in the simulations. However, the atomic positions could vary in our case due to the influence a different solvent, which is probably the reason for a bigger difference between the experimental and simulated spectra.

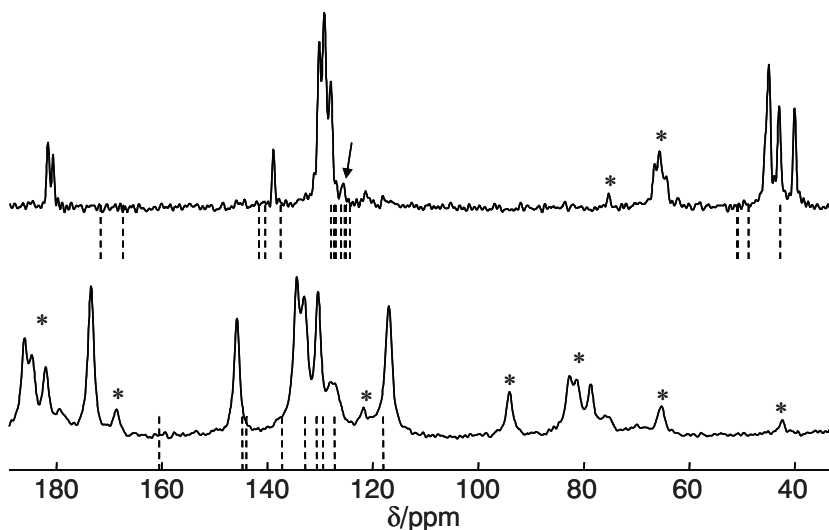


Figure 5.3 – ^{13}C CPMAS spectra of *m*-bromo cinnamic acid (bottom) and *m*-bromo truxillic acid (top). The dashed vertical lines represent the results of the Gaussian calculations. Asterisks mark spinning sidebands.

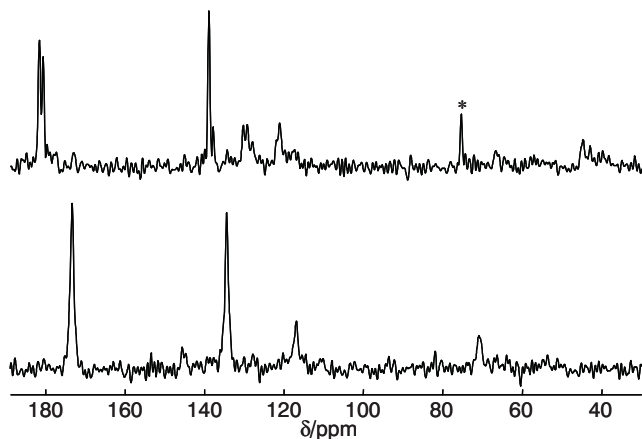


Figure 5.4 – ^{13}C CPMAS dephasing spectra of *m*-bromo cinnamic acid (bottom) and *m*-bromo truxinic acid (top). Asterisks mark spinning sidebands. Signals of protonated carbons are still present due to partial inefficiency of the dephasing experiment.

Table 5.2 – Resonance assignments for *m*-bromo cinnamic and truxinic acids together with the values obtained from the Gaussian calculations. Numbering from Scheme 5.1

Sample	Assignment	δ [ppm]	δ [ppm] theoretical
<i>m</i> -bromo cinnamic acid	C1	174	160
	C2	117	118
	C3	146	144
	C4	134	137
	C5/7	133	131/133
	C6/9	130	129/127
	C8	127	145
<i>m</i> -bromo truxinic acid	C1, C'1	181, 182	167, 172
	C2, C3, C'2 C'3	40, 43, 45	43, 49, 51
	C4, C'4	139	138, 140
	C5, C'5	126	124, 125
	C7, C6	128	125, 126
	C'9, C'6	129	126, 127
	C9, C'7	130	127, 128
	C8, C'8	122 (dephasing)	142

The *p*-bromo cinnamic acid and *p*-bromo truxinic acid spectra shown in Fig. 5.5. The photoproduct has four partially resolved cyclobutane ring signals, as well as two carboxyl and ipso signals, indicating a non-centrosymmetric photoproduct. The other aromatic signals are shifted to slightly lower ppm values. Some residual solvent (toluene) was also observed in the CPMAS spectrum with a peak around 20 ppm (not included in

Fig. 5.5). This peak was very small in intensity and other toluene peaks could not be identified in the aromatic region, probably due to an overlap with sample signals. The solvent is probably incorporated in the crystal structure on *p*-bromo truxinic acid, as in the *ortho* and *meta* cases.

The theoretical calculation of *p*-bromo cinnamic acid was performed without the X-ray crystal structure, since no published data exist, as described in section 5.1. The obtained results agree well with the experimental observations, in average within 2 ppm apart from the carboxyl carbon and the carbon atom attached to bromine. This procedure is only possible when a full geometry optimization is performed, since the starting atomic positions are a mere guess may not be reasonable. The full optimization will yield the gas phase molecule, which can be different from the solid one, since packing effects and hydrogen bonding are not present. Whereas this method was successful in the case of the cinnamic acids simulated, for the photoproducts this procedure could not be adopted. The full geometry optimization of a non-centrosymmetric photodimer yields a centrosymmetric photodimer, which is the most stable conformation (polymorph) when no neighbor molecules are present, as adopted in the solution state. For this reason, the photoproduct molecules can only be simulated when an X-ray crystal structure is available and only the proton positions are optimized. From the experimental spectra it can be concluded, that all the bromo-photoproducts are non-centrosymmetric.

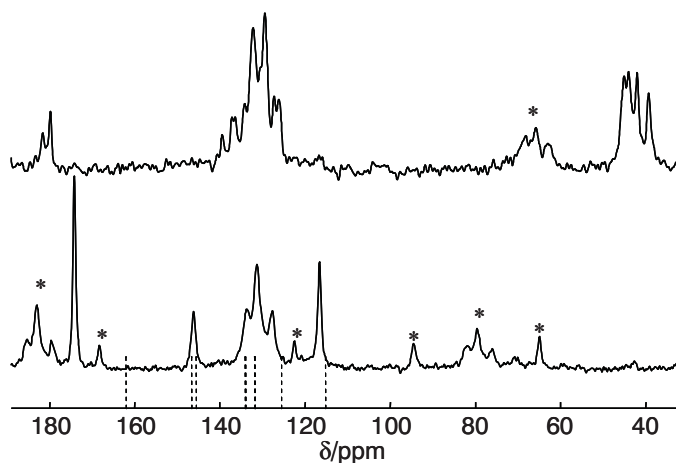


Figure 5.5 – ^{13}C CPMAS spectra of *p*-bromo cinnamic acid (bottom) and *p*-bromo truxillic acid (top). The dashed vertical lines represent the results of the Gaussian calculations. Asterisks mark spinning sidebands.

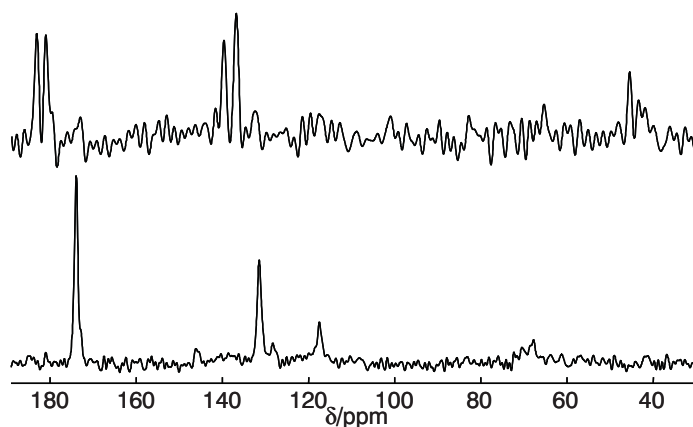


Figure 5.6 – ^{13}C CPMAS dephasing spectra of *p*-bromo cinnamic acid (bottom) and *p*-bromo truxillic acid (top). Signals of protonated carbons are still present due to partial inefficiency of the dephasing experiment.

Table 5.3 – Resonance assignments for *p*-bromo cinnamic and truxinic acids together with the values obtained from the Gaussian calculations. Numbering from Scheme 5.1

Sample	Assignment	$\delta[\text{ppm}]$	$\delta[\text{ppm}]$ theoretical
<i>p</i> -bromo cinnamic acid	C1	174	162
	C2	117	115
	C3	146	146
	C4	131	134
	C5, C6-9	128, 134	125, 132-134
	C7	128 (dephasing)	147
<i>p</i> -bromo truxinic acid	C1 C'1	182, 180	
	C2 C'2 C3 C'3	45, 42, 39	
	C4 C'4	139, 137	
	C5 C'5 C6-9 C'6-9	132, 129, 126	
	C7 C'7	Not resolved	

5.2.2 Kinetics of photoreaction

For studying the kinetics of photoreaction of the β -cinnamic acids, the *o*-, *m*-, and *p*-bromo cinnamic acid samples were irradiated and the corresponding ^{13}C CPMAS spectra can be seen in Figures 5.7, 5.9 and 5.11. The decrease of vinyl signal intensity and built-up of cyclobutane signal intensity can be followed as reaction takes place. Furthermore, the shift of certain resonances can be observed, for example the formation of two cyclobutane and

two ipso signals at higher chemical shift values in the case of the *p*-bromo cinnamic acid photoreaction. In order to obtain the kinetics curves, the ratio between the areas of vinyl and cyclobutane carbon signals is plotted versus time and the JMAK model [Joh, Avr1, Avr2, Avr3, Kol] was used to fit the curves and extract the parameters n and k , as in the previous chapters (see also section 2.4). The kinetics curve of *o*-bromo cinnamic acid is shown in Fig. 5.8, where $n = 0.79 \pm 0.11$ and $k = 0.014 \pm 0.002 \text{ min}^{-1}$. The fit parameters of *m*-bromo cinnamic acid (Fig. 5.10) curve are $n = 0.80 \pm 0.13$ and $k = 0.006 \pm 0.001 \text{ min}^{-1}$, and of *p*-bromo cinnamic acid (Fig. 5.12) are $n = 0.69 \pm 0.03$ and $k = 0.057 \pm 0.002 \text{ min}^{-1}$. For all the three samples the Avrami exponent is approximately 1, indicating a heterogenous one-dimensional linear growth with an initially fixed number of nuclei present, similar to unsubstituted β -cinnamic acid ($n = 0.89 \pm 0.11$). As already proposed for β - and *o*-methoxy cinnamic acid, exposure to UV radiation from natural light may have induced nucleation already during the crystallization. Even though the nucleation and growth mechanisms are similar for all the β -polymorphs, differences between the reaction rates are observed. For a better comparison, the three kinetic curve fits are plotted together with the one for unsubstituted β -cinnamic acid in Fig. 5.13.

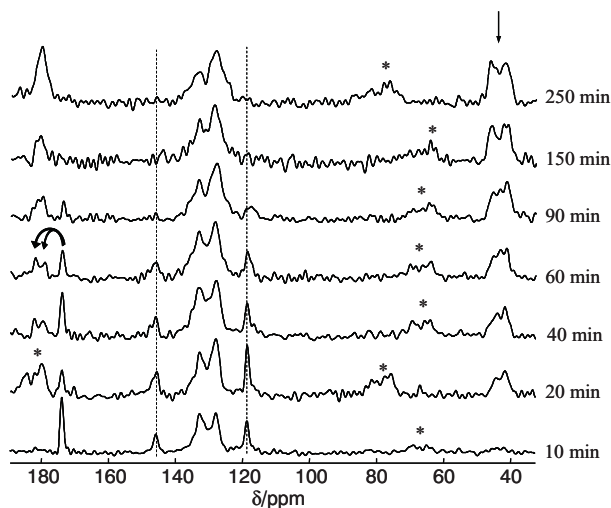


Figure 5.7 – ^{13}C CPMAS spectra of the irradiated samples of *o*-bromo cinnamic acid. The degree of conversion was calculated based on the intensity of the vinyl and cyclobutane carbon signals. The dashed lines mark the vinyl positions, the curved arrows mark the shift from one to two carboxyl signals upon photoreaction and the straight arrow indicates the cyclobutane peaks. Asterisks mark spinning sidebands.

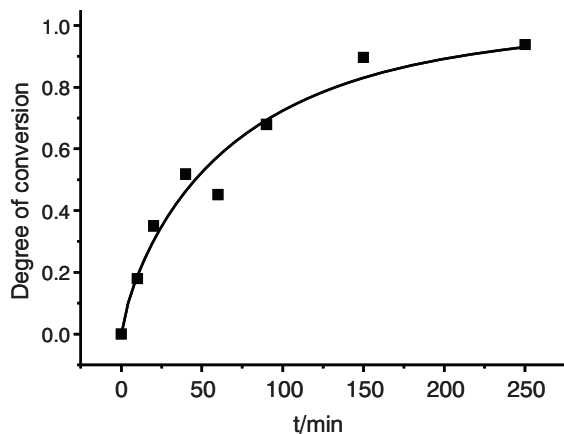


Figure 5.8 – Photodimerization kinetics of *o*-bromo cinnamic acid converting into *o*-bromo truxinic acid. The curve is the fit using the Johnson-Mehl-Avrami-Kolmogorov model with $k = 0.014 \pm 0.002 \text{ min}^{-1}$ and $n = 0.79 \pm 0.11$.

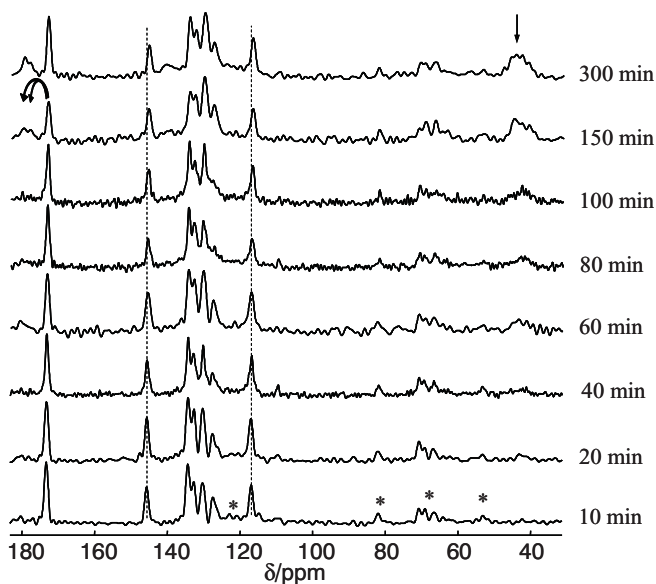


Figure 5.9 – ^{13}C CPMAS spectra of the irradiated samples of *m*-bromo cinnamic acid. The degree of conversion was calculated based on the intensity of the vinyl and cyclobutane carbon signals. The dashed lines mark the vinyl positions, the curved arrows mark the shift from one to two carboxyl signals upon photoreaction and the straight arrow indicates the cyclobutane peaks. To avoid confusion, spinning sidebands are marked with asterisks only for the first spectrum.

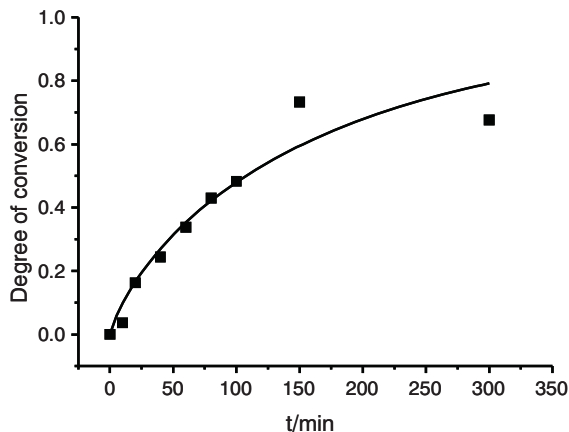


Figure 5.10 – Photodimerization kinetics of *m*-bromo cinnamic acid converting into *m*-bromo truxinic acid. The curve is the fit using the Johnson-Mehl-Avrami-Kolmogorov model with $k = 0.006 \pm 0.001 \text{ min}^{-1}$ and $n = 0.80 \pm 0.13$.

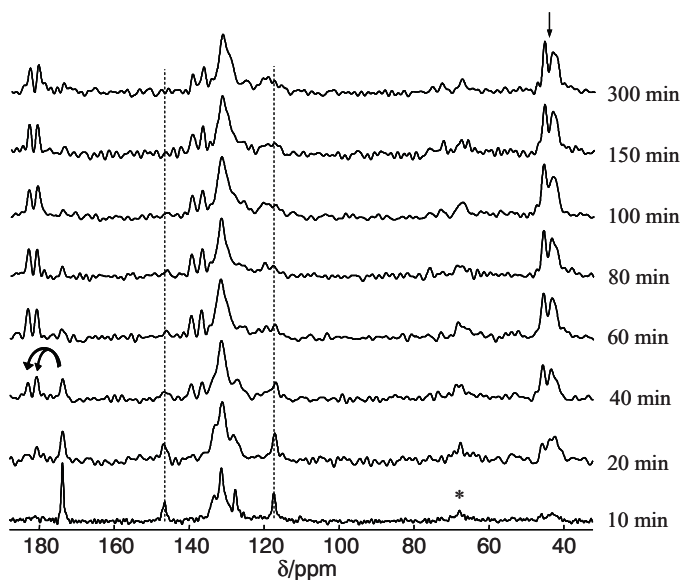


Figure 5.11 – ^{13}C CPMAS spectra of the irradiated samples of *p*-bromo cinnamic acid. The degree of conversion was calculated based on the intensity of the vinyl and cyclobutane carbon signals. The dashed lines mark the vinyl positions, the curved arrows mark the shift from one to two carboxyl signals upon photoreaction and the straight arrow indicates the cyclobutane peaks. To avoid confusion, spinning sidebands are marked with asterisks only for the first spectrum.

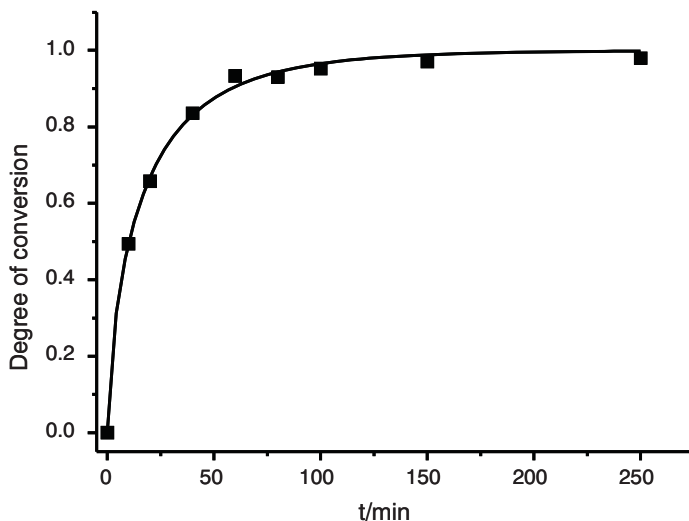


Figure 5.12 – Photodimerization kinetics of *p*-bromo cinnamic acid converting into *p*-bromo truxinic acid. The curve is the fit using the Johnson-Mehl-Avrami-Kolmogorov model with $k = 0.057 \pm 0.002 \text{ min}^{-1}$ and $n = 0.69 \pm 0.03$.

It can be observed that *o*- and *p*-bromo cinnamic acid react considerably faster than unsubstituted β -cinnamic acid, while *m*-cinnamic acid reacts the slowest. In order to investigate the reason for the observed differences, namely between the three derivatives, the solid-state UV absorption spectra of these samples were acquired. Figure 5.14 shows the UV spectra of *o*-, *m*- and *p*-bromo cinnamic acid thin films. No major differences in absorption of UV radiation between the derivatives are observed except that for *p*-bromo cinnamic acid the absorption tail starts at slightly higher wavelengths. Whereas this could contribute to some differences in kinetics behaviour of *p*-bromo cinnamic acid, it certainly is not sufficient to explain the considerable differences observed between the three derivatives.

As discussed in the previous chapters, the distance between the carbons that take part in the reaction of two parallel molecules could influence the photodimerization reaction. For *o*-bromo cinnamic acid the distance between C2 and C3 of two parallel molecules is 3.968 Å whereas for *m*-bromo cinnamic acid this distance is slightly higher 3.988 Å. Even though this could facilitate the photoreaction for *o*-bromo cinnamic acid, the differences in photoreaction are in comparison to *m*-bromo cinnamic acid still big. Since

the *p*-bromo cinnamic acid crystal structure is not available such a comparison cannot be done.

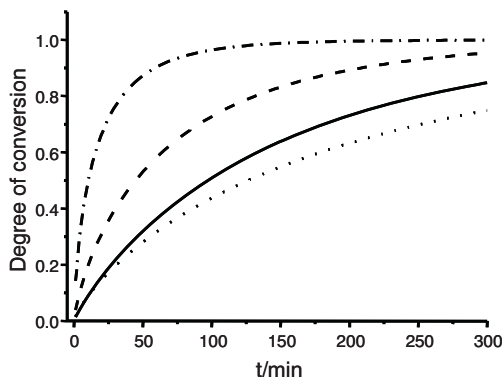


Figure 5.13 – Comparison between the fit functions of the photoreaction kinetics of β -cinnamic acid (solid curve), *o*-bromo cinnamic acid (dashed curve), *m*-bromo cinnamic acid (dotted curve), and *p*-bromo cinnamic acid (dash-dotted curve).

Another factor that could influence the kinetics of photoreaction is the crystallite size. In fact, the crystal shape and sizes of the three bromo cinnamic acids varied considerably. The *o*-bromo cinnamic acid consisted of transparent flat laths of 1-2 mm (high aspect ratio), the *m*-bromo cinnamic acid of semi-transparent cubic crystals also of 1-2 mm (with an aspect ratio close to 1), and finally the *p*-bromo cinnamic acid crystals were small white needles (<500 μm). As mentioned in the previous chapters, an influence of crystal size in the photodimerization rate has been observed for some cinnamic acid derivatives, where bigger crystals reacted slower than smaller ones. However, this was not observed in the *o*-methoxy and *o*-ethoxy systems, nor in the α - and β -polymorphs. Furthermore, β -cinnamic acid also crystallizes in thin needles, as does *p*-bromo cinnamic acid, and the α -cinnamic acid in flat laths as *o*-bromo and *o*-ethoxy cinnamic acids and the kinetics behaviour of these samples is quite different, so that a relation between crystal size and reaction rate cannot be established between different samples. Nevertheless, considering only each sample individually is it possible that a bigger crystal would take longer to fully convert. Using broad band irradiation the absorption of light is reduced to a surface layer, i. e. it does not penetrate deep into the bulk of the crystal. Once the photoreaction takes place, within this layer, there is a mismatch between the reactant and photoproduct crystal lattices. Eventually, the product lattice, concentrated at the surface of

the crystal, reaches its limit of solubility in the original lattice and the photoproduct separates from the reactant disintegrating in small crystalline particles [Enk]. Then, new cinnamic acid surfaces are exposed to light and further photoreaction can proceed. The *m*-bromo cinnamic acid crystals, being cubic, experience this effect more strongly than the thin laths or needles of the other derivatives, so that in this particular case the crystal size could have a considerable contribution for the much slower photoreaction. Nevertheless, other factors may as well contribute to the differences observed, such as the reorientation of groups near the reaction centre, as discussed in the previous chapters. Further discussion on the CSA tensor studies will be carried out below.

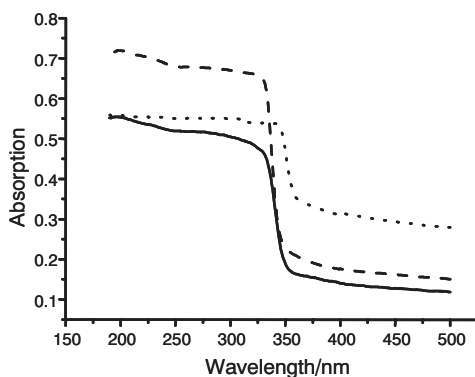


Figure 5.14 – Comparison between UV solid-state spectra of *o*-bromo cinnamic acid (solid curve), *m*-bromo cinnamic acid (dashed curve) and *p*-bromo cinnamic acid (dotted curve).

5.2.3 Chemical shift anisotropy

Changes in orientation of substituents near the reaction center upon photoreaction could help explain the different reaction kinetics of the three polymorphs. To get information about these orientational changes the chemical shift anisotropy (CSA) tensors have been analyzed using the 2D PASS sequence and the HBA software (see 2.2.3 for a more detailed description). The resulting 2D spectra along with the projection of the isotropic spectrum of *o*-bromo cinnamic acid and its photoproduct are shown in Figs. 5.12 and 5.13 and the CSA tensor values, reduced anisotropy, and asymmetry values obtained are given

in Tabs. 5.4 and 5.5 of the appendix, respectively. The theoretical CSA values *o*-bromo cinnamic acid obtained from the Gaussian simulation are also indicated in Tab. 5.4. The theoretically obtained values agree well with the experimentally obtained. The biggest difference is observed for the carboxyl carbon as discussed previously.

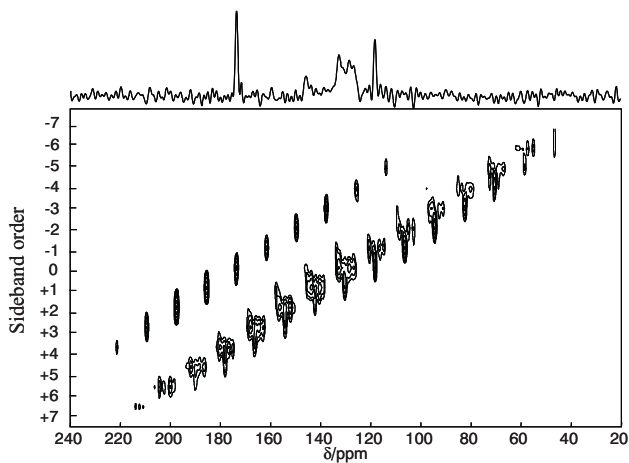


Figure 5.15 – 2D PASS of *o*-bromo cinnamic acid.

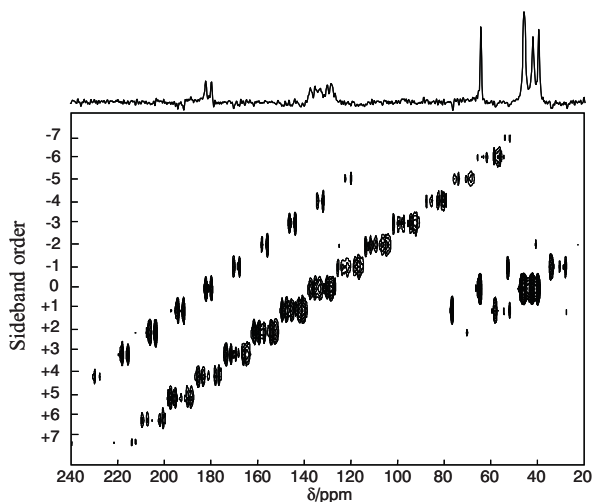


Figure 5.16 – 2D PASS of *o*-bromo truxinic acid.

The CSA tensor analysis of the carbons near to the reaction centre, i. e., carboxyl and aromatic carbons will give some insight into the orientational changes required during photoreaction. For an easier comparison, these CSA tensor values before and after photoreaction are plot together in Fig. 5.17. All the other aromatic carbons are not resolved for the photoproduct so a comparison is done considering an average of all. The changes observed are the biggest for C6 mainly due to δ_{33} . As for the carboxyl carbon, after photoreaction two signals are observed, where the isotropic chemical shifts changes are mostly due to δ_{11} .

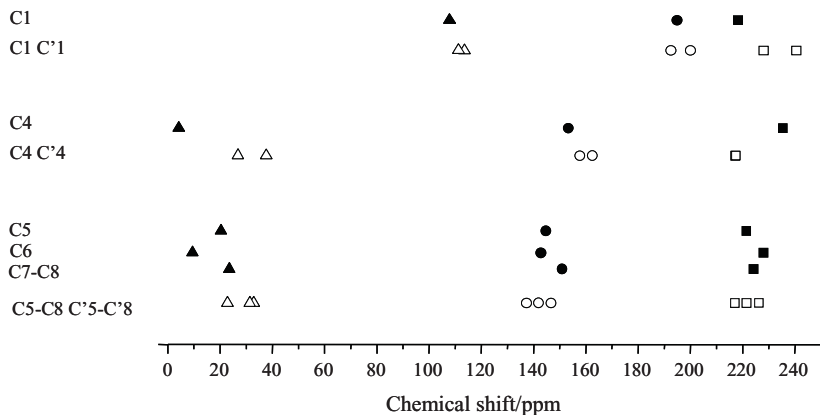


Figure 5.17 – Comparison of chemical shift tensor values of *o*-bromo cinnamic acid and *o*-bromo truxinic acid. Filled symbols refer to cinnamic acid and open symbols to truxinic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

For *m*-bromo cinnamic acid, the resulting 2D spectra along with the projection of the isotropic spectrum are shown in Figs. 5.18 and 5.19. The analysis resulted in the principal given in Tabs. 5.6 and 5.7 of the appendix for cinnamic acid and photoproduct respectively. The theoretical CSA values for *m*-bromo cinnamic acid and *m*-bromo truxinic acid obtained from the Gaussian simulation are also indicated in these tables. In the case of *m*-bromo cinnamic acid the obtained values agree quite well with the experimentally obtained ones, as seen in the other simulations. As for *m*-bromo truxinic acid the calculated isotropic chemical shifts show bigger differences to the experimental ones, as discussed above. Nevertheless, the calculated CSA values are still in reasonable agreement with the experimental ones.

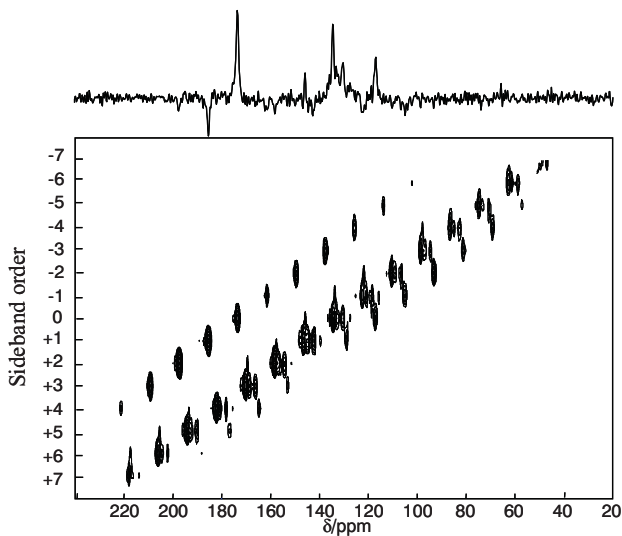


Figure 5.18 – 2D PASS of *m*-bromo cinnamic acid.

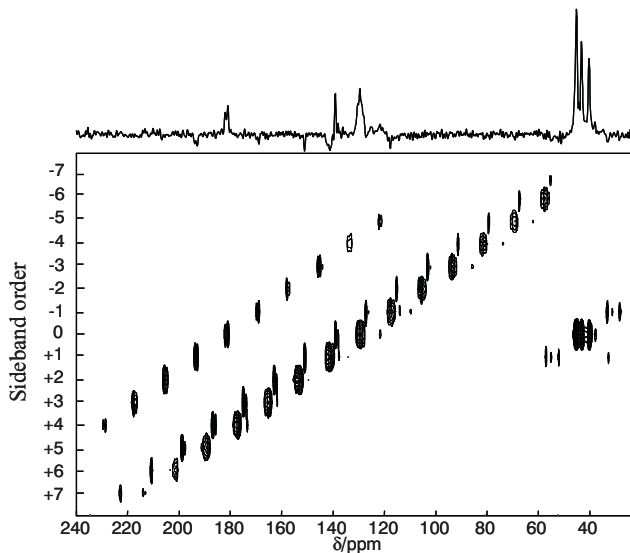


Figure 5.19 – 2D PASS of *m*-bromo truxinic acid.

The CSA tensor values of the aromatic and carboxyl carbons of the *m*-bromo cinnamic and truxinic acids are plotted together in Fig. 5.20, for an easier comparison. It

can be seen that for almost all the carbons the changes in CSA values are considerably and in all the principle tensor values. The changes observed for the *meta* photosystem, often from 20 to 30 ppm are considerably higher than the ones observed so far for other cinnamic acids, given the high number of carbons where this can be observed. Furthermore, a small change in chemical shift is not always connected to the amount of change in the CSA tensor values. This can be seen by comparing carbons C1 and C8 for example, where for carbon C1 there is bigger change in isotropic chemical shift (in fact there are two signals in the photoproduct) but much smaller in CSA tensor values.

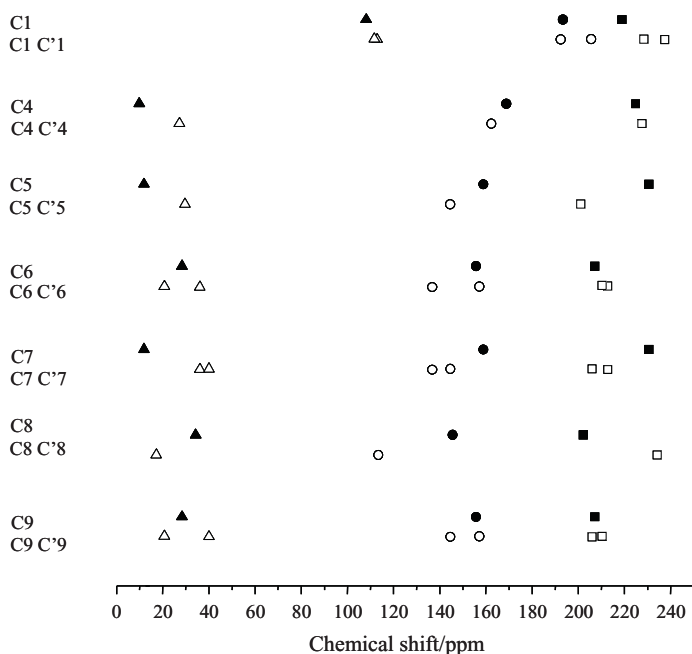


Figure 5.20 – Comparison of chemical shift tensor values of *m*-bromo cinnamic acid and *m*-bromo truxinic acid; Filled symbols refer to cinnamic acid and open symbols to truxinic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

The 2D spectra of *p*-bromo cinnamic acid and projection of the isotropic spectrum are shown in Figs. 5.21 and 5.22. The results of the sideband intensities analysis, where principal values of the chemical shift tensor as well as the reduced anisotropy and asymmetry were obtained, are given in Tabs. 5.8 and 5.9 of the appendix for cinnamic acid and photoproduct, respectively. The theoretical CSA values for *p*-bromo cinnamic acid

obtained from the Gaussian simulation are also indicated in Tab. 5.8. The theoretically obtained values for the CSA tensor still agree well with the experimentally obtained ones.

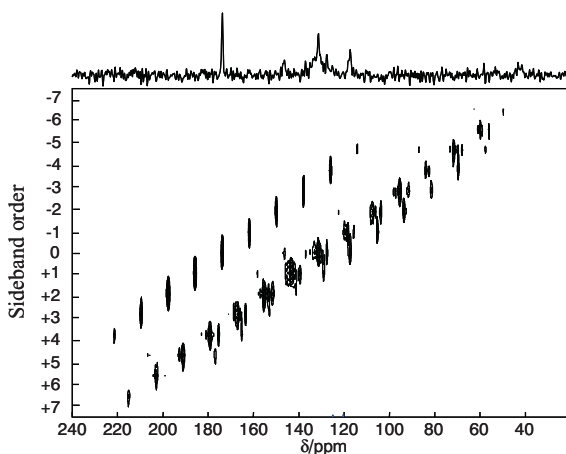


Figure 5.21 – 2D PASS of *p*-bromo cinnamic acid.

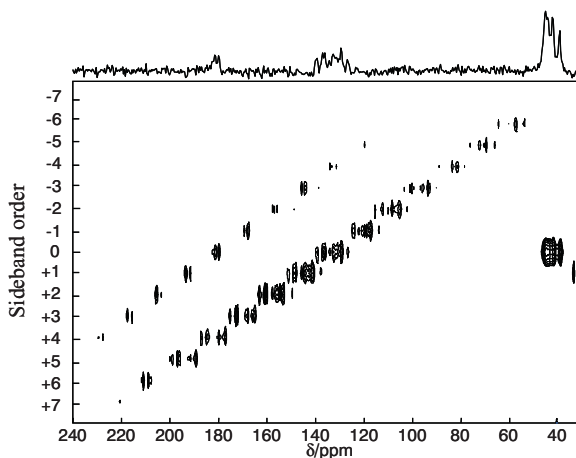


Figure 5.22 – 2D PASS of *p*-bromo truxinic acid.

Figure 5.23 compares the CSA tensor values of the carboxyl and aromatic carbons of *p*-bromo cinnamic acid and *p*-bromo truxinic acid. The biggest changes in CSA tensor values are observed for the carboxy carbon (C1) and are mostly due to changes in δ_{33} . The

ispo carbon (C4) changes are minor, and for the other aromatic carbons the changes are mostly in δ_{11} but also not very pronounced.

Overall the changes upon photoreaction of the carboxyl carbon are comparable for all the three derivatives. However, for the aromatic carbons, significantly more pronounced changes in CSA tensor and hence in orientation are observed for *m*-bromo cinnamic acid aromatic carbons. In the case of *o*- and *p*-bromo cinnamic acid the differences in CSA tensor values upon reaction was present, but smaller in comparison to *m*-bromo cinnamic acid. A comparison between *ortho* and *para* photosystems is not so straightforward in the case of carbons C5-9, because not all the correspondences are established in the *p*-bromo system. Nevertheless, for carbon C4 the differences upon photoreaction are quite bigger for the *o*-bromo system. This is consistent with the fact that *m*-bromo cinnamic acid is the one reacting slowest and *p*-bromo cinnamic acid fastest. As pointed out above, *m*-bromo cinnamic acid also has a bigger distance between reacting molecules in comparison the *o*-bromo cinnamic acid (this distance between is not available for *p*-bromo cinnamic acid), which requires a bigger reorientation of atoms (energy) for dimerization, therefore slowing down the reaction. Even though the difference in distance between the two derivatives is small, the comparatively bigger crystals (small aspect ratio) of *m*-bromo cinnamic acid slow down the reaction even more. A combined effect of different intermolecular distances and orientational changes upon photoreaction, as well as crystal sizes (for *m*-bromo cinnamic acid) could explain the different kinetic behavior observed.

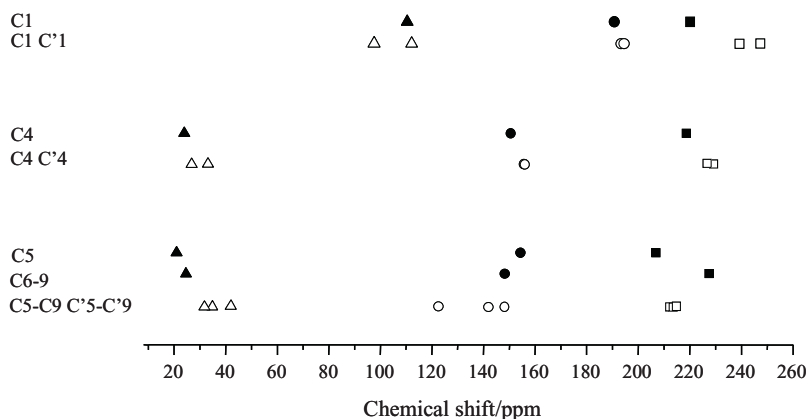


Figure 5.23 – Comparison of chemical shift tensor values comparison of *p*-bromo cinnamic acid and *p*-bromo truxinic acid; Filled symbols refer to cinnamic acid and open symbols to truxinic acid; δ_{11} is illustrated by squares, δ_{22} by circles, and δ_{33} by triangles.

5.3 ^1H High-speed MAS

5.3.1 ^1H chemical shift and intermolecular distances

Figure 5.24 shows the isotropic part of the ^1H MAS spectra of *o*-, *m*- and *p*-bromo cinnamic acid and their photodimers at a spinning speed of 30 kHz. The corresponding peak positions are summarized in Tab. 5.7. The assignment of overlapping signals was done by deconvolution of the peaks using the dmfit-Program [Mas].

Strong homonuclear dipolar couplings hinder resolution of all peaks. Nevertheless the carboxyl acid proton is well enough separated from the rest of the signals to enable a clear assignment and to resolve main connectivities (see below). The aromatic and vinyl proton signals of the cinnamic acids are strongly overlapping due to their similar isotropic chemical shifts, and deconvolution between the two signals was not possible. The two signals of the cyclobutane ring (carboxyl side and phenyl side) could be deconvoluted, even though they are still partially overlapping with the aromatic signals. Additional signals can be identified in the case of the photoproducts which cannot be assigned to the truxinic acid molecules, but to solvent molecules (as already seen from the ^{13}C spectra). Corresponding ether and toluene signals (ether: 7, 3.5 and 2.1 ppm, toluene: 7.4 to 7 and 2.3 ppm [SDBS]) can clearly be identified.

Upon photodimerization a shift of the carboxyl proton signal is observed, as seen previously for the other cinnamic acids. Furthermore, two carboxyl proton signals are present in all three photoproducts and the higher resolution of the photoproducts spectra could be an effect of the solvent. In the case of *o*-bromo truxinic acid, one of the carboxyl proton chemical shifts remains approximately unchanged and the second signal decreases in value. In the case of *m*-bromo truxinic acid both signals increase in chemical shift while for *p*-bromo truxinic acid, one of the signals slightly decreases and the other increases in chemical shift. As discussed in the previous chapters, this can be interpreted in terms of a stronger hydrogen bond if the shift is to higher ppm-values as for *o*-bromo truxinic acid or weaker hydrogen bond as in the case of *m*-bromo truxinic acid. For *p*-bromo truxinic acid one of the hydrogen bonded carboxyl groups has a slightly weaker hydrogen bond, whereas the other one is slightly stronger. The correlation between the isotropic chemical shift and the oxygen-oxygen distance was already discussed in Chapters 3 and 4, where the isotropic chemical shifts of several compounds (data taken from literature [Ber2]),

including the β -cinnamic acid derivatives are plotted versus oxygen-oxygen distance along the hydrogen bond in Fig. 3.14. As observed previously, for the cinnamic acid samples deviations from the theoretical curve are observed so a prediction of oxygen-oxygen distances based on the ^1H isotropic chemical shift is not accurate and the distances are underestimated. Nevertheless, for the β -bromo samples for which no crystal structure is available, the oxygen-oxygen distances are expected to fall within the range of the other cinnamic acid samples (260–270 pm) according to their isotropic chemical shifts. To obtain more structural information, double quantum excitation techniques are employed to indicate intra- and intermolecular connectivities as well as to correlate homonuclear dipolar couplings with structural details.

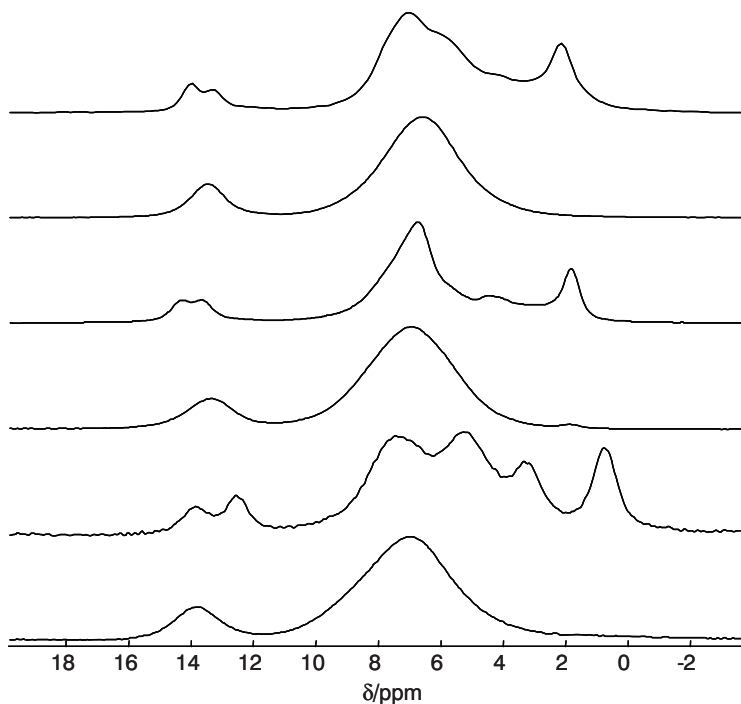


Figure 5.24 – ^1H MAS spectra at a spinning speed of 30 kHz showing the isotropic region only. Notification of samples from bottom to top: *o*-bromo cinnamic acid; *o*-bromo truxinic acid; *m*-bromo cinnamic acid; *m*-bromo truxinic acid; *p*-bromo cinnamic acid; *p*-bromo truxinic acid.

Table 5.7 – ^1H chemical shifts in the *o*-, *m*- and *p*-bromo cinnamic acid photosystems.

Sample	^1H Chemical shift		
	COOH	$\text{H}_{\text{arom}} + \text{H}_{\text{olef}}$	H_{cyclo}
<i>o</i> -bromo cinnamic acid	13.72	7.16	-
<i>o</i> -bromo truxinic acid	13.71, 12.36	7.26	3.10 ¹ , 5.04 ²
<i>m</i> -bromo cinnamic acid	13.36	6.97	-
<i>m</i> -bromo truxinic acid	14.13, 13.61	6.89	4.27 ¹ , 5.42 ²
<i>p</i> -bromo cinnamic acid	13.45	6.62	-
<i>p</i> -bromo truxinic acid	14.01, 13.28	7.13	4.98 ¹ , 5.70 ²

¹carboxyl side; ²phenyl side

5.3.2 ^1H - ^1H correlation experiments

The 2D BABA correlation spectra of *o*-bromo cinnamic acid and its photoproduct are shown in Figures 5.26 and 5.27, respectively. Some directly observable correlations are indicated by the dashed lines. In *o*-bromo cinnamic acid, the cross peaks between the carboxyl proton and the aromatics are clearly visible. This also includes the vinyl protons which are strongly overlapping with the aromatic ones, so there is no gain in resolution due to the 2D experiment. The *o*-bromo truxinic acid spectrum shows cross peaks between the two carboxyl protons and all the other signals, including the solvent signals. The aromatic and cyclobutane protons also have correlation peaks with the solvent. This is another indication that the solvent is included in the crystal structure of the photoproduct.

The 2D BABA correlation spectra of *m*-bromo cinnamic acid and its photoproduct are shown in Figs. 5.28 and 5.29, respectively. In the *m*-bromo cinnamic acid spectrum, the cross peaks between the carboxyl proton and the aromatics (including the vinyl protons) are clearly visible and well resolved. In the case of the photoproduct, *m*-bromo truxinic acid, cross peaks between the carboxyl protons and the aromatics, as well as with the signal at 2 ppm (solvent) are observed. Correlations between the carboxyl protons and the cyclobutane ones are not observed. However, there are crosspeaks between the 2 ppm signal and cyclobutane, as well as the aromatic protons.

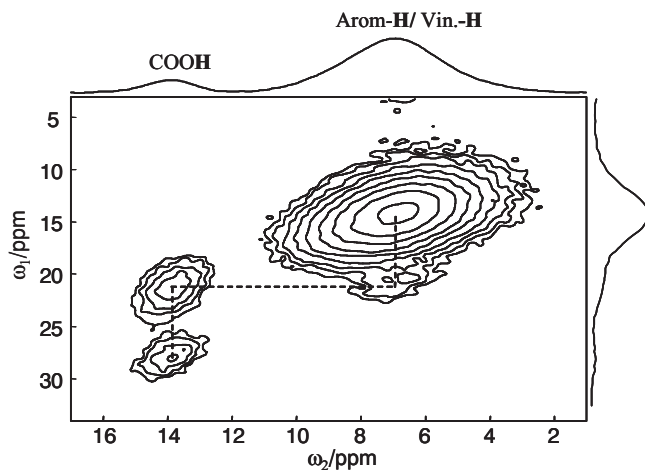


Figure 5.26 – 2D BABA of *o*-bromo cinnamic acid. General correlation peaks are indicated by dashed lines.

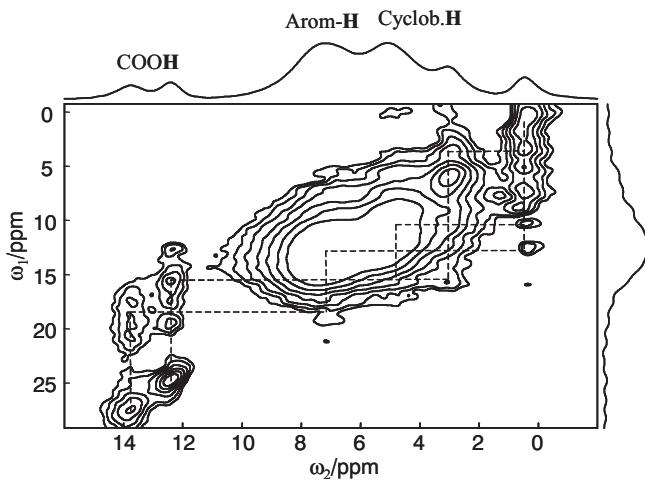


Figure 5.27 – 2D BABA of *o*-bromo truxinic acid. General correlation peaks are indicated by dashed lines.

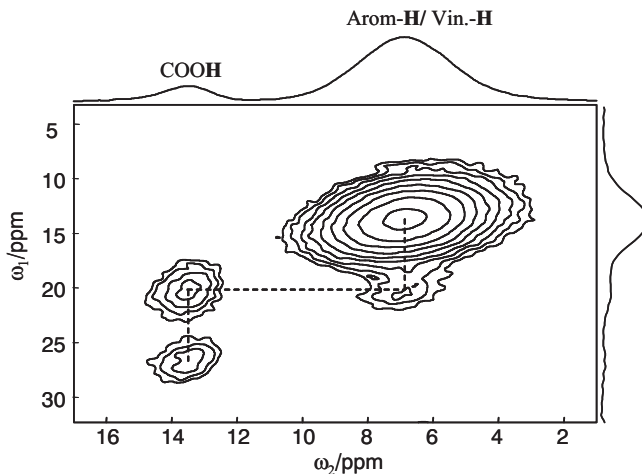


Figure 5.28 – 2D BABA of *m*-bromo cinnamic acid. General correlation peaks are indicated by dashed lines.

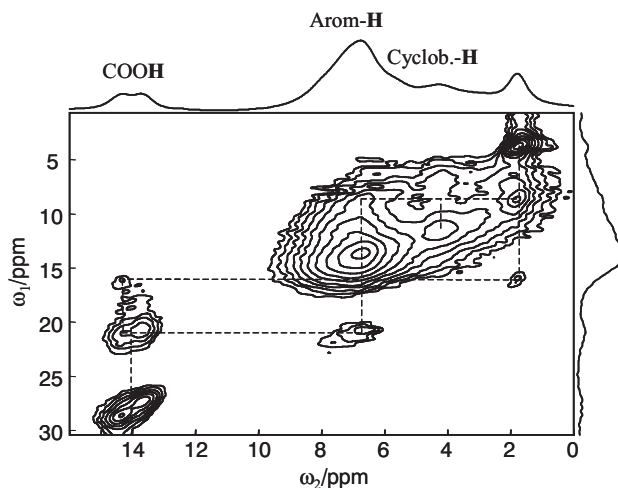


Figure 5.29 – 2D BABA of *m*-bromo truxinic acid. General correlation peaks are indicated by dashed lines.

In the case of *p*-bromo cinnamic acid and its photoproduct, the 2D BABA spectra are shown in Figs. 5.30 and 5.31, respectively. In the *p*-bromo cinnamic acid spectrum, the cross peaks between the carboxyl proton and the aromatics (including the vinyl protons) are clearly visible and well resolved, as seen for the other two derivatives. In the case of

the photoproduct, *p*-bromo truxinic acid, only cross peaks between the carboxyl protons and the aromatics protons are observed. In this case the correlations with the solvent peaks are not observed possibly due to the much broader spectrum when compared to the one of *o*- and *m*-bromo truxinic acids.

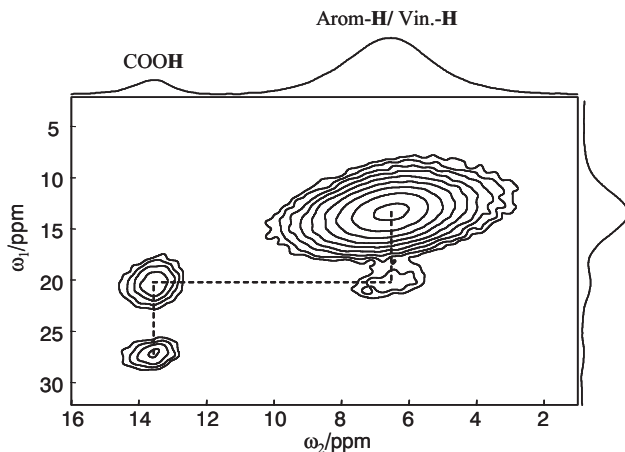


Figure 5.30 – 2D BABA of *p*-bromo cinnamic acid. General correlation peaks are indicated by dashed lines.

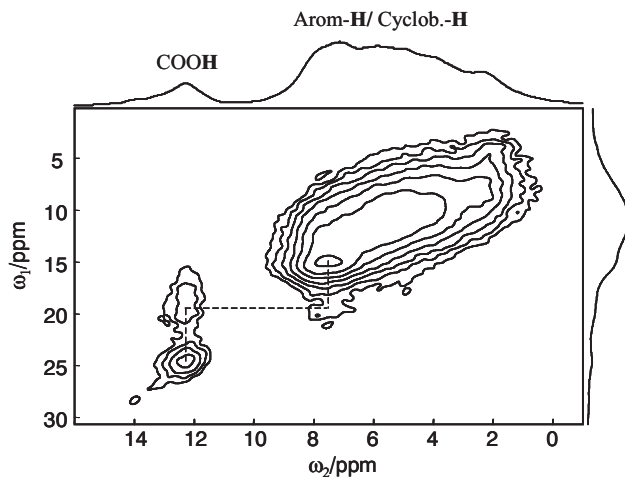


Figure 5.31 – 2D BABA of *p*-bromo truxinic acid. General correlation peaks are indicated by dashed lines.

The different F1-projections shown in Fig. 5.32 for the six samples only represent the intensity along the carboxyl proton position in the F2-dimension. The relative intensity ratios as obtained from a fit of the experimental F1-projections are 1:1.54 for *o*-bromo cinnamic acid, 1:0.9 for *o*-bromo truxinic acid, 1:1.37 for *m*-bromo cinnamic acid, 1:0.5 for *m*-bromo truxinic acid, 1:1.81 for *p*-bromo cinnamic acid, and 1:1.37 for *p*-bromo truxinic acid in terms of the carboxyl-to-other protons ratio, respectively. The calculated ratios do not account for the solvent peaks, except in the case of *p*-bromo truxinic acid, where deconvolution was not possible. Therefore, in this case the relative intensity of the other protons is higher when comparing to the *o*- and *m*-bromo photoproducts. Nevertheless, it can be observed that the intensity ratios for the photoproducts are always higher than for the reactants, meaning that the dipolar coupling between the carboxyl protons is stronger in relation to the other couplings. Since no crystal structure data exist, no definite explanation can be given. However, the presence of solvent molecules inside the crystal structure would weaken intermolecular dipolar couplings and favor carboxyl-carboxyl proton couplings. The solvent is actually in a close proximity to the truxinic acid molecules, since only protons with distances up to 0.4 nm contribute to the cross peak intensity. This was confirmed from the analysis of the second moments for the available crystal structure (Fig. 5.33), as also observed in the previous chapters.

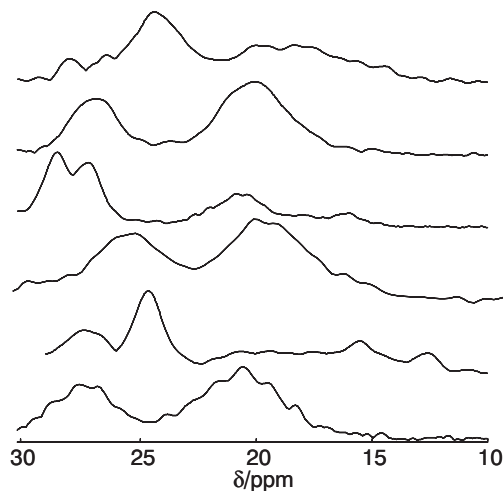


Figure 5.32 – F1-projections of the 2D BABA spectra corresponding to the carboxyl proton signal in F2. Notification of samples from bottom to top: *o*-bromo cinnamic acid; *o*-bromo truxinic acid; *m*-bromo cinnamic acid; *m*-bromo truxinic acid; *p*-bromo cinnamic acid; *p*-bromo truxinic acid.

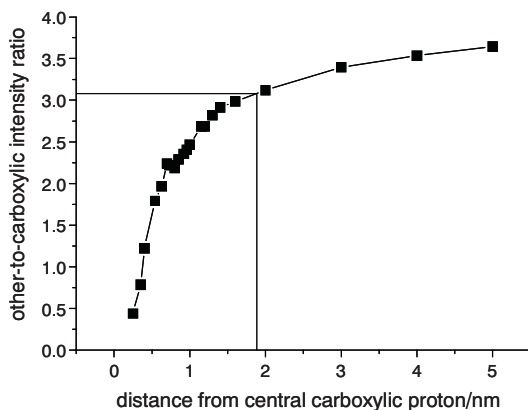


Figure 5.33 – Intensity ratio of aromatic and vinyl (other) protons relative to the carboxyl protons coupled to a central carboxyl proton as a function of distance as obtained from the crystal structure of *o*-bromo cinnamic acid. The solid and dashed lines represent the experimental intensity ratios multiplied by a factor of two.

5.4 Conclusions

As already seen in the previous chapters, the distinction between the three β -bromo-cinnamic acid derivatives, as well as their photoproducts was successfully carried out using ^{13}C solid-state NMR spectra with the support of theoretical calculations. Solvent molecules were observed in all spectra of the photoproducts. The photoreaction process of the three derivatives was explained based on the JMAK model, where in the three cases the growth of initially present nuclei proceeds one-dimensionally through the crystal. The photoreaction rate was observed to decrease in the order of *para*, *ortho*, and *meta* derivatives. This could in part be explained based on the comparative CSA tensor analysis of the three derivatives before and after photoreaction. The photodimerization of *m*-bromo cinnamic acid shows more severe changes to the principal values due to reorientation of groups near the reaction centre, which slows down the reaction. The *p*-bromo cinnamic acid was the one where smallest changes to the CSA tensor values were determined and it is also the one reacting fastest. A contribution to the observed reorientations is proposed to be related to the distance between the reacting molecules. This distance is available from

the crystal structure only for *o*- and *m*-bromo cinnamic acid, so only these two can be compared. The *m*-bromo cinnamic acid has a larger distance between reacting molecules which requires a bigger movement of atoms (reorientation) for dimerization, therefore slowing down the reaction, as seen for instance in the case β - vs. α -cinnamic acid. However, the difference in distance between the two derivatives is small. Considering the crystal sizes for a particular sample, the cubic crystals (small aspect ratio) of *m*-bromo cinnamic acid slow down the reaction even more, as if they were laths or needles (high aspect ratio) as the other two derivatives. So, only a combined effect of proximity between reacting molecules and orientational changes upon photoreaction, as well as crystal sizes (for *m*-bromo cinnamic acid) can explain the different kinetics behavior observed. The information gathered shows that aromatic substitution influences the photoreaction of β -cinnamic acids, which becomes more favorable for *para* and *ortho* substitution.

The ^1H spectra of these strongly coupled systems exhibited partial resolution at high magic angle spinning speeds, allowing resolution of the ^1H isotropic chemical shift of the carboxyl protons, involved in a hydrogen bond. This permitted a comparative evaluation of the hydrogen bond strength between two molecules. Only a rough correlation between the ^1H isotropic chemical shift and the oxygen-oxygen distance was possible since the theoretical prediction underestimates the values, as observed for the cases with known crystal structures. Nevertheless, this already gives some insight into structural information, in the cases where crystal structures are not available. Additionally, the ^1H - ^1H dipolar coupling can be employed to determine connectivities in these acid dimers using double quantum excitation techniques such as back-to-back, which represent intra- and intermolecular proton-proton couplings. The results obtained indicate that solvent molecules were included in the crystal structure of the photoproducts (as already suggested by the ^{13}C CPMAS and ^1H MAS spectra) and are in close proximity to the photoproduct molecules thereby reducing intermolecular dipolar couplings to other truxinic acid molecules. Because the solvent molecules are included in the crystal structure it is not possible to remove them. It should be noted that this solvent was included into the structures when chemical separation from the reactant was performed, i. e., after irradiation of the samples. Therefore it is of no influence to the photodimerization reaction kinetics. The techniques applied proved to yield significant information about these structures.

6. Summary and outlook

Stereoselective optically activated solid-state [2+2] photodimerization reactions are potential candidates for an optical switch in molecular optical storage systems. Small and relatively simply constructed molecules that belong to this category of photodimerizations are the *trans*-cinnamic acids. Solid-state NMR has been shown to be an essential tool in the characterization of these materials, which also serve as a model for the investigation of solid-state reactions in general. The great benefit of solid-state NMR compared to other characterization techniques is the possibility to study either crystalline or amorphous materials, without changing their properties (for example by dissolution), and the variety of techniques existent for accessing structural information.

In order to evaluate the general rules that influence the photodimerization reaction of *trans*-cinnamic acids, the α - and β -polymorphs and several of their derivatives were studied. The α -polymorph derivatives were varied in substitute size at the *ortho* position, and the β in substitute position. ^{13}C CPMAS spectra and theoretical calculations produced spectra in very good agreement that allowed the identification and assignment of the cinnamic acid polymorphs, their derivatives and photoproducts. Transformation of β -cinnamic acid into α -cinnamic acid was observed to occur even at room temperature on the contrary to what was initially proposed in the literature. At room temperature the transformation occurs at a slow rate, but temperature dependent measurements showed that high temperature accelerates this transformation. The ^{13}C CPMAS spectra of the photoproducts of the β -derivatives showed the presence of residual solvent molecules, which remained after chemical separation from the reactant and could not be removed by vacuum treatment. This however, was not observed in the α -derivatives.

The investigation of the photoreaction kinetics was possible with ^{13}C CPMAS spectroscopy, since the resonances of carbons that take place in the photoreaction are well resolved. The photoreaction process was explained based on the Johnson-Mehl-Avrami-Kolmogorov model for nucleation and growth. The results on the α -cinnamic acid

derivatives indicated that substitution in the *ortho* position strongly influences the photoreaction of α -cinnamic acid. The kinetics of the reaction slowed down from the unsubstituted α -cinnamic acid to the *o*-methoxy cinnamic acid, but sped up for *o*-ethoxy cinnamic acid. Whereas the growth of initially present nuclei of *o*-methoxy cinnamic acid proceeded one-dimensionally through the crystal as for the unsubstituted case, for the *o*-ethoxy cinnamic acid the reaction took place two-dimensionally through the crystal with a decreasing nucleation rate. In the case of β -cinnamic acid and its derivatives, *o*- *m*- and *p*-bromo cinnamic acid, the growth of initially present nuclei proceeds one-dimensionally through the crystal. The photoreaction rate was observed to decrease from *para*, via the *ortho*, to the *meta* derivative. The orientational changes upon photoreaction could be studied through a comparative analysis of the CSA tensor of reactants and photoproducts, which is another powerful technique of solid-state NMR. The general trend was that more pronounced changes in orientation led to slower reaction rates. However, the kinetic behaviour was observed to depend on a combination of several factors, not only the size and substitute position, but also the distance between reacting molecules, which induce more/less pronounced orientational changes upon reaction, and the size of crystals used for irradiation.

Another part of this work was to study the effects of hydrogen bonding on structure direction in the crystal arrangement, which play an important role in the cinnamic acids. The determination of hydrogen bonds and their strength via X-ray diffraction techniques is limited due to the small mass of the hydrogen. So, these studies are complementary to X-ray diffraction studies for an exact localization of proton positions within the crystal.

High magic angle spinning speeds enabled partial resolution in ^1H spectra of the strongly coupled organic acid dimer systems. The comparison of the ^1H isotropic chemical shift of the carboxyl protons, which form a hydrogen bond between two dimers, allowed a relative evaluation of the hydrogen bond strengths between the different cinnamic acids and photoproducts. The correlation between ^1H isotropic chemical shift and oxygen-oxygen distance, as described in the literature, was observed to slightly underestimate the distances for cinnamic acids and photoproducts. Additionally, the ^1H - ^1H dipolar coupling could be efficiently employed to determine connectivities in these acid dimers using double-quantum excitation techniques (rotor and non-rotor synchronized 2D BABA), which represent intra- and intermolecular proton-proton couplings. Furthermore, for *o*-methoxy cinnamic and truxillic acid samples (short longitudinal relaxation times) the determination of the hydrogen-hydrogen distance between two hydrogen bonded

molecules was possible. For the other samples, as the implementation of this experiment was not possible due to very long measurement times (long longitudinal relaxation times), an analysis of the relative intensities of cross peaks of the 2D BABA double-quantum dimension was performed, as a semi-quantitative approach. It was observed that homonuclear spins within a distance of 0.4 to 0.6 nm contribute to the double-quantum intensities, in agreement with the literature. For the particular case of β -cinnamic acid the relative intensities of the cross peaks were not characteristic of a head-to-head arrangement indicating that transformation to the α -polymorph occurred during the long measurement at high spinning speeds which induces a temperature increase. This is corroborated by the ^{13}C CPMAS experiments showing the conversion of β - to α -cinnamic acid with temperature. For the β -derivatives the 2D experiments confirmed that the solvent molecules are included in the crystal structures of the photoproducts (as was already suggested by the ^{13}C CPMAS and ^1H MAS spectra) and are in close proximity to the truxinic acid molecules (0.4 to 0.6 nm), since they originated peaks in these double-quantum experiments.

As an outlook, further studies on different derivatives with varying crystal sizes will bring more insights into the kinetics of photoreaction and the different influence on their reaction rate. Furthermore, NMR studies on partially deuterated samples could be done for the determination of ^1H - ^1H distances because of simplification of the large spin system. The other way round, ^2H measurements can be employed to get comparative information on C-H distances. Polymers which incorporate cinnamic acid molecules as side chain together with photodimerization exhibit very interesting properties that deserve further investigation. Examples have been shown for crack healing [Chu], shape memory effects [Len], and photopatternable films for photonic materials [Tan]. Light responsive molecular crystals based on diarylethene chromophores have been recently reported [Kob] to exhibit rapid and reversible macroscopic changes in shape and size induced by ultraviolet irradiation. These materials can move microscopic objects that make them promising materials for possible light-driven actuator applications. An investigation of cinnamic acids for such purpose certainly deserves consideration as upon photoreaction a crystal lattice mismatch between reactant and photoproduct was observed, which led to disintegration of the crystal under broadband irradiation. However, tail-irradiation has been observed to preserve the integrity of the crystals while photoreaction takes places. This has been reported in the literature [Enk] and also observed by the collaborators of this project (Washington University of St. Louis, USA).

The potential of solid-state NMR to study these photosystems has been demonstrated, where different techniques have been successfully applied yielding important new information about these samples and new insights into physical rules of the solid-state [2+2] photodimerization reaction. The results obtained will support the future design of materials that, such as these, undergo a solid-state stereoselective reaction and can be potentially used for molecular optical data storage systems.

Appendix

A.1 Chemical shift anisotropy tensor tables

The CSA tensor values presented here were calculated from fitting the spinning side band intensities obtained from the 2D PASS experiment combined with the HBA program (Herzfeld-Berger analysis). The total estimated uncertainty of the obtained values is less than 10%.

Table 3.3 – CSA values of α -cinnamic acid. Numbering of carbon atoms as in Scheme 3.1 and Table 3.1. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} (theo.)	δ_{11} (theo.)	δ_{22} (theo.)	δ_{33} (theo.)	Red. Aniso. (theo.)	Asymmetry (theo.)
C1	173 (161)	220.1 (253.4)	191.2 (129.0)	104.4 (100.5)	-67.5 (92.4)	0.43 (0.31)
C2	146 (145)	236.7 (246.7)	144.7 (142.3)	55.5 (47.1)	91.0 (101.4)	0.98 (0.94)
C3	119 (117)	198.2 (201.7)	106.3 (103.8)	50.4 (44.1)	79.9 (85.2)	0.70 (0.70)
C4	134 (136)	226.2 (222.5)	159.4 (170.6)	13.2 (13.6)	-119.7 (-122.0)	0.56 (0.42)
C5	131 (133)	227.5 (228.1)	139.9 (142.7)	24.8 (27.9)	-105.9 (-105.0)	0.83 (0.81)
C6-8	129	229.2	133.0	23.8	-104.8	0.92
(C6)	(129)	(230.9)	(140.8)	(14.0)	(-114.6)	(0.79)
(C7)	(130)	(232.2)	(145.5)	(12.5)	(-117.6)	(0.74)
(C8)	(128)	(230.8)	(141.1)	(13.5)	(-115.0)	(0.78)
C9	127 (125)	213.3 (224.0)	153.5 (141.1)	13.7 (8.9)	-113.2 (-115.8)	0.53 (0.72)

Table 3.4 – CSA values of α -truxillic acid. Numbering of carbon atoms as in Scheme 3.2 and Table 3.2. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} (theo.)	δ_{11} (theo.)	δ_{22} (theo.)	δ_{33} (theo.)	Red. Aniso. (theo.)	Asymmetry (theo.)
C'1	179 172	243.2 (270.9)	186.4 (149.9)	106.2 (94.6)	-72.4 (99.1)	0.78 (0.56)
C1	182 175	246.5 (276.8)	189.9 (155.1)	110.1 (94.4)	-72.0 (101.3)	0.79 (0.60)
C2	40 (46)	58.9 (63.6)	35.6 (44.4)	26.9 (30.5)	18.4 (17.5)	0.47 (0.80)
C'2	44 (48)	60.3 (69.1)	36.4 (42.7)	36.4 (32.6)	15.9 (20.9)	0.00 (0.48)
C'3	45 (53)	69.6 (72.3)	33.4 (56.7)	33.4 (29.1)	24.1 (-23.6)	0.00 (0.66)
C3	51 (51)	66.7 (65.4)	56.5 (54.9)	29.3 (32.9)	-21.6 (-18.2)	0.47 (0.58)
C4 C'4 (C4) (C'4)	137,138 (139) (141)	234.7 (228.9) (226.3)	163.9 (171.4) (179.8)	15.6 (17.4) (17.6)	-122.5 (-121.8) (-123.6)	0.58 (0.47) (0.38)
C'5	130 129	204.7 (229.6)	159.1 (143.3)	29.0 (14.6)	-101.9 (-114.6)	0.45 (0.75)
C'6 C'8 (C'6) (C'8)	129 (128) (127.7)	219.6 (231.5) (228.8)	139.6 (140.3) (140.0)	27.4 (12.8) (14.3)	-101.5 (-115.4) (-113.4)	0.79 (0.79) (0.78)
C7-C9 C5-6 C'7 C'9 (C5) (C6) (C'7) (C'9) (C7) (C9)	125 126 (125.9) (126.2) (126.4) (126) (123) (124)	217.2 (227.3) (228.6) (227.5) (223.1) (220.5) (219.7)	132.6 (140.1) (136.3) (140.4) (127.4) (137.8) (135.2)	29.3 (10.5) (13.7) (11.3) (27.4) (10.7) (15.6)	-97.1 (-115.4) (-112.5) (-115.1) (-98.5) (-112.3) (-107.9)	0.87 (0.76) (0.82) (0.76) (0.98) (0.74) (0.78)

Table 3.5 – CSA values of β -cinnamic acid. Numbering of carbon atoms as in Scheme 3.1 and Table 3.1. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} theo.	δ_{11} theo.	δ_{22} theo.	δ_{33} theo.	Red. Aniso. theo.	Asymmetry theo.
C1	174	224.0	188.9	109.5	-64.6	0.54
(C1)	162	(250.5)	(131.2)	(104.9)	(88.3)	(0.30)
C2	146	231.3	129.2	76.9	85.5	0.61
(C2)	147	(250.5)	(146.3)	(44.5)	(103.4)	(0.98)
C3	118	212.4	100.6	41.9	94.1	0.62
(C3)	(114)	(203.3)	(102.8)	(37.0)	(88.9)	(0.74)
C4	134	225.0	149.3	26.7	-107.0	0.70
(C4)	135	(222.3)	(170.6)	(13.2)	(-122.2)	(0.42)
C5-6	127	213.8	139.2	27.4	-99.4	0.75
(C5)	(125)	(223.7)	(139.9)	(10.2)	(-114.3)	(0.73)
(C6)	(128)	(230.6)	(140.8)	(13.5)	(-114.8)	(0.78)
C7-8	128	235.3	144.2	3.6	-124.1	0.73
C7-8	129	221.9	156.5	7.1	-121.3	0.54
(C7)	(130)	(232.3)	(145.8)	(12.6)	(-117.6)	(0.74)
(C8)	(129)	(230.9)	(141.0)	(14.0)	(-114.6)	(0.78)
C9	129	238.2	111.5	38.9	108.7	0.67
(C9)	134	(228.4)	(144.4)	(27.6)	(-105.9)	(0.79)
C9	129	238.2	111.5	38.9	108.7	0.67
(C9)	134	(228.4)	(144.4)	(27.6)	(-105.9)	(0.79)

Table 3.6 – CSA values of β -truxinic acid. Numbering of carbon atoms as in Scheme 3.2 and Table 3.2. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C2	41	48.9	48.9	24.4	-16.3	0.00
C'2 C3	45	53.2	53.2	29.3	-15.9	0.00
C'3	47	64.6	48.9	27.8	-19.2	0.83
C5-C9 C'5-C'9	125	250.0	114.7	12.0	124.4	0.83
C5-C9 C'5-C'9	128	228.3	145.1	11.4	-116.9	0.71
C5-C9 C'5-C'9	131	223.9	143.7	26.4	-104.9	0.76
C4	136	233.3	156.3	17.6	-118.1	0.65
C'4	138	232.8	169.0	12.8	-125.4	0.51
C1	175	243.7	173.7	107.7	68.6	0.96
C'1	179	250.6	176.8	109.0	71.8	0.94

Table 4.3 – CSA values of *o*-methoxy cinnamic acid. Numbering of carbon atoms as in Scheme 4.1 and Table 4.1. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C1	174	231.0	185.3	105.3	-68.6	0.67
	(162)	(250.0)	(131.5)	(105.6)	(87.6)	(0.30)
C2	116	199.4	104.7	45.1	83.0	0.72
	(112)	(199.6)	(101.2)	(36.6)	(87.2)	(0.74)
C3	140	241.6	151.8	29.6	-111.4	0.81
	(140)	(250.2)	(150.7)	(20.1)	(-120.2)	(0.83)
C4	122	195.3	152.9	18.9	-103.5	0.41
	(125)	(189.6)	(162.0)	(22.5)	(-102.2)	(0.27)
C5	127	213.0	142.6	26.8	-100.7	0.70
	(126)	(223.9)	(141.1)	(12.6)	(-113.2)	(0.73)
C6	121	210.4	125.9	27.9	-93.5	0.90
	(120)	(217.6)	(128.0)	(13.3)	(-106.4)	(0.84)
C7	131	229.1	152.5	13.2	-118.4	0.65
	(131)	(233.7)	(145.2)	(15.2)	(-116.1)	(0.76)
C8	111	192.6	128.4	12.8	-98.4	0.65
	(110)	(193.8)	(124.4)	(11.1)	(-98.7)	(0.70)
C9	157	235.6	166.6	69.8	-87.5	0.79
	(158)	(230.4)	(173.7)	(70.7)	(-87.6)	(0.65)
C10	56	75.7	75.7	16.0	-39.8	0.00
	(54)	(80.6)	(71.5)	(8.6)	(-44.9)	(0.20)

Table 4.4 – CSA values of *o*-methoxy truxillic acid. Numbering of carbon atoms as in Scheme 4.1 and Table 4.1. The values from the Gaussian calculation are indicated in brackets.

carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C1 C'1	180	233.1	198.8	109.9	-70.6	0.48
C2 C'2	31	47.6	33.3	13.8	-17.7	0.80
C3 C'3	47	54.8	54.8	30.4	-16.3	0.00
C4 C'4	129	213.7	153.7	19.7	-109.3	0.55
C5-C8 C'5-C'8	127	255.7	113.9	9.8	129.2	0.80
C5-C8 C'5-C'8	120	211.0	123.4	25.3	-94.6	0.93
C5-C8 C'5-C'8	109	188.2	122.7	18.0	-91.6	0.72
C9 C'9	157	234.7	161.3	74.8	-82.1	0.89
C10 C'10	55	71.6	71.6	19.9	-34.4	0.00
C10 C'10	54	93.2	60.6	7.0	-46.6	0.70

Table 4.5 – CSA values of *o*-ethoxy cinnamic acid. Numbering of carbon atoms as in Scheme 4.1 and Table 4.2. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C1	173 (162)	228.2 (250.0)	183.8 (131.7)	107.1 (105.8)	-65.9 (87.5)	0.67 (0.30)
C2	117 (112)	195.0 (199.4)	109.3 (100.9)	45.4 (36.8)	78.4 (87.1)	0.82 (0.7)
C3	139 (140)	243.9 (250.4)	151.8 (150.8)	21.3 (20.3)	-117.7 (-120.2)	0.78 (0.83)
C4, C6	121 (124)	200.3 (189.1)	149.1 (161.8)	14.5 (22.4)	-106.8 (-102.0)	0.48 (0.27)
(C4)	(120)	(217.4)	(127.9)	(13.3)	(-106.2)	(0.84)
(C6)						
C5	129 (126)	222.4 (224.3)	151.3 (140.9)	12.4 (12.7)	-116.3 (-113.3)	0.61 (0.74)
C7	132 (131)	228.4 (233.9)	149.4 (145.0)	17.3 (15.4)	-114.4 (-116.0)	0.69 (0.76)
C8	111 (111)	193.2 (194.4)	128.8 (124.2)	10.2 (13.0)	-100.6 (-97.5)	0.64 (0.72)
C9	157 (158)	234.6 (230.2)	168.9 (173.0)	68.5 (71.2)	-88.8 (-86.9)	0.74 (0.66)
C10	64 (65)	81.3 (89.1)	81.2 (78.7)	28.6 (27.2)	-35.1 (-37.8)	0.00 (0.28)
C11	15 (17)	20.1 (31.2)	20.1 (17.7)	3.9 (2.0)	-10.8 (-15.0)	0.00 (0.90)

Table 4.6 – CSA values of *o*-ethoxy truxillic acid. Numbering of carbon atoms as in Scheme 4.1 and Table 4.2. The values from the Gaussian calculation are indicated in brackets.

carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C1 C'1	182	242.5	196.6	107.5	-74.7	0.61
C2 C'2 C3 C'3	43	56.6	42.7	28.9	13.8	1.00
C4 C'4	127	205.0	152.6	22.8	-104.0	0.50
C5-C8 C'5-C'8	130	228.8	132.5	29.2	-100.9	0.95
C5-C8 C'5-C'8	128	229.2	143.9	10.7	-117.2	0.73
C5-C8 C'5-C'8	120	217.2	131.6	9.4	-110.0	0.78
C5-C8 C'5-C'8	109	196.4	128.1	2.6	-106.4	0.64
C9 C'9	158	237.6	166.3	68.8	-88.8	0.80
C10 C'10	63	82.0	81.2	24.1	-38.3	0.02
C11 C'11	13	18.0	18.0	2.1	-10.6	0.00

Table 5.4 – CSA values of *o*-bromo cinnamic acid. Numbering of carbon atoms as in Scheme 5.1 and Table 5.1. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} (theo.)	δ_{11} (theo.)	δ_{22} (theo.)	δ_{33} (theo.)	Red. Aniso. (theo.)	Asymmetry (theo.)
C1 (C1)	177 (162)	218.2 (250.1)	194.9 (129.7)	107.8 (105.3)	-65.9 (88.4)	0.35 (0.23)
C2 (C2)	118 (117)	200.6 (204.8)	108.1 (107.1)	46.3 (39.8)	123.4 (87.6)	0.75 (0.77)
C3 (C3)	146 (145)	259.0 (252.2)	147.0 (146.9)	30.9 (35.2)	-114.7 (-109.6)	0.98 (0.96)
C4 (C4)	131 (136)	235.2 (217.0)	153.1 (167.6)	4.2 (24.5)	-126.6 (-111.9)	0.68 (0.44)
C5 (C5)	129 (128)	221.2 (224.8)	144.5 (140.4)	20.3 (17.5)	-108.4 (-110.1)	0.71 (0.77)
C6 (C6)	127 (126)	227.7 (226.9)	142.6 (139.5)	9.4 (13.3)	-117.2 (-113.3)	0.73 (0.77)
C7-8 (C7) (C8)	132 (130) (133)	224.0 (229.8) (228.2)	150.7 (143.2) (134.0)	23.4 (17.5) (38.2)	-109.3 (-112.6) (-95.2)	0.67 (0.77) (0.99)

Table 5.5 – CSA values of *o*-bromo truxinic acid. Numbering of carbon atoms as in Scheme 5.1 and Table 5.1. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C1 C'1	182	240.5	192.5	113.6	-68.6	0.70
C1 C'1	180	228.0	200.0	111.3	-68.4	0.40
C2 C3 C'2 C'3	46	64.0	44.4	29.7	17.9	0.82
C2 C3 C'2 C'3	42	58.1	34.6	34.1	15.8	0.03
C2 C3 C'2 C'3	40	56.3	31.6	31.6	16.5	0.00
C4 C'4	137	217.0	157.5	37.6	-99.7	0.60
C4 C'4	135	217.2	162.3	26.8	-108.6	0.50
C5-C9 C'5-C'9	133	226.0	141.7	32.9	-100.6	0.84
C5-C9 C'5-C'9	130	221.3	146.5	22.8	-107.4	0.70
C5-C9 C'5-C'9	128	216.8	137.1	31.3	-97.1	0.82

Table 5.6 – CSA values of *m*-bromo cinnamic acid. Numbering of carbon atoms as in Scheme 5.1 and Table 5.2. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} (theo.)	δ_{11} (theo.)	δ_{22} (theo.)	δ_{33} (theo.)	Red. Aniso. (theo.)	Asymmetry (theo.)
C1	174	218.9	193.3	108.2	-65.2	0.39
(C1)	(160)	(253.1)	(128.0)	(100.4)	(92.6)	(0.30)
C2	117	199.7	102.4	49.2	82.6	0.64
(C2)	(118)	(204.0)	(105.6)	(44.4)	(86.0)	(0.71)
C3	146	240.9	139.7	56.9	95.1	0.87
(C3)	(144)	(244.8)	(140.6)	(46.6)	(100.8)	(0.93)
C4: 134	134	224.8	168.8	9.9	-124.6	0.45
(C4: 136)	(136)	(217.0)	(167.6)	(24.5)	(-111.9)	(0.44)
C5/7	133	230.6	158.88	11.9	-121.9	0.59
(C5)	(131)	(224.0)	(142.2)	(25.8)	(-104.9)	(0.78)
(C7)	(133)	(226.6)	(138.4)	(33.5)	(-99.3)	(0.89)
C6/9	130	207.1	155.7	28.3	-102.1	0.50
(C6)	(129)	(228.9)	(141.0)	(18.4)	(-111.0)	(0.79)
(C9)	(127)	(217.9)	(133.8)	(30.2)	(-97.1)	(0.87)
C8	127	202.1	145.6	34.3	-93.0	0.61
(C8)	(145)	(225.1)	(138.5)	(70.6)	(80.4)	(0.84)

Table 5.7 – CSA values of *m*-bromo truxinic acid. Numbering of carbon atoms as in Scheme 5.1 and Table 5.2. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} (theo.)	δ_{11} (theo.)	δ_{22} (theo.)	δ_{33} (theo.)	Red. Aniso. (theo.)	Asymmetry (theo.)
C'1	182 (172)	228.4 (275.2)	205.6 (145.4)	111.7 (94.5)	-70.2 (103.5)	0.32 (0.49)
C1	181 (167)	237.5 (266.3)	192.4 (144.9)	112.9 (90.8)	-68.0 (99.0)	0.66 (0.55)
C2	40 (43)	56.3 (66.0)	42.3 (35.71)	22.0 (26.2)	-18.2 (23.3)	0.77 (0.41)
C3	43 (49)	55.7 (67.4)	43.0 (43.9)	30.7 (34.6)	12.6 (18.8)	0.97 (0.50)
C'2 C'3 (C'2) (C'3)	45 (51) (51)	62.6 (67.4) (59.0)	36.4 (52.6) (56.0)	36.4 (32.5) (37.01)	17.5 (-18.3) (-13.7)	0.00 (0.81) (0.22)
C4 C'4 (C4) (C'4)	139 (138) (140)	227.5 (225.5) (224.6)	162.3 (170.0) (176.2)	27.3 (16.9) (20.4)	-111.7 (-120.5) (-120.0)	0.58 (0.461) (0.40)
C5 C'5 (C5) (C'5)	126 (124) (125)	201.0 (220.9) (222.2)	144.5 (134.2) (127.6)	29.7 (17.8) (25.4)	-95.4 (-106.5) (-99.6)	0.59 (0.81) (0.95)
C7 C6 (C7) (C6)	128 (125) (126)	212.8 (216.1) (217.1)	136.7 (129.1) (128.4)	36.1 (30.7) (32.4)	-92.4 (-94.6) (-93.5)	0.82 (0.92) (0.95)
C8 C'8 (C8) (C'8)	122 (142) (142)	234.2 (223.9) (225.0)	113.4 (134.9) (136.2)	17.2 (66.1) (63.7)	112.6 (82.3) (83.4)	0.85 (0.84) (0.87)
C9 C'7 (C9) (C'7)	130 (127) (128)	206.0 (222.4) (221.4)	144.6 (130.0) (130.3)	40.1 (29.6) (32.0)	-90.1 (-97.7) (-95.9)	0.68 (0.94) (0.95)
C'9 C'6 (C'9) (C'6)	129 (126) (127)	210.3 (224.4) (224.3)	157.1 (137.4) (139.7)	20.8 (16.3) (16.9)	-108.6 (-109.7) (-110.0)	0.49 (0.79) (0.77)

Table 5.8 – CSA values of *p*-bromo cinnamic acid. Numbering of carbon atoms as in Scheme 5.1 and Table 5.3. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso} (theo.)	δ_{11} (theo.)	δ_{22} (theo.)	δ_{33} (theo.)	Red. Aniso. (theo.)	Asymmetry (theo.)
C1	174 (162)	220.2 (250.3)	190.7 (130.8)	110.4 (104.9)	-63.3 (88.3)	0.47 (0.29)
C2	117 (115)	203.5 (204.3)	105.2 (103.7)	43.6 (37.3)	86.0 (89.2)	0.72 (0.74)
C3	146 (146)	238.0 (248.9)	149.5 (144.6)	51.8 (43.1)	-94.7 (103.4)	0.93 (0.98)
C4	131 (134)	218.8 (218.3)	150.7 (171.0)	24.2 (12.3)	-107.0 (-121.6)	0.64 (0.40)
C5	128 (125)	207.0 (221.6)	154.5 (139.7)	21.2 (15.0)	-106.4 (-110.4)	0.49 (0.74)
C6,8,9 (C6) (C8) (C9)	134 (132) (132) (134)	227.6 (225.8) (226.2) (226.0)	148.4 (134.2) (134.3) (144.0)	24.8 (34.8) (34.7) (32.0)	-108.8 (-96.8) (-97.0) (-102.0)	0.728 (0.94) (0.95) (0.80)

Table 5.9 – CSA values of *p*-bromo truxillic acid. Numbering of carbon atoms as in Scheme 5.1 and Table 5.3. The values from the Gaussian calculation are indicated in brackets.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Red. Aniso.	Asymmetry
C1 C'1	182	239.3	193.3	112.2	-69.4	0.66
C1 C'1	180	247.3	194.5	97.6	-82.2	0.64
C2 C'2 C3 C'3	45	57.6	38.4	38.0	13.0	0.03
C2 C'2 C3 C'3	42	60.9	32.5	32.5	18.9	0.00
C2 C'2 C3 C'3	39	55.7	31.1	31.1	16.4	0.00
C4 C'4	139	229.4	155.8	33.3	-106.2	0.69
C4 C'4	137	226.9	156.2	27.0	-109.7	0.64
C5 C'5 C6-9 C'6-9	132	212.4	148.3	35.1	-96.8	0.66
C5 C'5 C6-9 C'6-9	129	213.8	142.1	32.0	-97.3	0.74
C5 C'5 C6-9 C'6-9	126	215.0	122.7	42.2	88.4	0.91

A.2 SIMPSON simulation programs

The program given in A.2.1 is the input file used to calculate the 2D BABA F1-projection of the carboxyl proton for a 6 spin system [modified from an original version provided by Dr. Robert Graf, Max-Planck-Institut für Polymerforschung, Mainz which is greatly appreciated]. In A.2.2 the input file for calculation of the non-rotor synchronized 2D BABA spinning-side band pattern of a two spin-system *o*-methoxy cinnamic acid is given.

A.2.1 Simulation of the F1-projections of the 2D-BABA experiment

```
spinsys {  
#   1   2   3   4   5   6  
# 12H1 20H9 21H1 22H8 23H8 24H3  
#  
channels 1H  
nuclei   1H 1H 1H 1H 1H 1H  
dipole 1 2 -9381.07 0 64.206 -26.322  
dipole 1 3 -7066.7 0 147.48 130.19  
dipole 2 3 -1177 0 132.98 144.4  
dipole 1 4 -5356.5 0 40.102 -87.002  
dipole 2 4 -9882.3 0 60.305 -153.86  
dipole 3 4 -814.37 0 35.058 -71.022  
dipole 1 5 -3899.9 0 67.373 97.287  
dipole 2 5 -1385.3 0 87.566 120.66  
dipole 3 5 -2078 0 29.236 73.859  
dipole 4 5 -1084.9 0 101.42 95.633  
dipole 1 6 -3234.6 0 56.158 -148.16  
dipole 2 6 -1452.8 0 78.883 -172.9  
dipole 3 6 -979.33 0 35.875 -120.14  
dipole 4 6 -7760.4 0 96.891 171.82  
dipole 5 6 -1079.2 0 82.21 -114.64  
shift 1 6.62p 0 0 0 0 0  
shift 2 0.88p 0 0 0 0 0  
shift 3 6.62p 0 0 0 0 0
```

```
shift 4 0.88p 0 0 0 0 0
shift 5 0.88p 0 0 0 0 0
shift 6 0.88p 0 0 0 0 0
}
```

```
par {
  proton_frequency    500e6
  spin_rate            30000
  variable rs         1
  variable i          1
  variable j          1
  variable rf         150000
  variable sd         2.0
  variable loops      1
  sw                  spin_rate*rs
  np                  48
  crystal_file        repl68
  gamma_angles        21
  start_operator      Inz
  detect_operator     Hz
  verbose             1101
}
```

```
proc pulseseq {} {
  global par

  matrix set 1 coherence {{1 1 0 0 0 0} {-1 -1 0 0 0 0} {1 0 1 0 0 0} {-1 0 -1 0 0 0}
{1 0 0 1 0 0} {-1 0 0 -1 0 0} {1 0 0 0 1 0} {-1 0 0 0 -1 0} {1 0 0 0 0 1} {-1 0 0 0 0 -1}}

  maxdt 1.0

  set t90 [expr 0.25e6/$par(rf)]
  set tr2 [expr 0.5e6/$par(spin_rate)-2*$t90-$par(sd)]
  set dw [expr 1e6/$par(sw)]
```

```
for {set i 0} {$i < $par(rs)} {incr i} {  
  reset [expr $i*$dw]  
  delay $dw  
  store [expr $i+2*$par(rs)]  
  
  reset [expr $i*$dw]  
  delay [expr $par(sd)/2]  
  pulse $t90 $par(rf) 0  
  delay $tr2  
  pulse $t90 $par(rf) 180  
  delay $par(sd)  
  pulse $t90 $par(rf) 90  
  delay $tr2  
  pulse $t90 $par(rf) 270  
  delay [expr $par(sd)/2]  
  store $i  
  for {set j 1} {$j < $par(loops)} {incr j} {prop $i}  
  store $i  
  
  reset [expr $i*$dw]  
  delay [expr $par(sd)/2]  
  pulse $t90 $par(rf) 45  
  delay $tr2  
  pulse $t90 $par(rf) 225  
  delay $par(sd)  
  pulse $t90 $par(rf) 135  
  delay $tr2  
  pulse $t90 $par(rf) 315  
  delay [expr $par(sd)/2]  
  store [expr $i+$par(rs)]  
  for {set j 1} {$j < $par(loops)} {incr j} {prop [expr $i+$par(rs)]}  
  store [expr $i+$par(rs)]  
}
```

```
reset
prop 0
store [expr 3*$par(rs)]
filter 1
prop 0
acq
reset
prop 0
filter 1
prop [expr $par(rs)]
acq
for {set i 1} {$i < [expr $par(np)/2]} {incr i} {
    reset
    prop [expr 3*$par(rs)]
    prop [expr (( $i-1$ ) % $par(rs))+2*$par(rs)]
    store [expr 3*$par(rs)]
    filter 1
    prop [expr  $i$  % $par(rs)]
    acq
    reset
    prop [expr 3*$par(rs)]
    filter 1
    prop [expr  $i$  % $par(rs) + $par(rs)]
    acq
}
}

proc main {} {
    global par

    set f [fsimpson]
    set g [fdup $f]
    for {set i 1} {$i < $par(np)} {incr i 2} {
```

```
    set re [findex $f $i -re]
    set im [findex $f [expr $i+1] -re]
    fsetindex $g [expr ($i+1)/2] $re $im
  }
for {set i [expr $par(np)/2+1]} {$i <= $par(np)} {incr i} { #fsetindex $g $i 0.0e0 0.0e0}
fsave $g $par(name).fid -binary
fzerofill $g 2048
faddlb $g 2000 0
fft $g
fphase $g -rp 180
fsave $g $par(name).spe -binary
funload $f
funload $g
}
```

A.2.2 Simulation of the spinning side band pattern of the non-rotor synchronized 2D-BABA experiment

```
spinsys {
  channels 1H
  nuclei 1H 1H
  dipole 1 2 -8500 0 0 0
}

par {
  proton_frequency 500e6
  spin_rate 30000
  variable rs 20
  variable i 1
  variable j 1
  variable rf 100000
  variable sd 2.0
}
```

```
variable loops      1
sw                  spin_rate*rs
np                  1024
crystal_file        rep168
gamma_angles        21
start_operator       Inz
detect_operator      Ilz
verbose              1101
}

proc pulseseq {} {
  global par

  matrix set 1 coherence {{1 1} {-1 -1}}

  maxdt 1.0

  set t90 [expr 0.25e6/$par(rf)]
  set tr2 [expr 0.5e6/$par(spin_rate)-2*$t90-$par(sd)]
  set dw [expr 1e6/$par(sw)]

  for {set i 0} {$i < $par(rs)} {incr i} {
    reset [expr $i*$dw]
    delay $dw
    store [expr $i+2*$par(rs)]

    reset [expr $i*$dw]
    delay [expr $par(sd)/2]
    pulse $t90 $par(rf) 0
    delay $tr2
    pulse $t90 $par(rf) 180
    delay $par(sd)
    pulse $t90 $par(rf) 90
    delay $tr2
```

```
pulse $t90 $par(rf) 270
delay [expr $par(sd)/2]
store $i
for {set j 1} {$j < $par(loops)} {incr j} {prop $i}
store $i

reset [expr $i*$dw]
delay [expr $par(sd)/2]
pulse $t90 $par(rf) 45
delay $tr2
pulse $t90 $par(rf) 225
delay $par(sd)
pulse $t90 $par(rf) 135
delay $tr2
pulse $t90 $par(rf) 315
delay [expr $par(sd)/2]
store [expr $i+$par(rs)]
for {set j 1} {$j < $par(loops)} {incr j} {prop [expr $i+$par(rs)]}
store [expr $i+$par(rs)]
}

reset
prop 0
store [expr 3*$par(rs)]
filter 1
prop 0
acq
reset
prop 0
filter 1
prop [expr $par(rs)]
acq
for {set i 1} {$i < [expr $par(np)/2]} {incr i} {
    reset
```

```
prop [expr 3*$par(rs)]
prop [expr (($i-1) % $par(rs))+2*$par(rs)]
store [expr 3*$par(rs)]
filter 1
prop [expr $i % $par(rs)]
acq
reset
prop [expr 3*$par(rs)]
filter 1
prop [expr $i % $par(rs) +$par(rs)]
acq
}
}
proc main {} {
    global par

    set f [fsimpson]
    set g [fdup $f]
    for {set i 1} {$i < $par(np)} {incr i 2} {
        set re [findex $f $i -re]
        set im [findex $f [expr $i+1] -re]
        fsetindex $g [expr ($i+1)/2] $re $im
    }
    for {set i [expr $par(np)/2+1]} {$i <= $par(np)} {incr i} {
        fsetindex $g $i 0.0e0 0.0e0}
    fsave $g $par(name).fid
    fzerofill $g 2048
    faddlb $g 1500 0
    fft $g
    fphase $g -rp 180
    fsave $g $par(name).spe
    funload $f
    funload $g
}
```

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