Supplementary Material (ESI) for *PCCP*

Size effects of aromatic substitution in the *ortho* position on the photodimerization kinetics of α-*trans* cinnamic acid derivatives. A solid-state NMR study

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SUPPLEMENTARY INFORMATION

Spectral assignments of *o*-methoxy and *o*-ethoxy cinnamic acid and their photodimerization products

The α-polymorph structure is characterized by the head-to-tail arrangement of the two reacting molecules (see Scheme 1). Figures S1 and S2 show the ^{13}C CPMAS spectra of *o*-methoxy cinnamic acid and its photoproduct *o*-methoxy truxillic acid, respectively. The assignments of the spectra are summarized in Table S1 together with the results from DFT calculations. In addition to the DFT calculations, assignments were verified by combining the theoretical calculations with available data of solution spectra [S1] and by spectral editing techniques such as dipolar dephasing [S2] (included in Figures S1 and S2) or short contact times CPMAS. The dipolar dephasing spectra selectively show signals of quaternary and methyl carbons. In this case, these are the ipso carbon (C4), the methyl carbon (C10), the non-protonated aromatic carbon bound to the methoxy group (C9) as well as the carboxyl carbon (C1). The assignment of the signals to these four carbons is directly evident from their chemical shifts.

For the reactant *o*-methoxy cinnamic acid, all carbon signals are well separated from each other, and the individual chemical shifts are very close to the values from measurements in solution [S1], with the exception of the carboxyl carbon (see below). The DFT calculations also reflect the experimental values relatively well. For the carboxyl carbon, a deviation of about 12 ppm is present. This shift derives from the fact that in the solid-state, the carboxyl carbon is in a strong hydrogen bond with the carboxyl group of a neighbouring cinnamic acid molecule. However, in the simulations only one molecule was taken into account. As we focus on the reaction center, and the fact that the assignment of the carboxyl carbon is unambiguous, this is sufficient for our study. For the *o*-methoxy truxillic acid (Figure S2), two signals in the aliphatic region corresponding to the cyclobutane carbons are present, and the vinylic signals for the cinnamic acid are absent. The methoxy carbon signal does not overlap with the cyclobutane carbon signals and therefore provides an unambiguous indicator of the progress of the reaction. For the other carbons, small shift differences are observed in a similar manner to that previously presented for unsubstituted cinnamic acid [S3,S4]. In particular, a downfield shift of 6 and 7 ppm for the carbons next to the reaction center, i. e., the carboxyl and ipso-carbon, respectively, is observed. The shift differences for the other aromatic carbons are smaller than 2 ppm.

There are two interesting features present in the corresponding truxillic acid spectrum. On the one hand, two cyclobutane carbon signals are observed, which is expected if the cyclobutane ring is planar. In our previous investigations of unsubstituted α-cinnamic acid [S3,S5], it was observed that the planar ring structure is metastable and tends to become a kinked 4-membered ring. Substitution of a methoxy (or an ethoxy group, see below) in the *ortho*-position seems to stabilize the planar ring in the crystal structure. On the other hand, two signals are observed for the methoxy carbon (C10/C'10). This usually occurs when two crystallographic orientations are present, but it is not clear why this should be reflected here only for this one carbon atom. There could be two orientations of the methoxy group originating from a 180 degree rotation of the phenyl ring that yields two slightly different chemical shifts for the methoxy carbon signal. A solution ^{13}C NMR spectrum (not shown) yields only one methoxy carbon signal, thereby ruling out a side product or an impurity.

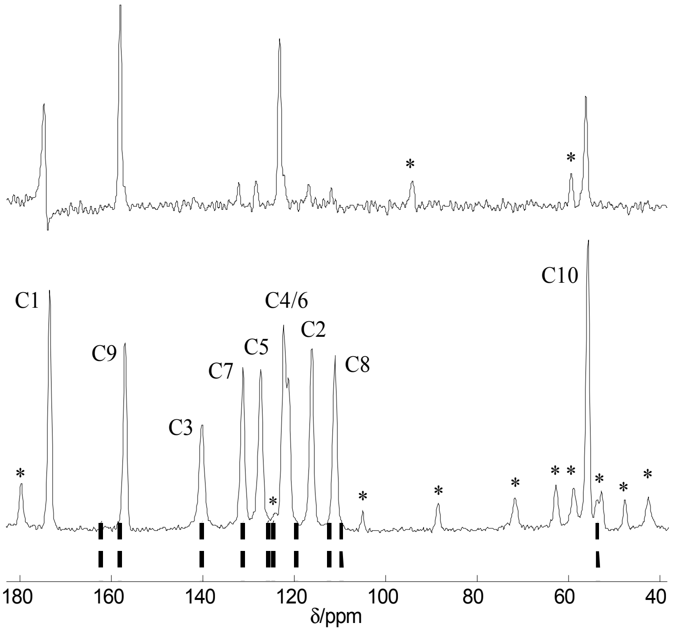

Figure S1 – ^{13}C CPMAS spectra of *o*-methoxy cinnamic acid (bottom) and the corresponding dipolar dephasing spectrum (top). Spinning sidebands are marked by asterisks. The small residual signal intensities from protonated carbons and the slight phase distortion for the peak at 174 ppm are due to partial inefficiency of the dephasing experiment. The dashed vertical lines represent the results of the Gaussian calculations.

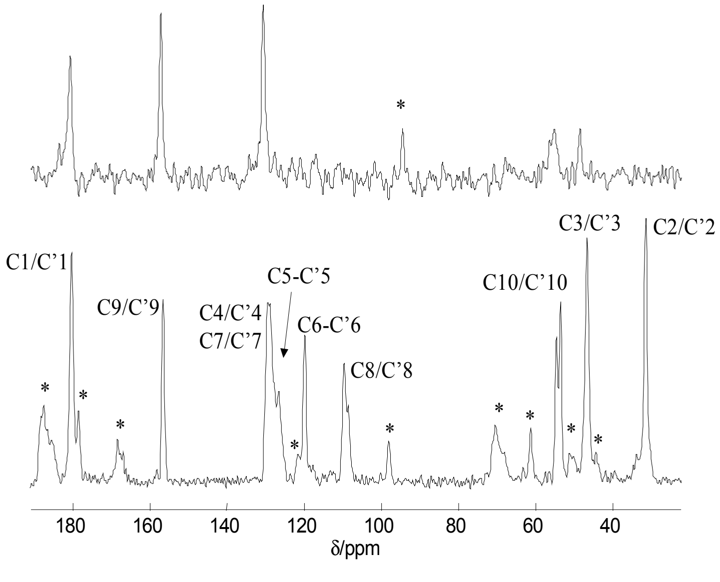

Figure S2 – ^{13}C CPMAS spectra of *o*-methoxy truxillic acid (bottom) and corresponding dipolar dephasing spectrum (top). Spinning sidebands are marked by asterisks.

Table S1 – Resonance assignments for *o*-methoxy cinnamic and truxillic acid together with values obtained from Gaussian calculations. Numbering of carbon atoms as from Scheme 1. Theoretical ppm-values are determined with higher accuracy but rounded for clarity.

Sample	**Assignment**	**δ [ppm]**	**$\delta_{theoretical}$ [ppm]**
o-methoxy-cinnamic acid	C1	174	162
	C2	116	112.5
	C3	140	140
	C4	122	125
	C5	127	126
	C6	121	120
	C7	131	131
	C8	111	110
	C9	157	158
	C10	56	54
o-methoxy-truxillic acid	C1/C’1	180	
	C2/C’2	47^{+}	
	C3/C3'	31^{+}	
	C4/C’4	129	
	C5/C’5	127^{*}	
	C6/C'6	120^{*}	
	C7/C'7	129^{*}	
	C8	109	
	C9/C’9	157	
	C10/C’10	54, 55	

$^{+}$: assignment based on chemical shift prediction

*: assignment ambiguous, based on comparison with *o*-methoxy cinnamic acid values

Figures S3 and S4 show the ^{13}C CPMAS spectra of *o*-ethoxy cinnamic acid and *o*-ethoxy truxillic acid, respectively. Due to the small structural difference to *o*-methoxy cinnamic acid, nearly identical chemical shifts are obtained for the signals of *o*-ethoxy cinnamic acid. Obviously, only the signals in the aliphatic region differ. Again, good agreement with the calculated values of the chemical shift is observed (Table S2). The similarity of the spectra of *o*-methoxy and *o*-ethoxy cinnamic acid is also reflected in that of the photoproducts. For the carboxyl carbon, the chemical shift of the *o*-ethoxy truxillic acid is shifted about 2 ppm to higher frequency. Interestingly, only one cyclobutane signal is observed in the photoproduct spectrum. That a single resonance is observed is quite unusual for 4-membered ring structures, and it might be simply a coincidence that the chemical shifts for both carbons are identical. The single resonance leads us to conclude that a planar cyclobutane ring is present.

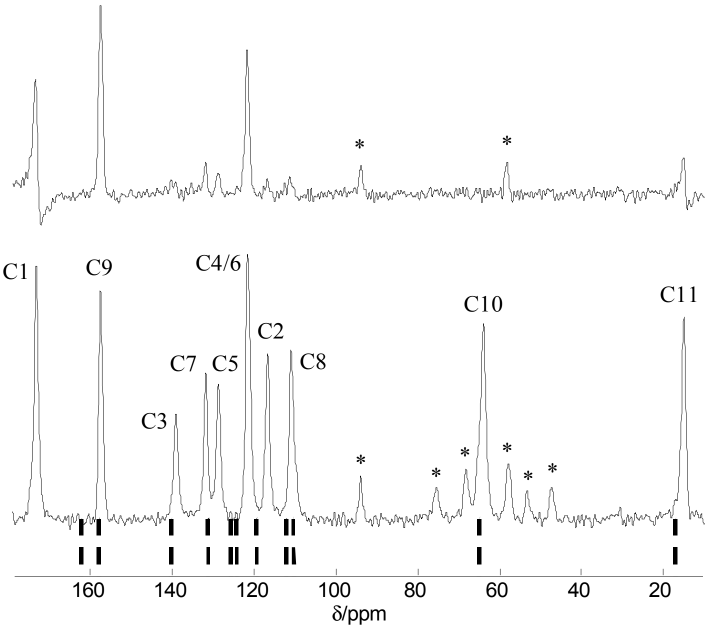

Figure S3 – ^{13}C CPMAS spectra of *o*-ethoxy cinnamic acid (bottom) and its respective dipolar dephasing spectrum (top). Spinning sidebands are marked by asterisks. The small protonated carbon signal intensities still present and the slight phase distortion for the peak at 173 ppm are due to partial inefficiency of the dephasing experiment. The dashed vertical lines represent the results of the Gaussian calculations.

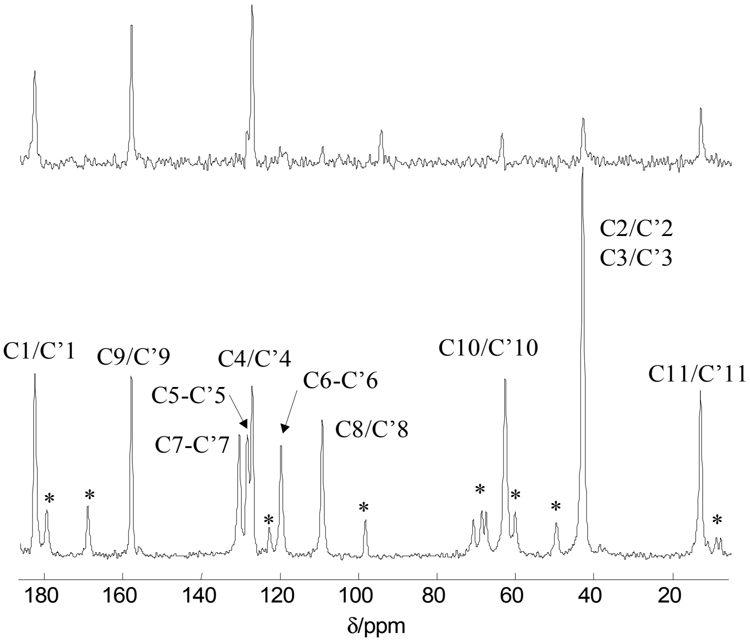

Figure S4 – ^{13}C CPMAS spectra of *o*-ethoxy truxillic acid (bottom) and respective dipolar dephasing spectrum (top). Spinning sidebands are marked by asterisks.

Table S2 – Resonance assignments for *o*-ethoxy cinnamic acid together with values obtained from Gaussian calculations. Numbering of carbon atoms follows Scheme 1.

Sample	**Assignment**	**δ [ppm]**	**$\delta_{theoretical}$ [ppm]**
o-ethoxy-cinnamic acid	C1	173	162.5
	C2	117	112
	C3	139	140.5
	C4	122	124
	C5	129	126
	C6	121	120
	C7	132	131
	C8	111	111
	C9	157	158
	C10	64	65
	C11	15	17
o-ethoxy-truxillic acid	C1/C’1	182	
	C2/C’2	43	
	C3/C’3	43	
	C4/C’4	127	
	C5/C’5	128*	
	C6/C'6	120*	
	C7/C'7	130*	
	C8	109	
	C9/C’9	158	
	C10/C’10	63	
	C11/C’11	13	

*: assignment ambiguous, based on comparison with o-ethoxy cinnamic acid values

Chemical shift anisotropy tensor values of *ortho*-substituted cinnamic and truxillic acids

Individual centerband and sideband intensities were taken from the slices of the 2D PASS spectra and fitted with the HBA software [S6]. The error for the principal tensor values δ11, δ22, and δ33 were determined by interactively varying the values for ρ and μ in the HBA software (Herzfeld-Berger convention [S7]) and with that the calculated sideband intensities which still fit the experimental ones reasonably good. For the aromatic and carboxylic carbon atoms the uncertainty of the values is on the order of 5 ppm, for the aliphatic carbons it is higher (about 10 ppm) due to low number of spinning sidebands even at the small spinning frequency of 1.5 kHz.

Table S3 – CSA values of *o*-methoxy cinnamic acid. Numbering of carbon atoms follows that of Scheme 1 and Table 1. The values from the Gaussian calculation are indicated in brackets. Values are given in ppm, except for the asymmetry parameter.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	δ_{CS}	η
C1	174 (162)	231.0 (250.0)	185.3 (131.5)	105.3 (105.6)	-68.6 (87.6)	0.67 (0.30)
C2	116 (112.5)	199.4 (199.6)	104.7 (101.2)	45.1 (36.6)	83.0 (87.2)	0.72 (0.74)
C3	140 (140)	241.6 (250.2)	151.8 (150.7)	29.6 (20.1)	-111.4 (-120.2)	0.81 (0.83)
C4	122 (125)	195.3 (189.6)	152.9 (162.0)	18.9 (22.5)	-103.5 (-102.2)	0.41 (0.27)
C5	127 (126)	213.0 (223.9)	142.6 (141.1)	26.8 (12.6)	-100.7 (-113.2)	0.70 (0.73)
C6	121 (120)	210.4 (217.6)	125.9 (128.0)	27.9 (13.3)	-93.5 (-106.4)	0.90 (0.84)
C7	131 (131)	229.1 (233.7)	152.5 (145.2)	13.2 (15.2)	-118.4 (-116.1)	0.65 (0.76)
C8	111 (110)	192.6 (193.8)	128.4 (124.4)	12.8 (11.1)	-98.4 (-98.7)	0.65 (0.70)
C9	157 (158)	235.6 (230.4)	166.6 (173.7)	69.8 (70.7)	-87.5 (-87.6)	0.79 (0.65)
C10	56 (54)	75.7 (80.6)	75.7 (71.5)	16.0 (8.6)	-39.8 (-44.9)	0.00 (0.20)

Table S4 – CSA values of *o*-methoxy truxillic acid. Numbering of carbon atoms follows that of Scheme 1 and Table 1. Values are given in ppm, except for the asymmetry parameter.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	δ_{CS}	η
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, C7/C'7*	129	213.7	153.7	19.7	-109.3	0.55
C5/C'5	127	255.7	113.9	9.8	129.2	0.80
C6/C'6	120	211.0	123.4	25.3	-94.6	0.93
C8/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
	54	93.2	60.6	7.0	46.6	0.70

*: separation of these two signals from 2D PASS spectra not possible due to signal overlap.

Table S5 – CSA values of *o*-ethoxy cinnamic acid. Numbering of carbon atoms follows that of Scheme 1 and Table 2. The values from the Gaussian calculation are indicated in brackets. Values are given in ppm, except for the asymmetry parameter.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	δ_{CS}	η
C1	173	228.2	183.8	107.1	-65.9	0.67
	(162.5)	(250.0)	(131.7)	(105.8)	(87.5)	(0.30)
C2	117	195.0	109.3	45.4	78.4	0.82
	(112)	(199.4)	(100.9)	(36.8)	(87.1)	(0.7)
C3	139	243.9	151.8	21.3	-117.7	0.78
	(140.5)	(250.4)	(150.8)	(20.3)	(-120.2)	(0.83)
C4, C6*	121	200.3	149.1	14.5	-106.8	0.48
(C4)	(124)	(189.1)	(161.8)	(22.4)	(-102.0)	(0.27)
(C6)	(120)	(217.4)	(127.9)	(13.3)	(-106.2)	(0.84)
C5	129	222.4	151.3	12.4	-116.3	0.61
	(126)	(224.3)	(140.9)	(12.7)	(-113.3)	(0.74)
C7	132	228.4	149.4	17.3	-114.4	0.69
	(131)	(233.9)	(145.0)	(15.4)	(-116.0)	(0.76)
C8	111	193.2	128.8	10.2	-100.6	0.64
	(111)	(194.4)	(124.2)	(13.0)	(-97.5)	(0.72)
C9	157	234.6	168.9	68.5	-88.8	0.74
	(158)	(230.2)	(173.0)	(71.2)	(-86.9)	(0.66)
C10	64	81.3	81.2	28.6	-35.1	0.00
	(65)	(89.1)	(78.7)	(27.2)	(-37.8)	(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)

*: separation of these two signals from 2D PASS spectra not possible due to signal overlap.

Table S6 – CSA values of *o*-ethoxy truxillic acid. Numbering of carbon atoms follow that of Scheme 1 and Table 2. Values are given in ppm, except for the asymmetry parameter.

Carbon	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	δ_{CS}	η
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/C'5	128	229.2	143.9	10.7	-117.2	0.73
C6/C'6	120	217.2	131.6	9.4	-110.0	0.78
C7/C'7	130	228.8	132.5	29.2	-100.9	0.95
C8/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

*: only one signal for all cyclobutane carbons.

References Supplementary Information

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