Crystal and Molecular Structures of a Low-Melting Polymorph of Allocinnamic Acid

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Synopsis. Crystals of a polymorph of allocinnamic acid having a melting point of 58 °C are monoclinic, space group $P2_1/c$ with a=6.2508(8), b=15.524(2), c=8.5067(5) Å, β=109.295(7)°, and Z=4. The structure was solved by direct methods and refined to a final R value of 0.042 for 1321 reflections [$I>3\sigma(I)$]. The molecules form centrosymmetric dimers with two O–H···O bonds of carboxylic acid groups [O···O distance, 2.666(1) Å, O···H–O angle, 160.79°]. The plane formed by the olefin group is twisted with respect to the phenyl ring at an angle of 37.8(2)°. The high-resolution solid-state ^{13}C NMR spectra were also measured and may be useful for distinguishing polymorphs of allocinnamic acid.

Polymorphism is a fairly widespread phenomenon among organic solids.[1] Although four polymorphic forms having different melting temperatures (32, 42, 58, and 68 °C) have been reported to exist for allocinnamic acid,[2] the crystal structures were not identified until recently. In our previous paper,[3] we identified the crystal structure of a polymorph of allocinnamic acid having a melting point of 68 °C (ACA-68) and studied its molecular structure. This study was undertaken to clarify differences in the crystal and molecular structures of allocinnamic acid having a melting point of 58 °C (ACA-58) from those of ACA-68 and to evaluate the usefulness of the solid state ^{13}C NMR spectroscopy for studying the polymorphism.

Experimental

Materials. Allocinnamic acid was taken from the same batch used in our previous work.[3] Its crystallization from hexane gave crystals which melted at 58 °C. The X-ray diffraction of the resulting crystal was measured.

NMR Measurements. The ^{13}C NMR spectra of the solid and solution samples were recorded with the same spectrometer and conditions as in our previous paper.[3]

X-Ray Crystal Structure Analysis. A colorless hexagonal crystal of approximate dimensions 0.46×0.43×0.43 mm was mounted on a glass fiber for a three-dimensional intensity data collection. A preliminary examination and data collection were done on a Rigaku AFC5R diffractometer equipped with a graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) and a 12 kW rotating anode generator. The crystal data are as follows: $C_9H_8O_2$ M=148.16, Monoclinic, a=6.2508(8), b=15.524(2), c=8.5067(5) Å, β=109.295(7)°, Space group, $P2_1/c$, V=779.1(2) Å^3, F(000)=312, D_c=1.263 g cm^{-3}, Z=4, Mo $K\alpha$ radiation, λ=0.71069 Å, μ=0.83 cm^{-1}, T=296 K.

The cell constants and an orientation matrix for the data collection were obtained using 25 reflections in the range of $44.29° < 2\theta < 54.44°$. Intensity data were collected at room temperature (23 °C) with an ω–2θ scan technique to a maximum 2θ values of 55.0° [scan speed 6° min^{-1} in ω, scan range in ω, $(1.68+0.30\tan\theta)°$]. Of the 2019 reflections observed, 1859 were unique. The intensities of three reflections measured after every 150 reflections declined by 7.30%. The intensities were corrected with the decay factor. An empirical absorption correction was applied, resulting in transmission factors ranging from 0.98 to 1.00. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods. All of the calculations were done with the TEXAN crystallographic software package.[4] The atomic scattering factors were taken from the International Table for X-Ray Crystallography Vol. IV.[5] The non-hydrogen atoms were refined anisotropically. All the H-atom positions were found from a difference Fourier map and refined isotropically except for the H1 atom, which was in an ideal position (O–H=0.96 Å) and not refined. The final cycle of the full-matrix least-squares refinements were done on 1321 observed reflections ($I>3\sigma(I)$) and 128 variables, which converged (largest parameter shifts were 0.01 times its esd) to R=0.042, R_w=0.051 where $w=4F_o^2/\sigma^2(F_o^2)$, and S=2.19.[6] The maximum and minimum peaks on the final difference Fourier map correspond to 0.13 and −0.24 e Å^{-3}, respectively.

Results and Discussion

Table 1 contains the final positional and equivalent thermal parameters for non-H atoms. Interatomic distances and angles are given in Table 2. The selected torsion angles are shown in Table 3. The molecular structure and packing in the unit cell are illustrated in Figs. 1 and 2. The molecules are linked together by the O···H–O′ hydrogen bonds (a prime denotes an atom of the inverted molecule) [O1···O2′ 2.666(1) Å, O1···H1′–O2′ angle 160.79°]. The hydrogen bonds between the carboxyl groups make a centrosymmetric dimer, which

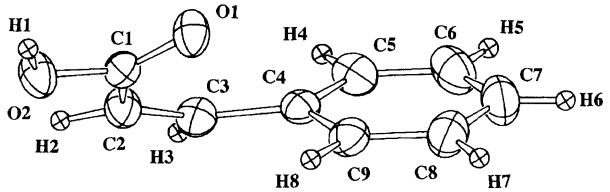

Fig. 1. A perspective view of the molecule with the atomic numbering.

Table 1. Fractional Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms

Atom	x	y	z	B_{eq}[a)]/Å^2
O1	−0.1070(2)	−0.04399(7)	0.1336(1)	4.64(5)
O2	−0.1448(2)	0.09270(7)	0.0498(1)	4.90(5)
C1	−0.1951(3)	0.0267(1)	0.1284(2)	3.72(5)
C2	−0.3743(3)	0.0475(1)	0.1979(2)	4.07(6)
C3	−0.4620(3)	−0.0024(1)	0.2287(2)	4.08(6)
C4	−0.3959(2)	−0.0863(1)	0.3691(2)	3.68(5)
C5	−0.5660(3)	−0.1408(1)	0.3834(2)	4.86(7)
C6	−0.5144(4)	−0.2174(1)	0.4684(3)	5.95(9)
C7	−0.2933(4)	−0.2404(1)	0.5447(3)	6.2(1)
C8	−0.1211(4)	−0.1871(1)	0.5338(2)	5.51(8)
C9	−0.1711(3)	−0.1107(1)	0.4463(2)	4.28(6)

a) $B_{eq}=(4/3)\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 2. Bond Lengths (Å) and Bond Angles (°)

O1–C1	1.222(2)	C4–C9	1.393(2)
O2–C1	1.317(2)	C5–C6	1.373(3)
C1–C2	1.466(2)	C6–C7	1.366(3)
C2–C3	1.333(2)	C7–C8	1.384(3)
C3–C4	1.466(2)	C8–C9	1.379(2)
C4–C5	1.395(2)		
O1–C1–O2	122.5(1)	C5–C4–C9	118.2(1)
O1–C1–C2	125.4(1)	C4–C5–C6	121.2(2)
O2–C1–C2	112.0(1)	C5–C6–C7	120.1(2)
C1–C2–C3	128.4(1)	C6–C7–C8	119.9(2)
C2–C3–C4	132.9(1)	C7–C8–C9	120.5(2)
C3–C4–C5	118.3(1)	C4–C9–C8	120.1(2)
C3–C4–C9	123.2(1)		

Table 3. Comparison of Selected Torsion Angles (°)

O1–C1–C2–C3	5.5(3)
O2–C1–C2–C3	−177.7(2)
C1–C2–C3–C4	10.0(3)
C2–C3–C4–C5	−148.7(2)
C2–C3–C4–C9	37.8(2)

is normally seen in carboxylic acids.[7)]

The carbonyl group (C1–O1) of ACA-58 is oriented towards the benzene ring as seen in molecules A and B of ACA-68.[3)] The O1 atom is placed in the *cis* conformation with respect to the C3 atom [O1–C1–C2–C3 torsion angle of ACA-58 is 5.5(3)° compared to −12.0(9)° for molecule A and −2.0(8)° for molecule B, respectively, of ACA-68]. Each of the benzene ring, the olefinic and the carboxylic acid group is essentially planar. There is a difference in the torsion angle around the C3–C4 bond between ACA-58 (−148.7(2)°) and ACA-68 (127.3(6)° for molecule A and −44.0(8)° for molecule B). If we view the molecule along the phenyl plane, the ACA-58 molecule is seen to be flatter than ACA-68. This leads to differences in the packing of the molecules. The different packing may account for a difference in densities between 1.263 g cm^{-3} for ACA-58 and 1.254 g cm^{-3} for ACA-68. The hydrogen bond is longer for ACA-58 [O1···O2′ is 2.666(1) Å for ACA-58, and O1A···O2B and O2A···O1B are 2.643(5) and 2.629(5) Å, respectively, for ACA-68].

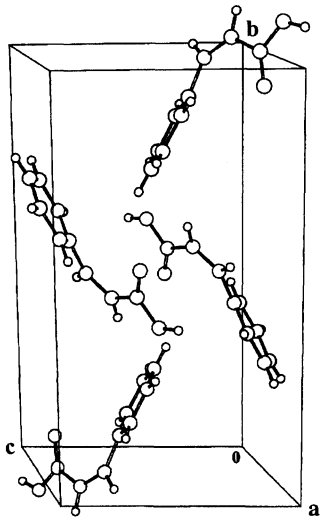

Fig. 2. Molecular packing in the unit cell.

For ACA-68, doublet features have been observed for the C2, C3, and C4 carbons in the solid state ^{13}C NMR spectra, reflecting the fact that there are two different molecules (A and B) in the asymmetric unit of the crystal. The corresponding signals for ACA-58 are observed as singlets, as shown in Fig. 3 and Table 4, in accord with the finding that the molecules form centrosym-

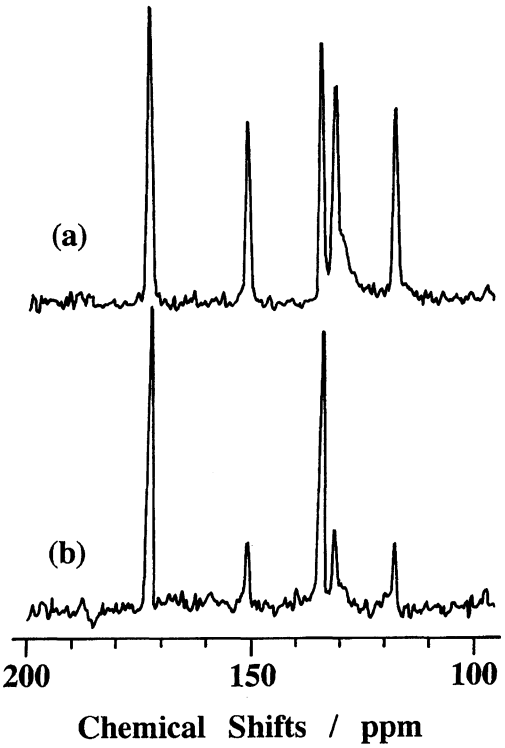

Fig. 3. Solid state ^{13}C NMR spectra of ACA-58. (a) TOSS, (b) TOSS/DD.

Table 4. ^{13}C NMR Chemical Shifts (ppm) and Assignments of ACA-58 in the Solid State

Assign.	TOSS	TOSS/DD[a)]
C1	172.8	172.7
C3	150.8	151.8*
C4	134.2	134.2
C5—C9	131.1	131.1*
	129.6	129.6*
C2	117.7	117.6*

a) Peaks denoted by asterisks reduce their intensities in the TOSS/DD mode.

metric dimers in a unit cell. The solid state ^{13}C NMR spectrum seems to be sensitive to the different molecular structures in the polymorphism. Thus, this spectroscopy could be used for distinguishing between organic polymorphs.

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