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Crystal and Molecular Structures of Allocinnamic Acid

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Synopsis. Crystals of allocinnamic acid having a melting point of 68 °C are monoclinic: space group $P2_1/n$ with $a=10.157(4)$, $b=9.798(2)$, $c=15.770(4)$ Å, $\beta=91.35(3)°$, and $Z=8$. The structure was solved by direct method and refined to a final R value of 0.059 for 3832 reflections $[I>3\sigma(I)]$. There are two independent molecules (A, B) in the asymmetric unit. The two molecules are hydrogen bonded through carboxylic acid groups [O1A···O2B 2.643(5) Å, O2A···O1B 2.629(5) Å]. Geometric differences between the two molecules are found in the torsion angle around the C(phenyl)–C(olefin) bond and the olefinic C=C bond length. In the high-resolution solid-state ^{13}C NMR spectra resonances for the C2, C3, and C4 carbons are observed as doublet features in accordance with the conformational variations observed in X-ray crystallography.

In our previous studies on the keto–enol tautomerism of phenylpyruvic acids, cinnamic and allocinnamic acids provided structural models for the enol form.[1—3] We have attempted to correlate the structures of the *trans*- and *cis*-olefinic moieties with the characteristics of the IR, Raman, and NMR spectra. In searching for literature concerning cinnamic acids, we noticed that no studies had been undertaken on the crystal structure of allocinnamic acid. Although the polymorphism of allocinnamic acid has been a subject of special interest, the conclusions seem to be controversial, as in Beilstein's Handbook.[4] Here, we repot for the first time on the X-ray crystal structure of allocinnamic acid having a melting point of 68 °C (ACA-68), and discuss its ^{13}C NMR characteristics.

Experimental

Materials. Allocinnamic acid was prepared by partial hydrogenation of phenylpropiolic acid, and purified by column chromatography on silica gel.[5] Its crystallization from hexane gave crystals which melted at 58 °C. When a small amount of the 58 °C acid was melted and cooled suddenly to 0 °C, crystals having a melting point 68 °C were obtained. A hexane solution of the 58 °C acid was seeded with the thus-obtained crystals. The resulting 68 °C crystal was used for an X-ray diffraction measurement.

NMR Measurements. The ^{13}C NMR spectra of the solid samples were recorded on a JEOL JNM-GSX 400 NMR spectrometer operating at 100.4 MHz for ^{13}C in the CPMAS mode. A TOSS (total suppression of spinning side bands) sequence was applied in order to eliminate any spinning side band. The spectra were also recorded in a combined pulse sequence of TOSS and dipolar dephasing (TOSS/DD) in order to distinguish between signals of non-hydrogen attached carbons from the others. The chemical shifts were calibrated using adamantane (29.5 ppm) as an external standard. ^{13}C NMR spectral measurement of a $CDCl_3$ solution was carried out on a JEOL JNM-EX 400 NMR spectrometer using standard pulse sequences; tetramethylsilane was used as an internal standard.

X-Ray Crystal Structure Analysis. A needle-shaped crystal of approximate dimensions (0.36×0.43×0.16 mm) was mounted on a glass capillary for a three-dimensional intensity data collection. A preliminary examination and data collection were performed on a Rigaku AFC5R diffractometer equipped with a graphite monochromated of Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) and a 12 kW rotating anode generator. The crystal data are as follows: $C_9H_8O_2$ $M=148.16$, Monoclinic, $a=10.157(4)$, $b=9.798(2)$, $c=15.770(4)$ Å, $\beta=91.35(3)°$, Space group $P2_1/n$, $V=1569.0(8)$ Å^3, $F(000)=624$, $D_c=1.25$ g cm^{-3}, $Z=8$, Mo $K\alpha$ radiation, $\lambda=0.71069$ Å, $\mu=0.83$ cm^{-1}.

The cell constants and an orientation matrix for the data collection were obtained from a least-squares refinement using the setting angles of 22 reflections in the $25.13°<2\theta<31.04°$ range.

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

Atom	x	y	z	$B_{eq}$$^{a)}$/Å^2
Molecule A				
O1	0.2215(3)	0.2339(3)	0.5304(2)	5.8(2)
O2	0.1433(4)	0.0294(3)	0.5573(3)	7.2(2)
C1	0.1401(5)	0.1596(5)	0.5645(3)	4.5(2)
C2	0.0282(5)	0.2116(5)	0.6124(3)	5.1(3)
C3	0.0102(5)	0.3388(5)	0.6380(3)	4.9(3)
C4	0.0996(4)	0.4567(4)	0.6344(3)	3.7(2)
C5	0.0556(5)	0.5772(5)	0.5976(3)	4.2(2)
C6	0.1365(7)	0.6899(5)	0.5954(4)	5.6(3)
C7	0.2603(7)	0.6847(7)	0.6310(4)	5.9(3)
C8	0.3052(6)	0.5673(7)	0.6694(4)	6.1(3)
C9	0.2254(5)	0.4530(6)	0.6711(3)	4.9(3)
Molecule B				
O1	0.3023(3)	−0.0665(3)	0.4425(2)	5.6(2)
O2	0.4099(3)	0.1296(3)	0.4375(2)	5.7(2)
C1	0.3936(5)	0.0039(5)	0.4155(3)	4.0(2)
C2	0.4878(5)	−0.0447(5)	0.3533(3)	4.4(2)
C3	0.4956(5)	−0.1686(5)	0.3173(3)	4.5(2)
C4	0.4252(4)	−0.2965(4)	0.3325(3)	3.7(2)
C5	0.4013(5)	−0.3472(5)	0.4132(3)	4.1(2)
C6	0.3437(5)	−0.4744(5)	0.4228(4)	4.8(3)
C7	0.3066(5)	−0.5502(6)	0.3529(4)	5.0(3)
C8	0.3282(5)	−0.5004(6)	0.2730(4)	5.0(3)
C9	0.3885(5)	−0.3762(6)	0.2633(4)	4.8(3)

a) $B_{eq}=(4/3)\sum_i\sum_j \beta_{ij}\,a_i\cdot a_j$.

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

	Molecule A	Molecule B		Molecule A	Molecule B
O1–C1	1.234(5)	1.239(5)	C4–C9	1.391(7)	1.386(6)
O2–C1	1.282(5)	1.290(5)	C5–C6	1.378(7)	1.387(7)
C1–C2	1.470(7)	1.466(6)	C6–C7	1.366(8)	1.374(7)
C2–C3	1.324(6)	1.343(6)	C7–C8	1.374(8)	1.373(7)
C3–C4	1.471(6)	1.465(6)	C8–C9	1.383(7)	1.373(7)
C4–C5	1.385(6)	1.392(6)			
O1–C1–O2	122.0(4)	122.1(4)	C5–C4–C9	118.7(5)	118.0(5)
O1–C1–C2	123.6(4)	123.7(4)	C4–C5–C6	120.5(5)	120.2(5)
O2–C1–C2	114.3(4)	114.1(4)	C5–C6–C7	120.3(6)	120.5(5)
C1–C2–C3	126.6(5)	128.5(5)	C6–C7–C8	120.4(6)	119.8(5)
C2–C3–C4	129.6(5)	132.1(4)	C7–C8–C9	119.9(6)	119.9(5)
C3–C4–C5	119.5(4)	123.4(4)	C4–C9–C8	120.3(5)	121.6(5)
C3–C4–C9	121.7(4)	118.4(4)			

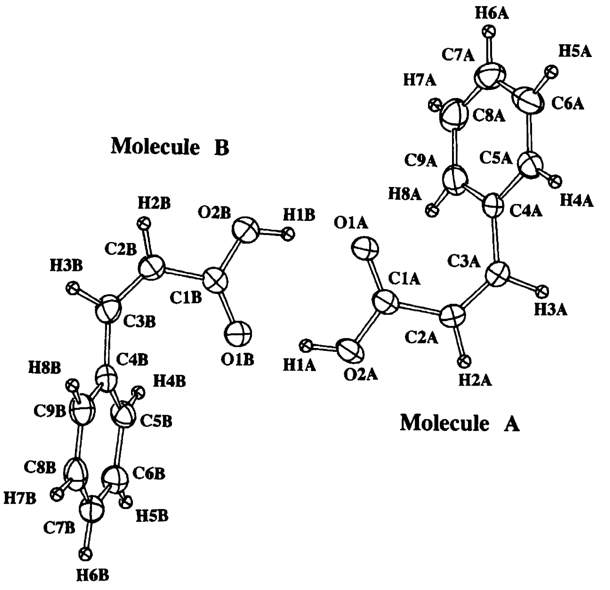

Fig. 1. A view of the two molecules of the asymmetric unit with the atom-numbering.

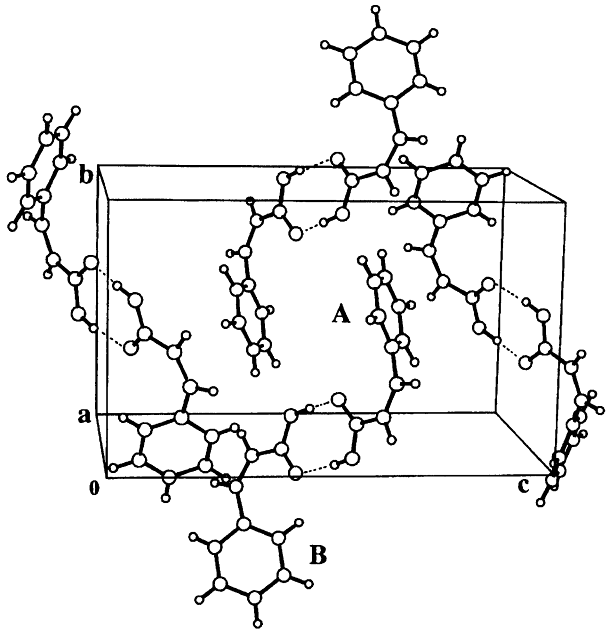

Fig. 2. Molecular packing in the unit cell. Dashed lines indicate the hydrogen bonding. O1A···O2B distance 2.643(5) Å, O1A···H–O2B angle 161(6)°, O2A···O1B distance 2.629(5), O2A–H···O1B angle 167(7)°.

Intensity data were collected at room temperature (23 °C) with a ω–2θ scan technique to a maximum 2θ value of 55.1° [scan speed, 6° min^{-1} in ω, scan range in ω, $(1.31+0.30\tan\theta)°$]. The weak reflections ($I<10.0\sigma(I)$) were rescanned (maximum of 2 rescans), and the counts were accumulated so as to assure good counting statistics. Stationary background counts were recorded on each side of the reflection.

Of the 4039 reflections observed, 3832 were unique. The intensities of three representative reflections measured after every 150 reflections declined by 22%. A linear correction factor was applied to the data in order to account for this phenomenon.

The linear absorption coefficient for Mo $K\alpha$ is 0.83 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, resulting in transmission factors ranging from 0.95 to 1.00. The data were corrected for both Lorentz and polarization effects.

The structure was solved by direct methods. All of the calculations were performed using the TEXAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. The final cycle of the full-matrix least-squares refinements were performed on 1556 observed reflections ($I>3\sigma(I)$) and 263 variables, which converged (the largest parameter shifts were 0.13 times its esd for H-atoms and 0.03 times its esd for non H-atoms) with both unweighted and weighted agreement factors:[6)]

$$R=\Sigma \mid\mid F_o \mid - \mid F_c \mid\mid / \Sigma \mid F_o \mid = 0.059$$

and

$$R_w = [(\Sigma w(\mid F_o \mid - \mid F_c \mid)^2/\Sigma w F_o^2)]^{1/2} = 0.074,$$

where $w=4F_o^2/\sigma^2(F_o^2)$.

The standard deviation of an observation of unit weight was 2.63. The weighting scheme was based on counting statistics and included a factor ($p=0.03$) in order to down-weight the intense reflections. Plots of $\Sigma w(|F_o|-|F_c|)^2$ ver-

Table 3. Comparison of ^{13}C NMR Chemical Shifts (ppm) Observed in the Solid State with Those in $CDCl_3$

Assign.	In the Solid		
	TOSS	TOSS/DD[a)]	in $CDCl_3$
C1	172.9	172.9	171.40
C3	150.4 149.6	151.1* 150.3*	145.87
C4	136.7 135.2	136.7 135.2	134.36
C5—C7	129.9 128.8	130.4* 128.7*	129.96 129.39 128.09
C2	120.5 117.9	121.2* 118.6*	118.67

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

sus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map correspond to 0.24 and −0.33 e/Å^{-3}.

Results and Discussion

The positional parameters for non-H atoms, and inter atomic distances and angles are given in Tables 1 and 2, respectively. The molecular structure and packing in the crystal are shown in Figs. 1 and 2. As shown in Fig. 2, the compound is crystallized in the monoclinic space group with eight molecules in a unit cell. There are two independent molecules (A,B) per asymmetric unit. The structure consists of an asymmetric dimer of hydrogen bonded through carboxylic acids [O1A···O2B 2.643(5) Å, O1A···H-O2B, 161(6)°, O2A···O1B 2.629 (5) Å, O2A-H···O1B, 167(7)°]. The O1 atoms of the carboxylic acids of molecules A and B are oriented in the *cis* conformation with respect to the C3 atoms. The asymmetry in the dimer is shown by the difference in the dihedral angles and the bond lengths. The plane of the carboxylic acid of molecule A is twisted by −12.0° from the plane of the olefinic moiety, whereas the corresponding planes of molecule B are nearly co-planar [O1–C1–C2–C3 is −12.1(9)° for molecule A and −1.9(8)° for molecule B]. The C3B–C4B–C5B angle is slightly larger than the C3A–C4A–C9A (123.4(4)° compared to 121.7(4)°), due to a steric interaction, which prevents the molecule from being planar. There is a marked difference in the torsion angle around the C3–C4 bond [C2A–C3A–C4A–C5A, 127.3(6)°, C2B–C3B–C4B–C5B, −44.0 (8)°]. The olefinic C2–C3 bond of molecule A is significantly shorter (1.324(6) Å) than that of molecule B (1.343(6) Å). The observed differences in the torsion angle and the bond length may be attributed to a difference in the conjugate interaction of the olefinic double bond and the benzene ring. Each of the benzene ring, the olefinic and the carboxylic group is essentially planar.

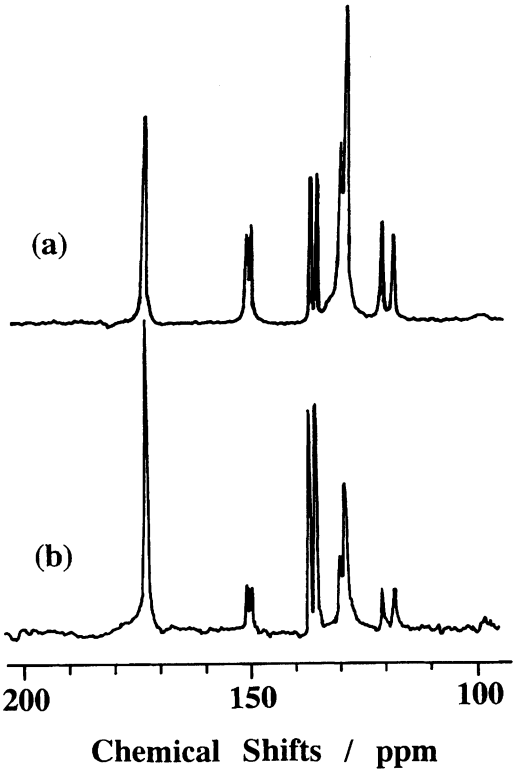

Fig. 3. Solid state ^{13}C NMR spectra of ACA-68. (a) TOSS, (b) TOSS/DD.

The solid-state ^{13}C NMR spectra of ACA-68 are shown in Fig. 3. The ^{13}C NMR chemical shifts are summarized in Table 3, together with those observed in solution. The peaks in the $CDCl_3$ solution spectrum were assigned based on the empirical chemical-shift values and the C–H COSY experiment. In accordance with the X-ray observation that there are two different molecules in a unit cell, ACA-68 exhibits doublet features for the C2, C3, and C4 carbons in the solid-state ^{13}C NMR. The assignments for the C1 and C4 carbons were confirmed by the finding that these peaks are enhanced in intensity in the TOSS/DD spectra. Work is in progress to assign to the split features to molecules A and B, and to elucidate the spectra-structure correlation.

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6) The lists of structure factors, the atomic parameters for hydrogen atoms and anisotropic thermal parameters for the non-hydrogen atoms are deposited as Document No. 67026 at the Office of the Editor of Bull. Chem. Soc. Jpn.