NOTES

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Topochemical Studies. II. The Crystal and Molecular Structure of the Second Polymorph of Chalcone, Ph-CH=CH-CO-Ph

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Crystals of chalcone are polymorphic and exist in many forms with different melting points.[1] Photochemistry of chalcone in solid state is of interest from a topochemical point of view because polymorphic modifications of this compound show significant differences in chemical behavior against ultraviolet light. Crystal structure of form I (mp 59°C) has been determined by Rabinovich,[2] the molecules are arranged in alternating layers related by the two-fold screw-axis along [001] and the shortest contact between C=C group is 5.2 Å so that crystals of this modification are light-stable. We have obtained crystals of form II and determined the crystal and molecular structure of this modification.

Experimental

The material was prepared by the condensation of benzaldehyde and acetophenone in alcoholic sodium hydroxide.[3] Crystals obtained by slow evaporation from ether solution were orthorhombic parallelepipeds elongated along the *b*-axis.

Crystal data: $C_{15}H_{12}O$; $M=208.2$; mp=56°C, orthorhombic, $a=10.90(2)$, $b=11.90(1)$, $c=17.93(1)$ Å, $V=2324.6$ Å^3, $Dm=1.179$, $Dc=1.178\ \text{g}\cdot\text{cm}^{-3}$, $Z=8$. Absorption coefficient for Cu $K\alpha$; $\mu=6.88\ \text{cm}^{-1}$. $F(000)=880$.

Systematically absent spectra: *h*0*l* when *l* odd, 0*kl* when *k* odd, *hk*0 when $h+k$ odd. Space group *Pbcn*.

Reflections were recorded with Cu$K\alpha$ radiation for the layers *h*0*l* to *h*8*l* and 0*kl* to 1*kl* by means of the equi-inclination Weissenberg technique. A total of 726 independent non-zero reflections were measured visually. Corrections for the Lorentz and polarization factors and for the spot-shape were applied.

Structure Determination and Refinement

Approximate positional parameters *y* and *z* of all the non-hydrogen atoms were obtained from a Harker section for the two-fold screw-axis along the *a*-axis. Approximate positional parameters *x* were estimated from a three-dimensional sharpened Patterson map.

Refinement was carried out by means of the block-diagonal least-squares method,[4] with anisotropic temperature factor for all the non-hydrogen atoms. The *R* index became 0.143 for all the observed reflections. A difference Fourier synthesis at this stage revealed all the hydrogen atoms. Further refinement including the hydrogen atoms with isotropic temperature factors reduced the *R* index to 0.110 for 726 observed reflections. The following weight system was adopted:

TABLE 1. ATOMIC PARAMETERS AND THEIR E.S.D.'S ($\times 10^4$) FOR NON-HYDROGEN ATOMS
Anisotropic thermal parameters are expressed as
$\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1048(7)	5176(7)	−884(4)	111(8)	114(8)	53(3)	−32(12)	5(8)	−35(8)
C(2)	531(8)	5963(7)	−1343(4)	187(12)	96(9)	60(3)	43(15)	3(11)	−10(10)
C(3)	1248(9)	6835(7)	−1655(4)	184(11)	136(9)	44(3)	19(16)	−12(10)	5(9)
C(4)	2470(9)	6886(7)	−1489(4)	184(11)	137(9)	48(3)	−19(18)	−3(11)	−17(8)
C(5)	3024(8)	6091(6)	−1012(4)	173(10)	93(8)	53(3)	−40(14)	18(10)	−22(9)
C(6)	2314(7)	5224(6)	−727(4)	155(9)	87(7)	38(2)	−3(13)	12(9)	−34(7)
C(7)	2949(7)	4411(6)	−231(4)	140(8)	97(8)	55(3)	−25(13)	−20(9)	−14(8)
C(8)	2445(7)	3543(6)	116(4)	104(8)	120(7)	44(3)	12(13)	−5(9)	−19(8)
C(9)	3224(6)	2763(7)	583(4)	105(8)	123(9)	56(3)	15(13)	3(9)	−23(9)
C(10)	2612(7)	1942(6)	1084(3)	116(8)	126(8)	31(2)	59(13)	−4(8)	−24(7)
C(11)	3350(8)	1449(8)	1633(5)	151(11)	179(11)	51(3)	82(17)	−4(10)	−16(10)
C(12)	2818(10)	678(8)	2114(4)	247(15)	179(11)	47(3)	182(21)	9(12)	29(10)
C(13)	1618(9)	337(8)	2030(5)	220(14)	145(11)	57(4)	107(19)	49(13)	18(10)
C(14)	939(9)	818(8)	1493(5)	193(12)	118(9)	60(3)	31(18)	12(11)	51(10)
C(15)	1403(7)	1605(7)	1003(4)	123(8)	134(8)	48(3)	40(14)	12(9)	1(9)
O(16)	4328(5)	2825(5)	547(4)	103(5)	178(8)	102(3)	−12(10)	−35(8)	48(9)

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1) C. Weygand, *Ann. Chem.*, **472**, 154, 174 (1929).

2) D. Rabinovich, *J. Chem. Soc.*, *B*, **1970**, 11.

3) E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Coll. Vol. I, p. 78 (1956).

4) Y. Okaya and T. Ashida, HBLS IV. The Universal Crystallographic Computing System (I), p. 65, The Crystallographic Society of Japan (1967).

Table 2. Atomic parameters and their e.s.d.'s for hydrogen atoms

Atom	x/a	y/b	z/c	B(Å^2)
H(17)	0.053(7)	0.442(6)	−0.073(4)	7.2
H(18)	−0.046(6)	0.587(5)	−0.146(3)	3.7
H(19)	0.082(6)	0.740(6)	−0.202(4)	2.7
H(20)	0.311(7)	0.748(7)	−0.174(4)	6.8
H(21)	0.399(7)	0.612(6)	−0.088(4)	4.1
H(22)	0.397(7)	0.437(6)	−0.018(4)	4.4
H(23)	0.158(7)	0.357(6)	0.008(4)	5.7
H(24)	0.416(8)	0.178(7)	0.175(4)	7.6
H(25)	0.334(7)	0.046(6)	0.247(5)	7.4
H(26)	0.140(9)	−0.035(8)	0.245(5)	10.2
H(27)	−0.008(9)	0.074(7)	0.153(5)	9.0
H(28)	0.081(7)	0.202(6)	0.058(4)	6.5

$$\sqrt{w}=14.0/F_o \qquad \text{when } F_o>14.0,$$

$$\sqrt{w}=1.0 \qquad \text{when } 14.0\geq F_o\geq 2.0$$

and

$$\sqrt{w}=0.0 \qquad \text{when } 2.0>F_o.$$

The final atomic parameters for non-hydrogen atoms and their estimated standard deviations are given in Table 1 and those for hydrogen atoms in Table 2.

The atomic scattering factors used were those of Hanson, Herman, Lea, and Skillman.[5] Computations were performed on the HITAC 5020E computer of the Computer Center of the University of Tokyo.

Results and Discussion

The average bond length of the C–C bonds in the two benzene rings is 1.386 Å. The bond lengths of the C–C single bonds between trigonal carbon atoms are 1.486, 1.511, and 1.486 Å for the C(6)–C(7), C(8)–C(9), and C(9)–C(10) bonds, respectively. They are slightly larger than the expected value 1.466 Å[6] for sp^2-sp^2 single bond. The C=C and C=O bond lengths are 1.325 and 1.208 Å respectively, which are comparable to the corresponding values, 1.319 and 1.206 Å, in form I of chalcone.[2] The average length of the C–H bonds is 1.07 Å.

The C(6)–C(7)–C(8) angle, 126.5°, is significantly greater than 120°. Similar results have been reported for several disubstituted ethylenes:[7] 127.6° for form I of chalcone[2] and 127.2° for *p*-methoxychalcone.[8] The C(1)–C(6)–C(5) angle, 120.1°, seems to be normal, although it has been pointed out[7] that a decrease in the corresponding angle is observed in the benzene ring with the –CH=CHR substituent: 118.2° in the form I of chalcone,[2] 117° in *p*-methoxychalcone[8] and 117.7° in 2,5-distyrylpyrazine.[7] In Table 3 the pertinent conformational details of form II are compared with those of form I[2] of chalcone.

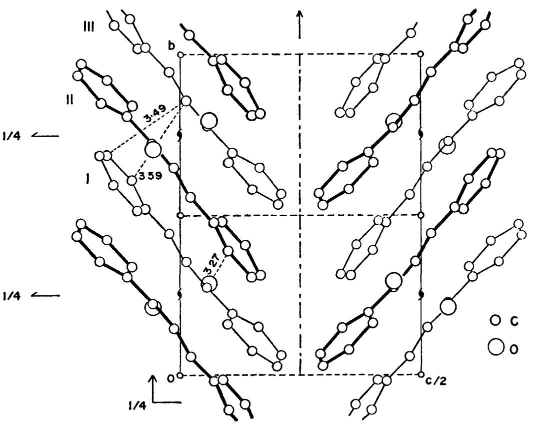

Fig. 1. Projection of the crystal structure along the *a*-axis. Short intermolecular contacts are shown by broken lines. Key for molecules I: x, y, z II: $1-x$, $1-y$, $1-z$ III: $1/2-x$, $1/2+y$, z.

The projection of the crystal structure along the *a*-axis is shown in Fig. 1 together with short intermolecular contacts. The long axis of the molecule declines by about 50° from the *a*-*c* plane and is nearly parallel to [021]. The pairs of molecules related by the *b*-glide plane are stacked along the *b*-axis. This mode of packing allows loose intermolecular contacts around the atoms C(6), C(9), and C(10); for which the C–H distances are 3.4, 3.4, and 3.6 Å, respectively. This is consistent with the fact that the density of the crystals of form II is smaller than that of form I.

The distances between neighboring ethylenic double-bonds are greater than 4.76 Å; thus the crystals of the second polymorph of chalcone might be light-stable.

Table 3. Comparison of the conformational details of the two forms of chalcone

	Form II[a]	Form I[b]
Maximum deviations of the non-hydrogen atoms from the mean molecular plane	+0.375 Å (C(12)) −0.354 Å (O(16))	+0.25 Å (C(8)) −0.20 Å (C(3))
Dihedral angle between two benzene rings	13.7°	11.1°
Rotation of the benzene ring		
C(1)—C(6) about C(6)—C(7) bond	0.6°	9.3°
C(10)—C(15) about C(9)—C(10) bond	21.6°	4.1°
Twist about C(8)—C(9) bond	9.7°	16.9°

a) This work. b) Ref. 2.

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