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Structure of 4-Bromochalcone

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Abstract. 3-(4-Bromophenyl)-1-phenyl-2-propen-1-one, C₁₅H₁₁BrO, $M_r = 287.16$, monoclinic, Cc , $a = 29.027$ (7), $b = 7.26$ (2), $c = 5.917$ (3) Å, $\beta = 101.38$ (3)°, $V = 1222$ (3) Å³, $Z = 4$, $D_x = 1.56$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 33.07$ cm⁻¹, $F(000) = 576$, $T = 296$ K, final $R = 0.058$ for 618 observed reflections with $I > 3\sigma(I)$. The structure of the title compound is non-centrosymmetric. The torsion angle O—C(3)—C(2)—C(1) of the central C₂H₂CO group is -16° . The dihedral angle between the two phenyl rings is 48.4° . The conjugated system of the molecule is disturbed.

Introduction. The title compound is a newly developed organic crystal with non-linear optical properties. The second harmonic generation (SHG) intensity of the compound, measured on a powder sample, is seven times larger than that of the urea standard (Goto, 1989). In order to explore the relationship between its structure and non-linear optical properties, we synthesized the title compound and determined its structure.

Experimental. The title compound was prepared by acyloin condensation of 4-bromobenzaldehyde with acetophenone at room temperature (Migrdichian,

1957). The crystals were obtained from ethanol solution. A colorless transparent needle crystal with approximate dimensions $2.0 \times 0.1 \times 0.1$ mm was mounted on a glass fiber in a random orientation. Preliminary examination and intensity data collection were performed on an AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell constants from 20 reflections, $18 < 2\theta < 22^\circ$. Space group determined to be Cc from systematic absences and from the absence of a center of symmetry (as required by the non-linear optical properties of the crystal). A total of 1341 reflections were collected, of which 1314 were unique. Data were collected in the range $1 < \theta < 26^\circ$ ($0 < h < 36$, $0 < k < 9$, $-7 < l < 7$) by ω - 2θ scan technique, ω -scan width $(1.5 + 0.3\tan\theta)^\circ$, scan speed $16^\circ \text{ min}^{-1}$. 631 observed reflections with $I > 3\sigma(I)$ were used for structure determination. Three standard reflections ($3\bar{3}\bar{1}$, $1\bar{2}$, $\bar{2}0$, $\bar{7}30$) were measured every 150 measurements and showed no significant intensity fluctuation. Lorentz and polarization corrections were applied. The linear absorption coefficient is 33.07 cm^{-1} for Mo $K\alpha$ radiation. DIFABS (Walker & Stuart, 1983) empirical absorption corrections were applied, yielding relative transmission coefficients ranging from 0.6394 to 1.3808.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses
$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_{ij}$$

	x	y	z	B_{eq}
Br	0	0.3070 (3)	0	4.1 (1)
O	0.2478 (5)	0.259 (2)	1.142 (2)	4.7 (8)
C(1)	0.1768 (8)	0.218 (4)	0.746 (3)	2 (1)
C(2)	0.2215 (8)	0.257 (3)	0.744 (3)	3 (1)
C(3)	0.2568 (7)	0.256 (3)	0.955 (3)	3 (1)
C(11)	0.1364 (7)	0.226 (3)	0.555 (3)	2.4 (9)
C(12)	0.1384 (6)	0.309 (3)	0.343 (3)	2.6 (9)
C(13)	0.0973 (7)	0.330 (3)	0.178 (3)	2.6 (9)
C(14)	0.0553 (6)	0.270 (3)	0.226 (4)	3 (1)
C(15)	0.0531 (6)	0.197 (3)	0.438 (2)	2.3 (8)
C(16)	0.093 (1)	0.171 (3)	0.593 (4)	2 (1)
C(21)	0.3083 (7)	0.254 (3)	0.930 (3)	3 (1)
C(22)	0.3409 (8)	0.318 (3)	1.117 (3)	3 (1)
C(23)	0.3879 (8)	0.313 (4)	1.098 (4)	5 (1)
C(24)	0.404 (1)	0.238 (4)	0.909 (5)	3 (1)
C(25)	0.3691 (7)	0.174 (3)	0.728 (3)	4 (1)
C(26)	0.321 (1)	0.184 (4)	0.741 (5)	4 (1)

Table 2. Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Br—C(14)	1.90 (2)	C(13)—C(14)	1.38 (3)
O—C(3)	1.18 (2)	C(14)—C(15)	1.37 (3)
C(1)—C(2)	1.33 (3)	C(15)—C(16)	1.34 (3)
C(1)—C(11)	1.46 (3)	C(21)—C(26)	1.34 (3)
C(2)—C(3)	1.45 (3)	C(21)—C(22)	1.39 (3)
C(3)—C(21)	1.53 (3)	C(22)—C(23)	1.39 (3)
C(11)—C(16)	1.38 (3)	C(23)—C(24)	1.41 (4)
C(11)—C(12)	1.40 (2)	C(24)—C(25)	1.40 (4)
C(12)—C(13)	1.39 (2)	C(25)—C(26)	1.43 (4)
C(2)—C(1)—C(11)	128 (2)	C(13)—C(14)—Br	118 (2)
C(1)—C(2)—C(3)	121 (2)	C(16)—C(15)—C(14)	119 (2)
O—C(3)—C(2)	124 (2)	C(15)—C(16)—C(11)	123 (2)
O—C(3)—C(21)	119 (2)	C(26)—C(21)—C(22)	123 (2)
C(2)—C(3)—C(21)	117 (2)	C(26)—C(21)—C(3)	121 (2)
C(16)—C(11)—C(12)	118 (2)	C(22)—C(21)—C(3)	116 (2)
C(16)—C(11)—C(1)	119 (2)	C(21)—C(22)—C(23)	117 (2)
C(12)—C(11)—C(1)	123 (2)	C(22)—C(23)—C(24)	124 (2)
C(13)—C(12)—C(11)	120 (2)	C(25)—C(24)—C(23)	115 (3)
C(14)—C(13)—C(12)	119 (2)	C(24)—C(25)—C(26)	121 (2)
C(15)—C(14)—C(13)	121 (2)	C(21)—C(26)—C(25)	119 (2)
C(15)—C(14)—Br	121 (1)		

All calculations were performed on a VAX computer with programs from the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). The structure was solved by direct methods using *DIRDIF* (Beurskens, 1984), the position of the Br atom being located in the *E* map. The structure was refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms, where the function minimized was $\sum w(|F_o| - |F_c|)^2$. The coordinates of H atoms were added according to theoretical models and were included in the structure-factor calculations. The final cycle of refinement included 152 variable parameters for 618 reflections with $I > 3\sigma(I)$.^{*} The final values of the discrepancy factors are $R = 0.058$, $wR = 0.066$, $S = 1.70$, $(\Delta/\sigma)_{\text{max}} = 0.04$. Maximum

^{*} Lists of H-atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54668 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0360]

Table 3. Selected least-squares planes

Plane 1	Distance (\AA)	E.s.d.			
Atoms defining plane					
C(11)	0.0057	0.0186			
C(12)	-0.0138	0.0200			
C(13)	0.0015	0.0171			
C(14)	0.0252	0.0206			
C(16)	0.0161	0.0212			
C(15)	-0.0172	0.0171			
Br	-0.0001	0.0014			
Additional atoms					
C(1)	-0.1583				
C(2)	-0.1467				
Mean deviation from plane 0.0114 \AA , $\chi^2 = 3.4$					
Plane 2					
Atoms defining plane					
C(1)	0.0414	0.0225			
C(2)	0.0159	0.0192			
C(3)	-0.0200	0.0180			
C(11)	-0.0229	0.0186			
Additional atoms					
O	-0.3065				
C(21)	0.3097				
C(12)	-0.3473				
C(13)	-0.5337				
Mean deviation from plane 0.0251 \AA , $\chi^2 = 7.4$					
Plane 3					
Atoms defining plane					
C(3)	-0.0067	0.0180			
O	0.0011	0.0139			
C(21)	0.0020	0.0188			
C(2)	0.0023	0.0192			
Additional atoms					
C(1)	-0.3016				
C(22)	0.4688				
C(26)	-0.4862				
Mean deviation from plane 0.0030 \AA , $\chi^2 = 0.2$					
Plane 4					
Atoms defining plane					
C(21)	-0.0018	0.0188			
C(22)	0.0134	0.0211			
C(23)	-0.0212	0.0256			
C(24)	0.0069	0.0273			
C(25)	0.0061	0.0203			
C(26)	-0.0086	0.0277			
Additional atoms					
C(3)	0.0732				
O	0.5107				
Mean deviation from plane 0.0097 \AA , $\chi^2 = 1.3$					
Dihedral angles between least-squares planes					
Plane	Plane	Angle ($^\circ$)	Plane	Plane	Angle ($^\circ$)
2	1	12.84	4	1	48.43
3	1	153.99	4	2	35.84
3	2	164.63	4	3	155.86

and minimum $\Delta\rho$ are 0.56 and 0.63 $e \text{\AA}^{-3}$ respectively. Scattering factors and f' , f'' were taken from Cromer & Waber (1974).

Discussion. The final atomic coordinates and thermal parameters are given in Table 1. The bond lengths and angles are listed in Table 2. Several least-squares planes are given in Table 3. The molecular configuration and the packing of molecules in the unit cell are shown in Figs. 1 and 2, respectively.

Discussion. The final atomic coordinates and thermal parameters are given in Table 1. The bond lengths and angles are listed in Table 2. Several least-squares planes are given in Table 3. The molecular configuration and the packing of molecules in the unit cell are shown in Figs. 1 and 2, respectively.

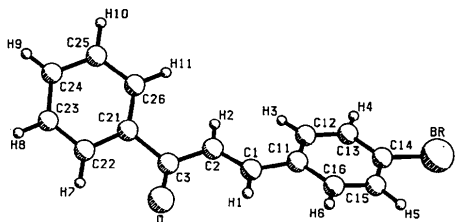


Fig. 1. The molecular structure of the title compound.

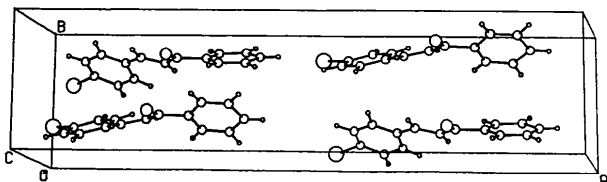


Fig. 2. The packing of the title compound in the unit cell.

Generally, bond lengths in conjugated systems are longer than double bonds and shorter than single bonds. Indeed, for the title compound, C(1)—C(11) and C(2)—C(3) are shorter than a typical single bond, and C(1)—C(2) and C(3)—O are slightly shorter than a typical double bond. It is therefore suggested that an extended π -electron conjugated system is induced in the BrC₆H₄C₂H₂CO group. The bond length C(3)—C(21) is 1.53 Å, which is a typical single bond. This implies that the conjugation of the molecule is interrupted and no intramolecular charge transfer over the whole molecule is expected. Therefore, the molecular dipole axis must lie close to the BrC(14)—C(11)C(1) axis in the molecule. The latter axis is inclined at about $\pm 70^\circ$ to the *b* axis in the

unit cell, see Fig. 2. The theoretically optimal angle between the two axes is 54.74° for non-linear optical effects to take place (Chemla & Zyss, 1987). The observation of efficient SHG shows that the packing of the molecules in the crystal is favorable for non-linear optical properties. The molecule consists of the phenyl ring C(11)—C(16), Br; the C(1), C(2), C(3), C(11) group; the C(3), O, C(21), C(2) group; and the phenyl ring C(21)—C(26), which are non-coplanar (Table 3). The dihedral angle between the phenyl rings is 48.4° . It is significant that the π -electron conjugated system is disturbed by the non-planarity of the molecule. This will produce a large hypsochromic shift of the cutoff wavelength of transmission. The cutoff wavelength is 380 nm (Goto, 1989).

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Structure of 3,5-Pyrazoledimethanol: an X-ray and ¹³C Solid-State NMR Study

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Abstract. C₅H₈N₂O₂, *M_r* = 128.1, monoclinic, *C*2/*c*, *a* = 12.9884 (5), *b* = 4.6517 (1), *c* = 20.7870 (11) Å, β = 102.436 (3)°, *V* = 1226.44 (9) Å³, *Z* = 8, *D_x* = 1.388 Mg m⁻³, λ (Cu *K* α) = 1.5418 Å, μ = 0.877 mm⁻¹, *F*(000) = 544, *T* = 293 K, *R* = 0.051 for 900 observed reflections. The hydroxyl groups are