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1-(4-Bromophenyl)-3-(4-methylphenyl)prop-2-en-1-one[1]

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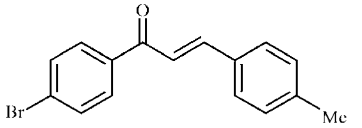
In the molecule of the title compound, $C_{16}H_{13}BrO$, the two benzene rings are rotated in opposite directions with respect to the central C—C═C—C part of the molecule. The phenone O atom deviates from the least-squares plane of the molecule by 0.300 (3) Å. In the crystal structure, molecules are paired through C—H···π interactions. The molecular pairs along [001] are hydrogen bonded through three translation-related co-operative hydrogen bonds in the 'bay area', forming molecular chains, which are further hydrogen bonded through C—H···Br weak interactions, forming (010) molecular layers. In the third direction, there are only weak van der Waals interactions. The co-operative hydrogen bonds in the 'bay area' are discussed briefly.

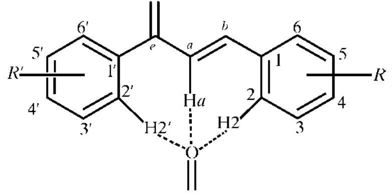
Comment

Chalcones with the general formula Ar–CH═CH–CO–Ar belong to an important class of compounds. The common and interesting part in the molecules of these compounds is the central part, *i.e.* —CH═CH—C═O—, in which the H atoms may or may not be substituted. The C═C double bond can be photoreactive, in which case it can react with suitable reagents through photocycloaddition to synthesize various products, and it is therefore widely used in organic solid photochemistry (Satish Goud *et al.*, 1995).

On the other hand, with appropriate substitutents, chalcones are a class of non-linear optical materials (Indira *et al.*, 2002). In these materials, the C═O bond acts as the electron-withdrawing group, and electron-rich substituents in the aromatic rings serve as electron-donating groups, forming a so-called *D*—π···*A*-type molecule. When the electron-rich groups are located on the 4 and/or 4′ positions, the electron flow follows a Λ-shaped path, and therefore the molecule is called a Λ-shaped molecule (Devia *et al.*, 1999). During our search for chalcone non-linear optical materials, the title compound, (I), was synthesized. We present here a study of the molecular packing in the crystal of (I) and a brief study of the C—H···O hydrogen bonds in (I) and some similar crystals.



(I)



(II)

The molecule of (I) (Fig. 1) is not planar. Taking the C1–C6 benzene ring as plane 1 (*P*1), the C7–C12 benzene ring as plane 2 (*P*2) and the central C1—C13═C14—C15 as plane 3 (*P*3), the dihedral angles between them, A_{12}, A_{13} and A_{23}, are 47.0 (1), 11.7 (0) and 35.4 (1)°, respectively, showing that the two benzene rings are rotated in opposite directions with respect to the central part, plane 3. The C1—C13═C14—C15 torsion angle is 175.1 (3)°. The angle between the C═O bond and plane 3 is 14.2 (3)°. Further geometric parameters are given in Table 1.

In the crystal structure of (I), molecules are paired through C—H···π interactions (Suezawa *et al.*, 2001) (Table 3). The shortest distance between parallel C═C double bonds is 4.557 (4) Å, much longer than the 4.2 Å reference value for a photoreactive crystal (Turowska-Tyrk *et al.*, 2003). The dihedral angle between plane 3 and the plane formed by the two C═C double bonds is 45.6 (3)°, which deviates significantly from the perfect value of 90° for 2+2 photocycloaddition. This is consistent with the fact that the crystal of (I) is photoinert.

The packing in (I) is illustrated in Fig. 2. The molecules along [001] interact *via* three C—H···O interactions (Desiraju, 1991), namely C12—H12···O1, C2—H2···O1 and C14—H14···O1 (Table 2), and form hydrogen-bonded molecular chains. These chains interact further through C5—H5···Br1 and C16—H16*A*···Br1 hydrogen bonds (Table 2), forming (010) molecular layers. In the third direction, [010], there are only weak ordinary van der Waals interactions.

The most interesting features in the structure of (I) are the above-mentioned co-operative hydrogen bonds, formed by the phenone O atom and the three C—H bonds in the 'bay

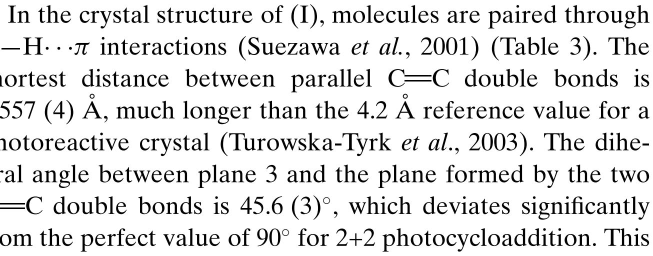


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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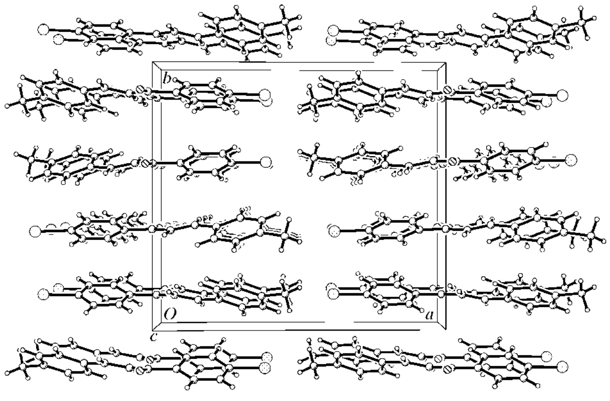

Figure 2
A packing diagram for (I), viewed down the *c* axis.

area', namely the area encircled by C2′—C1′—C_e—C_a=C_b—C1—C2. From the scheme, one can see that the three C—H bonds almost point to the same site. When this site is occupied by a phenone O atom from a neighbouring molecule, the formation of three C—H···O hydrogen bonds with nearly perfect geometries can be expected. Depending on the mutual arrangement of the two molecules involved, the most favourable symmetry relation between them is a translation vector, the size of which is dependent on the size of the substituents, followed by a screw axis and a glide plane. It is almost impossible for a centre of symmetry to connect the molecules in such a manner.

From the viewpoint of designing second-harmonic generating crystals (Desiraju, 1989), which must not be centrosymmetric, the above molecular self-assembling mode is desirable. Therefore, a brief study of some similar 4,4′-substituted chalcones was carried out, and the results are summarized in Tables 4 and 5.

As shown by Tables 4 and 5, the symmetry elements involved are indeed translation vectors and their size is around 6 Å. The co-operative C—H···O hydrogen bonds in the 'bay area' certainly play an important role in the crystal packing, as shown by the ESM% column in Table 5, which expresses the interaction energy between the molecules involved as a percentage of the total packing energy, as calculated using the program *OPEC* (Gavezzotti, 1983). However, this is not the unique factor determining the crystal packing. The dipole moment of the molecule of (I) is relatively large when compared with the others in Table 4, which leads to the molecules of (I) being arranged in an antiparallel fashion in the crystal. This may be the reason that the crystal of (I) is centrosymmetric.

Experimental

The synthesis of the (I) was carried out according to the procedure of Migrdichian (1957). An aqueous solution of sodium hydroxide (10%, 10 ml) was added to a solution of 4-bromoacetophenone (0.02 mol) and 4-methylbenzaldehyde (0.02 mol) in 95% ethanol (30 ml). The reaction mixture was stirred at room temperature for 4 h and yielded a light-yellow solid, and the mixture was then neutralized with hydrochloric acid (10%) and water. The product was recrystallized three times from dry acetone. After 3 d, light-yellow crystals of (I) were obtained by slow evaporation from dry acetone at 286 K. Elemental analysis (Perkin–Elmer 240C elemental analyzer): calculated for $C_{16}H_{13}BrO$: C 63.79, H 4.32%; found: C 63.66, H 4.19%. IR (KBr pellets, ν, cm^{-1}): 3030 (Ar-H), 2914 (C—H), 1658 (–C=O), 1598 (–CH=CH–), 1563 (Ph), 1332 (–CH_3), 1007 (–CH=C—H), 810 (Ar-H), 737 (Ar-H). ^{1}H NMR (Bruker AV-400 NMR spectrometer, $CDCl_3$, 399.97 MHz, ambient temperature, p.p.m.): 2.40 (*s*, 3H, –CH_3), 7.25 (*d*, 2H, Ph), 7.45 (*d*, 1H, –CH=CH–), 7.55 (*d*, 2H, Ph), 7.64 (*d*, 2H, Ph), 7.81 (*d*, 1H, –CH=CH–), 7.89 (*d*, 2H, Ph).

Crystal data

$C_{16}H_{13}BrO$
M_r = 301.17
Monoclinic, $P2_1/c$
a = 15.600 (3) Å
b = 14.235 (3) Å
c = 5.8621 (11) Å
β = 92.029 (4)°
V = 1301.0 (4) Å^3
Z = 4
D_x = 1.538 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4569 reflections
θ = 3.1–25.0°
μ = 3.14 mm^{-1}
T = 193 (2) K
Block, light yellow
0.35 × 0.31 × 0.30 mm

Data collection

Rigaku MercuryCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.356, T_{max} = 0.382
12 258 measured reflections

2267 independent reflections
2144 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 25.0°
$h = -18 \rightarrow 18$
$k = -16 \rightarrow 16$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.091
S = 1.24
2267 reflections
166 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 1.5303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C10	1.895 (3)	C4—C16	1.524 (4)
O1—C15	1.228 (4)	C7—C15	1.493 (4)
C1—C13	1.460 (4)	C13—C14	1.330 (4)
C3—C4	1.394 (4)	C14—C15	1.482 (4)
C2—C1—C6	117.8 (3)	C8—C7—C15	118.3 (3)
C2—C1—C13	122.9 (3)	C9—C10—C11	121.5 (3)
C6—C1—C13	119.2 (3)	C9—C10—Br1	119.1 (2)
C5—C4—C3	118.2 (3)	C11—C10—Br1	119.3 (2)
C5—C4—C16	121.4 (3)	C14—C13—C1	127.5 (3)
C3—C4—C16	120.3 (3)	C13—C14—C15	120.6 (3)
C12—C7—C8	119.0 (3)	O1—C15—C14	121.3 (3)
C12—C7—C15	122.6 (3)	O1—C15—C7	120.1 (3)
C13—C1—C2—C3	176.0 (3)	C1—C13—C14—C15	−175.1 (3)
C13—C1—C6—C5	−177.1 (3)	C13—C14—C15—O1	13.8 (5)
C15—C7—C8—C9	−178.1 (3)	C13—C14—C15—C7	−167.5 (3)
C8—C9—C10—Br1	−178.9 (2)	C12—C7—C15—O1	−154.7 (3)
Br1—C10—C11—C12	177.7 (2)	C8—C7—C15—O1	22.7 (5)
C15—C7—C12—C11	176.7 (3)	C12—C7—C15—C14	26.5 (4)
C2—C1—C13—C14	9.5 (5)	C8—C7—C15—C14	−156.1 (3)
C6—C1—C13—C14	−173.3 (3)		

H atoms were placed in geometrical positions and treated as riding, with C—H distances in the range 0.95–0.98 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2^{i}—H2^{i}···O1	0.95	2.82	3.627 (3)	144
C14^{i}—H14^{i}···O1	0.95	2.80	3.702 (4)	160
C12^{i}—H12^{i}···O1	0.95	2.91	3.722 (4)	145
C5^{ii}—H5^{ii}···Br1	0.95	3.17	3.953 (5)	141
C16^{ii}—H16*A*^{ii}···Br1	0.98	3.15	4.026 (4)	149

Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) *x* − 1, *y*, *z*.

Table 3
C—H···π interactions (Å, °) in (I).

*P*1 is the centre of plane 1 (the C1–C6 ring) and *P*2 is the centre of plane 2 (the C7–C12 ring).

C	H	*P*	H···*P*	C···*P*	C—H···*P*
C3	H3	*P*1^{i}	2.82	3.530 (4)	132
C11	H11	*P*2^{ii}	2.94	3.608 (3)	129
C8	H8	*P*2^{iii}	3.01	3.568 (4)	119
C13	H13	*P*2^{iv}	3.07	3.641 (4)	120

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, 1 - y, 1 - z$; (iii) $x, \frac{1}{2} - y, z + \frac{1}{2}$; (iv) $-x, 1 - y, -z$.

Table 4
Comparison of crystal data for (I) and analogous compounds.

A_{12} is the dihedral angle between planes 1 and 2 (defined in Table 3), and μ is the dipole moment, calculated by *MOPAC* (Dewar *et al.*, 1985).

	Space group	Shortest axis (Å)	A_{12} (°)	μ (D)	Substituents
(I)†	*P*2$_1$/*c*	5.862 (1)	47.0 (1)	4.91	4-CH$_3$, 4′-Br
(II)‡	*P*2$_1$2$_1$2$_1$	5.906	49	2.88	4,4′-CH$_3$
(III)§	*Pc*	5.991 (1)	48	3.75	4-Br, 4′-OCH$_3$
(IV)¶	*Cc*	5.917 (3)	48.6 (1)	1.95	4-Br

† This study. ‡ Rabinovich & Shakked (1974). § Li, Huang *et al.* (1992). ¶ Li, Pa & Su (1992).

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1246). Services for accessing these data are described at the back of the journal.

Table 5
Comparison of C—H···O hydrogen bonds (Å, °) in (I) and analogous compounds.

A, *B* and *C* represent C—H*a*···O, C—H2···O and C—H2′···O hydrogen bonds, respectively; see scheme in *Comment* for definitions of H*a*, H2 and H2′. ESM% is the interaction energy between the molecules involved, expressed as a percentage of the total packing energy.

	Bond	H···O	C···O	C—H···O	Type†	ESM%
(I)	*A*^{i}	2.80	3.702 (4)	160	T	9.73
	B^{i}	2.82	3.627 (5)	144	T	
	C^{i}	2.91	3.722 (6)	145	T	
(II)	*A*^{ii}	2.77	3.718 (3)	164	T	10.03
	B^{ii}	2.71	3.561 (5)	142	T	
	C^{ii}	3.06	3.841 (6)	140	T	
(III)	*A*^{iii}	2.97	3.876 (3)	158	T	9.24
	B^{iii}	2.90	3.761 (5)	150	T	
	C^{iii}	2.94	3.737 (4)	141	T	
(IV)	*A*^{iv}	2.87	3.787 (5)	161	T	9.86
	B^{iv}	2.80	3.622 (6)	144	T	
	C^{iv}	2.97	3.795 (4)	142	T	

† For type, T is a translation. Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) *x*, *y* − 1, *z*; (iii) *x*, *y*, *z* − 1; (iv) *x*, *y*, *z* + 1.

References

Desiraju, G. R. (1989). *Crystal Engineering*, ch. 9, pp. 225–260. Oxford: Elsevier Science.

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.

Devia, A. C., Feretti, F. H., Ponce, C. A. & Tomas, F. (1999). *J. Mol. Struct.* (*Theochem*), **493**, 187–197.

Dewar, M. S., Zeobisch, E. G., Healy, E. F. & Stewart, J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

Gavezzotti, A. (1983). *J. Am. Chem. Soc.* **105**, 5520–5225.

Indira, J., Prakash Karat, P. & Sarojini, B. K. (2002). *J. Cryst. Growth*, **242**, 209–214.

Jacobson, R. (1998). Private communication.

Li, Z.-D., Huang, L.-R., Su, G.-B. & Wang, H.-J. (1992). *Chin. J. Struct. Chem.* **11**, 1–4.

Li, Z.-D., Pa, F. & Su, G. (1992). *Acta Cryst.* C**48**, 712–714.

Migrdichian, V. (1957). *Org. Synth.* **1**, 171–173.

Rabinovich, D. & Shakked, Z. (1974). *Acta Cryst.* B**30**, 2829–2831.

Rigaku (2001). *CrystalClear* (Version 1.3) and *CrystalStructure* (Version 3.00). Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.

Satish Goud, B., Panneerselvam, K., Zacharias, D. E. & Desiraju, G. R. (1995). *J. Chem. Soc. Perkin Trans.* 2, pp. 325–330.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Suezawa, H., Yoshida, T., Hirota, M., Takahashi, H., Umezawa, Y., Honda, K., Tsuboyama, S. & Nishio, M. (2001). *J. Chem. Soc. Perkin Trans.* 2, pp. 2053–2058.

Turowska-Tyrk, I., Grzesniak, K., Trzop, E. & Zych, T. (2003). *J. Solid State Chem.* **174**, 459–465.