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Do C—H···O and C—H···π interactions help to stabilize a non-centrosymmetric structure for racemic 2,3-dibromo-1,3-diphenylpropan-1-one?

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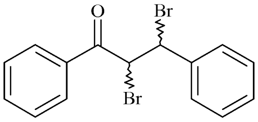
The racemic title compound, $C_{15}H_{12}Br_2O$, crystallizes in a non-centrosymmetric structure and displays a significant non-linear optical response to red light. The crystal packing is influenced by C—H···O and C—H···π interactions. One of the former bonds has a short H···O separation of 2.27 Å.

Comment

In order to display non-linear optical (NLO) effects, organic molecular crystals must possess suitable electronic and structural properties. The former effects, including strong donor–acceptor intermolecular interactions and delocalized *p*-electron systems, are reasonably well understood (Watson *et al.*, 1993). The latter effects – especially the ability to crystallize as a non-centrosymmetric structure – are harder to predict and control.

Among the many organic compounds reported for their NLO properties, chalcone derivatives are notable for their excellent blue light transmittance and good crystallizability. It is observed that the substitution of a bromo group on either of the benzene rings greatly influences the non-centrosymmetric crystal packing (Uchida *et al.*, 1998; Tam *et al.*, 1989; Indira *et al.*, 2002). Bromo groups improve the molecular first-order hyperpolarizabilities and can effectively reduce dipole–dipole interactions between the molecules (Zhao *et al.*, 2002). However, chalcone derivatives often have low melting temperatures, which can be a drawback with respect to the applications of these crystals in optical instruments. Chalcone dibromides usually have higher melting points and are thermally stable. We report here the synthesis and structure of the title compound, (I) (Fig. 1), which has a second harmonic generation (SHG) efficiency 0.4 times that of urea.

The non-centrosymmetric space group of (I) is consistent with the non-zero SHG signal observed. All the geometric parameters for (I) lie within their expected ranges (Allen *et al.*, 1995). A dihedral angle of 22.58 (16)° occurs between the mean planes of the two benzene rings. With respect to the C7—C8 bond, the atom pairs Br1/Br2, C6/C9 and H7/H8 are all *trans* (Table 1). Each molecule of (I) is chiral (the arbitrarily chosen asymmetric molecule has *R* and *S* configurations for atoms C7 and C8, respectively), but space-group symmetry generates a racemic 1:1 mix of enantiomers, as might be expected in terms of the bromination reaction used to prepare (I), *i.e. trans* addition of the two Br atoms has occurred. However, (I) does not crystallize in a space group with inversion symmetry and a substantial SHG response arises.



(I)

The crystal packing of (I) appears to be influenced by weak interactions, including C—H···O and C—H···π bonds (Table 2). The three C—H···O interactions in (I) all link to the same acceptor O atom. One of the resulting H···O separations is rather short, at 2.27 Å. It may be assumed that these three H atoms are all 'activated' (made more acidic) in terms of the identities of their adjacent atoms (Desiraju & Steiner, 1999). These C—H···O links result in parallel chains of molecules of (I) propagating in the *c* direction (Fig. 2). Within a chain, adjacent molecules, related by the *c*-glide operation, are enantiomers. For any adjacent pair of molecules in a chain, the dihedral angle between their C1-benzene rings is 50.50 (10)°. Fig. 2 shows that all the chains propagate in the same sense, *i.e.* all the C═O moieties point the same way, and it is tempting to assume that this 'lining up' effect plays a role in defining the SHG properties of (I).

Furthermore, two C—H···π interactions appear to consolidate the crystal packing in (I) in the *b* direction. The two H atoms involved in these interactions are both *trans* to the C—C bond to the rest of the molecule. When viewed along the *c* direction (Fig. 3), it is observed that a herring-bone-like array of molecules of (I) results, with the C—H···π bonds forming infinite ladder-like chains along [010].

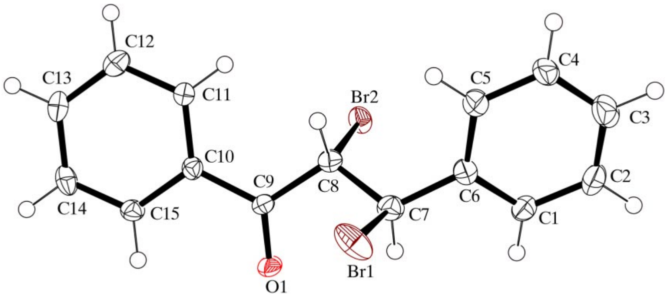


Figure 1
A view of (I), showing 50% probability displacement ellipsoids; H atoms are shown as arbitrary spheres.

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If the acceptor benzene ring is considered, then in each case it is notable that a Br atom is located roughly opposite the C—H$\cdots\pi$ interaction (Fig. 3) (H13$\cdots\pi$1$\cdots$Br2 = 168° and H3$\cdots\pi$2$\cdots$Br1 = 163°; π1 is the centroid of atoms C1–C6 and π2 is the centroid of atoms C10–C15). While this cannot be considered to be a Br$\cdots\pi$ 'bond' of any kind [the Br$\cdots\pi$ separations of 3.661 and 3.884 Å are greater than the van der Waals separation of 3.55 Å for Br (1.85 Å) plus the half-thickness (1.70 Å) of a benzene ring], it is possible that this kind of intermolecular contact influences the SHG response of (I). The crystal packing of (I), viewed approximately down [010], is available as a figure in the supplementary material.

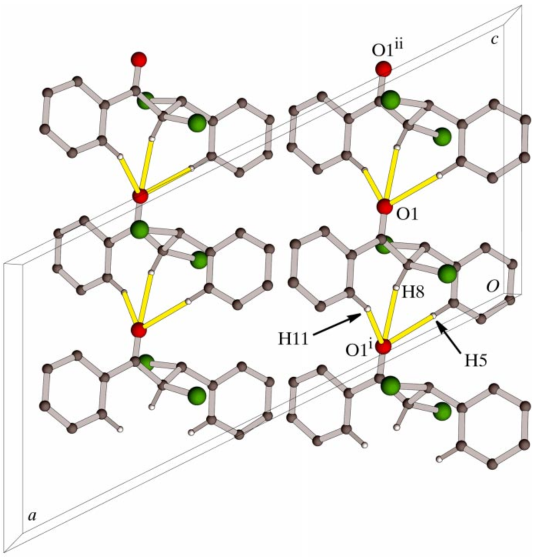

Figure 2
A view of (I), showing how the three C—H$\cdots$O interactions link adjacent molecules into parallel chains propagating in (001). H atoms not involved in the interactions shown have been omitted. [Symmetry codes: (i) x, $-y + 1$, $z - \frac{1}{2}$; (ii) x, $-y + 1$, $z + \frac{1}{2}$.]

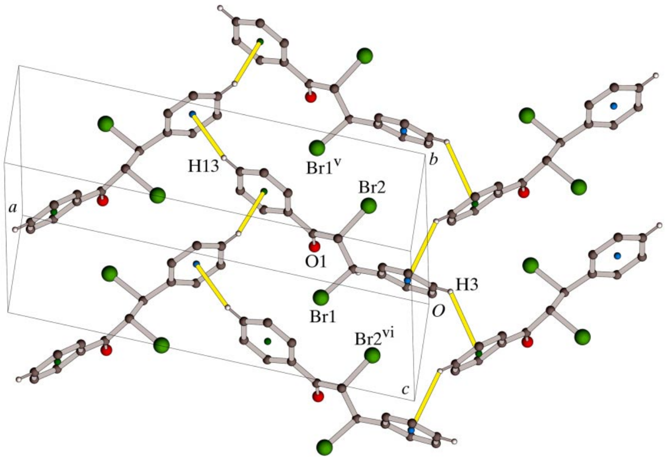

Figure 3
A detail of (I), showing how C—H$\cdots\pi$ interactions involving atoms H3 and H13 provide coherence between herring-bone-like sheets of molecules. Note also how a Br atom is positioned approximately *trans* to every C—H$\cdots\pi$ bond (see *Comment*). H atoms not involved in the interactions shown have been omitted. [Symmetry codes: (v) x, $y + 1$, z; (vi) x, $y - 1$, z.]

Experimental

Chalcone (1,3-diphenyl-2-propen-1-one) (20.8 g 0.1 mol) was treated with 30% bromine in acetic acid until the orange colour of the solution just persisted. After stirring for 30 min, the contents of the flask were poured onto crushed ice and the resulting crude solid was collected by filtration. The compound was dried and recrystallized as clear blocks of (I) from ethanol in 85% yield (m.p. 396–398 K). Analysis for $C_{15}H_{12}Br_2O$ requires: C 48.95, H 3.29%; found: C 48.91, H 3.26%. The SHG efficiency of (I), normalized to that of urea, was measured by a standard powder technique (Kurtz & Perry, 1968) using an Nd:YAG laser.

Crystal data

$C_{15}H_{12}Br_2O$
M_r = 368.07
Monoclinic, *Cc*
a = 20.6762 (7) Å
b = 7.2443 (2) Å
c = 10.3501 (3) Å
β = 116.575 (2)°
V = 1386.50 (7) Å^3
Z = 4

D_x = 1.763 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4476 reflections
θ = 2.9–27.5°
μ = 5.83 mm^{-1}
T = 120 (2) K
Block, colourless
0.48 × 0.32 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min}$ = 0.138, $T_{\max}$ = 0.350
9478 measured reflections
3011 independent reflections

2889 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.029
$\theta_{\max}$ = 27.5°
$h = -26 \rightarrow 26$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.058
S = 1.05
3011 reflections
164 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 3.0761P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.05 e Å^{-3}
$\Delta\rho_{\min}$ = −0.74 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0035 (2)
Absolute structure: Flack (1983), 1416 Friedel pairs
Flack parameter: 0.022 (11)

Table 1
Selected torsion angles (°).

C6—C7—C8—C9	169.9 (3)	Br1—C7—C8—Br2	175.33 (16)

Table 2
Intermolecular interactions (Å, °).

π1 is the centroid of the C1–C6 ring and π2 is the centroid of the C10–C15 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C5—H5$\cdots$O1$^{\rm i}$	0.95	2.55	3.469 (4)	162
C8—H8$\cdots$O1$^{\rm i}$	1.00	2.27	3.237 (4)	163
C11—H11$\cdots$O1$^{\rm i}$	0.95	2.57	3.370 (4)	142
C13—H13$\cdots\pi1^{\rm iii}$	0.95	2.91	3.629 (4)	133
C3—H3$\cdots\pi2^{\rm iv}$	0.95	2.99	3.590 (3)	123

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

The H atoms were positioned geometrically (C—H = 0.95–1.00 Å) and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier).

Harrison *et al.* • $C_{15}H_{12}Br_2O$ **o729**

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*, *DENZO* (Otwinowski & Minor, 1997) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997), *ATOMS* (Shape Software, 2003) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1880). Services for accessing these data are described at the back of the journal.

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