2,3-Dibromo-1-(4-methoxyphenyl)-3-[4-(methyl-sulfanyl)phenyl]propan-1-one

Ray J. Butcher,[a]* H. S. Yathirajan,[b] B. K. Sarojini,[c] B. Narayana[d] and A. Mithun[d]

[a]Department of Chemistry, Howard University, 525 College Street NW, Washington DC 20059, USA, [b]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, [c]Department of Chemistry, P. A. College of Engineering, Nadupadavu, Mangalore 574 153, India, and [d]Department of Chemistry, Mangalore University, Mangalagangotri 574 199, India

Correspondence e-mail:
raymond.butcher@nrl.navy.mil

The title compound, $C_{17}H_{16}Br_2O_2S$, crystallizes in a centrosymmetric space group and thus does not show any non-linear optical activity.

Comment

The non-linear optical (NLO) effect in organic molecules originates from a strong donor–acceptor intermolecular interaction, a delocalized π-electron system and the ability to crystallize in a non-centrosymmetric structure. Among several organic compounds exhibiting NLO effects, chalcone derivatives are important materials for their excellent blue light transmittance and good crystallizability. It has been observed that substitution of a bromo group on either of the phenyl rings greatly influences non-centrosymmetric crystal packing (Uchida *et al.*, 1998; Tam *et al.*, 1989; Indira *et al.*, 2002). Bromo substituents can obviously improve molecular first-order hyperpolarizabilities and can effectively reduce dipole–dipole interactions between molecules (Zhao *et al.*, 2002). Chalcone derivatives usually have lower melting points, which can be a drawback when their crystals are used in optical instruments. Chalcone dibromides usually have higher melting points and are thermally stable.
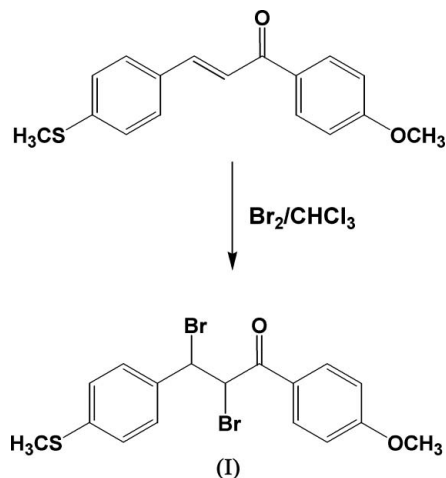
The crystal structure of the title compound, (I), $C_{17}H_{16}Br_2O_2S$, is reported. This compound was prepared by bromination and its second-harmonic generation (SHG) efficiency tested; it was found not to be active. This result is confirmed by the fact that (I) crystallizes in a centrosymmetric space group. Its geometrical parameters are similar to those observed in other chalcone derivatives (Butcher, Yathirajan, Anilkumar *et al.*, 2006; Butcher, Yathirajan, Mithun *et al.*, 2006).

Experimental

To a solution of 1-(4-methoxyphenyl)-3-[4-(methylthio)phenyl]prop-2-en-1-one (2.84 g, 0.01 mol) in chloroform (50 ml), bromine (1.60 g, 0.01 mol) in chloroform (10 ml) was added slowly with stirring. After completion of the addition of the bromine solution, the reaction mixture was stirred for 24 h. Excess chloroform was distilled off under reduced pressure. The solid obtained was dried and recrystallized from acetone (m.p. 379–381 K, yield 88%).

Crystal data

$C_{17}H_{16}Br_2O_2S$	$D_x = 1.741$ Mg m^{-3}
$M_r = 444.18$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 4400
$a = 10.7585$ (7) Å	reflections
$b = 13.5889$ (9) Å	$\theta = 2.3–28.5°$
$c = 11.6754$ (7) Å	$\mu = 4.91$ mm^{-1}
$\beta = 96.9710$ (10)°	$T = 376$ (2) K
$V = 1694.28$ (19) Å^3	Needle, colorless
$Z = 4$	$0.65 \times 0.25 \times 0.22$ mm

Data collection

Bruker APEX II CCD diffractometer	4532 independent reflections
	3415 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.039$
Absorption correction: multi-scan	$\theta_{max} = 29.1°$
(SADABS; Sheldrick, 1996)	$h = -12 \rightarrow 14$
$T_{min} = 0.118$, $T_{max} = 0.339$	$k = -18 \rightarrow 18$
18342 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 2.2098P]$
$wR(F^2) = 0.086$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
4532 reflections	$\Delta\rho_{max} = 0.97$ e Å^{-3}
201 parameters	$\Delta\rho_{min} = -0.95$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Br1—C8	1.997 (3)	O2—C14	1.358 (3)
Br2—C9	1.981 (3)	O2—C17	1.433 (3)
S—C2	1.758 (3)	C8—C9	1.496 (4)
S—C1	1.792 (3)	C9—C10	1.533 (4)
O1—C10	1.217 (3)		
C2—S—C1	103.46 (14)	C8—C9—C10	113.6 (2)
C14—O2—C17	117.7 (2)	C8—C9—Br2	108.02 (19)
C9—C8—C5	114.7 (2)	C10—C9—Br2	104.36 (18)
C9—C8—Br1	103.97 (19)	O1—C10—C11	122.6 (2)
C5—C8—Br1	110.53 (19)	O1—C10—C9	119.2 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C16—H16A$\cdots$O1^i	0.93	2.55	3.364 (3)	147

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

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—
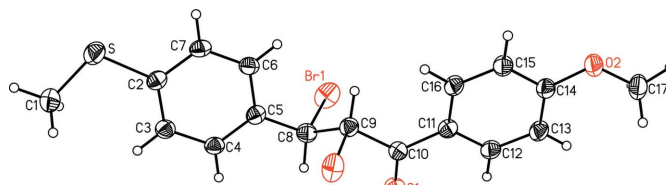

Figure 1
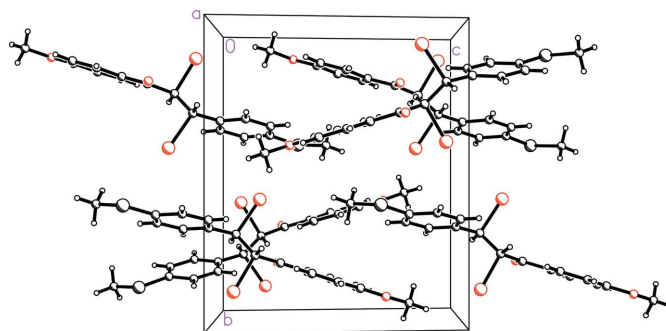View of the title compound (I), showing the atom-numbering scheme.

Figure 2
The molecular packing of (I), viewed down the a axis.

H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C—O or C—S bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

References

Bruker (1998). SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). SAINT-Plus and SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
Butcher, R. J., Yathirajan, H. S., Anilkumar, H. G., Sarojini, B. K. & Narayana, B. (2006). Acta Cryst. In the press.
Butcher, R. J., Yathirajan, H. S., Mithun, A., Narayana, B. & Sarojini, B. K. (2006). Acta Cryst. In the press.
Indira, J., Karat, P. P. & Sarojini, B. K. (2002). J. Cryst. Growth, 242, 209–214.
Sheldrick, G. M. (1996). SADABS. Version 2.03. University of Göttingen, Germany.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Tam, W., Guerin, B., Calabrese, J. C. & Stevenson, S. H. (1989). Chem. Phys. Lett. 154, 93–96.
Uchida, T., Kozawa, K., Sakai, T., Aoki, M., Yoguchi, H., Abduryim, A. & Watanabe, Y. (1998). Mol. Cryst. Liq. Cryst. 315, 135–140.
Zhao, B., Lu, W. Q., Zhou, Z. H. & Wu, Y. (2002). J. Mater. Chem. 10, 1513–1517.