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(2*E*)-1-(2,4-Dichlorophenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one

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The title compound, $C_{16}H_{12}Cl_2OS$, crystallizes in a non-centrosymmetric space group and shows a significant nonlinear optical activity. The source of the optical activity lies in the twist of the chalcone backbone, as exemplified by the dihedral angle of 42.45 (6)° between the two benzene rings. Weak intermolecular C—H$\cdots$O hydrogen bonds may contribute to the stabilization of the crystal structure.

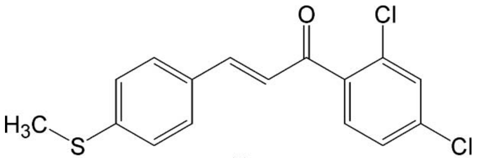
Key indicators

Single-crystal X-ray study
T = 103 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.071
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

A non-centrosymmetric crystal packing of molecules is a prerequisite for second-order nonlinear optical (NLO) activity, and much attention has been focused on this aspect of molecular structure (Long, 1995) and organic NLO materials due to their promising applications in optoelectronics technology and the much larger nonlinear response, extremely fast switching time and convenient optimization routes through molecular engineering compared with the currently studied inorganic materials. To have strong second-order NLO properties, the compound must possess a large first-order molecular hyperpolarizability, β, and also must crystallize in a non-centrosymmetric structure to have a non-zero χ^2. Besides the strong NLO properties, the materials must also fulfill some other requirements such as good transparency and high thermal stability (Zhao *et al.*, 2000).



(I)

Among several organic compounds reported for NLO properties, chalcone derivatives are noticeable materials for their excellent blue light transmittance and good crystallizability. They provide a necessary configuration to show NLO properties with two planar rings connected through a conjugated double bond (Goto *et al.*, 1991; Uchida *et al.*, 1998; Tam *et al.*, 1989; Indira *et al.*, 2002). Substitution on either of the phenyl rings greatly influences non-centrosymmetric crystal packing. It is speculated that in order to improve the activity, more bulky substituents should be introduced to increase the spontaneous polarization of non-centrosymmetric crystals (Fichou *et al.*, 1988). The molecular hyperpolarizability β is strongly influenced not only by the electronic effect but also by the steric effect of the substituent (Cho *et al.*, 1996). Recently, the crystal structures of 3-(4-chlorophenyl)-1-(2,4-dichlorophenyl)prop-2-en-1-one, 1-(2,4-dichlorophenyl)-3-(4-

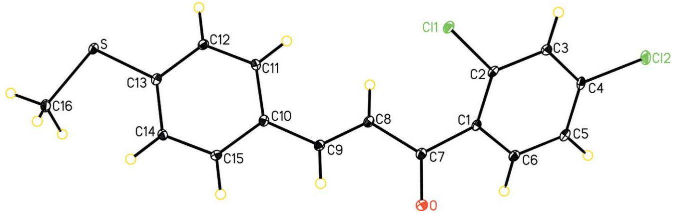


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

methoxyphenyl)prop-2-en-1-one and 1-(4-bromophenyl)-3-(2,4-dichlorophenyl)prop-2-en-1-one have been reported (Patil, Ng *et al.*, 2006; Patil, Rosli *et al.*, 2006; Patil, Teh *et al.*, 2006). In continuation of our quest to synthesize new chalcones (Butcher, Yathirajan, Sarojini *et al.*, 2006; Butcher *et al.*, 2006*a*,*b*), we have synthesized a new chalcone and studied its SHG efficiency. In view of the importance of the title compound, (I), its crystal structure is reported here.

The structure of (I) shows similar metrical parameters to those observed in other structurally characterized chalcones (Patil, Ng *et al.*, 2006; Patil, Rosli *et al.*, 2006; Patil, Teh *et al.*, 2006; Butcher, Yathirajan, Sarojini *et al.*, 2006; Butcher *et al.*, 2006*a*,*b*). Since these molecules do not posses a chiral center, the source of the optical activity lies in the twist of the chalcone backbone. This is best exemplified by the dihedral angle of 42.45 (6)°, between the planes of the two phenyl rings. There is a weak hydrogen bond between one of the methyl H atoms and the C═O group of an adjoining molecule (Table 2).

Experimental

To a mixture of 4-methylthiobenzaldehyde (1.52 g, 0.01 mol) and 2,4-dichloroacetophenone (1.89 g, 0.01 mol) in ethanol (5 ml), an aqueous solution of potassium hydroxide (5%, 5 ml) was added slowly with stirring. The mixture was stirred at room temperature for 24 h. The precipitated solid was filtered off, washed with water, dried and recrystallized from acetone (yield 70%; m.p. 384 K; SHG 0.44 × Urea). 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

$C_{16}H_{12}Cl_2OS$
$M_r = 323.22$
Monoclinic, $P2_1$
$a = 12.957$ (3) Å
$b = 3.8920$ (8) Å
$c = 14.135$ (3) Å
$\beta = 97.736$ (2)°
$V = 706.3$ (3) Å^3
$Z = 2$
$D_x = 1.520$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.60$ mm^{-1}
$T = 103$ (2) K
Rectangular fragment, colorless
0.55 × 0.26 × 0.11 mm

Data collection

Bruker APEX-II CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.712$, $T_{\max} = 0.937$
6061 measured reflections
2893 independent reflections
2811 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 28.1°$

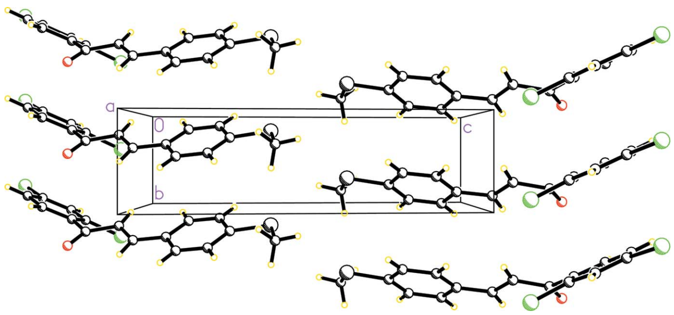


Figure 2
A packing diagram of (I).

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 1.05$
2893 reflections
182 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.1565P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Absolute structure: Flack (1983), with 926 Friedel pairs
Flack parameter: 0.16 (6)

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.7430 (19)	O—C7	1.227 (2)
Cl2—C4	1.7411 (19)	C1—C7	1.509 (2)
S—C13	1.7564 (18)	C7—C8	1.473 (2)
S—C16	1.801 (2)	C8—C9	1.343 (3)
C13—S—C16	103.49 (9)	C8—C7—C1	119.93 (17)
O—C7—C8	122.12 (17)	C9—C8—C7	119.70 (18)
O—C7—C1	117.89 (16)	C8—C9—C10	127.60 (18)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*B*···O$^{\rm i}$	0.98	3.21	3.852 (3)	125

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

H atoms were positioned geometrically, with C—H = 0.95 and 0.98 Å for Csp^2 and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = xU_{\rm eq}({\rm C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms. The value of the Flack parameter suggests possible partial inversion twinning.

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (2003). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison Wisconsin, USA.

Bruker (2006). *SMART* and *SAINT*. Bruker AXS Inc., Madison Wisconsin, USA.

Butcher, R. J., Yathirajan, H. S., Anilkumar, H. G., Sarojini, B. K. & Narayana, B. (2006*a*). *Acta Cryst.* E**62**, o1659–o1661.

Butcher, R. J., Yathirajan, H. S., Anilkumar, H. G., Sarojini, B. K. & Narayana, B. (2006*b*). *Acta Cryst.* E**62**, o1633–o1635.

Butcher, R. J., Yathirajan, H. S., Sarojini, B. K., Narayana, B. & Mithun, A. (2006). *Acta Cryst.* E**62**, o1629–o1630.

Cho, B. R., Je, J. T., Kim, H. S., Jean, S. J., Song, O. K. & Wang, C. H. (1996). *Bull. Korean Chem. Soc.* **17**, 693–695.

Fichou, D., Watanabe, T., Takeda, T., Miyata, S., Goto, Y. & Nakayama, M. (1988). *Jpn J. Appl. Phys.* **27**, 429–430.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Goto, Y., Hayashi, A., Kimura, Y. & Nakayama, M. (1991). *J. Cryst. Growth*, **108**, 688–698.

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

Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.

Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 21–38.

Patil, P. S., Ng, S.-L., Razak, I. A., Fun, H.-K. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o1463–o1465.

Patil, P. S., Rosli, M. M., Fun, H.-K., Razak, I. A., Dharmaprakash, S. M. & Shettigar, V. (2006). *Acta Cryst.* E**62**, o1707–o1709.

Patil, P. S., Teh, J. B.-J., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o1710–o1712.

Sheldrick, G. M. (1996). *SADABS*. 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., Zhoua, Z.-H. & Wub, Y. (2000). *J. Mater. Chem.* **10**, 1513–1517.

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