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3-[4-(Methylsulfanyl)phenyl]-1-(4-nitrophenyl)-prop-2-en-1-one

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.081
Data-to-parameter ratio = 16.6

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

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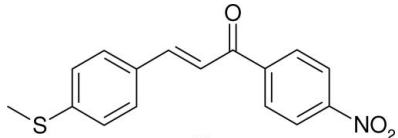
The geometrical parameters for the title compound, $C_{16}H_{13}NO_2S$, are normal. The non-centrosymmetric crystal packing, which is consistent with the non-zero second harmonic generation response, may be influenced by a weak intermolecular C—H···O interaction.

Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing studies (Harrison *et al.*, 2005, 2006) of the non-linear optical (NLO) properties and crystal structures of chalcone derivatives. It is known that substitution at either benzene ring of the chalcone skeleton substantially affects the optical response (Uchida *et al.*, 1998) and we are now exploring the role of the methylsulfanyl (H_3CS–) substituent (Butcher *et al.*, 2006) in this process.



(I)

The non-centrosymmetric polar space group of (I) is consistent with its significant second harmonic generation (SHG) response of 0.6 times that of urea (Watson *et al.*, 1993). The geometrical parameters for (I) fall within their expected ranges (Allen *et al.*, 1987). The molecule of (I) is distinctly twisted about the C6—C7 and the C9—C10 bonds (Table 1). The dihedral angle between the benzene ring mean planes (C1–C6 and C10–C15) in (I) is 45.84 (4)°, which is significantly smaller than the equivalent value of 68.15 (6)° in 2-bromo-1-(4-methylphenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one (Butcher *et al.*, 2006). The nitro group in (I) is well ordered and makes a dihedral angle of 12.94 (15)° with respect to the C10–C15 benzene ring. The C16 methyl group is almost in the plane of the C1–C6 benzene ring [deviation = 0.049 (4) Å].

A *PLATON* (Spek, 2003) analysis of the crystal structure of (I) indicates a possible intermolecular C—H···O interaction (Table 2) that might help to establish the crystal packing (Fig. 2). The C—H···O interaction forms extended chains of molecules propagating along [001]. Adjacent chains form pseudo-layers in (100), with all the molecules oriented in the same sense with respect to the polar axis.

Experimental

To a mixture of 4-(methylsulfanyl)benzaldehyde (1.52 g, 0.01 mol) and 4-nitroacetophenone (1.65 g, 0.01 mol) in ethanol (5 ml), a

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 an acetone–toluene (1:1 *v*/*v*) solvent mixture (yield 86%; m.p. 409 K). Analysis for $C_{16}H_{13}NO_3S$ found (calculated) (%): C 64.15 (64.20), H 4.32 (4.38), N 4.66 (4.68).

Crystal data

$C_{16}H_{13}NO_3S$
M_r = 299.33
Orthorhombic, *Aba*2
a = 13.7388 (4) Å
b = 33.5802 (8) Å
c = 5.9538 (2) Å
V = 2746.80 (14) Å^3
Z = 8
D_x = 1.448 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 120 (2) K
Plate, yellow
0.28 × 0.24 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.936, T_{max} = 0.993
27858 measured reflections
3173 independent reflections
2811 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 27.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.081
S = 1.06
3173 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 1.763P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 1416 Friedel pairs
Flack parameter: 0.04 (8)

Table 1
Selected torsion angles (°).

C5—C6—C7—C8	10.3 (3)	O1—C9—C10—C15	21.2 (3)
C7—C8—C9—O1	11.4 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O1^{i}	0.95	2.60	3.278 (3)	129

Symmetry code: (i) $x, y, z+1$.

A handful of reflections weakly violated the $h00$ ($h \neq 2n$) systematic absence condition for the space group *Aba*2. Attempts to develop a model in lower-symmetry space groups were not successful. The H atoms were positioned geometrically (C—H = 0.95–0.98 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl). The methyl group was allowed to rotate but not to tip to best fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *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); software used to prepare material for publication: *SHELXL97*.

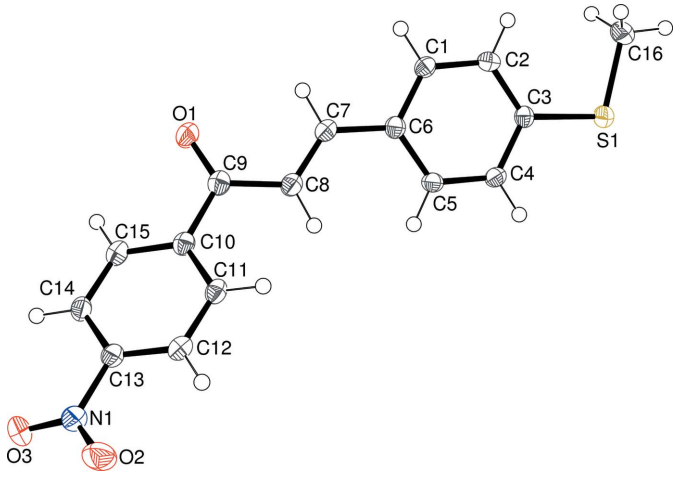


Figure 1
Molecular structure of (I) showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

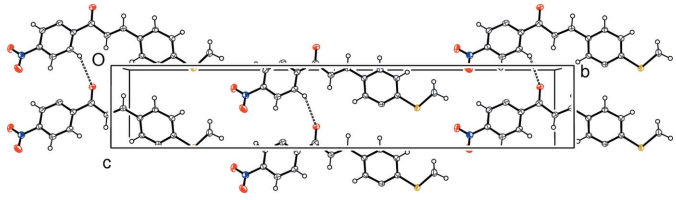


Figure 2
Part of a (100) sheet of molecules in (I) with C—H···O interactions shown as dashed lines.

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supporting information

Acta Cryst. (2006). E**62**, o4508–o4509 [https://doi.org/10.1107/S160053680603710X]

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Crystal data

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Orthorhombic, *Aba*2
Hall symbol: A 2 -2ac
$a = 13.7388$ (4) Å
$b = 33.5802$ (8) Å
$c = 5.9538$ (2) Å
$V = 2746.80$ (14) Å^3
$Z = 8$
$F(000) = 1248$
$D_x = 1.448$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6217 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.25$ mm^{-1}
$T = 120$ K
Plate, yellow
0.28 × 0.24 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
$T_{min} = 0.936$, $T_{max} = 0.993$
27858 measured reflections
3173 independent reflections
2811 reflections with $I > 2\sigma(I)$
$R_{int} = 0.063$
$\theta_{max} = 27.6°$, $\theta_{min} = 3.0°$
$h = -17\rightarrow17$
$k = -43\rightarrow43$
$l = -7\rightarrow7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.081$
$S = 1.06$
3173 reflections
191 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: none
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 1.763P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983), 1416 Friedel pairs
Absolute structure parameter: 0.04 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.33886 (12)	0.58404 (5)	0.0329 (4)	0.0197 (4)
H1	0.3126	0.5828	−0.1146	0.024*
C2	0.34598 (13)	0.62074 (6)	0.1380 (3)	0.0209 (4)
H2	0.3246	0.6442	0.0633	0.025*
C3	0.38469 (12)	0.62311 (6)	0.3537 (3)	0.0187 (4)
C4	0.41536 (13)	0.58797 (5)	0.4603 (3)	0.0201 (4)
H4	0.4422	0.5892	0.6072	0.024*
C5	0.40679 (13)	0.55163 (6)	0.3533 (4)	0.0207 (4)
H5	0.4271	0.5281	0.4288	0.025*
C6	0.36880 (14)	0.54878 (6)	0.1360 (4)	0.0201 (4)
C7	0.36326 (12)	0.51127 (5)	0.0127 (4)	0.0215 (4)
H7	0.3467	0.5129	−0.1420	0.026*
C8	0.37921 (13)	0.47485 (6)	0.0965 (3)	0.0222 (4)
H8	0.3892	0.4717	0.2534	0.027*
C9	0.38153 (13)	0.43940 (6)	−0.0505 (4)	0.0229 (4)
C10	0.38089 (13)	0.39913 (6)	0.0592 (3)	0.0208 (4)
C11	0.34357 (13)	0.39365 (6)	0.2756 (3)	0.0218 (4)
H11	0.3219	0.4160	0.3597	0.026*
C12	0.33801 (13)	0.35585 (6)	0.3683 (3)	0.0231 (4)
H12	0.3103	0.3518	0.5128	0.028*
C13	0.37387 (15)	0.32407 (6)	0.2449 (4)	0.0227 (4)
C14	0.41321 (13)	0.32839 (5)	0.0330 (4)	0.0229 (4)
H14	0.4383	0.3061	−0.0464	0.028*
C15	0.41513 (13)	0.36617 (6)	−0.0604 (3)	0.0230 (4)
H15	0.4401	0.3697	−0.2078	0.028*
C16	0.34877 (16)	0.70446 (6)	0.3191 (4)	0.0304 (5)
H16A	0.3535	0.7308	0.3888	0.046*
H16B	0.2804	0.6984	0.2866	0.046*
H16C	0.3862	0.7042	0.1790	0.046*
N1	0.36971 (13)	0.28424 (5)	0.3491 (3)	0.0287 (4)
O1	0.38403 (11)	0.44190 (4)	−0.2549 (3)	0.0295 (3)
O2	0.31977 (12)	0.28024 (4)	0.5189 (3)	0.0416 (4)
O3	0.41585 (12)	0.25723 (4)	0.2606 (3)	0.0373 (4)
S1	0.39700 (3)	0.667528 (13)	0.50812 (10)	0.02260 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0198 (8)	0.0229 (9)	0.0163 (9)	−0.0008 (6)	0.0022 (8)	0.0003 (9)
C2	0.0199 (9)	0.0219 (10)	0.0209 (10)	0.0015 (7)	−0.0007 (8)	0.0037 (8)

C3	0.0163 (8)	0.0199 (9)	0.0200 (9)	0.0006 (7)	0.0021 (7)	−0.0015 (8)
C4	0.0210 (8)	0.0229 (9)	0.0165 (11)	0.0006 (7)	−0.0006 (7)	0.0003 (8)
C5	0.0215 (9)	0.0217 (10)	0.0187 (10)	0.0034 (7)	0.0006 (8)	0.0025 (8)
C6	0.0191 (9)	0.0209 (10)	0.0202 (10)	0.0002 (7)	0.0016 (8)	−0.0012 (8)
C7	0.0212 (8)	0.0256 (9)	0.0176 (8)	−0.0002 (7)	−0.0003 (9)	−0.0015 (10)
C8	0.0229 (10)	0.0238 (10)	0.0199 (10)	−0.0002 (8)	−0.0011 (8)	−0.0022 (8)
C9	0.0186 (9)	0.0259 (10)	0.0243 (11)	−0.0009 (7)	−0.0009 (7)	−0.0035 (8)
C10	0.0175 (9)	0.0233 (9)	0.0217 (12)	−0.0020 (7)	−0.0030 (7)	−0.0024 (8)
C11	0.0185 (9)	0.0265 (10)	0.0204 (10)	0.0013 (7)	−0.0016 (8)	−0.0053 (8)
C12	0.0222 (9)	0.0286 (11)	0.0186 (10)	−0.0009 (8)	−0.0003 (8)	−0.0012 (8)
C13	0.0242 (9)	0.0227 (10)	0.0213 (10)	−0.0017 (8)	−0.0042 (8)	−0.0014 (8)
C14	0.0242 (9)	0.0223 (9)	0.0223 (11)	0.0014 (7)	−0.0029 (9)	−0.0051 (9)
C15	0.0218 (9)	0.0275 (11)	0.0197 (10)	−0.0020 (8)	0.0013 (7)	−0.0038 (8)
C16	0.0391 (12)	0.0203 (10)	0.0319 (13)	0.0037 (9)	−0.0054 (10)	0.0007 (9)
N1	0.0340 (9)	0.0258 (10)	0.0262 (10)	−0.0005 (7)	−0.0052 (8)	0.0000 (8)
O1	0.0413 (9)	0.0276 (8)	0.0197 (8)	−0.0001 (6)	0.0023 (7)	−0.0022 (6)
O2	0.0547 (9)	0.0352 (8)	0.0350 (8)	0.0026 (7)	0.0094 (10)	0.0107 (9)
O3	0.0524 (9)	0.0210 (8)	0.0385 (9)	0.0061 (7)	−0.0038 (8)	−0.0040 (7)
S1	0.0248 (2)	0.0203 (2)	0.0227 (2)	0.00036 (18)	−0.0015 (2)	−0.0021 (2)

Geometric parameters (Å, º)

C1—C2	1.386 (3)	C10—C15	1.398 (3)
C1—C6	1.395 (3)	C10—C11	1.399 (3)
C1—H1	0.9500	C11—C12	1.386 (3)
C2—C3	1.392 (3)	C11—H11	0.9500
C2—H2	0.9500	C12—C13	1.386 (3)
C3—C4	1.405 (3)	C12—H12	0.9500
C3—S1	1.760 (2)	C13—C14	1.380 (3)
C4—C5	1.382 (3)	C13—N1	1.475 (3)
C4—H4	0.9500	C14—C15	1.386 (3)
C5—C6	1.398 (3)	C14—H14	0.9500
C5—H5	0.9500	C15—H15	0.9500
C6—C7	1.460 (3)	C16—S1	1.801 (2)
C7—C8	1.339 (3)	C16—H16A	0.9800
C7—H7	0.9500	C16—H16B	0.9800
C8—C9	1.478 (3)	C16—H16C	0.9800
C8—H8	0.9500	N1—O3	1.225 (2)
C9—O1	1.220 (2)	N1—O2	1.229 (3)
C9—C10	1.502 (3)		
C2—C1—C6	122.4 (2)	C15—C10—C9	119.33 (17)
C2—C1—H1	118.8	C11—C10—C9	121.39 (17)
C6—C1—H1	118.8	C12—C11—C10	120.48 (18)
C1—C2—C3	119.60 (19)	C12—C11—H11	119.8
C1—C2—H2	120.2	C10—C11—H11	119.8
C3—C2—H2	120.2	C13—C12—C11	118.31 (19)
C2—C3—C4	118.92 (18)	C13—C12—H12	120.8

C2—C3—S1	124.52 (16)	C11—C12—H12	120.8
C4—C3—S1	116.55 (15)	C14—C13—C12	122.88 (18)
C5—C4—C3	120.52 (18)	C14—C13—N1	119.64 (17)
C5—C4—H4	119.7	C12—C13—N1	117.48 (19)
C3—C4—H4	119.7	C13—C14—C15	118.07 (19)
C4—C5—C6	121.26 (18)	C13—C14—H14	121.0
C4—C5—H5	119.4	C15—C14—H14	121.0
C6—C5—H5	119.4	C14—C15—C10	120.96 (19)
C1—C6—C5	117.31 (19)	C14—C15—H15	119.5
C1—C6—C7	119.72 (19)	C10—C15—H15	119.5
C5—C6—C7	122.93 (18)	S1—C16—H16A	109.5
C8—C7—C6	126.3 (2)	S1—C16—H16B	109.5
C8—C7—H7	116.8	H16A—C16—H16B	109.5
C6—C7—H7	116.8	S1—C16—H16C	109.5
C7—C8—C9	121.26 (19)	H16A—C16—H16C	109.5
C7—C8—H8	119.4	H16B—C16—H16C	109.5
C9—C8—H8	119.4	O3—N1—O2	124.16 (18)
O1—C9—C8	122.38 (19)	O3—N1—C13	118.04 (19)
O1—C9—C10	119.72 (18)	O2—N1—C13	117.80 (17)
C8—C9—C10	117.90 (17)	C3—S1—C16	102.82 (10)
C15—C10—C11	119.24 (17)		

C6—C1—C2—C3	0.3 (3)	C8—C9—C10—C11	23.6 (3)
C1—C2—C3—C4	−0.3 (3)	C15—C10—C11—C12	−1.8 (3)
C1—C2—C3—S1	−179.35 (14)	C9—C10—C11—C12	175.91 (16)
C2—C3—C4—C5	−0.3 (3)	C10—C11—C12—C13	2.6 (3)
S1—C3—C4—C5	178.83 (14)	C11—C12—C13—C14	−1.1 (3)
C3—C4—C5—C6	0.9 (3)	C11—C12—C13—N1	178.38 (16)
C2—C1—C6—C5	0.2 (3)	C12—C13—C14—C15	−1.1 (3)
C2—C1—C6—C7	−177.38 (16)	N1—C13—C14—C15	179.42 (16)
C4—C5—C6—C1	−0.8 (3)	C13—C14—C15—C10	1.9 (3)
C4—C5—C6—C7	176.70 (17)	C11—C10—C15—C14	−0.5 (3)
C1—C6—C7—C8	−172.30 (18)	C9—C10—C15—C14	−178.24 (17)
C5—C6—C7—C8	10.3 (3)	C14—C13—N1—O3	12.0 (3)
C6—C7—C8—C9	−173.50 (18)	C12—C13—N1—O3	−167.51 (18)
C7—C8—C9—O1	11.4 (3)	C14—C13—N1—O2	−167.74 (19)
C7—C8—C9—C10	−168.69 (17)	C12—C13—N1—O2	12.8 (3)
O1—C9—C10—C15	21.2 (3)	C2—C3—S1—C16	0.09 (18)
C8—C9—C10—C15	−158.66 (17)	C4—C3—S1—C16	−179.01 (14)
O1—C9—C10—C11	−156.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O1^{i}	0.95	2.60	3.278 (3)	129

Symmetry code: (i) *x*, *y*, *z*+1.