organic compounds

N-(Triphenylmethylsulfanyl)phthalimide

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The title compound, $C_{27}H_{19}NO_2S$, contains chains of fused $R_2^2(19)$ rings formed by intermolecular C—H···O=C hydrogen bonds and running along the [011] and [0$\bar{1}$1] directions. These chains are linked through short intermolecular C—H···π contacts, giving rise to sheets. The conformation of the title compound is dominated primarily by the nearly orthogonal lone-pair orbitals on the N and S atoms.

Comment

This paper forms part of our continuing study of the synthesis and structural characterization of divalent sulfur compounds. We are particularly interested in the utility of the title compound, (I) (Fig. 1 and Table 1), as a convenient reagent for sulfenamide synthesis (Harpp & Back, 1971). A search of the Cambridge Structural Database (CSD; Version 5.25; Allen, 2002) for the thiophthalimide fragment with an S-alkyl or S-aryl substituent yielded only two examples, viz. N-(2-nitrophenylthio)phthalimide (CSD refcode DETGOY; Iwasaki & Masuko, 1986) and N-(trichloromethylthio)phthalimide (GUHDUI; Carle et al., 2000).
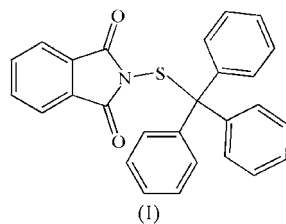
The thiophthalimide fragment in (I) is almost planar, with a dihedral angle of 2.1 (2)° between the N1/C20/C21/C26/C27 and C21–C26 planes. This value is similar to those found in N-(2-nitrophenylthio)phthalimide (1.4°; Iwasaki & Masuko, 1986). The six-membered ring of the phthalimide group is planar, with deviations within 0.020 (2) Å. The five-membered
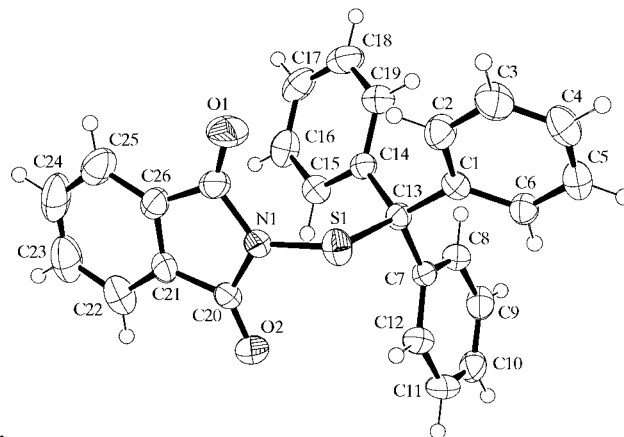
Figure 1
A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.
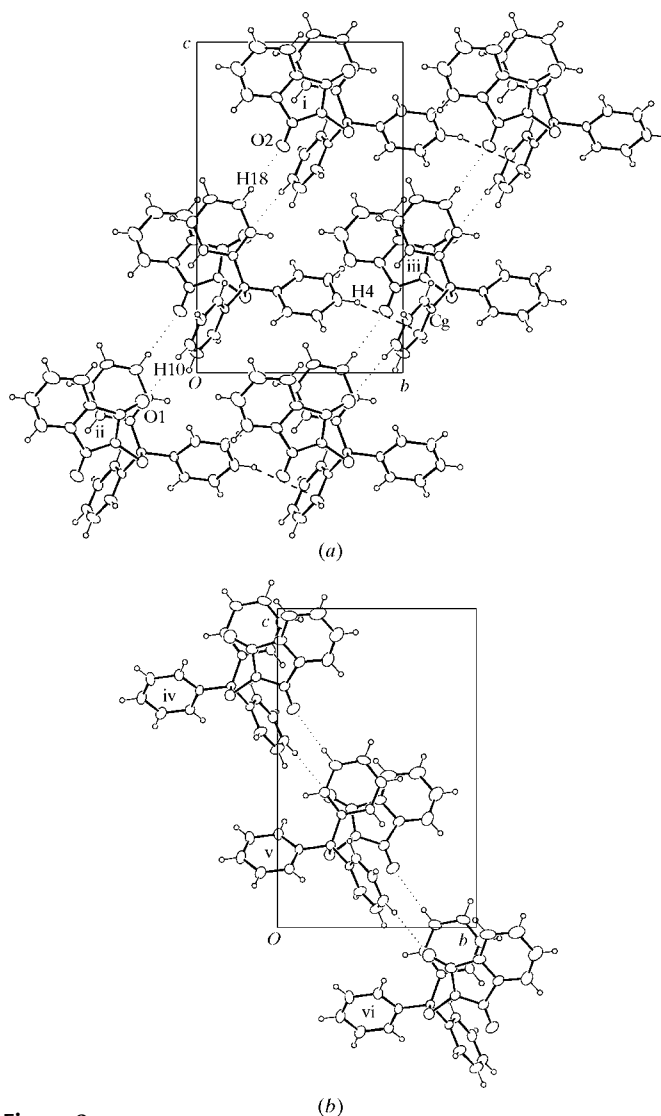
Figure 2
(a) A view of the packing of (I) along the a axis, showing the C—H···π interactions between the [011] chains. [Symmetry codes: (i) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$; (ii) $\frac{3}{2} - x$, $-\frac{1}{2} + y$, $-\frac{1}{2} + z$; (iii) x, $1 + y$, z.] (b) A view of the packing of (I) along the a axis, showing the [0$\bar{1}$1] chains. [Symmetry codes: (iv) $1 - x$, $-y$, $\frac{1}{2} + z$; (v) $-\frac{1}{2} + x$, $\frac{1}{2} - y$, z; (vi) $1 - x$, $1 - y$, $-\frac{1}{2} + z$.]
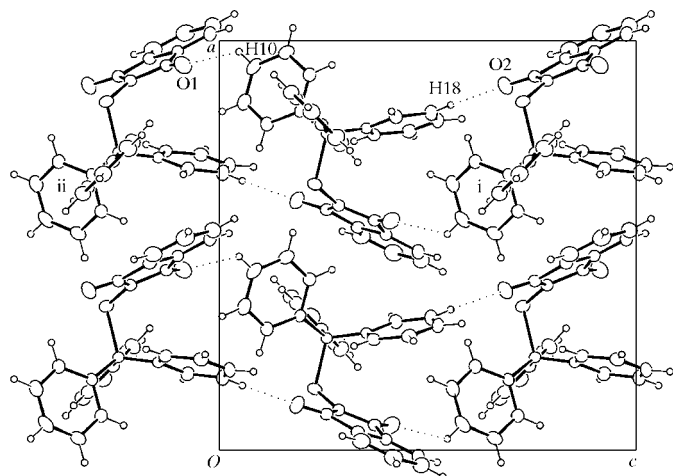
Figure 3
A view of the packing of (I) along the b axis, showing the [011] and [0$\bar{1}$1] chains. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$.]

ring is distorted, with significant out-of-plane deviations for atoms C20 [0.014 (1) Å] and C21 [0.015 (2) Å]. The S—N distance is shorter than the normal S—N single-bond length (1.74 Å), but is usual for this type of structure, many of which have S—N single bonds in the range 1.63–1.68 Å as a result of the π character of the S—N bond. The C13—Cn bonds [$n = 1$, 7 and 14; mean 1.537 (4) Å] are all well above the upper quartile value of 1.521 Å for Csp^3—C$_{aryl}$ bonds (Allen *et al.*, 1987). The mean of the 18 phenyl C—C distances is 1.381 (5) Å. The C—S distance is comparable to the value of 1.894 (2) Å found in *N,N*-dibenzyltriphenylmethanesulfen-amide (Brito *et al.*, 2004). The dihedral angles between phenyl rings C1–C6 and C7–C12, C1–C6 and C14–C19, and C7–C12 and C14–C19 in (I) are 81.9 (1), 57.5 (1) and 78.0 (1)°, respectively.

The crystal structure of (I) contains weak intermolecular C—H···O=C and C—H···π interactions (Table 2). The molecules act as double donors in C—H···O hydrogen bonds, linking molecules related by the *n*-glide planes (Fig. 2a and Table 2), thus generating chains of fused $R_2^2(19)$ rings (Bernstein *et al.*, 1995) along the [011] direction. Chains related by translation along [010] are linked through a C—H···π interaction, where the C4—H4 group at (x, y, z) acts as a donor to the centroid (Cg in Fig. 2a and Table 2) of the C7–C12 aryl ring at $(x, 1 + y, z)$, giving rise to sheets. An equivalent sheet, related to the other by the twofold screw axes along *c*, is generated in a similar way by means of chains running along the [0$\bar{1}$1] direction (Fig. 2b). The crystal structure is built up of these types of sheets, connected only by van der Waals interactions (Fig. 3).

Experimental

A heptane solution of trichloromethanesulfenyl chloride was added dropwise to a stirred dimethylformamide solution of phthalimide and triethylamine, producing (I) (Wunderly, 1972). Crystals suitable for X-ray analysis were grown by slow evaporation from dichloromethane–diethyl ether (1:1) at room temperature (m.p. 469 K). IR (KBr, cm^{-1}): 2360 (*m*), 1774 (*m*), 1718 (*vs*), 1440–1491 (*w*), 1340 (*w*),

1276 (*vs*), 1169 (*m*), 1089 (*w*), 1039 (*m*), 865 (*m*), 715–789 (*m*), 669 (*m*), 626 (*w*), 525–578 (*w*), 488 (*w*); UV–vis (CH$_2$Cl$_2$, nm): λ 285 (*sh*), 292, 302; MS(EI): *m/z*: 244, 243, 242, 241, 240, 239, 228, 166, 165, 147, 77, 76.

Crystal data

C$_{27}$H$_{19}$NO$_2$S	Mo Kα radiation
$M_r = 421.49$	Cell parameters from 2257
Orthorhombic, $Pna2_1$	reflections
$a = 14.790$ (15) Å	$\theta = 2.6$–27.5°
$b = 9.373$ (8) Å	$\mu = 0.18$ mm^{-1}
$c = 15.01$ (3) Å	$T = 298$ (2) K
$V = 2081$ (5) Å^3	Prism, colourless
$Z = 4$	$0.40 \times 0.25 \times 0.19$ mm
$D_x = 1.345$ Mg m^{-3}	

Data collection

Nonius KappaCCD area-detector diffractometer	4484 independent reflections
	3966 reflections with $I > 2\sigma(I)$
φ scans, and ω scans with κ offsets	$R_{int} = 0.053$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SORTAV*; Blessing, 1995)	$h = -19 \rightarrow 18$
$T_{min} = 0.943$, $T_{max} = 0.960$	$k = -12 \rightarrow 11$
17 690 measured reflections	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2$
$R(F) = 0.048$	$+ 0.1932P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.19$	$(\Delta/\sigma)_{max} = 0.004$
4484 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983)
	Flack parameter = 0.01 (7)

Table 1
Selected geometric parameters (Å, °).

S1—N1	1.685 (2)	O2—C20	1.193 (3)
S1—C13	1.894 (3)	C1—C13	1.543 (3)
N1—C20	1.412 (3)	C7—C13	1.534 (3)
N1—C27	1.419 (4)	C13—C14	1.533 (4)
O1—C27	1.191 (3)	C21—C26	1.379 (4)
N1—S1—C13	107.44 (10)	C14—C13—C1	114.43 (18)
C14—C13—C7	109.36 (18)	C7—C13—C1	111.87 (18)
C13—S1—N1—C20	−88.2 (2)	C13—S1—N1—C27	90.02 (19)

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

Cg is the centroid of the C7–C12 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C18—H18···O2^i	0.93	2.55	3.478 (5)	177
C10—H10···O1^{ii}	0.93	2.65	3.369 (5)	135
C4—H4···Cg^{iii}	0.93	2.87	3.778 (8)	164

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

The H atoms were positioned geometrically (C—H = 0.93 Å), riding on their carrier atoms, with U_{iso}(H) values set at 1.2 times U_{eq} of the parent atom. The orientation of the structure with respect to the polar axis (Jones, 1986) was determined on the basis of 2010 Friedel pairs. The number of unique reflections in the merged set is 2457.

organic compounds

Data collection: *COLLECT* (Nonius, 1998); cell refinement and data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997); program used to solve structure: *SIR97* (Altomare *et al.*, 1999); program used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1360). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C. & Guagliardi, A. R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brito, I., Vargas, D., León, Y., Cárdenas, A., López-Rodríguez, M. & Wittke, O. (2004). *Acta Cryst.* E**60**, o1668–o1670.
Carle, A. B., Krause Bauer, J. A. & Wilson, R. M. (2000). *Acta Cryst.* C**56**, 97–98.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Harpp, D. & Back, T. (1971). *Tetrahedron Lett.* **52**, 4957–4960.
Iwasaki, F. & Masuko, Y. (1986). *Acta Cryst.* C**42**, 124–127.
Jones, P. G. (1986). *Acta Cryst.* A**42**, 57.
Nonius (1998). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Wunderly, S. (1972). Unpublished results.