Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

O-(2-*tert*-Butyl-6-dimethylthiocarbamoyl-4-methylphenyl) *N*,*N*-dimethylthiocarbamate dichloromethane solvate

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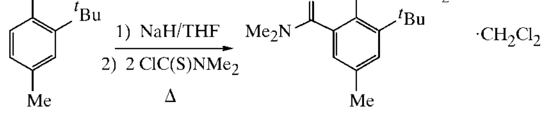
Received 14 July 2003
Accepted 28 August 2003
Online 23 September 2003

In the title compound, $C_{17}H_{26}N_2OS_2\cdot CH_2Cl_2$, the C=S distances are 1.650 (4) and 1.679 (3) Å, and the torsion angle between the planes of the thiocarbamate and carbonothioyl fragments is 54.4 (2)°. The steric and electronic effects that these substituents exert on one another determine the observed *anti* configuration with respect to the phenyl C atoms to which they are attached.

Comment

The synthesis of substituted thiophenols from the corresponding phenols requires the initial preparation and purification of substituted *O*-phenyl thiocarbamates. The latter compounds are necessary for the Newman–Kwart thermal rearrangement, which is the key step in the transformation of *O*-phenyl thiocarbamates to the corresponding *S*-phenylthiocarbamates (Newman & Karnes, 1966). In order to prepare a series of substituted thiophenols, we decided to undertake the synthesis and structural characterization of *O*-substituted thiocarbamates. We report here the preparation of the title compound, (I).



(I)

Compound (I) crystallizes with a disordered molecule of dichloromethane in the monoclinic space group $P2_1/c$ by slow evaporation of a concentrated dichloromethane solution. A search of the Cambridge Structural Database (*ConQuest*, Version 1.4; Cambridge Structural Database, 2002) revealed that there are no solid-state structure reports of aromatic compounds possessing both thiocarbamate and carbonothioyl moieties. Thus, compound (I) is the first of its kind to be crystallographically characterized.

The crystal structure features distinct C13=S1 and C7=S2 bond distances (Table 1). The shorter C13=S1 bond distance, which corresponds to the thiocarbamate group, is associated with the marginally longer C13—N1 bond, while the longer C7=S2 bond, which corresponds to the carbonothioyl group, is associated with the marginally shorter C7—N2 bond (Fig. 1).

The bond lengths and angles of the thiocarbamate group of (I) are comparable to those of the related compounds 2-[(diethylamino)carbonyl]-3-formylphenyl *N*,*N*-diethylthiocarbamate (Stanetty *et al.*, 2002) and the sterically demanding *O*-{2-[bis(pyrazol-1′-yl)methyl]-6-*tert*-butyl-4-methylphenyl}-*N*,*N*-dimethylthiocarbamate (Higgs & Carrano, 2002). Thus, the bond angles around the sp^2-hybridized C atoms of the thiocarbamate moieties of all three compounds are very similar, with values of 109.4 (3), 110.1 (2) and 110.1 (2)° for the N—C—O angle, 126.5 (2), 126.9 (2) and 126.5 (2)° for the N—C=S angle, and 124.0 (2), 123.0 (2) and 123.4 (2)° for the O—C=S angle, respectively. Although the corresponding bond lengths are comparable for the three compounds, the thiocarbamate C=S bond length of (I) [1.650 (4) Å] is shorter than that found for any related thiocarbamate (Bandarage *et al.*, 1994; Rao *et al.*, 2000). The geometric parameters of the carbonothioyl fragment, on the other hand, are comparable to those of the related compounds *N*,*N*-dimethylthiobenzamide (Walter *et al.*, 1976) and 2-hydroxy-*N*,*N*-dimethylthiobenz-

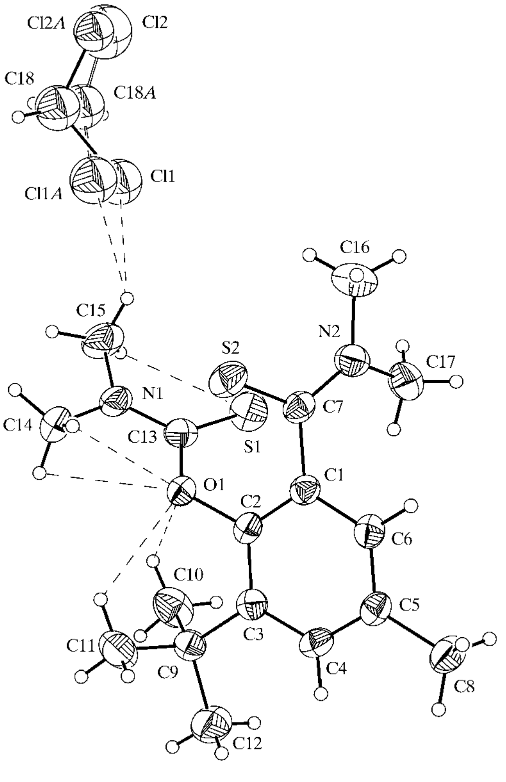


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 40% probability level. The CH_2Cl_2 molecule is disordered (see text).

DOI: 10.1107/S010827010301905X

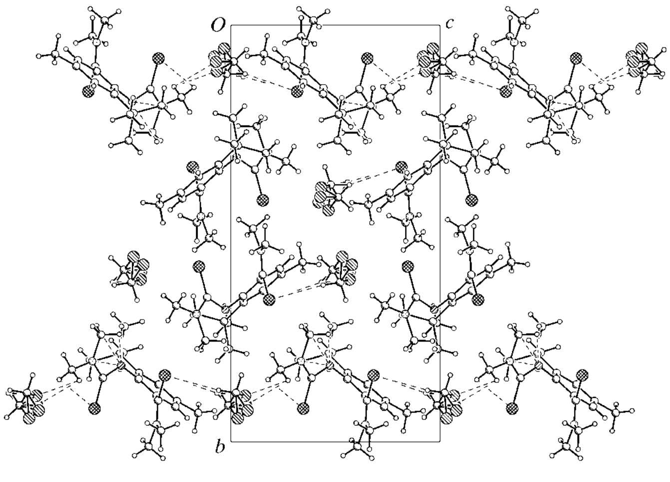


Figure 2
A view of the pseudo-channels along the [100] direction containing the CH_2Cl_2 molecules.

amide (Pertlik, 1990). The dihedral angle between the S1/O1/N1/C13–C15 thiocarbamate plane and the plane of the aromatic C1–C6 ring is 70.2 (1)°, which reflects the steric congestion due to the presence of the bulky *tert*-butyl and the sulfur-containing groups. This effect is further reflected in the dihedral angle between the planes of the carbonothioyl moiety and the aromatic ring [62.8 (2)°]. The corresponding dihedral angle between the planes of the thiocarbamate and carbonothioyl moieties is 54.4 (2)°.

Interestingly, the dichloromethane molecules pack along pseudo-channels, which can be viewed along the [100] axis in Fig. 2. Examination of the structure with *PLATON* (Spek, 2003) shows that there are intermolecular interactions between atoms Cl1 and Cl1*A* on the dichloromethane molecule and atom H15*A* on the dimethylamine group of the thiocarbamate functionality, as well as between atom Cl2 and atom H17*A* on atom C17 of the carbonothioyl fragment. Another interaction is observed between atom Cl2*A* and atom H6 on atom C6 of the aromatic ring. These interactions, together with the weak S2···H18*A* hydrogen bond (S···H = 2.86 Å), are probably responsible for stabilizing the dichloromethane molecule in the observed position. There are also short intramolecular contacts that need comment. There are three C—H···O1 interactions, to atoms H10*A*, H11*A* and H14*C* (H···O = 2.36, 2.42 and 2.43 Å, respectively). The first two interactions appear to be determined by the proximity of the *tert*-butyl group to atom O1, whereas the interaction involving atom H14*C* appears to be determined by the planarity of the thiocarbamate fragment, which brings the C14 methyl group close to atom O1. The latter geometric feature is also responsible for the short contact between atoms H15*C* (on C15) and S1, with an H···S distance of 2.78 Å, some 0.16 Å shorter than the sum of the van der Waals radii (Bondi, 1964). An analogous intramolecular contact between atoms H16*C* and S2 (H···S = 2.81 Å) arises as a result of the planarity of the carbonothioyl moiety.

Experimental

To a stirred solution of 2-*tert*-butyl-4-methylphenol (2.00 g, 12.17 mmol) in anhydrous tetrahydrofuran (75 ml) was added solid NaH (0.30 g, 12.17 mmol) in small portions. After the mixture had been stirred for 1 h, dimethylthiocarbamoyl chloride (3.01 g, 24.35 mmol) was added. The mixture was stirred for a further 1 h at room temperature and was then heated under reflux for 12 h, after which the mixture was cooled to room temperature and quenched with water (30 ml). The organic phase was diluted with diethyl ether (75 ml) and washed successively with water (30 ml) and a saturated Na_2CO_3 solution (30 ml). The organic layer was then dried with Na_2SO_4, filtered and concentrated with a rotary evaporator. The yellow solid obtained was dissolved in dichloromethane (25 ml), and slow evaporation of the solvent afforded yellow crystals of (I) (yield 0.66 g, 16.1%; m.p. 360–363 K). IR ($CHCl_3$, cm^{-1}): 3022, 2970, 2875, 1596, 1523, 1482, 1433, 1397, 1365, 1289, 1137, 1060, 930, 865, 824; ^{1}H NMR (300 MHz, $CDCl_3$, TMS internal reference): δ 7.18 (1H, *d*, ArH), 6.73 (1H, *d*, ArH), 3.47 (3H, *s*, NMe), 3.42 (3H, *s*, NMe), 3.39 (3H, *s*, NMe), 3.34 (3H, *s*, NMe), 2.3 (3H, *s*, ArMe), 1.36 (9H, *s*, ^{t}Bu); EI mass spectrum: *m*/*z* 338 (M^+, 70%).

Crystal data

$C_{17}H_{26}N_2OS_2{\cdot}CH_2Cl_2$
$M_r = 423.44$
Monoclinic, $P2_1/c$
$a = 9.5032$ (5) Å
$b = 21.4599$ (10) Å
$c = 11.7601$ (7) Å
$\beta = 113.791$ (1)°
$V = 2194.5$ (2) Å^3
$Z = 4$

$D_x = 1.282$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5414 reflections
$\theta = 2.5$–31.0°
$\mu = 0.50$ mm^{-1}
$T = 291$ (2) K
Prism, colorless
0.30 × 0.22 × 0.16 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
17 814 measured reflections
3851 independent reflections
2621 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.051$
$\theta_{\rm max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -25 \rightarrow 25$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.167$
$S = 0.99$
3851 reflections
230 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.096P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.50$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C13	1.650 (4)	N1—C13	1.327 (4)
S2—C7	1.679 (3)	N2—C7	1.316 (4)
O1—C13	1.358 (3)	C1—C7	1.499 (4)
O1—C2	1.395 (3)		
C13—O1—C2	122.2 (2)	N1—C13—O1	109.4 (3)
N2—C7—C1	118.1 (3)	N1—C13—S1	126.5 (2)
N2—C7—S2	123.1 (2)	O1—C13—S1	124.0 (2)
C1—C7—S2	118.4 (2)		

The positional parameters of the H atoms were calculated geometrically and refined as riding, with a fixed $U_{\rm iso}$ value ($1.2U_{\rm eq}$ of the parent atom) and C—H distances in the range 0.93–0.97 Å. The dichloromethane solvent molecule was refined isotropically at two positions, each with an occupancy of 0.5.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

IC and AFF thank CONACYT for financial support (Proyecto de Instalación No. 39130-E).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1269). Services for accessing these data are described at the back of the journal.

References

Bandarage, U. K., Simpson, J., Smith, R. A. J. & Weavers, R. T. (1994). *Tetrahedron*, **50**, 3463–3472.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bruker (2000). *SMART* (Version 5.625) and *SHELXTL* (Version 6.1). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SAINT*. Version 6.04. Bruker AXS Inc., Madison, Wisconsin, USA.

Cambridge Structural Database (2002). Version 5.19. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Higgs, T. C. & Carrano, C. J. (2002). *Eur. J. Org. Chem.* pp. 3632–3645.

Newman, M. S. & Karnes, H. A. (1966). *J. Org. Chem.* **31**, 3980–3984.

Pertlik, F. (1990). *Monatsh. Chem.* **121**, 129–139.

Rao, P., Enger, O., Graf, E., Hosseini, M. W., De Cian, A. & Fischer, J. (2000). *Eur. J. Inorg. Chem.* pp. 1503–1508.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Stanetty, P., Mons, M.-C. & Mereiter, K. (2002). Private communication.

Walter, V. W., Harto, S. & Voss, J. (1976). *Acta Cryst.* B**32**, 2876–2877.