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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.037

wR factor = 0.096

Data-to-parameter ratio = 13.1

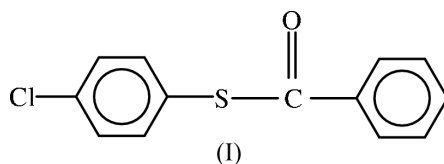
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

4-Chlorophenyl thiobenzoate

The title compound, $\text{C}_{13}\text{H}_9\text{ClOS}$, crystallizes in the orthorhombic system in the non-centrosymmetric space group $P2_12_12_1$, with one molecule in the asymmetric unit. The repulsion between two Cl atoms of neighbouring molecules is minimized by a 2_1 screw arrangement of the asymmetric unit.

Comment

Thiol esters constitute a group of natural products (Halcomb *et al.*, 1995) which function as coenzyme derivatives with a critical role in biochemical transformations (Stryer, 1988). These compounds are involved in the synthesis of proteins by chemical ligation of benzyl thiol esters (Baca *et al.*, 1995, and references therein), and are used as acyl donors in the resolution of secondary alcohols catalysed by ligase, in solid phase peptide synthesis (Benz, 1994) and as cephalosporin derivatives, which have been tested as elastic inhibitors (Alpegiani *et al.*, 1992). The role of thiol esters as acylating agents in biochemical processes and their high reactivity have made them attractive intermediates in a variety of synthetic transformations. The use of these compounds in the lactonization process (Nicolaou, 1977) involved in the synthesis of macrocyclic natural products and asymmetric C—C bond formation (Hirama *et al.*, 1979), achieved through the metal enolates derived from thiol esters, has added a new dimension to the utility of these esters. Thiol esters also play an important role in the development of thiol drugs; they protect the thiol group, increase the activity of the drug, and mask the undesired odour and taste of the native thiol (Bolasco, 1980). They are used as intermediates in the synthesis of ketones (McGarvey *et al.*, 1986), Grignard reagents (Conrow & Portoghese, 1986) and silylacetylenes (Kawanami *et al.*, 1983). Macrolactonization through thiol esters is accomplished in the preparation of a variety of natural products (Masamune *et al.*, 1977; Mohanraj & Ford, 1985).



Recently, we have synthesized a set of substituted thiol esters, and their structural features have been investigated with the help of ^1H NMR and melting points. In continuation, the crystallographic study of thiol esters has been carried out.

In the present work, the structural elucidation of the title compound, 4-chlorophenyl thiobenzoate, (I), has been undertaken (Fig.1 and Table 1). The 2_1 screw-related

Received 4 January 2005

Accepted 11 January 2005

Online 22 January 2005

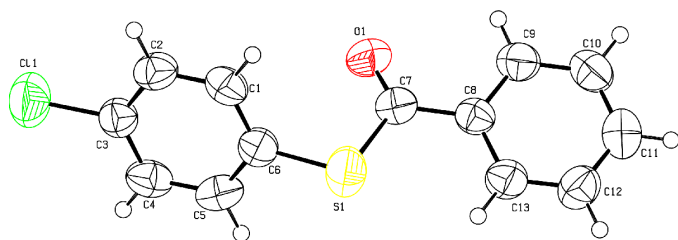


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids (ORTEP; Johnson, 1976).

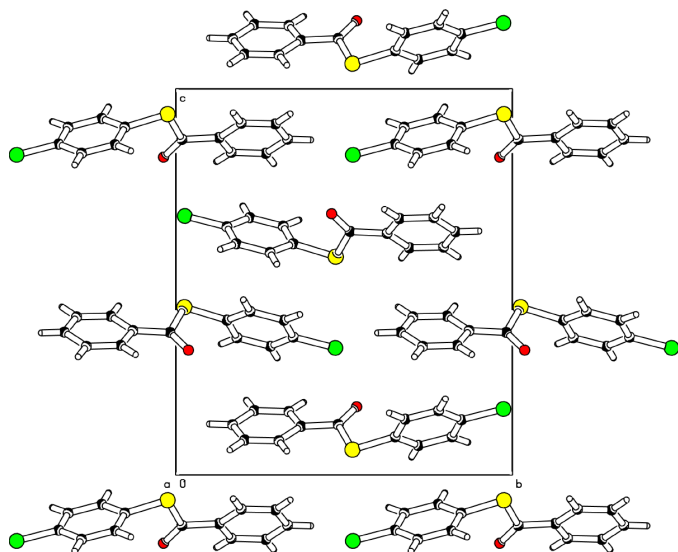


Figure 2
A packing diagram of the molecule, viewed down the *a* axis.

arrangement of the molecules in the unit cell is such that it minimizes the repulsion between two Cl atoms of neighbouring molecules (Fig. 2). Chlorine, being a highly electronegative atom, tries to pull the electrons away from sulfur through the benzene ring. Therefore the C–S bond length increases (1.771 Å) and hence bond strength decreases. The dihedral angle between the two benzene rings is 57.43 (9)°. The carbonyl group is slightly twisted from the plane of the C8–C13 benzene ring, having a torsion angle of 11.6 (5)° (Table 1). This twisting of the carbonyl group leads to short contacts between the aromatic H and carbonyl O atoms. There seems to be no hydrogen-bonding network in this structure. The bond length of the carbonyl group, 1.200 (4) Å, is normal.

Experimental

4-Chlorophenyl thiobenzoate was prepared using hydrotalcite (Cavani *et al.*, 1991) as a base catalyst. In a typical procedure, a 1:1 mixture of 4-chlorothiophenol (0.144 g, 1 mmol) and benzoyl chloride (0.093 ml, 1 mmol) was mixed intimately with hydrotalcite clay catalyst (250 mg) and heated as a solid mixture in an oil bath for about 4 h at 353 K. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction, the mixture was extracted with dichloromethane and recrystallized from methanol.

Crystal data

C₁₃H₉ClOS
M_r = 248.71
 Orthorhombic, *P*2₁2₁2₁
a = 5.8414 (4) Å
b = 13.3621 (8) Å
c = 15.3130 (13) Å
V = 1195.24 (15) Å³
Z = 4
D_x = 1.381 Mg m⁻³

Data collection

Nonius MACH3 four-circle diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.862, *T_{max}* = 0.932
 2084 measured reflections
 1912 independent reflections
 1338 reflections with *I* > 2 σ (*I*)

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.037
wR(*F*²) = 0.096
S = 1.02
 1912 reflections
 146 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.4019P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 10.1–14.1°
 μ = 0.47 mm⁻¹
T = 293 (2) K
 Needle, colourless
 0.25 × 0.2 × 0.15 mm

R_{int} = 0.029
 θ_{\max} = 27.0°
h = -1 → 7
k = -1 → 17
l = -1 → 19
 3 standard reflections
 frequency: 60 min
 intensity decay: none

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max}$ = 0.26 e Å⁻³
 $\Delta\rho_{\min}$ = -0.27 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0085 (14)
 Absolute structure: Flack (1983),
 388 Friedel pairs
 Flack parameter: 0.04 (13)

Table 1

Selected geometric parameters (Å, °).

C6–S1	1.771 (3)	C7–O1	1.200 (4)
S1–C7	1.780 (4)		
C6–S1–C7	101.00 (16)	O1–C7–S1	122.3 (3)
O1–C7–C8	122.7 (3)		
Cl1–C3–C4–C5	179.9 (3)	O1–C7–C8–C9	11.7 (5)

The H atoms were placed in geometrically calculated positions and included in the refinement in the riding-model approximation, with *U*_{iso}(H) equal to 1.2*U*_{eq} of the carrier atom (C–H = 0.93 Å).

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, (1994)); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The authors thank the Department of Science and Technology, Government of India, for establishing the Single Crystal Diffractometer facility at the School of Physics, Madurai Kamaraj University, Madurai, through the FIST programme.

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