

Structure of 2-[2-(3,4-Dimethoxyphenylthio)phenyl]-1-methylethylamine Hydrochloride

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Abstract. $C_{17}H_{22}NO_2S^+Cl^-$, $M_r = 339.88$, monoclinic, $C2/c$, $a = 28.276(8)$, $b = 9.567(2)$, $c = 12.766(3)$ Å, $\beta = 91.23(2)^\circ$, $V = 3453(2)$ Å³, $Z = 8$, $D_x = 1.308$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 31.40$ cm⁻¹, $F(000) = 1440$, $T = 295$ K, $R = 0.041$, $wR = 0.070$ for 2324 observed reflections. Pairs of diphenyl sulfide molecules related by C_2 axes are held together by bifurcated hydrogen bonds. The dimers bridged by Cl anions are arranged into layers parallel to the ab crystal plane. The dihedral angle between phenyl rings is $81.27(6)^\circ$ and the torsion angles about S—C bonds are C(2)—S(1)—C(12)—C(13) $-99.7(2)$ and C(3)—C(2)—S(1)—C(12) $2.0(2)^\circ$. The 2-aminopropyl side chain is approximately perpendicular to the phenyl ring [C(2)—C(7) inclusive] with the torsion angle C(6)—C(7)—C(8)—C(9) = $104.3(3)^\circ$.

Introduction. Recently, derivatives of diphenyl sulfides were found to be potentially antidepressive (Jilek *et al.*, 1989). They show a high affinity to both imipramine and desipramine binding sites in the rat brain and inhibit the re-uptake of 5-hydroxytryptamine as well as of noradrenaline in the rat-brain structures. For a better understanding of the relationships between structure and biological activity of these compounds we have focused on an analysis of the structural behaviour of diphenyl sulfides on the basis of their known three-dimensional structures (Schneider, 1989) and on the basis of X-ray structure determination of some prominent original derivatives. The title compound is a relatively weak inhibitor of serotonin and norepinephrine re-uptake receptors.

Experimental. Colourless plate-like crystals were grown from ethanol–heptane solution (9:1) by slow evaporation at room temperature. Crystal dimensions $0.4 \times 0.3 \times 0.2$ mm; Syntex $P2_1$ diffractometer; graphite-monochromated Cu $K\alpha$ radiation. Cell con-

stants by least squares using 24 reflections with $6 < 2\theta < 28^\circ$. Cell dimensions and space group also determined independently by Weissenberg and oscillation techniques. Unique data set collected using $\omega/2\theta$ scan; 2403 unique reflections, 2324 with $F > 3.92\sigma(F)$, $0 < 2\theta < 116^\circ$, $-18 \leq h \leq 18$, $0 \leq k \leq 10$, $0 \leq l \leq 13$. No absorption corrections applied ($\mu r = 0.94$). No significant variation observed in three standard reflections (800, 020, 004) measured after every 47 reflections.

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) in the space group $C2/c$ and refined with *SHELX76* (Sheldrick, 1976). The atomic scattering factors were taken from *SHELX76* (Sheldrick, 1976) without any changes. An isotropic refinement based on $|F|$ with all non-H atoms gave $R = 0.13$. H atoms were added at geometrically idealized positions and refined without any constraints to $R = 0.11$. Finally, anisotropic refinement of non-H atoms and isotropic of H atoms (287 variables) converged at $R = 0.041$ and $wR = 0.070$, $S = 2.2$ using 2324 F 's with $F > 3.92\sigma(F)$ and at $R = 0.042$ and $wR = 0.071$ for all unique reflections $\{w = [\sigma(F)^2 + 0.0009F^2]^{-1}\}$. $(\Delta/\sigma)_{\max} = 0.24$. A final difference Fourier map did not contain any peaks higher than 0.27 and lower than -0.32 e Å⁻³.

Discussion. The final fractional coordinates and equivalent isotropic temperature factors for non-H atoms and for some structurally important H atoms are listed in Table 1 along with their e.s.d.'s.* A *PLUTO* (Motherwell & Clegg, 1978) drawing of a pair of molecules of the title compound, related by a twofold axis, is depicted in Fig. 1 and a packing

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52762 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^5$ for S, Cl, x of C atoms; $\times 10^4$ for y, z of C atoms), equivalent isotropic temperature factors for non-H atoms ($\text{\AA}^2 \times 10^4$) and isotropic temperature factors for H atoms ($\text{\AA}^2 \times 10^3$) with their *e.s.d.*'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}/U_{iso}
S(1)	44050 (2)	18565 (6)	96062 (4)	525 (2)
Cl(22)	28513 (2)	21053 (6)	23553 (5)	644 (3)
C(2)	41758 (7)	3175 (2)	8755 (2)	434 (7)
C(3)	44681 (8)	4017 (2)	8162 (2)	486 (7)
C(4)	42781 (9)	5046 (2)	7505 (2)	554 (8)
C(5)	38003 (10)	5242 (2)	7438 (2)	613 (9)
C(6)	35063 (9)	4410 (3)	8030 (2)	565 (8)
C(7)	36817 (8)	3375 (2)	8691 (2)	462 (7)
C(8)	33427 (8)	2529 (3)	9338 (2)	540 (8)
C(9)	32421 (8)	1052 (2)	8962 (2)	500 (8)
N(10)	30630 (7)	1068 (2)	7841 (1)	480 (7)
C(11)	28658 (11)	346 (3)	9623 (2)	656 (10)
C(12)	50339 (8)	2002 (2)	9501 (2)	455 (7)
C(13)	52727 (8)	1067 (2)	8849 (2)	458 (7)
C(14)	57549 (7)	1166 (2)	8764 (1)	424 (6)
O(15)	60330 (5)	305 (2)	8172 (1)	561 (5)
C(16)	58223 (10)	-855 (2)	7652 (2)	542 (8)
C(17)	60080 (7)	2203 (2)	9328 (2)	450 (7)
O(18)	64827 (5)	2232 (2)	9151 (1)	549 (5)
C(19)	67636 (10)	3260 (3)	9702 (3)	677 (10)
C(20)	57675 (9)	3097 (2)	9985 (2)	534 (8)
C(21)	52840 (9)	2998 (2)	10068 (2)	544 (7)
H(101)	328 (1)	139 (3)	740 (2)	60 (7)
H(102)	275 (1)	157 (3)	774 (2)	86 (9)
H(103)	302 (1)	30 (3)	764 (2)	76 (10)
H(161)	611 (1)	-146 (4)	752 (2)	91 (9)
H(162)	561 (1)	-55 (2)	709 (2)	56 (6)
H(163)	564 (1)	-140 (3)	817 (2)	71 (8)
H(191)	709 (1)	300 (3)	964 (2)	87 (10)
H(192)	678 (1)	311 (3)	1049 (2)	75 (9)
H(193)	666 (1)	426 (3)	955 (2)	82 (9)

diagram is shown in Fig. 2. Intra- and intermolecular geometrical parameters were computed by the program *PARST* (Nardelli, 1983).

Two diphenyl sulfide molecules related by twofold axes are held together by bifurcated hydrogen bonds, $N(10) \cdots H(101) \cdots O(15^i), O(18^i)$ [$N(10) \cdots O(15^i)$ 2.980 (3), $N(10) \cdots O(18^i)$ 3.092 (3) Å; $N(10) \cdots H(101) \cdots O(15^i)$ 129 (2), $N(10) \cdots H(101) \cdots O(18^i)$ 153 (2)°], where (i) = 1 - $x, y, 1.5 - z$. Cl anions are located between pairs of dimers of diphenyl sulfide molecules, related by twofold screw axes, and these layers are parallel to the *ab* crystal plane [$N(10) \cdots Cl(22)$ 3.126 (2), $N(10) \cdots Cl(22^{ii})$ 3.153 (2) Å; $N(10) \cdots H(102) \cdots Cl(22)$ 171 (3), $N(10) \cdots H(103) \cdots Cl(22^{ii})$ 170 (3)°], where (ii) = 0.5 - $x, y - 0.5, 1.5 - z$. The layers have only van der Waals contacts.

The principal bond lengths, bond angles and torsion angles are listed in Table 2. The skeleton of the molecule has all the characteristic features of diphenyl sulfides (Schneider, 1989), as determined from a comparison of structures retrieved from the Cambridge Structural Database (Allen *et al.*, 1979).

The torsion angles around the S—C bonds are $C(2) \cdots S(1) \cdots C(12) \cdots C(21)$ 81.6 (2) and $C(3) \cdots C(2) \cdots$

$S(1) \cdots C(12)$ 2.0 (2)°. The angle between the mean planes of the two phenyl rings is 81.27 (6)°. The phenyl ring, $C(2) \cdots C(7)$ inclusive, is planar [$\chi^2 = 1.2$] with greatest deviation -0.001 (2) Å for C(3). The S(1) and C(8) atoms lie near this plane [deviations are -0.0075 (6) and -0.041 (3) Å respectively]. The C atoms of the 2-aminopropyl moiety are almost planar and are approximately perpendicular to the mean plane of the phenyl ring.

The second phenyl ring, $C(12) \cdots C(13) \cdots C(14) \cdots C(17) \cdots C(20) \cdots C(21)$, is more distorted from planarity [greatest deviation for C(17): 0.009 (2) Å].

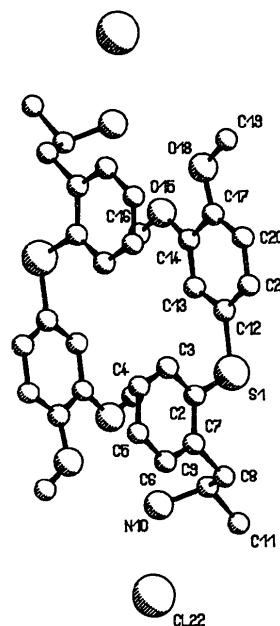


Fig. 1. Perspective view of a pair of 2-[2-(3,4-dimethoxyphenylthio)phenyl]-1-methylethylamine hydrochloride molecules related by a twofold axis and linked by bifurcated H bonds, see text. The labelling scheme is also shown for one molecule in the pair. Hydrogen atoms are omitted for clarity.

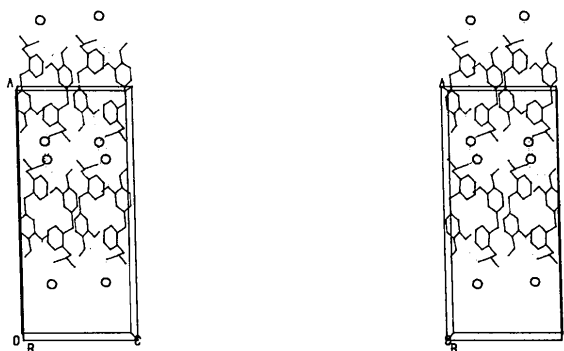


Fig. 2. Stereoscopic packing diagram showing the view down the unique *b* axis. Hydrogens are omitted for clarity. Dotted lines show hydrogen-bonded contacts.

Table 2. Selected bond lengths (Å), angles (°) and torsion angles (°)

S(1)—C(2)	1.779 (2)	C(9)—C(11)	1.530 (4)
S(1)—C(12)	1.791 (2)	C(14)—O(15)	1.376 (2)
C(7)—C(8)	1.514 (3)	C(17)—O(18)	1.366 (2)
C(8)—C(9)	1.518 (3)	O(15)—C(16)	1.418 (3)
C(9)—N(10)	1.508 (3)	O(18)—C(19)	1.438 (3)
C(2)—S(1)—C(12)	104.4 (1)	N(10)—C(9)—C(11)	107.8 (2)
S(1)—C(2)—C(7)	118.6 (2)	C(13)—C(14)—C(17)	120.1 (2)
S(1)—C(2)—C(3)	122.1 (2)	C(14)—C(17)—C(20)	119.5 (2)
S(1)—C(12)—C(13)	119.0 (2)	C(13)—C(14)—O(15)	125.6 (2)
S(1)—C(12)—C(21)	120.8 (2)	C(20)—C(17)—O(18)	125.7 (2)
C(3)—C(2)—C(7)	119.3 (2)	O(15)—C(14)—C(17)	114.3 (2)
C(13)—C(12)—C(21)	120.1 (2)	O(18)—C(17)—C(14)	114.8 (2)
C(7)—C(8)—C(9)	116.2 (2)	C(14)—O(15)—C(16)	119.1 (2)
C(8)—C(9)—N(10)	110.3 (2)	C(17)—O(18)—C(19)	117.9 (2)
C(8)—C(9)—C(11)	111.3 (2)		
C(12)—S(1)—C(2)—C(7)	-177.5 (2)	C(13)—C(14)—O(15)—C(16)	-4.8 (3)
C(12)—S(1)—C(2)—C(3)	2.0 (2)	C(20)—C(17)—O(18)—C(19)	1.1 (3)
C(2)—S(1)—C(12)—C(13)	-99.7 (2)	C(14)—O(15)—C(16)—H(161)	-160 (2)
C(2)—S(1)—C(12)—C(21)	81.6 (2)	C(14)—O(15)—C(16)—H(162)	69 (2)
S(1)—C(2)—C(3)—C(4)	-179.7 (2)	C(14)—O(15)—C(16)—H(163)	-52 (2)
S(1)—C(2)—C(7)—C(8)	1.4 (3)	C(17)—O(18)—C(19)—H(191)	166 (2)
S(1)—C(12)—C(13)—C(14)	-179.9 (2)	C(17)—O(18)—C(19)—H(192)	66 (2)
C(2)—C(7)—C(8)—C(9)	-77.5 (3)	C(17)—O(18)—C(19)—H(193)	-59 (2)
C(7)—C(8)—C(9)—N(10)	-55.7 (3)	C(8)—C(9)—N(10)—H(103)	179 (3)
C(7)—C(8)—C(9)—C(11)	-175.4 (2)	C(8)—C(9)—C(11)—H(112)	-177 (2)

The S1 atom as well as the non-H atoms of both methoxy groups lie nearly in this plane with greatest deviations for C(16): -0.187 (3) and C(19): 0.070 (3) Å. Angles O(15)—C(14)—C(17) and O(18)—C(17)—C(14) (see Table 2) are lower than their ideal value of 120° because of repulsion between the methoxy groups and the phenyl ring,

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Structure of 3-Phenyl-3-piperidino-2,4-pentanedione Monooxime

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Abstract. C₁₆H₂₂N₂O₂, *M_r* = 274.4, monoclinic, *P*2₁/*a*, *a* = 14.253 (9), *b* = 9.994 (6), *c* = 10.468 (4) Å, β = 93.70 (4)°, *V* = 1488.0 Å³, *Z* = 4, *D_m* = 1.21, *D_x* = 1.22 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.076 mm⁻¹, *F*(000) = 592, *T* = 293 K, *R* = 0.06 for 2341 observed reflections. The conformation of the piperidine ring is a chair. The dihedral angle between the least-squares planes through the benzene and the six-membered heterocyclic rings is 56.7 (1)°. Crystal cohesion is mainly governed by van der Waals contacts, although there is a weak intermolecular H bond.

and attraction between the O(15) and O(18) atoms and the H(101ⁱ) atom. H atoms of the methyl groups minimize overlap with the phenyl ring [see Table 2; H(131)⋯H(162) 2.47 (3), H(131)⋯H(163) 2.36 (4), H(201)⋯H(192) 2.48 (4), H(201)⋯H(193) 2.33 (4) Å].

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