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4-(2′-Hydroxythiobenzoyl)morpholine

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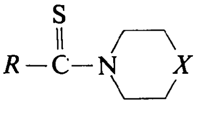
Abstract. $C_{11}H_{13}NO_2S$, orthorhombic, $P2_12_12_1$, a = 13·447 (2), b = 18·186 (3), c = 8·980 (1) Å, Z = 8, d_c = 1·35 Mg m^{-3}. The two molecules in the asymmetric unit have similar geometry, with a torsion angle of nearly 65° about the bond joining the phenyl and thiocarbonyl groups. Distortions of the thioamide moiety from strict planarity appear to be significant. The two intermolecular hydrogen bonds have O···S distances of 3·199 (6) and 3·180 (7) Å.

Introduction. The barrier to rotation about the C—N bond in thioamides has been studied by a number of authors using NMR techniques. In two classes of *N*,*N*-dialkylthiobenzamides, Berg (1976) and Krueger & Fulea (1975) have shown that *o*-hydroxy substituents decrease the barrier ($\Delta G^{\ddagger}$) by 10–20 kJ mol^{-1}, while *o*-methoxy groups raise the barrier by a similar amount. A paucity of structural data on compounds of this type has hampered the interpretation of spectroscopic data.

This study is part of a series of crystallographic investigations of thioamides of the type



where *R* is a group capable of conjugation with the thiocarbonyl group and N is part of a morpholine or piperidine ring. A comparison of structural parameters may provide new insights into the relative importance of electronic and steric effects.

An additional point of interest in 4-(2′-hydroxythiobenozyl)morpholine[†] is the possibility for O—H···S hydrogen bonding. The IR spectra of the *o*-hydroxy derivatives have been interpreted in favour of an *intra*-molecular hydrogen bond in both the *N*,*N*-dimethylthiobenzamide and in the thiobenzoylmorpholine derivatives. It is reported to be weak in the former and strong in the latter.

4-(2′-Hydroxythiobenzoyl)morpholine crystallizes from benzene as transparent crystals with a slightly yellow cast. The form {210} is developed with [001] elongated. A crystal of dimensions 0·15 × 0·10 × 0·25 mm was cut from a longer one and mounted parallel to the c axis. Data were collected using Ni-filtered Cu $K\alpha$ radiation (λ = 1·5418 Å) on an automated Picker FACS-1 diffractometer operated in the θ–2θ scan mode with a scan rate of 0·5° min^{-1} and a scan range of $\Delta 2\theta = (1{\cdot}2 + 0{\cdot}285\tan\theta)^{\circ}$. Background was measured for 20 s at either end of the scan. Application of an analytical absorption correction [μ(Cu $K\alpha$) = 2·387 mm^{-1}] resulted in coefficients in the range 1·104 to 1·316. Of the 1885 independent reflections measured

Table 1. *Atomic coordinates* (× 10^4) *for* 4-(2′-*hydroxythiobenzoyl*)*morpholine*

	x	*y*	*z*
S	1273 (2)	9101 (1)	11171 (3)
C(1)	1874 (7)	8850 (5)	9586 (10)
C(2)	2510 (7)	8190 (5)	9644 (10)
C(3)	2289 (8)	7557 (5)	8813 (11)
O(1)	1444 (5)	7596 (3)	7968 (8)
C(4)	2881 (9)	6939 (5)	8964 (13)
C(5)	3701 (9)	6957 (6)	9842 (12)
C(6)	3940 (8)	7571 (7)	10639 (11)
C(7)	3345 (9)	8183 (5)	10553 (11)
N	1771 (6)	9222 (4)	8320 (8)
C(8)	1077 (10)	9828 (5)	8108 (12)
C(9)	508 (9)	9709 (6)	6738 (12)
O(2)	1077 (7)	9628 (4)	5451 (8)
C(10)	1685 (9)	9005 (6)	5630 (10)
C(11)	2365 (8)	9097 (5)	6979 (11)
S′	1032 (2)	6092 (1)	6271 (3)
C(1)′	516 (7)	6323 (5)	4641 (10)
C(2)′	−121 (7)	6997 (5)	4541 (9)
C(3)′	157 (7)	7628 (5)	3803 (10)
O(1)′	1038 (5)	7597 (3)	2986 (7)
C(4)′	−413 (7)	8256 (5)	3918 (11)
C(5)′	−1259 (8)	8248 (6)	4735 (11)
C(6)′	−1571 (9)	7639 (7)	5481 (12)
C(7)′	−1008 (8)	7024 (6)	5406 (10)
N′	653 (6)	5921 (4)	3395 (8)
C(8)′	1300 (9)	5283 (5)	3359 (12)
C(9)′	2005 (9)	5393 (6)	2049 (15)
O(2)′	1510 (6)	5485 (4)	673 (8)
C(10)′	909 (9)	6138 (6)	764 (11)
C(11)′	127 (8)	6065 (6)	1974 (10)

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[†] This structure has been reported as part of papers presented at the 61st Canadian Chemical Conference and the 11th International Congress of Crystallography (Van Roey & Kerr, 1978*a*,*b*). Crystal data for a different crystalline form have been published (Sarkar & Sen Gupta, 1978).

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with $2\theta \leq 120°$, 982 had intensities greater than $3\sigma(I)$ where $\sigma^2(I) = T + B + (0{\cdot}02I)^2$, T is the total peak count and B is the background count normalized to the time interval of the scan.

The structure was solved by direct methods. The E map from *MULTAN* showed 26 of the 30 non-hydrogen atoms. Those remaining were located in a difference Fourier map. Refinement by full-matrix least squares (one molecule/cycle) converged with $R = 0{\cdot}0667$ for the observed reflections.

During the final stages of refinement, H atoms were included in the model in calculated positions with the C—H distance set to 1·04 Å and an isotropic temperature parameter $U_{\rm iso} = 0{\cdot}06$ Å^2. Hydroxyl H atoms were not located in the difference map and so were not included in the model. The function minimized was $\sum w\Delta^2$ where $w = [\sigma^2(I) + 0{\cdot}002F^2]^{-1/2}$. Reflections with $I \leq 3\sigma(I)$ were given zero weight if $F_{\rm calc} \leq F_{\rm obs}$. At convergence the value of $R_w = (\sum w\Delta^2/\sum wF^2_{\rm obs})^{1/2} = 0{\cdot}0905$ for the 1598 reflections of non-zero weight. The standard deviation of an observation of unit weight is 1·185. Final atomic coordinates of the non-hydrogen atoms are given in Table 1.* The scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The molecular geometry of 4-(2'-hydroxythiobenzoyl)morpholine and the numbering scheme used in the text are shown in Fig. 1. The two molecules of the asymmetric unit are related by a pseudo twofold screw axis parallel to **z** at $x = 0{\cdot}125$, $y = 0{\cdot}750$. The molecules are linked in extended chains by hydrogen bonds, as illustrated in Fig. 2. Molecule 1 donates a proton to the S of molecule 2 forming a hydrogen bond with an O(1)···S' distance of 3·199 (6) Å. Molecule 1 accepts a proton from O(1)' in the cell adjacent in the

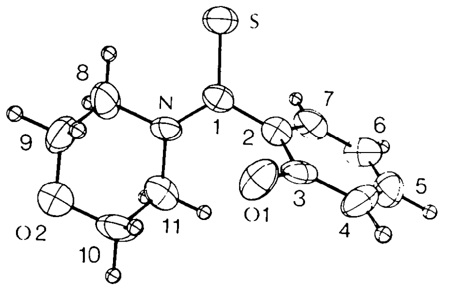

Fig. 1. A perspective view of a molecule of 4-(2'-hydroxythiobenzoyl)morpholine showing the numbering scheme used in the text. The boundary ellipsoids have been drawn at the 50% probability level.

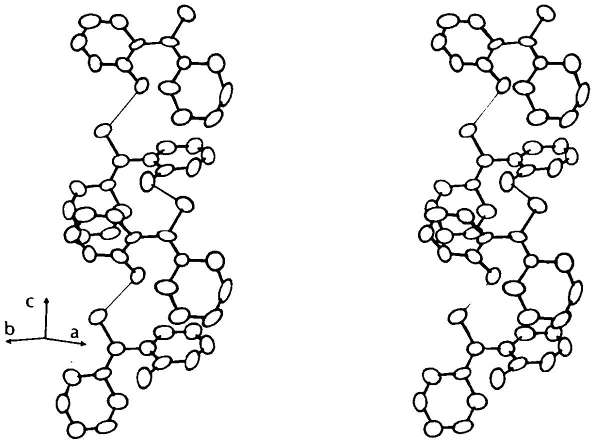

Fig. 2. Intermolecular hydrogen bonding in 4-(2'-hydroxythiobenzoyl)morpholine. The two molecules in the middle correspond to the coordinates listed in Table 1. Thus the order is 2(+z), 1, 2, 1(−z).

Table 2. *Bond distances* (Å) *and angles* (°)

	Molecule 1	Molecule 2
S—C(1)	1·699 (9)	1·673 (9)
C(1)—C(2)	1·47 (1)	1·50 (1)
C(1)—N	1·33 (1)	1·35 (1)
C(2)—C(3)	1·40 (1)	1·38 (1)
C(2)—C(7)	1·39 (2)	1·42 (1)
C(3)—O(1)	1·37 (1)	1·40 (1)
C(3)—C(4)	1·38 (1)	1·38 (1)
C(4)—C(5)	1·36 (2)	1·35 (1)
C(5)—C(6)	1·36 (2)	1·36 (2)
C(6)—C(7)	1·37 (2)	1·35 (2)
N—C(8)	1·46 (1)	1·45 (1)
N—C(11)	1·46 (1)	1·48 (1)
C(8)—C(9)	1·46 (2)	1·52 (2)
C(9)—O(2)	1·39 (1)	1·41 (2)
O(2)—C(10)	1·41 (1)	1·44 (1)
C(10)—C(11)	1·53 (1)	1·52 (2)
S—C(1)—C(2)	117·7 (7)	119·6 (6)
S—C(1)—N	122·0 (7)	122·3 (7)
C(2)—C(1)—N	120·3 (8)	118·1 (8)
C(1)—C(2)—C(3)	121·8 (9)	123·8 (8)
C(3)—C(2)—C(7)	118·4 (9)	117·4 (8)
C(1)—C(2)—C(7)	119·8 (8)	118·3 (8)
C(2)—C(3)—O(1)	115·3 (8)	116·7 (8)
O(1)—C(3)—C(4)	125·0 (9)	123·0 (8)
C(2)—C(3)—C(4)	119·5 (9)	120·2 (9)
C(3)—C(4)—C(5)	120 (1)	119·9 (9)
C(4)—C(5)—C(6)	121 (1)	122 (1)
C(5)—C(6)—C(7)	120 (1)	118 (1)
C(6)—C(7)—C(2)	120·7 (9)	121·7 (9)
C(1)—N—C(8)	124·3 (8)	122·2 (8)
C(1)—N—C(11)	124·6 (8)	123·6 (8)
C(8)—N—C(11)	111·1 (7)	114·1 (7)
N—C(8)—C(9)	109·5 (8)	106·5 (8)
C(8)—C(9)—O(2)	115 (1)	113 (1)
C(9)—O(2)—C(10)	108·1 (8)	108·2 (8)
O(2)—C(10)—C(11)	110·5 (8)	111·0 (8)
C(10)—C(11)—N	110·1 (8)	107·6 (8)

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* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34571 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°)

	Molecule 1	Molecule 2
S–C(1)–C(2)–C(3)	115·2 (8)	109·6 (8)
S–C(1)–C(2)–C(7)	−64·1 (8)	−62·2 (8)
S–C(1)–N–C(8)	−6·2 (7)	−3·4 (7)
S–C(1)–N–C(11)	171 (1)	174 (1)
C(1)–C(2)–C(3)–O(1)	−0·6 (9)	6·8 (8)
N–C(1)–C(2)–C(3)	−63·8 (9)	−70·4 (9)
N–C(1)–C(2)–C(7)	117 (1)	118 (1)
C(8)–N–C(1)–C(2)	173 (1)	177 (1)
C(11)–N–C(1)–C(2)	−9·7 (9)	−6·5 (8)

Table 4. *Selected intramolecular non-bonded distances* (Å)

	Molecule 1	Molecule 2
S···C(8)	3·06 (1)	3·02 (1)
S···H(8)	2·57*	2·50*
S···C(7)	3·30 (1)	3·32 (1)
S···H(7)	3·13*	3·19*
O(1)···C(11)	3·13 (1)	3·18 (1)
O(1)···N	3·01 (1)	3·11 (1)
O(1)···C(1)	2·76 (1)	2·84 (1)
C(2)···H(11)	2·43*	2·39*
C(2)···C(11)	2·91 (1)	2·88 (1)
C(3)···N	3·14 (1)	3·20 (1)
C(3)···H(11*A*)	2·56*	2·58*
C(3)···C(11)	3·25 (1)	3·28 (1)

* Hydrogen positions not refined.

+**z** direction with an O(1)′···S distance of 3·180 (7) Å. Contrary to the conclusions from IR spectroscopy, these are *inter*- rather than *intra*-molecular hydrogen bonds. Since the distances are considerably shorter than the sum of the van der Waals radii for O and S, 3·25 Å, these are strong hydrogen bonds of their class (Hamilton & Ibers, 1968). These O···S distances are among the shortest in the literature (Srinivasan & Chacko, 1967).

The thioamide moiety shows the short C–N bond, the long C–S bond and the planar N that typify this class of compounds (Table 2). The torsion angle between the phenyl and thiocarbonyl groups is close to 65° in both molecules (Table 3), thus allowing little overlap between the two π systems. Hydrogen bonding does not appear to have had much influence on the conformation since the torsion angle reported here is very close to the 64·8 (2)° observed in the parent compound, 4-thiobenzoylmorpholine (Kerr & Van Roey, 1979). The dominant influence appears to be the short intramolecular contacts involving the phenyl ring. These are listed in Table 4.

In spite of the large distortions in the bond angles, the N atom is within 0·02 Å of the plane defined by C(1), C(8) and C(11). This implies that the hybridization is essentially sp^2 with the lone-pair electrons in a *p*-type orbital perpendicular to that plane. However, the thioamide group is significantly distorted with the plane C(2), C(1), S rotated with respect to the plane C(1), C(8), C(11) so that the angle between the normals is about 8° for molecule 1 and about 5° for molecule 2.

Computer programs used include *MULTAN* (Germain, Main & Woolfson, 1971), *CUDLS* (J. Stephens), *ORTEP* (Johnson, 1965) and several from the Los Alamos Scientific Laboratory system of programs (A. C. Larson).

References

Berg, U. (1976). *Acta Chem. Scand. Ser. B*, **30**, 695–704.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*. New York, Amsterdam: Benjamin.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kerr, K. A. & Van Roey, P. M. A. O. (1979). *Acta Cryst.* B**35**, 2344–2347.

Krueger, P. J. & Fulea, A. O. (1975). *Tetrahedron*, **31**, 1813–1816.

Sarkar, P. B. & Sen Gupta, S. P. (1978). *Z. Kristallogr.* **147**, 151–152.

Srinivasan, R. & Chacko, K. K. (1967). *Conformation in Biopolymers*, Vol. II, edited by G. N. Ramachandran, pp. 607–616. London, New York: Academic Press.

Van Roey, P. M. A. O. & Kerr, K. A. (1978*a*). 61st Canadian Chemical Conference, Winnipeg, Canada, 4–7 June. Abstract PH-54.

Van Roey, P. M. A. O. & Kerr, K. A. (1978*b*). *Acta Cryst.* A**34**, S100.