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The Structure of 1-(2-Hydroxythiobenzoyl)piperidine: Room-Temperature X-ray Diffraction and 20 K Neutron Diffraction Study

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Abstract

1-(2-Hydroxythiobenzoyl)piperidine, $C_{12}H_{15}NOS$, orthorhombic, *Pbca*, $Z = 8$, $a = 13{\cdot}526\,(6)$, $b = 19{\cdot}256\,(6)$, $c = 8{\cdot}868\,(2)$ Å, $V = 2309{\cdot}4$ Å^3, $D_c = 1{\cdot}273$ Mg m^{-3} at 293 K, $R = 4{\cdot}51$, $R_w = 4{\cdot}91\%$ for 1497 reflections; $a = 13{\cdot}387\,(5)$, $b = 18{\cdot}947\,(5)$, $c = 8{\cdot}831\,(2)$ Å, $V = 2239{\cdot}9$ Å^3, $D_c = 1{\cdot}312$ Mg m^{-3} at 20 K, $R = 8{\cdot}1$, $R_w = 7{\cdot}1\%$ for 2107 reflections. Intramolecular steric contacts cause the *o*-hydroxyphenyl group to be rotated out of the plane of the thioamide moiety by 68·5 (2)° at 293 K and by 66·4 (3)° at 20 K. This conformation is similar to those observed for other *N*,*N*-dialkylthiobenzamides and shows that intermolecular hydrogen bonding and differences in packing arrangements do not have large effects on the molecular conformation. The neutron diffraction study shows the geometry of the O—H···S hydrogen bond to be typical of hydrogen bonds of intermediate strength.

Introduction

NMR studies by Fulea & Krueger (1975) and Berg (1976) have shown the barrier to rotation about the C—N bond of the thioamide moiety in *N*,*N*-dialkyl(*o*-hydroxy)thiobenzamides to be 10 to 20 kJ mol^{-1} lower than in the corresponding *N*,*N*-dialkylthiobenzamides. This decrease in barrier height is attributed to an intramolecular O—H···S hydrogen bond, which is stronger in the transition state than in the ground state and thus stabilizes the former.

We previously reported the crystal structures of 4-thiobenzoylmorpholine, TBM (Kerr & Van Roey, 1979*a*), and 4-(2-hydroxythiobenzoyl)morpholine, HTBM (Kerr & Van Roey, 1979*b*). These compounds have similar conformations with an angle of approximately 65° between the normals to the planes of the phenyl ring and the thioamide moiety. This conformation appears to be determined mainly by the short intramolecular contacts involving the *ortho* C atoms of the phenyl ring. One of these has a short contact with the S atom while the other interacts with a C attached to N in the morpholine ring. A similar conformation was also observed for *N*,*N*-dimethylthiobenzamide (Walter, Harto & Voss, 1976). The crystal structure of the *o*-hydroxy derivative, HTBM, shows an intermolecular O—H···S hydrogen bond; however, the infrared spectra have been interpreted in terms of an intramolecular hydrogen bond in $CDCl_3$ solutions (Fulea & Krueger, 1977).

Although both the piperidine derivative, HTBP, and the morpholine derivative, HTBM, crystallize in the orthorhombic system with similar dimensions, HTBP crystallizes in the centrosymmetric space group *Pbca* while HTBM crystallizes in the noncentrosymmetric $P2_12_12_1$. Comparison of the two structures provides a measure of the influence of packing arrangements on conformation.

The structure of HTBP was studied by neutron diffraction to establish the geometry of the O—H···S hydrogen bond. Hydrogen bonds of this type are not well documented. The few examples of neutron diffraction studies found in the literature all refer to

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inorganic complexes where the water of hydration forms hydrogen bonds with S ligands (Mereiter, Preisinger & Guth, 1979). The neutron diffraction data were collected at 20 K to reduce the amplitude of the thermal motion from the large values observed in the room-temperature X-ray structure.

Experimental

X-ray diffraction

1-(2-Hydroxythiobenzoyl)piperidine crystallizes from benzene as colourless needles. Weissenberg and precession photography indicated the orthorhombic space group *Pbca*. The crystal used for the data collection had approximate dimensions 0·17 × 0·17 × 0·28 mm and was cut from a longer one. The orientation matrix and the lattice parameters (see *Abstract*) were refined from the positional parameters of 12 high-angle reflections (Busing & Levy, 1967).

The data were collected on an automated Picker FACS-1 diffractometer using Mo *Kα* radiation ($\lambda = 0{\cdot}71069$ Å) with a graphite monochromator. The data were collected in the $\theta/2\theta$ scan mode with a scan width of $\Delta 2\theta = (1{\cdot}3 + 0{\cdot}692\tan\theta)^\circ$ and a scan rate of 1° min^{-1}. Backgrounds were measured for 20 s at either end of the scan. In total, 2667 independent reflections were measured with $2\theta \le 55^\circ$. Of these, 1497 had an intensity greater than $3\sigma(I)$, where $\sigma(I) = [T + B + (0{\cdot}02I)^2]^{1/2}$; T is the total peak count and B the background count normalized to the time interval of the scan. Lorentz and polarization corrections were applied to the data but no absorption correction was made ($\mu_{\mathrm{Mo}\,K\alpha} = 0{\cdot}251$ mm^{-1}).

The structure was solved by direct methods, using the program *MULTAN* (Germain, Main & Woolfson, 1971). Atomic scattering factors and anomalous-dispersion correction terms were taken from *International Tables for X-ray Crystallography* (1974).

The structure was refined by full-matrix least squares. The function minimized was $\sum w\Delta F^2$ where $w = [2\sigma(I)^2 + 0{\cdot}0005F^2]^{-1}$ for the observed reflections and $w = 0$ for the reflections with $I \le 3\sigma(I)$. All H atoms, except for the hydroxyl H atom, were found in a difference Fourier map calculated at the end of the refinement with isotropic thermal parameters for the heavier atoms. The H atoms were included in the model but were not refined until the refinement with anisotropic thermal parameters had converged. The largest peak in the difference Fourier map at this point corresponded to the position of the H atom of the hydroxyl group.

The final values of the weighted and unweighted residuals for the observed reflections were 4·91 and 4·51% respectively. The unweighted residual for all reflections was 9·48%. The standard deviation of an observation of unit weight is 1·241. The final atomic coordinates are listed in Table 1.* The equivalent isotropic temperature factor, U_{eq}, corresponds to $\frac{1}{3}$ of the trace of the diagonalized U_{ij} matrix. The e.s.d. of U_{eq} is about $1{\cdot}5 \times 10^{-3}$ Å^2.

Table 1. *Atomic coordinates* ($\times 10^4$, *for* S $\times 10^5$) *for HTBP* (*X-ray data at* 293 K)

	x	y	z	U_{eq} (Å$^2 \times 10^3$)
S	32991 (6)	39158 (4)	17577 (8)	49
C(1)	2744 (2)	3796 (1)	81 (3)	37
C(2)	1928 (2)	3274 (1)	2 (3)	38
C(3)	2051 (2)	2642 (1)	−718 (3)	41
O	2919 (1)	2537 (1)	−1456 (2)	57
C(4)	1297 (2)	2154 (1)	−672 (4)	53
C(5)	419 (2)	2305 (2)	40 (4)	62
C(6)	292 (2)	2933 (2)	737 (4)	63
C(7)	1047 (2)	3407 (1)	738 (4)	52
N	2968 (2)	4152 (1)	−1143 (3)	47
C(8)	3739 (2)	4689 (2)	−1191 (4)	63
C(9)	4466 (2)	4545 (2)	−2424 (5)	70
C(10)	3957 (3)	4484 (2)	−3935 (4)	66
C(11)	3154 (3)	3938 (2)	−3854 (3)	66
C(12)	2444 (2)	4083 (1)	−2591 (4)	49

Neutron diffraction

The crystal used for the data collection had a volume of approximately 1·42 mm^3 and was grown by vapour diffusion of hexane in a concentrated chloroform solution. The data were collected on an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor. The incident beam was monochromated by reflection from the (002) plane of a beryllium crystal. The selected wavelength of 1·1173(1) Å was calibrated against a standard KBr crystal ($a = 6{\cdot}6000$ Å). A temperature of 20·0 ± 0·5 K was maintained by means of a Displex closed-cycle helium refrigerator (Air Products and Chemicals, Inc.).

The cell dimensions (see *Abstract*) were determined from the least-squares refinement of the setting angles of 26 high-angle reflections.

The data were collected in the $\theta/2\theta$ step-scan mode. The reflections with $2\theta \le 50^\circ$ were measured over a fixed scan width of 3·0° with 75 steps per scan. For the reflections with $2\theta > 50^\circ$, the scan width was varied according to $\Delta 2\theta = (1{\cdot}12 + 4{\cdot}75\tan\theta)^\circ$. The parameters for this dispersion correction were determined experimentally. The number of steps per scan in the high 2θ region was allowed to vary from 65 to 100,

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* Tables of structure factors and anisotropic thermal parameters for both the X-ray and neutron structures as well as H-atom coordinates for the X-ray structure have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35970 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

which resulted in a step size ranging from 0·06 to 0·12°.

All 1516 independent reflections with $2\theta < 75°$ were measured and an additional 591 reflections in the range $75° < 2\theta < 105°$ were selected for measurement. These high-angle reflections had calculated intensities greater than an arbitrarily chosen limit. The model for this calculation included the non-hydrogen atoms placed at the positions from the refined X-ray structure and the H atoms placed at 1·04 Å from the C atoms. The hydroxyl H atom was omitted from the model. The isotropic thermal parameters were set at $B = 0{\cdot}75$ Å^2 for the non-hydrogen atoms and $B = 1{\cdot}50$ Å^2 for the H atoms. In view of the large numbers of unobserved reflections, this seemed to be a reasonable method for obtaining the maximum number of data without using excessive amounts of reactor time.

The background counts were estimated from 10% of the steps at either end of the scan. Lorentz and analytical absorption corrections were applied to the data. The linear absorption coefficient $\mu = 0{\cdot}2193$ mm^{-1} was calculated on the basis of an atomic mass-absorption coefficient for H of $(\mu/\rho)_{\lambda=1\cdot1173\,\text{Å}} = 2521{\cdot}8$ mm^2 g^{-1} (Koetzle & McMullan, 1979). The transmission coefficients ranged from 0·781 to 0·907.

Table 2. *Atomic coordinates* ($\times 10^4$) *for HTBP* (*neutron data at* 20 K)

	x	y	z	U_{eq} (Å^2 $\times 10^4$)/U (Å^2 $\times 10^3$)
S	3272 (4)	3944 (2)	1781 (5)	75
C(1)	2711 (1)	3809 (1)	79 (2)	59
C(2)	1886 (1)	3281 (1)	27 (2)	57
C(3)	2001 (1)	2630 (1)	−725 (2)	73
O	2863 (2)	2523 (1)	−1500 (3)	81
C(4)	1242 (1)	2127 (1)	−650 (2)	82
C(5)	353 (1)	2278 (1)	115 (3)	96
C(6)	229 (1)	2923 (1)	833 (2)	87
C(7)	998 (1)	3415 (1)	801 (2)	70
N	2945 (1)	4162 (1)	−1175 (2)	70
C(8)	3718 (2)	4714 (1)	−1216 (2)	85
C(9)	4484 (2)	4566 (1)	−2467 (3)	97
C(10)	3962 (2)	4482 (1)	−4003 (2)	96
C(11)	3159 (2)	3911 (1)	−3894 (2)	85
C(12)	2417 (2)	4073 (1)	−2632 (2)	79
H(1)	2856 (3)	2075 (2)	−2040 (5)	24
H(4)	*1351* (3)	*1624* (2)	−*1214* (6)	25
H(5)	−244 (3)	1882 (2)	119 (6)	25
H(6)	−465 (3)	3040 (2)	1449 (6)	28
H(7)	917 (3)	3913 (2)	1397 (6)	25
H(8*A*)	4071 (4)	4742 (2)	−103 (5)	27
H(8*B*)	3332 (4)	5216 (2)	−1438 (5)	24
H(9*A*)	4890 (3)	4069 (2)	−2187 (5)	26
H(9*B*)	5028 (4)	5003 (3)	−2482 (6)	27
H(10*A*)	4505 (4)	4344 (2)	−4873 (5)	27
H(10*B*)	3615 (4)	4988 (2)	−4336 (5)	23
H(11*A*)	3495 (3)	3393 (2)	−3695 (5)	24
H(11*B*)	2746 (4)	3870 (2)	−4964 (5)	25
H(12*A*)	1861 (3)	3650 (2)	−2528 (5)	22
H(12*B*)	2031 (4)	4576 (2)	−2859 (5)	23

A structure factor calculation based on the above-mentioned model, followed by an inverted difference Fourier map revealed the position of the hydroxyl H atom. The atomic scattering lengths used are those published by Koester (1977).

The refinement was based on F^2 with minimization of the function $\sum w(F_o^2 - k^2F_c^2)^2$ where $w = [\sigma^2(I) + (0{\cdot}01F^2)^2]^{-1}$ and k is the scale factor. All 2107 measured reflections were included in the refinement. Refinement with anisotropic thermal parameters was conducted in two blocks. The scale factor and the isotropic-extinction parameter were included in both blocks while the atoms included were varied from cycle to cycle. The extinction parameter used, g, was a type 1 isotropic correction with Lorentzian distribution (Becker & Coppens, 1974) and refined to $0{\cdot}22(2) \times 10^{-4}$.

The final weighted and unweighted residuals based on F^2 are 7·1 and 8·1% respectively. The standard deviation of an observation of unit weight is 1·106. The final atomic coordinates and the equivalent isotropic thermal parameters, U_{eq}, are listed in Table 2.[*] The e.s.d. of U_{eq} is about $1{\cdot}5 \times 10^{-4}$ Å^2 for the heavy atoms and about 3×10^{-3} Å^2 for H.

Discussion

Bond lengths and bond angles for the non-hydrogen atoms as determined by the low-temperature neutron study and the room-temperature X-ray study are compared in Table 3. The room-temperature bond-length values are systematically shorter than the low-temperature values owing to the effects of thermal motion (Cruickshank, 1956). Bond lengths and angles involving H atoms are listed in Table 4. Bond lengths from the two experiments are compared, but bond angles refer to the neutron experiment. The molecular conformation and the numbering scheme used in the text are shown in Fig. 1.

Intermolecular OH···S hydrogen bonds connect the molecules in extended chains parallel to the c axis, as

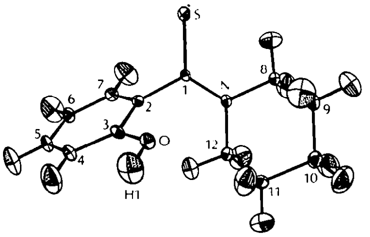

Fig. 1. *ORTEP* drawing (Johnson, 1965) of 1-(2-hydroxythiobenzoyl)piperidine as determined by neutron diffraction at 20 K. Thermal ellipsoids correspond to 75% probability.

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[*] See previous footnote.

Table 3. *Bond lengths* (Å) *and angles* (°) *for HTBP*

	Neutron	X-ray		Neutron	X-ray		Neutron	X-ray
S—C(1)	1·700 (5)	1·681 (3)	C(3)—C(4)	1·394 (3)	1·387 (4)	N—C(12)	1·478 (2)	1·473 (4)
C(1)—C(2)	1·490 (3)	1·495 (3)	C(4)—C(5)	1·398 (3)	1·377 (4)	C(8)—C(9)	1·534 (3)	1·497 (5)
C(1)—N	1·332 (2)	1·319 (3)	C(5)—C(6)	1·386 (3)	1·369 (5)	C(9)—C(10)	1·534 (3)	1·510 (5)
C(2)—C(3)	1·411 (2)	1·383 (4)	C(6)—C(7)	1·390 (3)	1·370 (4)	C(10)—C(11)	1·528 (3)	1·513 (5)
C(2)—C(7)	1·394 (3)	1·383 (4)	N—C(8)	1·471 (2)	1·469 (4)	C(11)—C(12)	1·524 (3)	1·502 (5)
C(3)—O	1·356 (3)	1·360 (3)						
S—C(1)—C(2)	117·1 (2)	117·6 (2)	O—C(3)—C(4)	122·8 (2)	123·2 (2)	C(1)—N—C(12)	123·6 (1)	124·0 (2)
S—C(1)—N	123·8 (2)	123·6 (2)	C(2)—C(3)—C(4)	119·7 (2)	119·6 (2)	C(8)—N—C(12)	113·3 (1)	112·4 (2)
C(2)—C(1)—N	119·1 (2)	118·7 (2)	C(3)—C(4)—C(5)	120·2 (2)	120·4 (3)	N—C(8)—C(9)	111·0 (2)	110·9 (3)
C(1)—C(2)—C(3)	121·4 (2)	121·6 (2)	C(4)—C(5)—C(6)	120·2 (2)	120·1 (3)	C(8)—C(9)—C(10)	110·5 (2)	111·3 (3)
C(1)—C(2)—C(7)	119·7 (2)	119·3 (2)	C(5)—C(6)—C(7)	119·6 (2)	119·7 (3)	C(9)—C(10)—C(11)	109·8 (2)	109·8 (3)
C(3)—C(2)—C(7)	118·9 (2)	119·0 (2)	C(6)—C(7)—C(2)	121·3 (2)	121·2 (3)	C(10)—C(11)—C(12)	111·3 (2)	111·4 (3)
C(2)—C(3)—O	117·4 (2)	117·2 (2)	C(1)—N—C(8)	122·9 (2)	123·6 (2)	C(11)—C(12)—N	110·4 (2)	111·0 (2)

Table 4. *Bond distances* (Å) *and angles* (°) *involving* H

(*a*) Bond distances

	Neutron	X-ray
O—H(1)	0·975 (5)	0·83 (2)
C(4)—H(4)	1·085 (5)	0·93 (2)
C(5)—H(5)	1·096 (5)	0·94 (3)
C(6)—H(6)	1·100 (5)	0·90 (2)
C(7)—H(7)	1·086 (5)	0·94 (2)
C(8)—H(8*A*)	1·092 (5)	0·94 (3)
C(8)—H(8*B*)	1·100 (5)	1·04 (3)
C(9)—H(9*A*)	1·114 (5)	0·96 (3)
C(9)—H(9*B*)	1·104 (6)	0·94 (3)
C(10)—H(10*A*)	1·090 (5)	0·94 (3)
C(10)—H(10*B*)	1·106 (5)	0·94 (3)
C(11)—H(11*A*)	1·093 (5)	0·93 (3)
C(11)—H(11*B*)	1·098 (5)	1·03 (3)
C(12)—H(12*A*)	1·097 (5)	0·98 (2)
C(12)—H(12*B*)	1·102 (5)	0·98 (2)

(*b*) Bond angles (neutron data only)

C(3)—O—H(1)	111·6 (3)	C(9)—C(10)—H(10*A*)	110·1 (3)
C(3)—C(4)—H(4)	118·7 (3)	C(9)—C(10)—H(10*B*)	109·7 (3)
C(5)—C(4)—H(4)	121·1 (3)	C(11)—C(10)—H(10*A*)	110·1 (3)
C(4)—C(5)—H(5)	118·8 (3)	C(11)—C(10)—H(10*B*)	109·6 (3)
C(6)—C(5)—H(5)	120·9 (3)	C(10)—C(11)—H(11*A*)	110·8 (3)
C(5)—C(6)—H(6)	120·4 (3)	C(10)—C(11)—H(11*B*)	110·5 (3)
C(7)—C(6)—H(6)	120·0 (3)	C(12)—C(11)—H(11*A*)	109·3 (3)
C(6)—C(7)—H(7)	120·0 (3)	C(12)—C(11)—H(11*B*)	108·4 (3)
C(2)—C(7)—H(7)	118·7 (3)	C(11)—C(12)—H(12*A*)	110·9 (3)
N—C(8)—H(8*A*)	108·4 (3)	C(11)—C(12)—H(12*B*)	110·2 (3)
N—C(8)—H(8*B*)	106·8 (3)	N—C(12)—H(12*A*)	109·6 (3)
C(9)—C(8)—H(8*A*)	111·5 (3)	N—C(12)—H(12*B*)	106·4 (3)
C(9)—C(8)—H(8*B*)	110·1 (3)	H(8*A*)—C(8)—H(8*B*)	108·8 (4)
C(8)—C(9)—H(9*A*)	108·7 (3)	H(9*A*)—C(9)—H(9*B*)	108·4 (4)
C(8)—C(9)—H(9*B*)	108·2 (3)	H(10*A*)—C(10)—H(10*B*)	107·5 (4)
C(10)—C(9)—H(9*A*)	109·3 (3)	H(11*A*)—C(11)—H(11*B*)	106·4 (4)
C(10)—C(9)—H(9*B*)	111·6 (3)	H(12*A*)—C(12)—H(12*B*)	109·2 (4)

Table 5. *Torsional angles* (°) *in HTBP*

	Neutron (20 K)	X-ray (293 K)
S—C(1)—N—C(8)	−0·2 (3)	0·9 (2)
S—C(1)—N—C(12)	−176·4 (2)	−176·0 (3)
S—C(1)—C(2)—C(3)	−110·3 (3)	−108·0 (2)
S—C(1)—C(2)—C(7)	66·4 (3)	68·5 (2)
C(1)—C(2)—C(3)—O	−5·0 (3)	−5·0 (2)
C(7)—C(2)—C(3)—O	178·3 (2)	178·6 (3)
N—C(1)—C(2)—C(3)	72·1 (2)	74·2 (3)
N—C(1)—C(2)—C(7)	−111·2 (2)	−109·4 (3)
C(2)—C(3)—O—H(1)	−175·9 (3)	
C(4)—C(3)—O—H(1)	4·1 (4)	

shown in Fig. 2. Extended hydrogen-bonded chains are also observed in HTBM but the arrangement of the molecules is different in the two cases. In HTBP, alternating enantiomers are related by a *c* glide, while in HTBM only a single enantiomer is present with successive members of the chain related by an approximate twofold screw axis. The latter arrangement results in a smaller volume: 274·5 Å^3/molecule in HTBM compared to 288·7 Å^3/molecule in HTBP. The difference in packing has only a small influence on molecular conformation. The S—C(1)—C(2)—C(7) torsional angle of 68·5 (2)° in the room-temperature study of HTBP is slightly larger than corresponding angles in HTBM [−64·1 (8) and −62·2 (8)°] and TBM [64·8 (2)°]. The angle in the low-temperature structure is about 2° smaller. The decrease can be attributed to reduced librational motion at lower temperature (see Table 5).

The geometry of the thioamide moiety in HTBP is very similar to that observed in TBM. The three determinations are of comparable precision. Bond lengths S—C(1) and C(1)—N indicate strong participation of the N lone pair in the π system of the

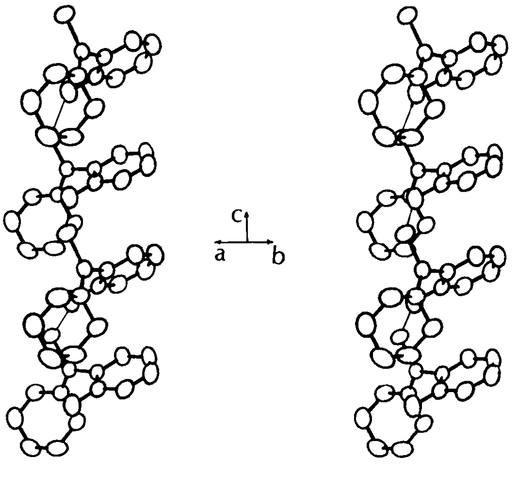

Fig. 2. Stereoview of the hydrogen-bonded chain of 1-(2-hydroxythiobenzoyl)piperidine.

thiocarbonyl group. The large torsional angle about the C(1)–C(2) bond precludes resonance interaction between the phenyl ring and the thioamide moiety. This angle is determined mainly by the non-bonded contacts noted in Table 6. When the less sterically demanding styryl group is introduced in place of the phenyl group as in 4-thiocinnamoylmorpholine (Kerr & Van Roey, 1979*c*) the torsional angle is reduced below 2° with a consequent lengthening of the C–N bond to 1·339 (3) Å.

Winkler & Dunitz (1971) have shown that most amides deviate from the planar conformation normally assumed to be the lowest-energy form. The wide range of distortions observed prompted these authors to conclude that such deformation is possible with little energy cost. A similar situation is likely for the thioamides. The estimated standard deviation of the best plane through the thioamide moiety is 0·021 Å for HTBP, which is considerably smaller than the 0·09 Å in TBM or the 0·08 and 0·05 Å found in HTBM.

Table 6. *Intramolecular non-bonded contacts* (Å) *for HTBP*; *short contacts are underlined*

	Neutron (20 K)	X-ray (293 K)
S···C(8)	3·082 (5)	3·067 (3)
S···H(8*A*)	2·490 (6)	2·53 (3)
S···C(7)	3·319 (5)	3·325 (3)
S···H(7)	3·171 (7)	3·14 (2)
C(2)···C(12)	2·875 (3)	2·864 (4)
C(2)···H(12*A*)	2·362 (5)	2·38 (2)
C(3)···C(12)	3·259 (3)	3·275 (4)
C(3)···H(12*A*)	2·510 (5)	2·62 (2)
O···C(12)	3·158 (3)	3·207 (3)
O···H(12*A*)	2·678 (5)	2·81 (2)

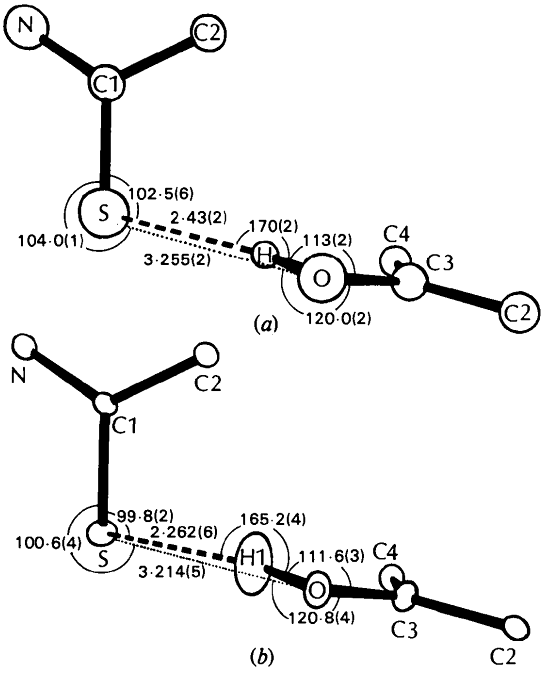

Fig. 3. Geometry of the O–H···S hydrogen bond in 1-(2-hydroxythiobenzoyl)piperidine. (*a*) Room-temperature X-ray structure. (*b*) 20 K neutron structure.

The geometry of the OH···S hydrogen bond as determined in the X-ray and neutron experiments is shown in Fig. 3. Comparison of O···S and H···S distances with van der Waals radii suggests that the hydrogen bond is of intermediate strength. The O···S distance is slightly longer than the 3·180 (7) and 3·199 (6) Å determined for the two intermolecular hydrogen bonds in HTBM. However, the OH···S hydrogen bonds in these two compounds are among the shortest bonds of this class so far observed (Mereiter *et al.*, 1979).

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