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The α Form of Piperidinium 1-Piperidinecarbodithioate

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Abstract

$[C_5H_{12}N]^+[C_6H_{10}NS_2]^-$ is orthorhombic, space group $Pbc2_1$, with $a = 6{\cdot}466\,(1)$, $b = 14{\cdot}941\,(2)$, $c = 27{\cdot}665\,(4)$ Å, $Z = 8$, $V = 2672{\cdot}6$ Å^3, $D_x = 1{\cdot}225$ Mg m^{-3}, phase transition $\alpha \rightarrow \beta$ at *ca* 354 K. The non-centrosymmetric structure has been refined to $R(F^2) = 0{\cdot}108$ for 3167 reflections and 446 parameters. Two cations and two anions are linked by eight N—H···S hydrogen bonds to form a dimer with pseudosymmetry $2/m$. The dimers are packed at van der Waals distances, mainly as close-packed layers between which the distances are fairly long. The most notable interdimeric distances are six S···S contacts per dimer, two of each of 3·853 (3), 3·871 (3) and 3·922 (3) Å.

Introduction

The present investigation forms part of a series of polymerism studies on amphiphilic $[R_2NH_2]^+[R_2NCS_2]^-$ salts, where R is an alkyl substituent (Wahlberg, 1978*a*,*b*,*c*, 1979, 1980).

In preparing crystals of piperidinium 1-piperidinecarbodithioate, two phases, α and β, were obtained simultaneously (Wahlberg, 1980), and the structure of the β form was determined.

The crystals of the α form appeared as very thin pale-yellow flakes. The polar direction [001] was perpendicular to the flakes. On heating, the crystals lost their brightness at the phase-transition temperature of *ca* 354 K as a zone passed through them. Some crystals remained up to *ca* 5 K higher and then shattered. The phases in the transition $\alpha \rightarrow \beta$ were identified by powder diffraction. The reverse transition could not be established. Systematically absent reflections among $0kl$ for k odd and $h0l$ for l odd indicated the space groups $Pbcm$ or $Pbc2_1$ [non-standard form of $Pca2_1$; the present symmetry relations are: x,y,z; $\bar{x}, \bar{y}, \frac{1}{2}+z$; $\bar{x}, \frac{1}{2}+y, z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$]. The statistical distribution of normalized structure factors indicated non-centrosymmetry. $Pbcm$ is inconsistent with the final structure. The cell parameters were based on 53 lines

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from a Guinier–Hägg powder photograph. The internal standard was CoP$_3$ (a = 7·70778 Å) and the radiation was Cr $K\alpha_1$ (λ = 2·289753 Å).

A crystal of thickness 0·05 mm was sealed in a thin-walled glass capillary. The plate edges were situated 0·11 to 0·12 mm from the centre of the crystal. Intensities were collected on a Stoe–Philips four-circle PDP 8/I computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The count rate was reduced by a factor 2^n, $0 \le n \le 3$ (scan time and one filter). Reflections within the ranges $0 \le h \le 8$, $0 \le k \le 19$ and $-36 \le l \le 0$ were measured in the ω–2θ mode. The longest scan time, for the weakest reflections, was 173 s. The background was measured on each side of a reflection for 25 s. The intensities of three standard reflections, measured at intervals of 40 reflections, decreased by 1·5 to 5%. Corrections were applied for background and for Lorentz, polarization and absorption effects [μ(Mo $K\alpha$) = 0·356 mm^{-1}], but not for the decrease of the standard reflections. The transmission factor varied from 0·94 to 0·99. 3485 reflections within $0{\cdot}060 < (\sin\theta)/\lambda \le 0{\cdot}650$ Å^{-1} were reduced to 3167 structure factors with $F_m^2 \ge 2{\cdot}30\sigma(F^2)$; 1606 had $F_m^2 < 3{\cdot}0\sigma(F^2)$.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The H atoms were introduced empirically. The structure was initially refined by the full-matrix least-squares program *UPALS* (Lundgren, 1976). F_m was corrected for non-hydrogen-atom f' anomalous-dispersion terms (*International Tables for X-ray Crystallography*, 1974), and F_c was kept on an absolute scale. The refinement then proceeded by a local version of the block-diagonal *ORFLS* program (Busing, Martin & Levy, 1962), with scaling on F_c. Four independent ions formed separate blocks. The thermal parameters of the non-hydrogen atoms were anisotropic. The coordinates and the isotropic thermal parameters of all the H atoms were varied. All the structure factors were included in the last cycles, where 446 parameters were varied. The expression minimized was $\sum w\delta^2$, where $\delta = F_m^2 - F_c^2$ and $w^{-1} = \sigma^2(F^2) = \sigma^2_{\text{count}}(F^2) + (0{\cdot}03F_m^2)^2$. The refinement converged at $R(F^2) = \sum|\delta|/\sum F_m^2 = 0{\cdot}108$ and $R_w(F^2) = (\sum w\delta^2/\sum wF_m^4)^{1/2} = 0{\cdot}124$. The final coordinates are given in Table 1.* The largest parametric $|\Delta|/\sigma$ was 0·7 for x[4H(7)], 0·6 for x[3H(7)] and 0·5 for U_{33}[4C(3)], y[1H(12)] and x[2H(6)]; the average value was 0·107. $|\delta|/\sigma(F^2)$ was $\ge 2{\cdot}0$ for 237 reflections. A normal δR probability plot (Abrahams & Keve, 1971) had a slope of 1·24 and an intercept of 0·15. A difference synthesis showed some peaks of density $\le 0{\cdot}51$ eÅ^{-3}. Scattering factors were taken from *International Tables for X-ray*

Table 1. *Decimal parts of the fractional coordinates and isotropic thermal parameters B* (Å^2) *defined from* $\exp\{-B[(\sin\theta)/\lambda]^2\}$

For the non-hydrogen atoms the alternative values B_{eq} (Å^2) corresponding to the anisotropic temperature factor coefficients are given. $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$. The atomic labels are preceded by the numbering of the molecular ions.

	x	y	z	B
1S(1)	1958 (3)	48038 (13)	24550	4·00
1S(2)	6228 (3)	43350 (13)	21675 (7)	3·86
1N	5075 (8)	4561 (4)	3076 (2)	3·19
1C(1)	4459 (11)	4608 (4)	2607 (2)	3·32
1C(2)	3673 (15)	4833 (7)	3473 (3)	4·43
1C(3)	3541 (13)	4109 (6)	3846 (3)	4·57
1C(4)	5638 (16)	3855 (8)	4024 (3)	5·43
1C(5)	7088 (14)	3610 (7)	3608 (3)	4·78
1C(6)	7156 (13)	4369 (6)	3248 (3)	4·47
1H(3)	452 (17)	533 (7)	359 (4)	8 (4)
1H(4)	282 (8)	504 (4)	341 (2)	−2 (1)
1H(5)	252 (12)	426 (5)	410 (3)	4 (2)
1H(6)	252 (8)	356 (4)	373 (2)	0 (1)
1H(7)	614 (12)	426 (5)	416 (3)	1 (2)
1H(8)	549 (9)	337 (4)	428 (2)	1 (1)
1H(9)	813 (11)	360 (5)	372 (3)	2 (2)
1H(10)	664 (9)	296 (4)	343 (2)	1 (1)
1H(11)	772 (9)	493 (4)	342 (2)	0 (1)
1H(12)	778 (8)	436 (3)	301 (2)	−2 (1)
2S(1)	−1006 (3)	32066 (12)	10627 (7)	3·86
2S(2)	3243 (3)	26985 (13)	07872 (7)	4·02
2N	0132 (9)	2863 (4)	0159 (2)	3·76
2C(1)	0698 (10)	2960 (4)	0627 (2)	2·66
2C(2)	−1929 (11)	3167 (5)	−0013 (3)	4·04
2C(3)	−1718 (13)	3918 (7)	−0377 (3)	4·67
2C(4)	−0199 (14)	3680 (6)	−0800 (3)	4·74
2C(5)	1788 (14)	3375 (8)	−0584 (3)	5·06
2C(6)	1564 (15)	2616 (7)	−0237 (3)	4·81
2H(3)	−284 (8)	262 (4)	−009 (2)	0 (1)
2H(4)	−263 (5)	336 (2)	034 (1)	−3 (1)
2H(5)	−321 (12)	396 (6)	−055 (3)	4 (2)
2H(6)	−206 (17)	438 (7)	−025 (4)	6 (4)
2H(7)	−104 (10)	304 (4)	−100 (2)	3 (2)
2H(8)	001 (9)	424 (4)	−093 (2)	0 (1)
2H(9)	242 (13)	317 (6)	−077 (3)	3 (2)
2H(10)	255 (12)	398 (5)	−044 (3)	4 (2)
2H(11)	065 (10)	200 (5)	−040 (3)	3 (2)
2H(12)	225 (10)	251 (5)	−007 (3)	1 (2)
3N	3090 (11)	4843 (4)	1262 (2)	4·08
3C(2)	4905 (14)	5132 (7)	0966 (3)	4·95
3C(3)	4247 (18)	5221 (8)	0439 (3)	5·30
3C(4)	2436 (14)	5853 (6)	0386 (3)	4·61
3C(5)	0642 (12)	5558 (6)	0694 (3)	4·46
3C(6)	1327 (12)	5466 (6)	1223 (3)	4·43
3H(1)	410 (14)	456 (6)	174 (4)	8 (3)
3H(2)	279 (10)	435 (5)	118 (2)	1 (2)
3H(3)	535 (10)	566 (5)	108 (3)	2 (2)
3H(4)	628 (10)	480 (5)	104 (3)	3 (2)
3H(5)	551 (9)	538 (4)	026 (2)	−1 (1)
3H(6)	407 (13)	476 (5)	031 (3)	2 (2)
3H(7)	252 (11)	649 (5)	044 (3)	3 (2)
3H(8)	190 (8)	587 (4)	005 (2)	0 (1)
3H(9)	−065 (7)	604 (3)	068 (2)	−1 (1)
3H(10)	−003 (9)	505 (4)	063 (2)	−1 (1)
3H(11)	153 (10)	612 (5)	129 (2)	2 (2)
3H(12)	−016 (8)	531 (3)	142 (2)	−1 (1)
4N	2064 (10)	2693 (4)	1991 (2)	3·81
4C(2)	3895 (14)	2073 (6)	2039 (3)	4·75

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35993 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1 (*cont.*)

	x	y	z	B
4C(3)	4382 (14)	1968 (6)	2571 (3)	4·70
4C(4)	2532 (17)	1676 (6)	2859 (3)	5·62
4C(5)	0727 (15)	2291 (6)	2782 (3)	5·28
4C(6)	0193 (15)	2416 (7)	2267 (3)	5·24
4H(1)	176 (8)	272 (3)	168 (2)	−1 (1)
4H(2)	211 (10)	336 (5)	211 (2)	2 (2)
4H(3)	350 (6)	149 (3)	190 (1)	−2 (1)
4H(4)	560 (14)	247 (7)	183 (3)	8 (3)
4H(5)	569 (12)	172 (5)	258 (3)	4 (2)
4H(6)	517 (9)	260 (4)	273 (2)	1 (1)
4H(7)	178 (15)	098 (8)	274 (4)	9 (3)
4H(8)	300 (12)	171 (5)	314 (3)	3 (2)
4H(9)	−085 (9)	215 (4)	294 (2)	0 (1)
4H(10)	108 (9)	296 (4)	294 (2)	2 (1)
4H(11)	−066 (13)	200 (6)	209 (3)	6 (3)
4H(12)	−075 (10)	282 (4)	222 (2)	1 (1)

Crystallography (1974). No attempt was made to determine the absolute configuration by the inclusion of f'' anomalous-dispersion terms (*cf.* Wahlberg, 1979). Lundgren (1976) has described the computer programs. The calculations were performed on the IBM 370/155–158 and IBM 1800 computers in Uppsala.

Discussion

The non-centrosymmetric structure is built up of dimers, Fig. 1, which possess the approximate symmetry $2/m$. The dimer is very similar to those in the β form. The intradimeric N—H···S hydrogen-bond distances are given in Table 2. The ions are shown in Figs. 2 and 3. Table 3 gives the deviations from the least-squares plane through the dithiocarbamate plane atoms S(1), S(2), C(1), N, C(2) and C(6). The position of 3H(1) is unexpected (Fig. 2, Table 2). This might be an effect of minor systematic errors. The positions of some of the other H atoms are also uncertain (Figs. 2 and 3).

Table 2. N—H···S *hydrogen bonds* (Å)

	H···S	N···S
3H(1)···1S(1)*	2·43 (10)	3·380 (6)
4H(2)···1S(1)	2·36 (7)	3·406 (7)
3H(1)···1S(2)*	1·84 (9)	3·312 (7)
4H(2)···1S(2)†	3·04 (6)	3·675 (7)
3H(2)···2S(1)†	3·01 (7)	3·647 (7)
4H(1)···2S(1)	2·58 (5)	3·335 (6)
3H(2)···2S(2)	2·72 (7)	3·465 (7)
4H(1)···2S(2)	2·65 (6)	3·416 (6)

* Concerning 3H(1), see text.

† Weak bond.

Table 3. *Deviations* (Å) *from the least-squares plane through the dithiocarbamate plane atoms* [C(3), C(4) *and* C(5) *are situated on the positive side*]

	Molecule (1)	Molecule (2)
S(1)	0·003 (2)	−0·004 (2)
S(2)	0·000 (2)	0·003 (2)
C(1)	−0·046 (6)	0·033 (6)
N	0·029 (5)	−0·058 (6)
C(2)	−0·079 (10)	0·111 (8)
C(6)	0·038 (9)	−0·075 (11)

The dimers are packed at van der Waals distances (Bondi, 1964). The longest extension of the dimer is essentially oriented along **c**; projections in the *ac* and *bc* planes of the angle between **c** and a line through 1C(4) and 2C(4) are 15·79 and 1·12°, respectively. The

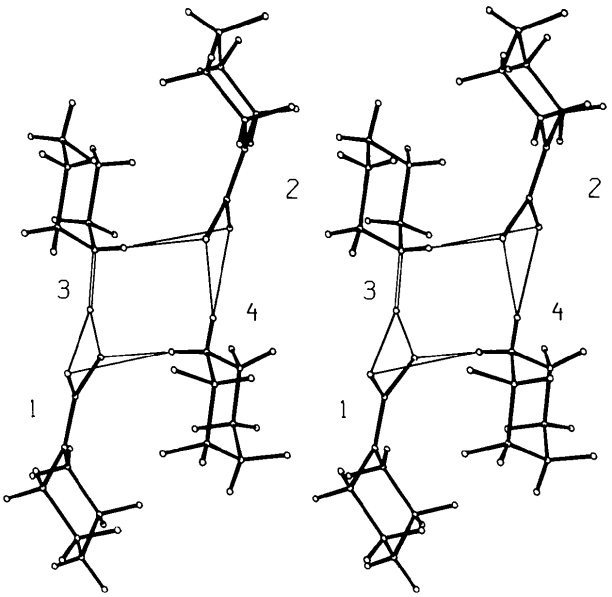

Fig. 1. The pseudo-centrosymmetric dimer. The numbering refers to the molecular ions. The vectors 1N → 3N and 1N → 4N are parallel to the corresponding vectors in the figures of the dimers of the β form (Wahlberg, 1980).

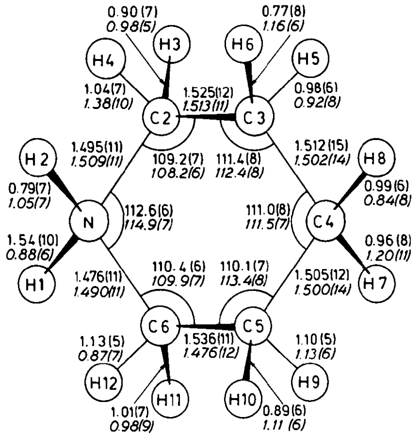

Fig. 2. Distances (Å) and angles (°) in the piperidinium cations. The upper value of a pair refers to molecule (3), the lower value (italic print) to molecule (4). Concerning 3H(1), see text.

intramolecular S···S vectors lie roughly along **a**. Close-packed layers occur parallel to *ab*; a dimer at x,y,z is surrounded by six others at $x \pm 1, y, z$; $\bar{x}, y \pm \frac{1}{2}, z$ and $1 - x, y \pm \frac{1}{2}, z$. The very thin crystal flakes are parallel to these layers. The layers are stacked along the polar axis **c** by 2_1 screw-axis operations. This gives the dimer another eight fairly long contacts, giving 14 neighbours in all. The position of the pseudo centre of symmetry in the dimer at approximately 0·261, 0·376, 0·162 differs from screw axes along **c**, which excludes the space group *Pbcm*.

The presence of the phase transition $\alpha \rightarrow \beta$, with unchanged dimers, justifies a more thorough examination of the dimeric packing arrangement. There are two important observations in this context. Firstly, the packing of dimers along **a** by translational repetition gives rise to three short interdimeric S···S contacts per two adjacent dimers (six per dimer): 1S(1)···1S(2$^{\rm i}$) of 3·853 (3), 2S(1)···2S(2$^{\rm i}$) of 3·871 (3) and 2S(1)···1S(2$^{\rm i}$) of 3·922 (3) Å. These distances are longer than twice the van der Waals radius of S of 1·83 Å, but are comparable to twice the ion radius of S in ionic dithiocarbamates of the order of *ca* 1·94 Å (Wahlberg, 1976). A short S···S distance of 3·762 Å occurs between chains in dimethylammonium dimethyldithiocarbamate (Wahlberg, 1978*a*). The shortest interdimeric S···S distance in the β form is 4·740 Å. Secondly, Table 4 shows that the S atoms participate in many of the shortest interdimeric distances (17 of 40). The table also shows that the contacts between the close-packed layers in general are long (3 of 40). Thus, the relative packing density is not very homogeneous, and is highest around the S atoms. In the β form the relative packing density is more uniform, and the overall packing density is 2·5% smaller. A concluding speculation – not verified – is that the phase transition is initiated by vibrational entropy involving the S atoms.

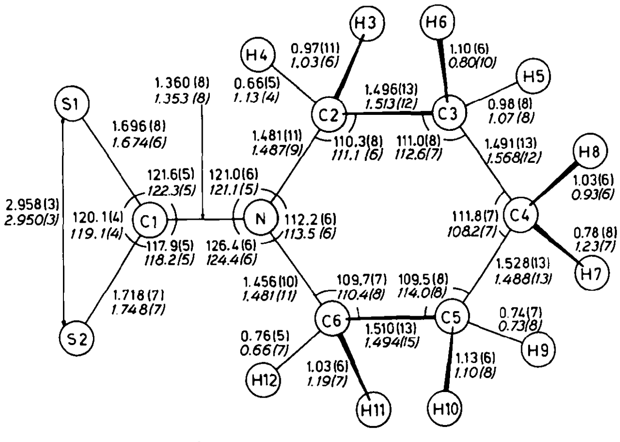

Fig. 3. Distances (Å) and angles (°) in the 1-piperidinecarbodithioate anions. The upper value of a pair refers to molecule (1), the lower value (italic print) to molecule (2).

Table 4. *The shortest interdimeric contacts*

The van der Waals distances *d* are obtained (Bondi, 1964) from the radii S = 1·83, N = 1·55, C = 1·70 and H = 1·17 Å.

	Distance D (Å)	$100\,(D-d)/d$ (<10·0, %)	Neighbouring dimer*
1S(1)···1S(2)	3·853 (3)	5·3	2
1C(6)	3·857 (9)	9·3	2
1H(12)	3·18 (5)	6·0	2
4H(5)	3·27 (8)	8·9	4
4H(7)	3·09 (10)	3·0	3
1S(2)···2S(1)	3·922 (3)	7·2	1
4C(6)	3·86 (1)	9·2	1
4H(7)	3·19 (11)	6·5	4
4H(12)	2·99 (7)	−0·4	1
2S(1)···2S(2)	3·871 (3)	5·8	2
3H(4)	2·95 (7)	−1·6	2
3H(7)	3·24 (8)	8·1	5
3H(11)	3·19 (7)	6·4	5
4H(4)	3·24 (9)	8·1	2
2S(2)···2H(4)	3·10 (4)	3·3	1
3H(3)	3·28 (7)	9·2	6
3H(9)	3·01 (5)	0·3	5
1N···4C(4)	3·57 (1)	9·8	4
2N···3C(4)	3·49 (1)	7·3	5
3H(7)	2·79 (8)	2·5	5
1C(1)···4C(3)	3·61 (1)	6·1	4
4C(4)	3·72 (1)	9·4	4
1C(5)···2H(7)	2·96 (7)	3·1	7
4H(9)	3·14 (6)	9·6	1
1C(6)···4C(4)	3·62 (1)	6·4	4
4H(7)	2·87 (11)	0·0	4
2C(1)···3C(5)	3·70 (1)	8·7	5
3H(7)	3·07 (8)	7·1	5
3H(9)	2·87 (5)	0·2	5
2C(2)···3C(4)	3·64 (1)	7·2	5
3H(7)	2·83 (8)	−1·3	5
2C(3)···1H(5)	3·13 (8)	9·0	8
3C(4)···2H(3)	2·97 (6)	3·6	3
4C(4)···1H(11)	3·05 (6)	6·1	6
1H(8)···2H(3)	2·52 (9)	7·6	7
1H(10)···4H(9)	2·42 (8)	3·6	1
1H(11)···4H(7)	2·48 (12)	5·8	4
1H(12)···4H(7)	2·54 (12)	8·7	4
2H(3)···3H(7)	2·26 (10)	−3·3	5
4H(5)···4H(9)	2·53 (10)	8·1	1

* Central dimer at x,y,z. No symmetry duplicates are included.

(1) $1 + x, y, z$
(2) $x - 1, y, z$
(3) $\bar{x}, \frac{1}{2} + y, z$
(4) $1 - x, \frac{1}{2} + y, z$
(5) $\bar{x}, y - \frac{1}{2}, z$
(6) $1 - x, y - \frac{1}{2}, z$
(7) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
(8) $\bar{x}, 1 - y, z - \frac{1}{2}$.

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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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