Table 8. *Some dihedral angles (°) between planes defined by three atoms*

Plane 1	Plane 2	Dihedral angle between planes 1 and 2 (*a*,*e*)-(2)	 (*a*,*a*)-(2)
S(2)P(2)O	S(1)P(1)O	39·0 (2)	103·4 (3)
S(2)P(2)O	P(1)OP(2)	55·9 (2)	45·4 (3)
S(1)P(1)O	P(1)OP(2)	69·3 (3)	39·9 (3)

the axially sited S atoms [106·7 (3) *versus* 105·0 (2), 104·2 (3) and 104·7 (3)°].

(3) The P(1)—O—P(2) angle in (*a*,*e*)-(2) is 5·6° larger than that in (*a*,*a*)-(2), presumably as a result of the shorter S···S contact in this isomer [3·99 *versus* 4·10 Å].

These conclusions are similar to those drawn for the axial–equatorial and equatorial–equatorial bis(4-methyl-2-thioxo-1,3,2-dioxaphosphorinanyl) oxide isomers [(*a*,*e*)-(1) and (*e*,*e*)-(1)]. The P—O ring bonds for the rings with an axial P=S bond are significantly longer than those in rings with an equatorial thiophosphoryl group. The P=S bond lengths are within the range (1·85–1·96 Å) typically observed for substituted phosphates (Corbridge, 1974).

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The Crystal and Molecular Structure of 4-Thiobenzoylmorpholine at 200 K

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Abstract

$C_{11}H_{13}NOS$ crystallizes from benzene as yellow needles elongated in the *c* direction with space group $P2_12_12_1$. Crystal data at 200 K are: a = 10·770 (3), b = 17·401 (5), c = 5·661 (2) Å, V = 1060·9 Å^3, D_c = 1·298 Mg m^{-3}, Z = 4. The structure refined to an *R* value of 0·0364. The C—N length of 1·326 (3) Å and the C—S length of 1·683 (2) Å indicate extensive delocalization of the N lone pair. However the torsional angle of 64·8 (2)° between the phenyl and thiocarbonyl groups minimizes interaction between the two π systems.

Introduction

Substituents capable of conjugation with the thiocarbonyl group in thioamides can influence the interaction of the N lone pair with the π system of the thiocarbonyl. It has been shown by IR and NMR studies (Krueger & Fulea, 1975; Berg, 1976) that such substituents can either raise or lower the barrier to rotation about the C—N bond. This work is part of a crystallographic study of several related thioamides undertaken to provide a structural basis for evaluating the interaction between the thioamide moiety and the substituents in terms of electronic and steric effects in this class of compounds.

Since the structure of 4-thiobenzoylmorpholine was intended to be the reference structure for the series it was disappointing to find extremely high thermal motion in the room-temperature structure. In order to gain the required precision, the data were recollected at 200 K. Although the amplitude of vibration is considerably reduced at this temperature, thermal parameters are still significantly anisotropic.

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Experimental

Yellow needle-shaped crystals of 4-thiobenzoylmorpholine were obtained from benzene solutions. Preliminary Weissenberg and precession photographs indicated the orthorhombic space group $P2_12_12_1$. For the low-temperature data set, a crystal of dimensions 0·20 × 0·10 × 0·25 mm was cut from a larger crystal and mounted parallel to the c axis. The orientation matrix and the lattice parameters were refined from the parameters of 12 high-angle reflexions (Busing & Levy, 1967). A comparison of cell dimensions at 298 K and 200 K is given in Table 1.

Data were collected on an automated Picker diffractometer equipped with a graphite monochromator and operated in the θ–2θ scan mode with a scan rate of 1° min^{-1} and a scan range of $\Delta 2\theta = (1{\cdot}4 \times 0{\cdot}692 \tan\theta)°$. Background was measured for 20 s at either end of the scan. Of the 1790 independent reflections accessible with Mo $K\alpha$ radiation (λ = 0·71069 Å) in the range $3{\cdot}0° \le 2\theta \le 60{\cdot}0°$, 1533 had significant intensities [$I \ge 3\sigma(I)$; where $\sigma(I) = (T + B)^{1/2}$, T is the total peak count and B is the background count normalized to the time interval of the scan]. Data were corrected for Lorentz and polarization effects, but not for absorption [μ(Mo $K\alpha$) = 0·206 mm^{-1}]. The low temperature was maintained by means of a Cryo-tip low-temperature apparatus on loan from Dr M. N. G. James of the University of Alberta.

Structure determination and refinement

The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971) applied to the room-temperature data set. Full-matrix refinement of the room-temperature structure converged at an R value of 0·0657. Coordinates from this refinement were used as a starting point for the refinement of the low-temperature structure.

All H atoms were located in a difference synthesis computed at the end of isotropic refinement. These were included in the model but were not refined until the anisotropic refinement of the heavy atoms had converged (maximum shift/error 0·11; average shift/error 0·005). The function minimized was $\sum w\Delta^2$ where $w = [4\sigma^2(I) + 0{\cdot}0006F^2]^{-1/2}$ for observed and zero for the unobserved reflections. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Crystal data*

	298 K	200 K
a	10·920 (4) Å	10·770 (3) Å
b	17·395 (4)	17·401 (5)
c	5·657 (2)	5·661 (2)
V	1074·57 Å^3	1060·92 Å^3
D_c	1·282 Mg m^{-3}	1·298 Mg m^{-3}

Refinement was terminated with R = 0·0364 for the 1533 observed data and R = 0·0466 for the full data set; $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ = 0·0414. The standard deviation of an observation of unit weight is 0·992. The refined value of the extinction parameter is g = 2·9 (8) × 10^{-4}. Atomic parameters of the non-hydrogen atoms are given in Table 2.* There were no significant features in the difference Fourier map calculated after the refinement was complete. Maximum and minimum values were 0·27 and −0·21Δ e Å^{-3}.

The Joule–Thomson cooling device used here has been described in some detail by Rudman (1976). During the experiment, the temperature was monitored by recording the output of a thermocouple mounted on the copper block supporting the sample. Although the temperature of the block was measured as 200 ± 2 K for the duration of the experiments, Ito & Sakurai (1973) measured temperature differences between sample and block as high as 10 K in this temperature range. In this experiment it is more important that the temperature is well controlled than the exact value known.

Discussion

The geometry of the molecule is displayed in Fig. 1 with bond distances and angles listed in Table 3. A principal feature of this structure is the torsional angle of 64·8 (2)° between the thiocarbonyl group and the phenyl ring. This conformation is intermediate between

Table 2. *Positional parameters* (×10^5 *for* S, ×10^4 *for others*)

	x	y	z
S	11874 (6)	21519 (4)	03027 (13)
C(1)	2230 (2)	2182 (1)	2515 (4)
C(2)	3002 (2)	1485 (1)	2953 (4)
C(3)	2838 (2)	1065 (1)	5057 (5)
C(4)	3504 (2)	0387 (1)	5394 (5)
C(5)	4345 (2)	0143 (1)	3727 (5)
C(6)	4521 (2)	0563 (1)	1660 (5)
C(7)	3844 (2)	1233 (1)	1275 (4)
N	2378 (2)	2779 (1)	3942 (4)
C(8)	3413 (2)	2878 (1)	5622 (5)
C(9)	4118 (2)	3601 (1)	4979 (7)
O	3331 (2)	4260 (1)	4951 (5)
C(10)	2364 (3)	4162 (1)	3267 (7)
C(11)	1581 (2)	3469 (1)	3871 (6)

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* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34531 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

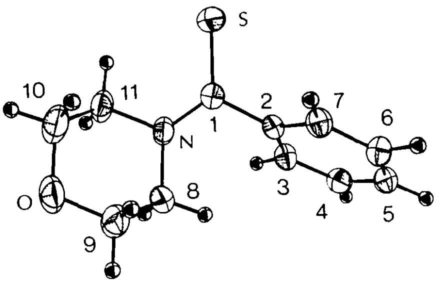

Fig. 1. A perspective view of 4-thiobenzoylmorpholine showing the numbering scheme used in the text. Thermal ellipsoids correspond to 50% probability.

those of 1-(4-chlorophenyl)-2-morpholino-2-thioxoethanone (Kerr & van Roode, 1979) where $\tau \simeq 90°$ and 4-thiocinnamoylmorpholine (Kerr & Van Roey, 1979*a*) where $\tau \simeq 0°$.

Consistent with the torsional angles (Table 4), the C—N distance is shorter, and the C—S distance longer than the values of 1·339 (4) and 1·675 (3) Å for the corresponding bonds in the thiocinnamoyl compound where τ[S—C(1)—C(2)—C(7)] = 1·7 (2)°. Although the sum of the bond angles at N is close to 360°, there appears to be significant pyramidal distortion since N lies +0·041 (2) Å from the plane defined by C(1), C(8) and C(11). Atoms S and C(2) lie −0·216 (1) and +0·208 (2) Å from this plane. This corresponds to a rotation of the plane S, C(1), C(2) out of the plane C(1), C(8), C(11) by 9·0°. Such a distortion is clearly a compromise between electronic and steric factors. The non-bonded intramolecular distances listed in Table 5 show that the S atom is involved in short contacts both with the phenyl ring and with the morpholine ring. The 9·0° rotation relieves the short contact between S and C(11) with minimal disruption of the π system of the thioamide group.

Although the near planarity of the N atom suggests that hybridization must be predominantly sp^2, the bond angles show considerable deviations from 120°. The distortion is not as extreme as it seems at first sight. If there were no steric effects, one would expect an sp^2-hybridized N in a six-membered ring to have an internal bond angle of about 112° and two equal exocyclic angles of about 124°. In 4-thiobenzoylmorpholine a slight expansion of the C(1)—N—C(8) angle to 125° relieves the short contacts between C(8) and the phenyl ring. However, in view of the extremely short contact between S and C(11) it is somewhat unexpected to find C(1)—N—C(8) larger than C(1)—N—C(11).

The molecular packing illustrated in Fig. 2 shows no unusual intermolecular contact. The conformation is largely the same as that observed for *N*,*N*-dimethylthiobenzamide (Walter, Harto & Voss, 1976), 4-(2-hydroxythiobenzoyl)morpholine (Kerr & Van Roey, 1979*b*) and 1-(2-hydroxythiobenzoyl)piperidine (Kerr

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

S—C(1)	1·683 (2)	C(3)—H(3)	1·03 (2)
C(1)—N	1·326 (3)	C(4)—H(4)	0·90 (2)
C(1)—C(2)	1·491 (3)	C(5)—H(5)	1·00 (2)
C(2)—C(3)	1·409 (3)	C(6)—H(6)	0·98 (2)
C(2)—C(7)	1·385 (3)	C(7)—H(7)	0·96 (2)
C(3)—C(4)	1·394 (3)	C(8)—H(8)	1·01 (2)
C(4)—C(5)	1·374 (4)	C(8)—H(8′)	1·05 (2)
C(5)—C(6)	1·393 (4)	C(9)—H(9)	0·92 (3)
C(6)—C(7)	1·391 (3)	C(9)—H(9′)	0·98 (2)
N—C(8)	1·475 (3)	C(10)—H(10)	1·04 (3)
N—C(11)	1·475 (3)	C(10)—H(10′)	1·00 (2)
C(8)—C(9)	1·513 (3)	C(11)—H(11)	0·97 (3)
C(9)—O	1·426 (3)	C(11)—H(11′)	1·05 (3)
O—C(10)	1·422 (4)		
C(10)—C(11)	1·512 (4)		
S—C(1)—C(2)	118·1 (2)	C(5)—C(6)—C(7)	120·0 (2)
S—C(1)—N	123·9 (2)	C(6)—C(7)—C(2)	120·1 (2)
C(2)—C(1)—N	118·0 (2)	C(1)—N—C(8)	125·1 (2)
C(1)—C(2)—C(3)	119·5 (2)	C(1)—N—C(11)	123·4 (2)
C(1)—C(2)—C(7)	120·6 (2)	C(8)—N—C(11)	111·3 (2)
C(3)—C(2)—C(7)	119·8 (2)	N—C(8)—C(9)	108·7 (2)
C(2)—C(3)—C(4)	119·4 (2)	C(8)—C(9)—O	111·9 (2)
C(3)—C(4)—C(5)	120·4 (2)	C(9)—O—C(10)	110·3 (2)
C(4)—C(5)—C(6)	120·3 (2)	O—C(10)—C(11)	110·6 (3)
		C(10)—C(11)—N	109·4 (2)

Table 4. *Torsional angles* (°)

S—C(1)—C(2)—C(3)	−112·7 (2)
S—C(1)—C(2)—C(7)	64·8 (2)
S—C(1)—N—C(8)	−169·1 (3)
S—C(1)—N—C(11)	4·6 (2)
C(1)—C(2)—C(3)—C(4)	176·0 (3)
C(3)—C(2)—C(1)—N	65·1 (2)
C(7)—C(2)—C(1)—N	−117·4 (2)
C(2)—C(1)—N—C(8)	13·3 (2)
C(2)—C(1)—N—C(11)	−173·1 (3)

Table 5. *Selected intramolecular non-bonded distances* (Å)

S···H(11)	2·53 (3)	S···C(3)	3·739 (3)
S···C(11)	3·084 (3)	C(3)···N	3·090 (3)
S···H(7)	3·21 (2)	C(3)···C(8)	3·232 (3)
S···C(7)	3·324 (2)		

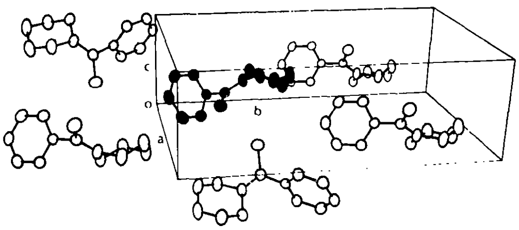

Fig. 2. Crystal structure of 4-thiobenzoylmorpholine. The darkened molecule is that whose coordinates are listed in Table 2. The shortest intermolecular contacts are S···H(9′) 2·91 (3) Å and O···H(6) 2·62 (3) Å which are not significant.

& Van Roey, 1979*c*). This suggests that the conformation observed in the crystal is the result of intramolecular interactions and therefore will probably persist in solution.

Thermal motion

The shapes of the thermal ellipsoids refined from the room-temperature data suggest that librational motion makes a dominant contribution to the thermal parameters of the thiobenzoyl portion of the molecule. In the morpholine ring, the main component of the thermal parameters is a large amplitude of vibration perpendicular to the plane of the ring. It would appear that this is indeed thermal motion rather than static disorder since the amplitude of vibration is considerably reduced at 200 K. An examination of the thermal ellipsoids in Fig. 1 suggests that the librational motion of the molecule has been largely frozen out at 200 K. However, the U_{33} parameters of four atoms on the morpholine ring remain high. For C(9), O, C(10) and C(11), the values are 0·064, 0·082, 0·075 and 0·067 Å^2, respectively (e.s.d. $\simeq$ 0·002 Å^2). These can be compared with the room-temperature values of 0·122, 0·138, 0·138 and 0·124 Å^2.

Computer programs used in this study include *CUDLS* (J. Stephens), *ORTEP* (Johnson, 1965) and several from the Los Alamos Scientific Laboratory system of programs (A. C. Larson). The authors would like to thank Drs M. N. G. James and M. Cowie of the University of Alberta for providing various components of the cooling systems used in this work.

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Etude Structurale et Energétique à l'Etat Cristallin du Composé Smectogène Hexanoyl-7 Nonyl-2 Dihydro-9,10 Phénanthrène

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Abstract

The crystal structure of the smectogenic compound 7-hexanoyl-2-nonyl-9,10-dihydrophenanthrene, $C_{29}H_{40}O$, has been established. It crystallizes in space group $P2_1/c$ with a = 12·774 (5), b = 36·66 (1), c = 5·439 (4) Å, β = 100·58 (8)°. The molecules are nonlinear and adopt a 'banana'-type conformation, unlike other smectogenic molecules with similar formulae. Molecules are stacked in the Ox direction with an average separation of 3·6 Å and quite a high association energy of $-130{\cdot}5$ kJ mol^{-1} resulting from

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