

Table 4. Bond angles ( $^{\circ}$ ) with *e.s.d.*'s in parentheses

O(1)–C(1)–C(2)	125.7 (5)	O(3)–C(4)–C(5)	109.2 (4)
C(1)–C(2)–C(3)	121.5 (5)	C(4)–O(3)–C(11)	118.5 (4)
C(2)–C(3)–C(4)	109.5 (4)	O(3)–C(11)–C(12)	110.9 (5)
C(3)–C(4)–C(5)	108.7 (4)	O(3)–C(11)–O(7)	122.0 (5)
C(4)–C(5)–O(1)	109.4 (4)	O(7)–C(11)–C(12)	127.0 (5)
C(5)–O(1)–C(1)	113.8 (4)	C(4)–C(5)–C(6)	112.1 (4)
C(2)–C(3)–O(2)	110.0 (5)	O(1)–C(5)–C(6)	107.5 (4)
O(2)–C(3)–C(4)	106.5 (4)	C(5)–C(6)–O(4)	107.7 (4)
C(3)–O(2)–C(9)	116.3 (4)	C(6)–O(4)–C(7)	116.3 (4)
O(2)–C(9)–O(6)	121.6 (5)	O(4)–C(7)–O(5)	123.0 (5)
O(2)–C(9)–C(10)	111.7 (5)	O(4)–C(7)–C(8)	110.3 (5)
O(6)–C(9)–C(10)	126.7 (5)	C(8)–C(7)–O(5)	126.7 (6)
C(3)–C(4)–O(3)	107.9 (4)		

for other unsaturated sugars (López de Lerma, Martínez-Carrera & García-Blanco, 1973; Stokhuyzen & Chung Chieh, 1976; Gould, Gould, Rees & Wight, 1976). The bond lengths are: C( $sp^2$ )–C( $sp^2$ ) 1.311 (7), C( $sp^2$ )–C( $sp^3$ ) 1.501 (7), and C( $sp^3$ )–C( $sp^3$ ) 1.516 (7) Å. The lengths of both C–O bonds are somewhat different, depending on the C atom hybridization: C( $sp^3$ )–O 1.433 (6) and C( $sp^2$ )–O 1.364 (6) Å. The geometries of the acetyl groups do not deviate from those of other structures reported in the literature.

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### *N*-Thiocinnamoylmorpholine

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**Abstract.** C<sub>13</sub>H<sub>15</sub>NOS, monoclinic,  $P2_1/c$ ,  $a = 11.382$  (5),  $b = 6.163$  (4),  $c = 17.550$  (8) Å,  $\beta = 102.16$  (3) $^{\circ}$ ;  $Z = 4$ ,  $d_c = 1.288$  Mg m<sup>-3</sup>. The planarity of the molecule together with the geometry of the thioamide fragment and the non-planar geometry of the N atom indicate competition between the N lone pair and the styrene moiety for the  $\pi$  orbital of the thiono group.

**Introduction.** The rotational barrier about the C–N bond of amides (Rogers & Woodbrey, 1962) and

thioamides (Sandström, 1962) is generally attributed to interaction between the lone-pair electrons on N and the  $\pi$  orbital of the thiono group. Such barriers can be measured by NMR spectroscopy through the coalescence temperatures of methyl or methylene protons of substituents on N. The introduction of groups capable of conjugation with the thiono group is reported to lower the barrier dramatically. For example, the activation energy for rotation in *N,N*-dimethylthioacetamide is 182.7 kJ mol<sup>-1</sup> (Neuman & Young, 1965), but only 64.4 kJ mol<sup>-1</sup> in *N,N*-dimethylthio-benzamide (Schwenker & Rosswag, 1967). A systematic study of the influence of conjugating

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substituents in a series of thioamides (Krueger & Fulea, 1975) has been hampered by lack of information on the ground-state conformation of such molecules. This work is part of a series of structural studies on representative thioamides where the N atom is part of a morpholine or piperidine ring.

The space group  $P2_1/c$  was uniquely determined by systematic absences of the type:  $h0l$ ,  $l = 2n + 1$ , and  $0k0$ ,  $k = 2n + 1$  observed in Weissenberg and precession photographs. A crystal of approximate dimensions  $0.25 \times 0.18 \times 0.10$  mm was cut from a longer crystal and mounted parallel to the  $b$  axis. Data were collected on a Picker FACS-1 diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) and a graphite monochromator. Intensity measurements were made at a scan speed of  $1^\circ \text{ min}^{-1}$  with a scan width of  $\Delta 2\theta = (1.4 + 0.692 \tan \theta)^\circ$  for reflections with  $2\theta \leq 20^\circ$  and  $\Delta 2\theta = (1.0 + 0.692 \tan \theta)^\circ$  for reflections  $20 < 2\theta \leq 50^\circ$ . Backgrounds were measured for 20 s at either end of the scan. Of the 2138 independent reflections measured, 1332 had intensities greater than  $3\sigma(I)$  where  $\sigma(I) = [T + B + (0.02I)^2]^{1/2}$ .  $T$  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 using *MULTAN* (Germain, Main &

Woolfson, 1971) and refined by a full-matrix least-squares procedure.

H atoms were located in a difference Fourier synthesis at the end of the isotropic refinement and were included in the model during the anisotropic refinement, but their parameters were not allowed to vary until the refinement of the heavy atoms had converged. Unit weights were used throughout. The final values of the conventional  $R$  value are 0.0403 for observed reflections and 0.0511 for all 2138 independent reflections with  $2\theta \leq 50^\circ$ . The standard deviation of an observation of unit weight is 0.79.

Positional parameters for all atoms and temperature parameters for H atoms are given in Table 1.\* The C—H distances range between 0.91 and 1.12 Å with a mean value of 1.00 (7) Å.

Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). Computer programs used include: *MULTAN* (Germain, Main & Woolfson, 1971), *CUDLS* (J. S. Stephens), *ORTEP* (Johnson, 1965) and several programs of the Los Alamos Scientific Laboratory System of Programs (A. C. Larson).

**Discussion.** The  $E$  configuration about the C(2)—C(3) bond allows the molecule to assume a planar conformation. The orange colour of the crystals and the observed geometry are consistent with an extended  $\pi$  system.

Table 1. Positional parameters ( $\times 10^4$ ; for H  $\times 10^3$ ) with estimated standard deviations in parentheses

	$x$	$y$	$z$	$U_{\text{iso}}$ ( $\text{Å}^2 \times 10^3$ )
S	7831.8 (9)	0751 (2)	4604.9 (6)	
C(1)	7800 (3)	3204 (5)	5011 (2)	
C(2)	6868 (3)	4794 (6)	4677 (2)	
C(3)	6002 (3)	4433 (6)	4074 (2)	
C(4)	5045 (3)	5919 (6)	3710 (2)	
C(5)	4294 (3)	5338 (7)	3004 (2)	
C(6)	3388 (3)	6723 (9)	2642 (2)	
C(7)	3220 (3)	8675 (9)	2979 (3)	
C(8)	3946 (3)	9277 (7)	3673 (2)	
C(9)	4848 (3)	7900 (7)	4036 (2)	
N	8604 (2)	3796 (4)	5648 (2)	
C(10)	9460 (3)	2199 (6)	6076 (2)	
C(11)	10622 (3)	3232 (7)	6420 (2)	
O	10482 (2)	4994 (4)	6916 (1)	
C(12)	9756 (4)	6602 (6)	6467 (2)	
C(13)	8541 (3)	5786 (6)	6111 (2)	
H(2)	684 (4)	604 (7)	495 (2)	120 (13)
H(3)	600 (3)	30. (5)	382 (2)	67 (10)
H(5)	440 (2)	398 (5)	276 (2)	61 (9)
H(6)	294 (3)	628 (6)	213 (2)	87 (12)
H(7)	259 (3)	962 (6)	275 (2)	92 (12)
H(8)	383 (3)	1070 (6)	394 (2)	75 (10)
H(9)	528 (2)	835 (5)	452 (2)	63 (9)
H(10A)	964 (3)	110 (6)	563 (2)	85 (12)
H(10B)	911 (3)	163 (6)	658 (2)	80 (11)
H(11A)	1102 (3)	376 (6)	594 (2)	100 (13)
H(11B)	1111 (3)	218 (6)	671 (2)	97 (13)
H(12A)	1012 (3)	703 (6)	594 (2)	92 (12)
H(12B)	971 (3)	779 (6)	686 (2)	82 (11)
H(13A)	806 (3)	689 (6)	580 (2)	90 (12)
H(13B)	811 (3)	542 (7)	659 (2)	101 (13)

\* Lists of structure factors, anisotropic thermal parameters and C—H distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34124 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å) and angles ( $^\circ$ )

S—C(1)	1.675 (3)	S—C(1)—C(2)	120.7 (2)
C(1)—C(2)	1.472 (4)	S—C(1)—N	121.9 (2)
C(1)—N	1.339 (4)	C(2)—C(1)—N	117.4 (3)
C(2)—C(3)	1.305 (4)	C(1)—C(2)—C(3)	124.6 (3)
C(3)—C(4)	1.463 (5)	C(2)—C(3)—C(4)	127.8 (3)
C(4)—C(5)	1.395 (4)	C(5)—C(4)—C(3)	119.2 (3)
C(4)—C(9)	1.386 (6)	C(9)—C(4)—C(3)	122.8 (3)
		C(5)—C(4)—C(9)	118.0 (3)
C(5)—C(6)	1.386 (6)	C(4)—C(5)—C(6)	120.5 (4)
C(6)—C(7)	1.372 (8)	C(5)—C(6)—C(7)	120.0 (4)
C(7)—C(8)	1.371 (6)	C(6)—C(7)—C(8)	120.6 (4)
C(8)—C(9)	1.380 (5)	C(7)—C(8)—C(9)	119.6 (4)
		C(8)—C(9)—C(4)	121.4 (3)
N—C(10)	1.474 (4)	C(1)—N—C(10)	120.4 (3)
N—C(13)	1.481 (5)	C(1)—N—C(13)	125.4 (3)
		C(10)—N—C(13)	112.2 (2)
C(10)—C(11)	1.478 (5)	N—C(10)—C(11)	111.0 (3)
C(11)—O	1.421 (5)	C(10)—C(11)—O	111.9 (3)
O—C(12)	1.418 (4)	C(11)—O—C(12)	108.8 (3)
C(12)—C(13)	1.480 (5)	O—C(12)—C(13)	112.4 (3)
		C(12)—C(13)—N	111.3 (3)

Bond lengths and angles for non-hydrogen atoms are listed in Table 2. The distances C(1)–N, C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(1)–S are indicative of partial double-bond character. The C–N and C–S bond lengths are well within the range observed for other thioamides (Walter & Voss, 1970).

Although there are no significant intermolecular contacts, the short intramolecular distances shown in Fig. 1 are probably responsible for distortion of the following bond angles from the unstrained value of  $120^\circ$ : C(2)–C(1)–N  $117.4$ , C(1)–N–C(13)  $125.4$ , C(1)–C(2)–C(3)  $124.6$ , C(2)–C(3)–C(4)  $127.8^\circ$  ( $\sigma = 0.3^\circ$ ). The molecular packing is illustrated in Fig. 2.

The torsional angles listed in Table 3 suggest that there are small deviations from planarity which minimize interactions between H atoms (Fig. 1) without disrupting the  $\pi$  system. The standard deviation of the

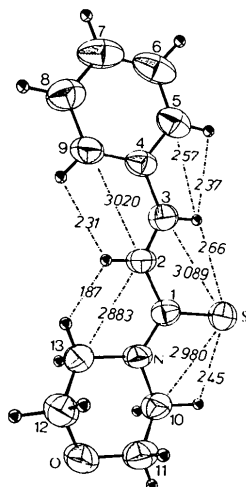


Fig. 1. Molecular geometry of *N*-thiocinnamoylmorpholine showing some non-bonded intramolecular distances and the numbering scheme used in the text. Thermal ellipsoids of heavier atoms correspond to 50% probability. Estimated standard deviations for the intramolecular distances are as follows: S–C  $0.004$  Å; C–C  $0.005$  Å; S–H  $0.04$  Å; C–H  $0.03$  Å; H–H  $0.05$  Å.

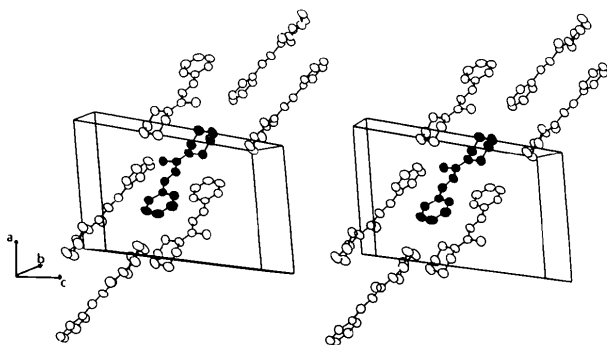


Fig. 2. Stereoscopic view of molecular packing. The darkened molecule is the one whose coordinates are given in Table 1.

Table 3. Torsion angles ( $^\circ$ )

S–C(1)–C(2)–C(3)	1.7 (2)
S–C(1)–N–C(10)	–7.2 (2)
S–C(1)–N–C(13)	–171.2 (4)
C(1)–C(2)–C(3)–C(4)	179.8 (5)
C(2)–C(3)–C(4)–C(5)	172.4 (5)
C(2)–C(3)–C(4)–C(9)	–7.6 (4)
C(2)–C(1)–N–C(10)	172.4 (4)
C(2)–C(1)–N–C(13)	8.4 (3)
C(3)–C(2)–C(1)–N	–178.0 (4)

least-squares plane through the atoms S, C(1), C(2), C(3), C(4) and N is  $0.011$  Å. Atoms C(5) and C(9) of the phenyl ring are displaced above and below this plane by  $+0.15$  and  $-0.14$  Å respectively, while atoms C(10) and C(13) of the morpholine ring are both displaced by  $-0.21$  Å to the same side of the plane. Thus the phenyl ring is rotated by  $6.9^\circ$  out of this plane and the N atom is slightly pyramidal.

The geometry at N appears to be significant. In other thioamides in this series where the group attached to the thiono function is not conjugated with it, the N atom is planar. [See for example 1-(4-chlorophenyl)-2-morpholino-2-thioxoethanone (Kerr & van Roode, 1979).] This implies that the hybridization at N, and hence the barrier to rotation about the C–N bond, is determined by how well the attached group competes for the  $\pi$  orbital on the thiono group. No competition corresponds to a high barrier to rotation, a short C–N bond and  $sp^2$  hybridization at nitrogen. Strong competition tends to reduce the barrier, lengthen the C–N bond and decrease the  $p$  character of the lone pair on N.

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