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1-(4-Chlorophenyl)-2-morpholino-2-thioethanone

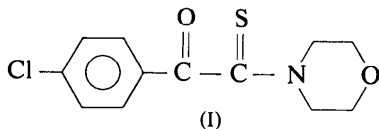
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Abstract. $C_{12}H_{12}ClNO_2S$, orthorhombic, $Pn2_1a$, $a = 7.3211$ (9), $b = 11.315$ (2), $c = 15.336$ (2) Å, $Z = 4$, $D_c = 1.410$ Mg m⁻³. The molecule consists of two independent π systems with an O–C(2)–C(1)–S torsion angle of 92°. This lack of conjugation across the C(1)–C(2) bond is consistent with the high barrier to rotation about the C–N bond reported in NMR studies.

Introduction. The high barrier to rotation about the C–N bond in thioamides is generally attributed to participation of the N lone pair in the π system of the thiono group. Groups capable of conjugation with the thiono group can reduce this barrier (Sandström, 1967; Brown & Katekar, 1969). For example, the activation energy for rotation in *N,N*-dimethylthioacetamide is 183 kJ mol⁻¹ (Neuman & Young, 1965) compared with 64.4 kJ mol⁻¹ in *N,N*-dimethylthiobenzamide ($T_c = 356$ K) (Schwenker & Rosswag, 1967). The coalescence temperature for the title compound (I) is above 443 K (Krueger & Fulea, 1975), implying that the rotational barrier in this compound is among the highest so far observed. The X-ray study was undertaken to explain this apparent anomaly.



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The title compound was obtained from benzene as yellow crystals. The specimen used for analysis was approximately 0.22 mm on each side and was cut from a larger crystal. Intensity data were collected on a Picker FACS I diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å), the θ – 2θ scan mode, a scan range of $\Delta 2\theta = (1.7 + 0.285 \tan \theta)^\circ$ and a scan of 1° min^{-1} . Background was measured for 40 s at either end of the scan. Both hkl and $hk\bar{l}$ reflections were measured to a maximum 2θ value of 100° . These were averaged to give 698 independent reflections of which 535 had intensities greater than $3\sigma(I)$, where $\sigma^2(I) = T + B + (0.02I)^2$. T is the total peak count and B is the background count normalized to the time interval of the scan. Reflections $0kl$, $k + l \neq 2n$ and $hk0$, $h \neq 2n$ were systematically absent, indicating space group $Pnma$ or $Pn2_1a$. The latter was chosen on the basis of intensity statistics. No absorption correction was made [$\mu(\text{Cu } K\alpha) = 4.06 \text{ mm}^{-1}$].

The structure was solved by direct methods and refined by least squares with the y coordinate of C(1) fixed. Owing to the small number of observed reflections, the refinement was performed in two large blocks, with parameters of the 4-chlorobenzoyl group in one block and those of the thiono group and the morpholine ring in the other block. The scale factor and the parameters of C(1) and C(2) were included in both blocks. Extinction was not included and unit weights were used throughout. H atoms were located in difference maps and included in the model but were not refined. The final conventional R value was 0.0387 for the 535 observed reflections and 0.0632 for the full

data set. The standard deviation of an observation of unit weight is 1.26. 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). Computer programs used include *MULTAN* (Germain, Main & Woolfson, 1971), *CUDLS* (J. Stephens), *ORTEP* (Johnson, 1965), and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34131 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions ($\times 10^4$)

The y coordinate of C(1) was not refined.

	x	y	z
S	1730 (4)	3035 (4)	5471 (2)
Cl	-702 (5)	186 (4)	1276 (2)
O(1)	-1796 (11)	4248 (7)	4388 (5)
C(1)	-474 (13)	2790	5305 (6)
C(2)	-1160 (10)	3240 (9)	4425 (6)
C(3)	-949 (14)	2478 (9)	3655 (6)
C(4)	-1280 (13)	2958 (10)	2829 (6)
C(5)	-1152 (15)	2282 (11)	2096 (7)
C(6)	-808 (14)	1088 (12)	2204 (6)
C(7)	-480 (16)	584 (9)	3009 (6)
C(8)	-549 (14)	1284 (10)	3746 (6)
N	-1683 (11)	2326 (8)	5839 (5)
C(9)	-3616 (14)	2125 (10)	5613 (6)
C(10)	-4087 (13)	855 (9)	5824 (6)
O(2)	-3714 (9)	586 (6)	6715 (4)
C(11)	-1815 (14)	714 (11)	6884 (6)
C(12)	-1193 (15)	1959 (10)	6702 (7)

Table 2. Bond lengths (Å) and angles ($^\circ$)

C(1)–S	1.657 (10)	C(2)–C(1)–S	113.6 (6)
C(1)–C(2)	1.527 (13)	C(2)–C(1)–N	117.6 (8)
C(1)–N	1.315 (12)	S–C(1)–N	128.8 (7)
C(2)–O(1)	1.233 (12)	O(1)–C(2)–C(3)	123.0 (9)
C(2)–C(3)	1.471 (14)	O(1)–C(2)–C(1)	118.3 (8)
		C(3)–C(2)–C(1)	118.6 (8)
C(3)–C(4)	1.399 (14)	C(2)–C(3)–C(4)	118.7 (9)
C(3)–C(8)	1.389 (15)	C(2)–C(3)–C(8)	120.7 (9)
		C(4)–C(3)–C(8)	120.4 (9)
C(4)–C(5)	1.364 (16)	C(3)–C(4)–C(5)	121.1 (10)
C(5)–C(6)	1.385 (18)	C(4)–C(5)–C(6)	117.4 (10)
C(6)–Cl	1.753 (12)	Cl–C(6)–C(5)	118.6 (8)
C(6)–C(7)	1.380 (15)	Cl–C(6)–C(7)	118.6 (10)
C(7)–C(8)	1.382 (14)	C(5)–C(6)–C(7)	122.8 (10)
		C(6)–C(7)–C(8)	119.3 (10)
N–C(9)	1.474 (13)	C(7)–C(8)–C(3)	118.8 (9)
N–C(12)	1.433 (13)	C(1)–N–C(9)	124.1 (8)
C(9)–C(10)	1.513 (15)	C(1)–N–C(12)	121.5 (8)
C(10)–O(2)	1.426 (11)	C(9)–N–C(12)	114.3 (8)
O(2)–C(11)	1.422 (12)	N–C(9)–C(10)	108.4 (8)
C(11)–C(12)	1.506 (16)	C(9)–C(10)–O(2)	111.3 (8)
		C(10)–O(2)–C(11)	109.9 (7)
		O(2)–C(11)–C(12)	110.9 (9)
		C(11)–C(12)–N	111.5 (8)

several from the Los Alamos Scientific Laboratory system of programs (A. C. Larson).

Discussion. Interatomic distances and angles are given in Table 2. Fig. 1 presents the molecular geometry and some important non-bonded interactions. Fig. 2 shows the molecular packing. The torsion angle between the carbonyl and thiono groups is 92° . The carbonyl group has been rotated slightly ($\approx 10^\circ$) out of the plane of the benzene ring, thus relieving a potential close contact between O(1) and H(4). The group S, C(1), N, C(9), C(12) is rigorously planar with an estimated standard deviation of only 0.008 Å. C(2) is displaced -0.123 Å from this plane. The angle between this plane and the plane of the benzene ring is 86° .

The strict planarity of the thioamide group results in steric interactions between S and C(12). In spite of the expansion of the S–C(1)–N angle to 128.8° , the contacts $S \cdots C(12) = 3.10$ and $S \cdots H(12) = 2.58$ Å are remarkably short. The C–N distance of 1.31 Å and the C–S distance of 1.66 Å are well within the

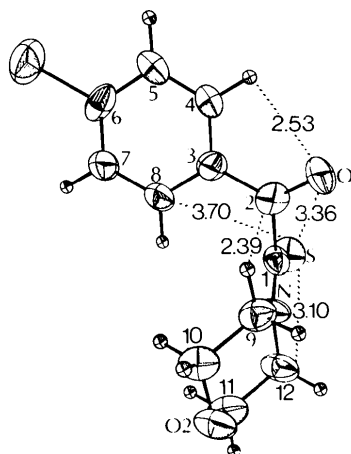


Fig. 1. A perspective drawing of the title compound, showing the numbering scheme. Thermal ellipsoids of the heavier atoms are plotted at the 50% probability level. Some non-bonded distances (Å) are given.

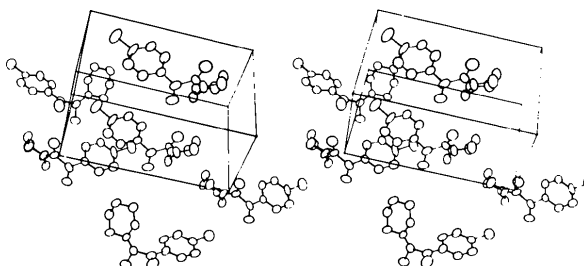


Fig. 2. Molecular packing. There are no unusually short contacts. The origin is at the lower rear left-hand corner, a is up the page, and c is to the right.

range of values reported for thioamides (Walter & Vos, 1970).

The long C(1)–C(2) bond of 1.53 Å, and the 92° torsion angle are consistent with the high coalescence temperature reported by Fulea & Krueger. Since there is no cross-conjugation between the benzoyl and thiono groups, barrier reduction of the type reported in dimethylthiobenzamide cannot occur. On the contrary, it seems likely that the inductive effect of the electro-positive carbonyl would enhance the barrier. These two effects would explain why the title compound apparently has one of the highest C–N rotational barriers so far encountered in thioamides.

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o*-Terphenyl by Neutron Diffraction

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Abstract. C₁₈H₁₄, orthorhombic, *P*2₁2₁2₁, *a* = 18.583 (3), *b* = 6.024 (1), *c* = 11.728 (2) Å (at 295–297 K, by neutron diffraction, based on *a* = 5.64037 Å for NaCl), *Z* = 4, $\rho_c = 1.65 \text{ Mg m}^{-3}$ [*cf.* Clews & Lonsdale (1937). *Proc. R. Soc. London Ser. A*, **161**, 493–504]. One of the end rings is twisted 42.1 and the other 62.1° in the same sense from the (physically impossible) conformation with all three rings coplanar. Other consequences of overcrowding in the molecule are shown by the significant bending, in and out of the ring planes, at the ends of the inter-ring bonds C(1)–C(1') and C(1'')–C(2') (IUPAC atom numbering rules). Angles C(1)–C(1')–C(2') and C(1'')–C(2')–C(1') are opened to 123.6 (3) and 123.0 (3)°.

Introduction. A crystal specimen† was shaped to an approximate rectangular parallelepiped ~4.8 × 3.5 × 3.7 mm (61.4 mm³, 68.5 mg), carefully examined for quality by X-ray precession photography, enclosed in a

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thin-walled quartz tube to prevent sublimation, and mounted on the neutron diffractometer at the Oak Ridge High Flux Isotope Reactor. The cell parameters (see *Abstract*) were determined by the least-squares method from the first moments of 108 neutron 2θ scans ($70.1 < 2\theta < 83.4^\circ$). Standard procedures (Lisensky, Johnson & Levy, 1976; Spirlet & Busing, 1978) were used to collect intensity data for the 1891 independent reflections of one octant of reciprocal space to the $(\sin \theta)/\lambda$ limit 0.665 \AA^{-1} ($\lambda = 1.0155 \text{ \AA}$). Absorption corrections on $|F_o|^2$ ranging from 1.795 to 1.996 were computed by Gaussian integration (Busing & Levy, 1957). The coefficient used, $\mu = 0.1924 \text{ mm}^{-1}$, was obtained by calculation using the total scattering cross-section 551 fm^2 for C (*International Tables for X-ray Crystallography*, 1962) and the cross-section 3800 fm^2 for H. The latter has been found empirically to yield good approximations to μ for hydrogenous compounds. The solution for the structure was obtained with ease by use of the 210 *E* values >1.50 and the direct-method program *MULTAN* of Main, Woolfson & Germain (1971), the indicated best set of phases yielding all 18 C atoms among the highest 22 peaks of the *E* map. Approximate coordinates for the 14 H

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