

| | | | |
|------------|-----------|-------------|-----------|
| C10—O4—C12 | 113.9 (2) | C6—C7—C8 | 115.3 (2) |
| C10—O5—C14 | 114.7 (2) | C7—C8—C9 | 110.8 (3) |
| O1—C1—O2 | 121.4 (2) | C8—C9—C10 | 110.0 (2) |
| O1—C1—C2 | 117.0 (2) | O4—C10—O5 | 110.5 (2) |
| O2—C1—C2 | 121.5 (2) | O4—C10—C5 | 106.6 (2) |
| C1—C2—C3 | 118.7 (3) | O4—C10—C9 | 111.4 (2) |
| C1—C2—C4 | 117.2 (2) | O5—C10—C5 | 104.8 (2) |
| C3—C2—C4 | 123.8 (3) | O5—C10—C9 | 110.3 (2) |
| C2—C4—C5 | 116.0 (2) | C5—C10—C9 | 113.0 (2) |
| C4—C5—C6 | 108.9 (2) | O4—C12—C13 | 112.6 (2) |
| C4—C5—C10 | 109.5 (2) | C12—C13—C14 | 107.7 (2) |
| C4—C5—C11 | 109.6 (2) | C12—C13—C15 | 110.0 (2) |
| C6—C5—C10 | 108.5 (2) | C12—C13—C16 | 110.0 (3) |
| C6—C5—C11 | 109.8 (2) | C14—C13—C15 | 108.7 (3) |
| C10—C5—C11 | 110.6 (2) | C14—C13—C16 | 109.7 (3) |
| O3—C6—C5 | 120.1 (3) | C15—C13—C16 | 110.6 (3) |
| O3—C6—C7 | 120.7 (3) | O5—C14—C13 | 111.6 (2) |
| C5—C6—C7 | 119.0 (2) | | |

A total of 20 atoms were located from an *E* map. The remaining atoms were located in succeeding difference Fourier syntheses. H atoms were located and their positions and isotropic displacement parameters were refined. The structure was refined by full-matrix least squares.

Data collection and cell refinement were performed using *CAD-4 Software* (Enraf-Nonius, 1989). The structure was solved by direct methods (*SIR88*; Burla *et al.*, 1989). All calculations were performed on a VAX computer using *MoLEN* (Fair, 1990). Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 6-Benzoyl-3,5-diphenyl-1,4-thiomorpholine-2-carboxylate 1,1-Dioxide

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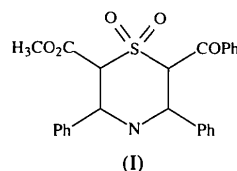
(Received 19 December 1994; accepted 1 May 1995)

Abstract

The crystal structure determination of C₂₅H₂₃NO₅S reveals that the thiomorpholine ring adopts a slightly distorted chair conformation. All the substituents on heterorings are equatorially oriented. There are no short intermolecular distances and the structure is stabilized with van der Waals interactions.

Comment

Thiomorpholine derivatives have attracted considerable interest because of their various chemotherapeutic properties, such as the antihistaminic activity of promethazine, the psychotherapeutic action of chlorpromazine and the insecticidal and anthelmintic properties of prothiazine (Katritzky & Boulton, 1968). Since the chemical and physiological characteristics of these compounds are directly defined by the conformation of their molecules and their relevant structural data are limited, X-ray crystallographic studies on a series of thiomorpholine derivatives have been undertaken. Here, we report the crystal and molecular structure of the title compound, (I).



The torsion angles indicate that the thiomorpholine ring adopts a slightly distorted chair conformation. The deviations of S(1), C(1), C(2), C(3) and C(4) from the mean plane passing through the atoms are -0.136 , 0.360 , -0.301 , 0.110 and 0.400 Å, respectively. Based on these atomic displacements from the mean plane through the non-H atoms, it can be inferred that the thiomorpholine ring adopts a slightly distorted chair conformation. When compared with the half-chair conformation for thiomorpholine itself (Ramasubbu, Parthasarathy & Tsoucaris, 1988), the full chair in the present case is preferred because the bulky substituents of the heterocyclic ring are all equatorial. The substituents of the aroyl group at C(1), aryl groups at C(2) and C(3), and the alkoxy carbonyl group at C(4) are equatorial. Their respective planes are almost perpendicular to the plane of the heteroring thus avoiding short intermolecular contacts. The C—S bond lengths of 1.793 (3) and 1.798 (3) Å in the present structure are comparable with the corresponding distances of 1.795 (3) and 1.795 (3) Å in the thiomorpholine-3-one structure (Ramasubbu, Parthasarathy & Tsoucaris, 1988). However, the endocyclic bond distances C(1)—C(2) 1.543 (4), C(3)—C(4) 1.543 (4), C(2)—N 1.466 (4) and C(3)—N 1.470 (4) Å in our structure are different from the corresponding distances of 1.490 (3), 1.505 (3), 1.452 (3) and 1.322 (3) Å, respectively, in the thiomorpholine-3-one structure (Ramasubbu, Parthasarathy & Tsoucaris, 1988). The slight differences in the C—C and C—N bond lengths in our structure compared with those in the thiomorpholine ring structure (Ramasubbu, Parthasarathy & Tsoucaris, 1988) can be attributed to the effect of the bulky substituents at these C atoms of the thiomorpholine ring.

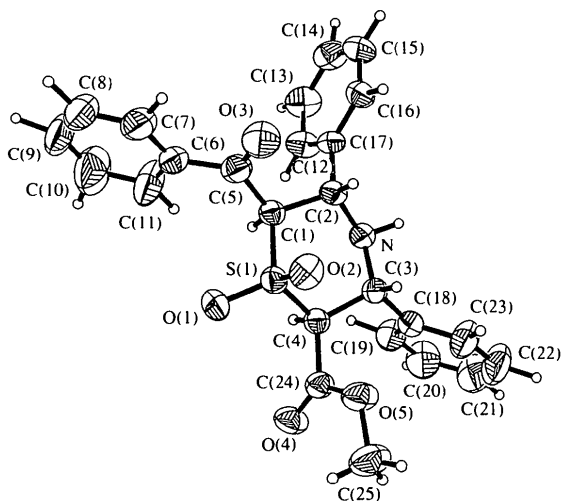


Fig. 1. View of the title molecule with displacement ellipsoids plotted at the 50% probability level.

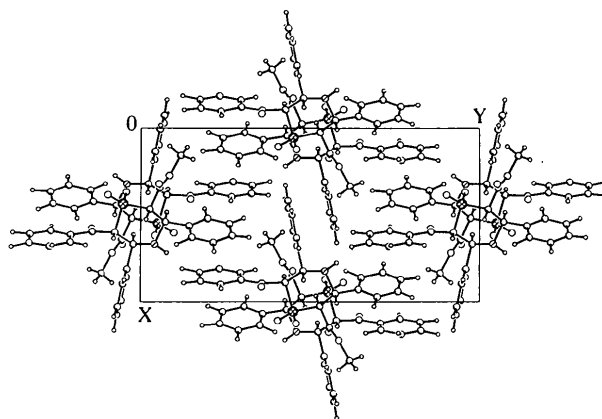


Fig. 2. Packing diagram of the unit cell.

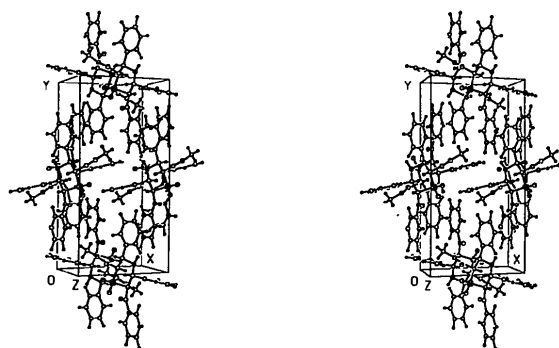


Fig. 3. Stereoview of the molecules in the unit cell.

Experimental

Crystals of the title compound were grown from a mixture of methanol/toluene (2:1) by slow evaporation of the solvent. The density D_m was measured by flotation.

Crystal data

$C_{25}H_{23}NO_5S$

$M_r = 449.55$

Monoclinic

$P2_1/n$

$a = 10.989$ (4) Å

$b = 20.086$ (3) Å

$c = 11.058$ (3) Å

$\beta = 110.5$ (3)°

$V = 2287$ (2) Å³

$Z = 4$

$D_x = 1.303$ Mg m⁻³

$D_m = 1.30$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25

reflections

$\theta = 10$ – 22.5 °

$\mu = 0.169$ mm⁻¹

$T = 293$ K

Needle

$0.4 \times 0.3 \times 0.2$ mm

White

Data collection

CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

none

$\theta_{max} = 25$ °

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 23$

$l = -12 \rightarrow 12$

4461 measured reflections
 3200 independent reflections
 3200 observed reflections
 $[I > 3\sigma(I)]$
 $R_{\text{int}} = 0.0221$

2 standard reflections
 monitored every 100
 reflections
 intensity decay: <2%

Refinement

Refinement on F^2
 $R = 0.056$
 $wR = 0.073$
 $S = 1.46$
 3199 reflections
 289 parameters
 H-atom parameters not
 refined
 $w = 1/[\sigma^2(F_o) + 0.003F_o^2]$

$(\Delta/\sigma)_{\text{max}} = 0.52$
 $\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = 0.06 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

| | | | |
|-------------------|-----------|-------------------|------------|
| C(10)—C(11) | 1.412 (7) | C(12)—C(13) | 1.394 (5) |
| C(12)—C(17) | 1.391 (4) | C(13)—C(14) | 1.376 (6) |
| C(14)—C(15) | 1.360 (5) | C(15)—C(16) | 1.406 (5) |
| C(16)—C(17) | 1.384 (5) | C(18)—C(19) | 1.375 (4) |
| C(18)—C(23) | 1.375 (4) | C(19)—C(20) | 1.394 (5) |
| C(20)—C(21) | 1.356 (6) | C(21)—C(22) | 1.371 (6) |
| C(22)—C(23) | 1.391 (5) | | |
| O(1)—S(1)—O(2) | 118.5 (1) | O(1)—S(1)—C(1) | 109.2 (1) |
| O(2)—S(1)—C(1) | 109.4 (1) | O(1)—S(1)—C(4) | 109.4 (1) |
| O(2)—S(1)—C(4) | 109.5 (1) | C(1)—S(1)—C(4) | 99.0 (1) |
| C(24)—O(5)—C(25) | 116.2 (3) | C(2)—N—C(3) | 116.7 (2) |
| S(1)—C(1)—C(2) | 109.6 (2) | S(1)—C(1)—C(5) | 107.5 (2) |
| C(2)—C(1)—C(5) | 112.5 (3) | N—C(2)—C(1) | 109.8 (2) |
| N—C(2)—C(17) | 107.3 (2) | C(1)—C(2)—C(17) | 110.4 (2) |
| N—C(3)—C(4) | 107.3 (2) | N—C(3)—C(18) | 108.0 (2) |
| C(4)—C(3)—C(18) | 111.6 (3) | S(1)—C(4)—C(3) | 108.9 (2) |
| S(1)—C(4)—C(24) | 110.6 (2) | C(3)—C(4)—C(24) | 115.6 (2) |
| O(3)—C(5)—C(1) | 118.3 (3) | O(3)—C(5)—C(6) | 121.1 (3) |
| C(1)—C(5)—C(6) | 120.6 (3) | C(5)—C(6)—C(7) | 117.0 (3) |
| C(5)—C(6)—C(11) | 123.5 (3) | C(7)—C(6)—C(11) | 119.5 (3) |
| C(6)—C(7)—C(8) | 121.3 (4) | C(7)—C(8)—C(9) | 119.7 (4) |
| C(8)—C(9)—C(10) | 120.0 (5) | C(9)—C(10)—C(11) | 119.5 (5) |
| C(6)—C(11)—C(10) | 119.8 (4) | C(13)—C(12)—C(17) | 120.6 (3) |
| C(12)—C(13)—C(14) | 119.3 (3) | C(13)—C(14)—C(15) | 120.7 (3) |
| C(14)—C(15)—C(16) | 120.9 (4) | C(15)—C(16)—C(17) | 119.0 (3) |
| C(2)—C(17)—C(12) | 120.3 (3) | C(2)—C(17)—C(16) | 120.1 (2) |
| C(12)—C(17)—C(16) | 119.6 (3) | C(3)—C(18)—C(19) | 120.1 (2) |
| C(3)—C(18)—C(23) | 120.5 (2) | C(19)—C(18)—C(23) | 119.3 (3) |
| C(18)—C(19)—C(20) | 120.4 (3) | C(19)—C(20)—C(21) | 120.3 (3) |
| C(20)—C(21)—C(22) | 119.6 (4) | C(21)—C(22)—C(23) | 120.7 (4) |
| C(18)—C(23)—C(22) | 119.7 (3) | O(4)—C(24)—O(5) | 124.93 (3) |
| O(4)—C(24)—C(4) | 123.2 (2) | O(5)—C(24)—C(4) | 111.9 (3) |

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|-------|-------------|------------|------------|-----------------|
| S(1) | 0.0561 (1) | 0.4477 (1) | 0.7666 (1) | 0.041 (1) |
| O(1) | 0.1093 (2) | 0.4030 (1) | 0.6971 (2) | 0.058 (1) |
| O(2) | 0.1252 (2) | 0.4573 (1) | 0.9016 (2) | 0.054 (1) |
| O(3) | -0.0844 (3) | 0.3551 (1) | 0.9221 (2) | 0.074 (1) |
| O(4) | 0.1747 (2) | 0.5536 (1) | 0.5809 (2) | 0.058 (1) |
| O(5) | 0.2230 (2) | 0.5835 (1) | 0.7867 (2) | 0.063 (1) |
| N | -0.1738 (2) | 0.5414 (1) | 0.7320 (2) | 0.043 (1) |
| C(1) | -0.1086 (3) | 0.4237 (1) | 0.7419 (2) | 0.038 (1) |
| C(2) | -0.1741 (3) | 0.4778 (1) | 0.7969 (2) | 0.040 (1) |
| C(3) | -0.0463 (3) | 0.5718 (1) | 0.7532 (2) | 0.040 (1) |
| C(4) | 0.0253 (3) | 0.5268 (1) | 0.6866 (2) | 0.039 (1) |
| C(5) | -0.1039 (3) | 0.3562 (1) | 0.8070 (3) | 0.049 (1) |
| C(6) | -0.1231 (3) | 0.2938 (2) | 0.7309 (3) | 0.055 (1) |
| C(7) | -0.0982 (4) | 0.2343 (2) | 0.7997 (5) | 0.075 (2) |
| C(8) | -0.1167 (5) | 0.1752 (2) | 0.7391 (6) | 0.092 (2) |
| C(9) | -0.1666 (5) | 0.1729 (2) | 0.6054 (7) | 0.106 (3) |
| C(10) | -0.1870 (7) | 0.2305 (3) | 0.5356 (6) | 0.122 (3) |
| C(11) | -0.1638 (5) | 0.2923 (2) | 0.6007 (4) | 0.093 (2) |
| C(12) | -0.3994 (3) | 0.4475 (2) | 0.6472 (3) | 0.057 (1) |
| C(13) | -0.5299 (3) | 0.4331 (2) | 0.6233 (3) | 0.065 (1) |
| C(14) | -0.5746 (3) | 0.4313 (2) | 0.7249 (4) | 0.062 (1) |
| C(15) | -0.4931 (3) | 0.4437 (2) | 0.8475 (4) | 0.063 (1) |
| C(16) | -0.3610 (3) | 0.4577 (2) | 0.8737 (3) | 0.050 (1) |
| C(17) | -0.3149 (3) | 0.4598 (1) | 0.7722 (3) | 0.040 (1) |
| C(18) | -0.0688 (3) | 0.6411 (1) | 0.6948 (3) | 0.044 (1) |
| C(19) | -0.1359 (4) | 0.6493 (2) | 0.5649 (3) | 0.059 (1) |
| C(20) | -0.1644 (5) | 0.7129 (2) | 0.5122 (4) | 0.081 (2) |
| C(21) | -0.1260 (6) | 0.7673 (2) | 0.5886 (4) | 0.091 (2) |
| C(22) | -0.0576 (5) | 0.7595 (2) | 0.7179 (4) | 0.094 (2) |
| C(23) | -0.0273 (5) | 0.6963 (2) | 0.7716 (4) | 0.074 (2) |
| C(24) | 0.1494 (3) | 0.5555 (1) | 0.6771 (3) | 0.044 (1) |
| C(25) | 0.3393 (4) | 0.6160 (2) | 0.7854 (4) | 0.075 (2) |

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-----------|------------|-----------|
| S(1)—O(1) | 1.433 (3) | S(1)—O(2) | 1.431 (2) |
| S(1)—C(1) | 1.798 (3) | S(1)—C(4) | 1.793 (3) |
| O(3)—C(5) | 1.215 (4) | O(4)—C(24) | 1.190 (4) |
| O(5)—C(24) | 1.324 (3) | O(5)—C(25) | 1.440 (5) |
| N—C(2) | 1.466 (4) | N—C(3) | 1.470 (4) |
| C(1)—C(2) | 1.543 (4) | C(1)—C(5) | 1.527 (4) |
| C(2)—C(17) | 1.518 (4) | C(3)—C(4) | 1.543 (4) |
| C(3)—C(18) | 1.517 (4) | C(4)—C(24) | 1.518 (4) |
| C(5)—C(6) | 1.483 (4) | C(6)—C(7) | 1.391 (5) |
| C(6)—C(11) | 1.350 (6) | C(7)—C(8) | 1.344 (6) |
| C(8)—C(9) | 1.385 (9) | C(9)—C(10) | 1.365 (8) |

The structure was solved by direct methods and refined by full-matrix least-squares methods. After non-H atoms were refined anisotropically, positions of all H atoms were calculated but were not refined further.

Data collection: Nonius CAD-4 diffractometer software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Molecular graphics: *ORTEP* (Johnson, 1976).

Lists of structure factors, torsion angles, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: CR1183). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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