

Tableau 4. *Plans moyens d'atomes*

Plan 1: $0,4880x + 0,3882y + 0,7817z - 5,2813 = 0$
 Atomes définissant le plan
 N(3), N(5), C(4), S(7)
 Distances à ce plan des autres atomes (Å)
 O(1) 1,14 (1) C(6) 0,03 (1)
 C(2) 0,15 (1)

Plan 2: $0,5143x + 0,3623y + 0,7773z - 5,2809 = 0$
 Atomes définissant le plan
 C(4), N(5), C(6)

Plan 3: $0,8994x - 0,3794y - 0,2172z + 0,6455 = 0$
 Atomes définissant le plan
 N(3), C(2), O(1)

A l'exception de l'atome d'oxygène et des atomes d'hydrogène, tous les atomes sont pratiquement dans le plan 1 défini par N(5)C(4)S(7)N(3) (Tableau 4).

Ainsi l'angle dièdre formé entre les plans 3 et 1 est de $79,9 (7)^\circ$ alors qu'il n'est que de $1,3 (7)^\circ$ entre les plans 1 et 2.

La structure cristalline est caractérisée par des chaînes formées de molécules de Noxythioline liées deux à deux par deux liaisons hydrogène: N(3)I—O(1)III 2,866 (9); N(3)III—O(1)I 2,866 (9) Å, et trois liaisons de van der Waals: C(2)I—O(1)III

3,44 (1); S(7)I—O(1)III 3,202 (6); C(6)III—O(1)I 3,36 (1) Å.

Les liaisons hydrogène intermoléculaires non linéaires font intervenir l'atome H(03) relié à l'atome d'azote N(3) avec un angle N(3)—H(03)—O(1) de 156° .

Du point de vue de l'arrangement, nous pouvons observer que la cohésion du réseau cristallin est assuré par deux types de liaisons de van der Waals: N(5)III—C(6)VI 3,41 (1); N(5)III—S(7)IV 3,388 (7) Å.

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8-Chloro-1-methyl-6-phenyl-1,2,3,4-tetrahydro-1,5-benzodiazocin-2-one

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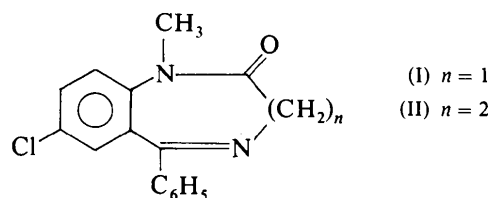
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Abstract. $C_{17}H_{15}ClN_2O$, $M_r = 298.77$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 13.374 (11)$, $b = 15.951 (8)$, $c = 7.056 (9)$ Å, $V = 1505.2 (3.9)$ Å³. The structure was solved by the heavy-atom method and refined by full-matrix least squares to $R = 0.079$ for 1089 observed reflections. The eight-membered ring has a boat-shape conformation.

Introduction. 1,2,3,4-Tetrahydro-1,5-benzodiazocin-2-ones and their lower cyclic homologues – 1,3-dihydro-2H-1,4-benzodiazepines – possess marked psychotropic effects. Structural features of the latter were studied in a series of works (Karle & Karle, 1967; Camerman & Camerman, 1972). Nevertheless, in their

activity level and pharmacological spectra, the members of the classes given above, such as 7-chloro-1-methyl-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepin-2-one (I, diazepam) and 8-chloro-1-methyl-6-phenyl-1,2,3,4-tetrahydro-1,5-benzodiazocin-2-one (II), are considerably different, which may be explained by their structural differences:



In order to determine the structure and spatial form of (II) an X-ray analysis was performed (Fig. 1). Benzodiazocine (II) was synthesized by condensing 5-chloro-2-methylaminobenzophenone with β -alanyl chloride-hydrogen chloride (Bogatsky & Andronati, 1979).

The colourless C₁₇H₁₅ClN₂O crystals are stable in air. Unit-cell dimensions and the space group were determined by the photographic method. The lattice parameters have been refined by use of a three-circle single-crystal diffractometer DAR-UMB (Kheiker,

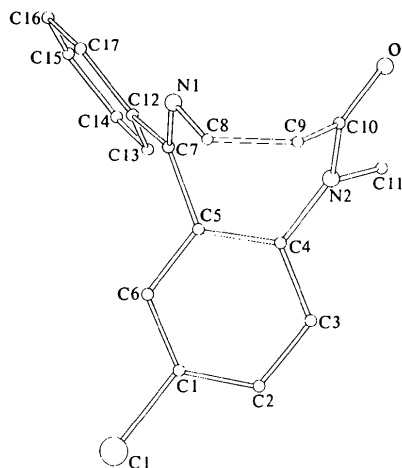


Fig. 1. The projection of the molecule on the C(1)–C(6) plane.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eq} * |
|-------|----------|-----------|------------|--------------------------|
| Cl | 3193 (2) | −192 (2) | 4913 (3) | 4.11 (7) |
| N(1) | 2493 (5) | −2888 (4) | 10682 (8) | 3.2 (2) |
| N(2) | 448 (4) | −2623 (4) | 8414 (9) | 3.2 (2) |
| O | −188 (5) | −3303 (4) | 10937 (:0) | 5.0 (2) |
| C(1) | 2377 (6) | −925 (5) | 5913 (10) | 2.7 (2) |
| C(2) | 1367 (7) | −796 (5) | 5720 (10) | 3.4 (2) |
| C(3) | 707 (6) | −1366 (5) | 6579 (11) | 3.2 (2) |
| C(4) | 1097 (6) | −2030 (5) | 7600 (11) | 2.8 (2) |
| C(5) | 2143 (6) | −2161 (5) | 7745 (9) | 2.3 (2) |
| C(6) | 2777 (5) | −1581 (4) | 6884 (9) | 2.5 (2) |
| C(7) | 2541 (5) | −2876 (4) | 8824 (11) | 2.8 (2) |
| C(8) | 2049 (7) | −2165 (6) | 11624 (12) | 3.6 (2) |
| C(9) | 902 (7) | −2136 (7) | 11637 (13) | 4.7 (3) |
| C(10) | 371 (5) | −2752 (6) | 10341 (12) | 4.0 (2) |
| C(11) | −174 (6) | −3162 (4) | 7065 (11) | 4.8 (3) |
| C(12) | 3010 (4) | −3567 (4) | 7835 (11) | 2.6 (2) |
| C(13) | 2793 (4) | −3705 (5) | 5889 (12) | 3.2 (2) |
| C(14) | 3182 (5) | −4407 (5) | 4881 (13) | 4.3 (2) |
| C(15) | 3812 (7) | −4932 (6) | 5825 (15) | 4.5 (3) |
| C(16) | 4084 (7) | −4814 (6) | 7694 (19) | 5.6 (3) |
| C(17) | 3666 (7) | −4127 (5) | 8724 (14) | 4.3 (3) |

* *B*_{eq} is defined as $B_{eq} = \frac{1}{3} \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j B(ij)$, where the \mathbf{a}_i 's are cell constants in direct space.

1973). The intensity measurements were carried out on a crystal of approximately 0.4 × 0.9 × 0.6 mm, with graphite-monochromated Mo *K* α radiation and combined ω and $\theta/2\theta$ scan ($2 \leq \theta \leq 50^\circ$). 1570 symmetry-independent reflections were collected; 1089 of them were taken [$I \geq 2\sigma(I)$] as observed. The structure was solved by the heavy-atom method with CRYSTAL (Tovbis & Shchedrin, 1970). H atom positions were determined from the difference-Fourier syntheses. The final *R* factor was 0.079, $R_w = [(\sum w^{1/2} \Delta) / \sum w^{1/2} F_o] = 0.095$. The weighting scheme was $w = 1/[\sigma^2(F) + F^2 E_{ap}^2]$, where E_{ap} is the apparatus error. The final atomic coordinates are given in Table 1.*

Discussion. The structure consists of molecules packed with contacts no shorter than the sums of the van der Waals radii. The molecular structure is given in Fig. 1. The bond distances and angles are given in Tables 2 and 3. The eight-membered ring has a boat con-

* Lists of structure factors, anisotropic thermal parameters and hydrogen atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36188 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA) with *e.s.d.*'s in parentheses

| | | | |
|-------------|----------|-------------|----------|
| Cl–C(1) | 1.75 (1) | C(1)–C(2) | 1.37 (2) |
| C(2)–C(3) | 1.40 (2) | C(3)–C(4) | 1.38 (2) |
| C(4)–C(5) | 1.42 (2) | C(5)–C(6) | 1.39 (2) |
| C(6)–C(1) | 1.36 (2) | C(4)–N(2) | 1.41 (2) |
| N(2)–C(11) | 1.53 (2) | N(2)–C(10) | 1.38 (2) |
| C(10)–O | 1.23 (2) | C(10)–C(9) | 1.52 (2) |
| C(9)–C(8) | 1.54 (2) | C(8)–N(1) | 1.46 (2) |
| N(1)–C(7) | 1.31 (2) | C(7)–C(5) | 1.47 (2) |
| C(7)–C(12) | 1.45 (2) | C(12)–C(13) | 1.42 (2) |
| C(13)–C(14) | 1.42 (2) | C(14)–C(15) | 1.36 (2) |
| C(15)–C(16) | 1.38 (2) | C(16)–C(17) | 1.43 (2) |
| C(17)–C(12) | 1.40 (2) | | |

Table 3. Bond angles ($^\circ$) with *e.s.d.*'s in parentheses

| | | | |
|------------------|---------|-------------------|---------|
| Cl–C(1)–C(2) | 118 (1) | C(10)–C(9)–C(8) | 116 (2) |
| Cl–C(1)–C(6) | 118 (1) | C(9)–C(8)–N(1) | 116 (2) |
| C(1)–C(2)–C(3) | 119 (2) | C(8)–N(1)–C(7) | 118 (2) |
| C(2)–C(3)–C(4) | 119 (2) | N(1)–C(7)–C(5) | 121 (2) |
| C(3)–C(4)–C(5) | 121 (2) | C(7)–C(5)–C(6) | 121 (2) |
| C(4)–C(5)–C(6) | 118 (2) | C(7)–C(5)–C(4) | 121 (2) |
| C(5)–C(6)–C(1) | 119 (2) | N(1)–C(7)–C(12) | 119 (2) |
| C(6)–C(1)–C(2) | 124 (2) | C(5)–C(7)–C(12) | 120 (2) |
| C(3)–C(4)–N(2) | 120 (2) | C(7)–C(12)–C(13) | 120 (2) |
| C(5)–C(4)–N(2) | 119 (2) | C(7)–C(12)–C(17) | 123 (2) |
| C(4)–N(2)–C(11) | 117 (2) | C(12)–C(13)–C(14) | 122 (2) |
| C(4)–N(2)–C(10) | 123 (2) | C(13)–C(14)–C(15) | 118 (2) |
| C(11)–N(2)–C(10) | 119 (2) | C(14)–C(15)–C(16) | 123 (2) |
| N(2)–C(10)–O | 119 (2) | C(15)–C(16)–C(17) | 119 (2) |
| N(2)–C(10)–C(9) | 118 (2) | C(16)–C(17)–C(12) | 120 (2) |
| O–C(10)–C(9) | 123 (2) | C(17)–C(12)–C(13) | 118 (2) |

Table 4. *Deviations of atoms from least-squares planes*

Atoms with an asterisk are not used to define plane.

| Atom | Distance (Å) | Atom | Distance (Å) |
|--|--------------|-------|--------------|
| Plane A: $0.083x + 8.815y + 5.881z - 2.676 = 0$ | | | |
| C(1) | 0.005 (8) | C(2) | -0.003 (8) |
| C(3) | -0.006 (8) | C(4) | 0.012 (8) |
| C(5) | -0.009 (8) | C(6) | 0.001 (6) |
| Cl* | 0.071 (3) | | |
| Plane B: $10.415x + 8.976y - 1.957z + 1.588 = 0$ | | | |
| C(12) | -0.012 (6) | C(13) | 0.019 (7) |
| C(14) | -0.008 (8) | C(15) | -0.009 (10) |
| C(16) | 0.015 (11) | C(17) | -0.005 (9) |
| Plane C: $-0.048x + 8.612y + 5.939z - 2.744 = 0$ | | | |
| N(2) | -0.008 (6) | C(4) | 0.016 (8) |
| C(5) | -0.016 (8) | C(7) | 0.008 (7) |
| Plane D: $1.339x + 15.804y + 0.642z + 3.591 = 0$ | | | |
| N(2) | 0.045 (6) | C(10) | -0.045 (8) |
| N(1) | 0.047 (6) | C(7) | -0.047 (7) |
| O* | -0.952 (7) | C(11) | -0.976 (7) |
| Plane E: $-1.212x - 9.407y + 5.662z - 8.430 = 0$ | | | |
| N(1) | 0.033 (6) | C(8) | -0.060 (9) |
| C(9) | 0.059 (10) | C(10) | -0.031 (8) |

Angles between planes (°)

| | |
|-----------------|-------------|
| Planes A and B: | 85.2 (1.2) |
| Planes C and D: | 127.7 (1.8) |
| Planes C and E: | 69.0 (1.9) |
| Planes D and E: | 121.3 (1.4) |

formation and its atomic displacements from the least-squares planes of some parts of the molecule are shown in Table 4. The conformation, bond distances and valence angles of the molecule are in agreement with those found in 8-bromo-1-methyl-6-phenyl-1,2,3,4-tetrahydro-1,5-benzodiazocin-2-one (Andronati, Dvorkin, Simonov, Danilin, Malinovsky & Bogatsky, 1979).

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The Structure of Aniline at 252 K

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Abstract. C₆H₇N, monoclinic, $P2_1/c$, $a = 21.822$ (8), $b = 5.867$ (4), $c = 8.386$ (6) Å, $\beta = 101.01$ (5)°, $V = 1053.9$ (10) Å³, $Z = 8$, $D_x = 1.174$ Mg m⁻³ at 252 K, $M_r = 93.13$, m.p. = 267.18 K. The structure was solved by direct methods and refined by a least-squares

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procedure to an R of 0.063 for 834 reflections. The asymmetric unit contains two crystallographically independent molecules I and II. Both N atoms are out of the benzene plane by about 0.12 Å and the average dihedral angle between the amino (NH₂) plane and the

benzo group. In the eight-membered ring there is a shortening of the bonds N(2)–C(4) and N(2)–C(10) to 1.41 (2) and 1.38 (2) Å, respectively. A similar effect was noted in studies of the structures of diazepam (Camerman & Camerman, 1972) and medazepam (Gilli, Bertolasi, Sacerdoti & Borea, 1978). This shortening is due to resonance interaction between the amide fragment and the benzo group. The main difference between the structures of the title compound and its 8-bromo analogue is the orientation of the phenyl ring in position 6. This causes a principal reconstruction of the molecular packing. The distinctive increase in angles at C(8) and C(9) to 116° is probably due to the ring expansion from a seven- to an eight-membered one. The corresponding angle in diazepam is 110.5°. In spite of differences in conformation and some bond distances for the compounds (I) and (II) the projections on the fused benzene ring are similar.

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