There is a noticeable shortening effect for one bond in each ring, i.e. C(7)-C(8) 1.370 (6) and C(1)-C(6) 1.366 (7) Å; no explanation can be offered for this, but exactly the same effect was observed in the 2-chloro derivative (Shefter, 1976) where the two bonds are 1.376 and 1.361 Å, respectively. S-C(7) at 1.775 (4) Å agrees with 1.766/i, found in sodium naphthionate tetrahydrate (Brown & Corbridge, 1966) and S-N(1) at 1.661 (3)/i, agrees with 1.666/k in γ-sulphanilamide (Alléaume & Decap, 1965). The other bonds in the molecule are similar to those found in other sulphanilamides and sulphadiazines; a table of comparisons is given by Cook & Turner (1975).

The two rings are effectively planar, for C(1)-(6) the r.m.s. deviation is 0.030(5) Å and for C(7)-(12) 0.012(4) Å. The dihedral angle between them is 50.65 (5)°.

References


Structure of 1-Diphenylmethyl-3-hydroxyazetidinium Chloride,* C16H18NO+.Cl−

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(Received 17 October 1983; accepted 4 January 1984)

Abstract. Mr=275.8, monoclinic, P21/a, a = 12.356 (5), b = 9.054 (4), c = 14.043 (4) Å, β = 100.34 (3)°, V = 1545.5 Å3, Z = 4, Dm = 1.14, Dc = 1.185 Mg m−3, µ(Mo Kα) = 2.77 mm−1, F(000) = 584-0, T = 293 K, R = 0.053 for 1088 reflections. The four-membered ring is buckled 13.0° (0= 167.0°). The azetidinium moiety is linked to the Cl− ion through a hydrogen bond [O–H…Cl = 3.166 (5) Å].

Introduction. Structural studies on compounds containing the azetidine ring are important for the interpretation of their stereochemical and biological significance. In this connection our findings on the molecular geometry of the title compound (DPHA) are presented. The samples of DPHA were provided by Dr Joseph John of the Department of Science and Technology, India.

Experimental. Small, pale-yellow needles (from acetone solution). Dm by flotation in bromoform/benzene. Crystal 0.38 × 0.25 x 0.5 mm. Enraf–Nonius CAD-4/11M single-crystal X-ray diffractometer. Lattice parameters from 2θ reflections (12° < 2θ < 26°). Data collection: h, k, +l with 2θ < 60°; Mo Kα radiation, graphite monochromator; θ/2θ scan mode. Three standard reflections every 200 s: no significant variation. 2707 independent reflections, 1088 with F > 3σ(F). Lp correction. No absorption or decay corrections. P21/a, general positions ±(x, y, z; ½−x, ½+y, −z), from systematic absences 0k0, k = 2n and h0l, h ≠ 2n. Direct methods (MULTAN78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Anisotropic full-matrix refinement for non-H atoms (LALS; Gantzel, Sparks & Trueblood, 1961). H from stereochemical considerations and verified from AF synthesis, only positions refined, R = 0.053, Rw = 0.057; Σw[(Fobs)−(Fc)]2 minimized, where w = 1/[σ2 + (bF2 + cF4)] with a = 3.5, b = 1.0 and c = 0.025. (Δρ)max = 0.01. Final Δρ map featureless. No correction for

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secondary extinction. Atomic scattering factors from 

Table 1. Fractional atomic coordinates \((\times 10^4)\) and 
equivalent isotropic thermal parameters for non-H atoms with e.s.d.'s in parentheses

\[
B_{eq} = \frac{1}{2} \sum_i \sum_j U_{ij} \alpha_i \alpha_j \beta_{ij}
\]

<table>
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<th>X</th>
<th>Y</th>
<th>Z</th>
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<tr>
<td>1</td>
<td>1102 (1)</td>
<td>4130 (2)</td>
<td>8744 (1)</td>
</tr>
<tr>
<td>O1</td>
<td>1876 (4)</td>
<td>2096 (6)</td>
<td>10332 (3)</td>
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<td>1473 (5)</td>
<td>3137 (5)</td>
<td>9580 (5)</td>
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<td>97 (6)</td>
<td>1791 (8)</td>
<td>9916 (5)</td>
</tr>
<tr>
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<td>923 (6)</td>
<td>1252 (8)</td>
<td>8862 (5)</td>
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<td>C4</td>
<td>1882 (5)</td>
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<td>7724 (5)</td>
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<td>1964 (8)</td>
<td>5346 (5)</td>
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<td>515 (8)</td>
<td>5149 (5)</td>
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<td>C15</td>
<td>1507 (7)</td>
<td>5765 (5)</td>
<td>678 (5)</td>
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<tr>
<td>C16</td>
<td>154 (7)</td>
<td>1273 (6)</td>
<td>6623 (5)</td>
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Table 2. Bond distances (Å) and angles (°) for non-H atoms with e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Angle</th>
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<td>O1—C2</td>
<td>1.413 (8)</td>
<td>89.7 (5)</td>
</tr>
<tr>
<td>N1—C3</td>
<td>1.559 (9)</td>
<td>89.1 (5)</td>
</tr>
<tr>
<td>C5—C6</td>
<td>1.517 (9)</td>
<td>115.8 (5)</td>
</tr>
<tr>
<td>C11—C12</td>
<td>1.388 (8)</td>
<td>113.5 (5)</td>
</tr>
<tr>
<td>C17—C18</td>
<td>1.505 (9)</td>
<td>89.9 (5)</td>
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<tr>
<td>C2—C3</td>
<td>1.537 (9)</td>
<td>89.9 (5)</td>
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<tr>
<td>C4—N1—C1</td>
<td>1.549 (5)</td>
<td>115.8 (5)</td>
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<td>C5—C6—C7</td>
<td>119.9 (7)</td>
<td>119.9 (5)</td>
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<td>119.7 (8)</td>
<td>119.7 (5)</td>
</tr>
<tr>
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<td>112.1 (6)</td>
<td>112.1 (5)</td>
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<tr>
<td>C12—C13—C14</td>
<td>119.5 (6)</td>
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</tr>
<tr>
<td>C14—C15—C16</td>
<td>112.0 (6)</td>
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</tr>
<tr>
<td>O1—C1—C2</td>
<td>112.4 (5)</td>
<td>112.4 (5)</td>
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Discussion. | Atomic coordinates are given in Table 1.* Bond lengths and bond angles involving non-H atoms are given in Table 2. Table 3 gives some important torsion angles. Fig. 1 gives an *ORTEP* plot (Johnson, 1965) of the molecule.

The endocyclic N—C bonds (1.559 (9) and 1.525 (8) Å) are significantly longer than the exocyclic one which is 1.468 (8) Å. This feature is generally found in similar structures, such as 1-diphenylmethyl-azetidin-3-ol (hereafter DPAO) (Ramakumar, Venkatesan & Rao, 1977) and 3-hydroxy-2-methyl-1-(1-methyl-2-phenylethyl)azetidinium chloride (hereafter MPHA) (Wetherington & Moncrief, 1974). However, these bonds are particularly sensitive to the nature of the hydrogen-bond formation. In DPAO, the endocyclic bonds average 1.496 (7) Å while in MPHA these are 1.546 (15) and 1.457 (15) Å. DPAH has a hydrogen bond of the type O—H...Cl \(|O(1)...Cl| = 3.166 (5), O(1)—H(O1) = 1.01 (5), Cl...H(O1) = 2.19 (6) Å, O(1)—H(O1)...Cl = 166.5°\), while DPAO has a hydrogen bond of the type O—H...N \(|O...N| = 3.159 (7) Å\) and in MPHA there are two hydrogen bonds of the types O—H...Cl \(|O...Cl| = 3.083 (11) Å\) and N—H...Cl \(|N...Cl| = 3.095 (9) Å\).

The angles within the four-membered ring in DPAH are close to 90° — in DPAO and MPHA one of the angles deviates significantly [86.4 (4)° and 86.9 (8)° respectively].

The four-membered ring is buckled. The angle between the planes N(1),C(1),C(3) and C(1),C(2),C(3) is 13° (the angle of puckering, \(\theta = 167.0°\)). This compares well with the structures of L-azetidine-2-carboxylic acid (\(\theta = 169.0°\); Berman, McGandy, Burgner & Van Etten, 1969), *N*-tert-butyl-3-hydroxy-N-methylazetidinium methanesulphonate (\(\theta = 166.0°\); McGandy, Berman, Burgner & Van Etten, 1969) and falls within the predicted values of Towns & Trefonas (1971). However, DPAO and MPHA differ significantly (\(\theta = 154.0°\) in both cases) and this can be attributed

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39116 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

![Fig. 1](image-url) | A perspective view of the molecule.
Structure of 8-Chloro-1-[(dimethylamino)methyl]-6-phenyl-4H-imidazo-[1,2-a][1,4]benzodiazepine, C_{20}H_{19}ClN_{4}*

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(Received 14 November 1983; accepted 13 January 1984)

Abstract. \( M_r = 350.8 \), triclinic, \( P\overline{1}, a = 9.036(4), \)
\( b = 9.888(3), c = 11.035(7) \AA, \alpha = 94.62(4), \beta = 
100.40(5), \gamma = 106.75(3)\), \( U = 919.4 \AA^3, Z = 2, \)
\( D_x = 1.267 \text{ Mg m}^{-3}, \mu(\text{Mo }K\alpha) = 
0.18 \text{ mm}^{-1}, F(000) = 368, \) room temperature, \( R = 
0.042 \) for 1361 observed reflections. The seven-membered
ring adopts a boat conformation and the angle between
the phenyl ring and the fused benzene moiety is 66.5 (5) \(^\circ\). Bond
lengths and angles agree with those found in other 1,4-benzodiazepines. The benzo
and imidazo rings are effectively planar.

Introduction. Many 5-phenyl-1,4-benzodiazepines
exhibit a broad range of psychotherapeutic properties.
The title compound (Gall & Kamdar, 1981) is of the
type possessing a five-membered hetero-ring fused
across the N(1)-C(2) bond of the parent system. It has
a rather low affinity for the benzodiazepine receptor
in vitro in comparison with the analogous triazoloben-
zodiazepine triazolam† (Hester, Rudzik & Kamdar,
1971) and estazolam‡ (Meguro & Kuwada, 1970)
which bind considerably better, approximately 100
times more strongly in the case of estazolam (Braestrup
& Squires, 1978). The structure of the title compound is
reported as part of a study of structure–activity
relationships for benzodiazepines.

Experimental. Crystal size 0.025 \( \times \) 0.15 \( \times \) 0.5 mm,
Enraf–Nonius CAD-4 diffractometer, cell dimensions
from setting angles of 25 reflections, graphite-
monochromated Mo K\( \alpha \) radiation, no absorption
correction, 3237 reflections scanned by \( \omega \)-\( 2\theta \) scans up to
\( \theta = 25^\circ \), 1361 reflections considered observed \( |I| > 
2.5\sigma(I) \), index range \( h \) = 10 to 9, \( k \) = 11 to 11, \( l \) = 12.
Two standard reflections, measured every 2 h; no
significant intensity variation. Structure solved by direct
methods; H atoms apart from those of methyl groups
located from Fourier difference map; least-squares
refinement, \( \sum w(|F|)^2 \) minimized, methyl groups refined
as rigid groups, other H atoms refined isotropically and
non-H anisotropically; final calculated shifts all <0.1 \( \AA; \)
\( R = 0.042, wR = 0.052 \); weighting scheme, \( w = 1/ 
[\sigma^2(F) + 0.0015|F|^2]; \) residual electron density in final
difference map within \( \pm 0.2 \text{ e} \AA^{-3}; \) no correction for
secondary extinction.

Computations were carried out with SHELX
(Sheldrick, 1978) using complex neutral-atom scatter-
ing factors (International Tables for X-ray Crystal-
lography, 1974) and PLUTO (Motherwell & Clegg,
1978).