

(3) absorbs at 353 nm under the same conditions (Camilleri, Gilmore & Cole-Hamilton, 1985).

The more positive reduction potential for (2) in relation to (3) may be due to the S in the heteropentalene moiety being more electron withdrawing than O. This is consistent with Hammett σ values for substituents such as SH ($\sigma_p = 0.15$) and OH ($\sigma_p = -0.37$) or SCH₃ ($\sigma_p = 0.00$) or OCH₃ ($\sigma_p = -0.27$).

The molecules in crystals of (2) pack in parallel sheets but with no short interlayer contacts. There are, however, some notable intrasheet non-bonded intermolecular S...N contacts (Fig. 2) between crystallographically independent molecules. The shortest contacts are S(8)...N(7')*, 3.04 Å, and S(8')...N(7)*, 3.17 Å. These can be ascribed to weak $d\pi$ - $p\pi$ interactions.

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Structural Studies of Some Benzodiazepines. I. The Structure of 3-(Benzylamino)-4,5-dihydro-1H-2,4-benzodiazepine Hydrochloride (1)

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Abstract. C₁₆H₁₈N₃⁺.Cl⁻, $M_r = 287.8$, orthorhombic, $P2_12_12_1$, $a = 11.474$ (2), $b = 22.212$ (2), $c = 5.810$ (1) Å, $V = 1480.7$ (4) Å³, $Z = 4$, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 22 \text{ cm}^{-1}$, $D_x = 1.2909$ (3) g cm⁻³, $F(000) = 624$. Diffractometer data at room temperature. $R = 6.15\%$ for 1641 reflections with $I > 3\sigma(I)$, max. $\Delta/\sigma = 1.772$. The benzodiazepine ring has an envelope conformation; both diazepine N atoms are protonated - compound (1) exists in the ionic form, stabilized by hydrogen bonds between all N atoms and the Cl ion.

Introduction. The wide range of biological activity of derivatives of 3-amino-2,4-benzodiazepine (2) is the main reason for the many chemical and pharmacological studies of these compounds. For example, 3-amino-4,5-dihydro-1H-2,4-benzodiazepine (Rodriguez, Zitho & de Stevens, 1968) and its derivatives

(Ciba Ltd, 1970) act on coronary vasa and show bacteriostatic activity. Other compounds of this type, synthesized by Schnettler & Suh (1975), had in pharmacological tests a depressive effect on the central nervous system. This variety of properties of these and similar compounds prompted our studies of several new benzodiazepines, which should enable us to design the most pharmacologically favourable derivative of (2).

The title compound, (1), was obtained with good efficiency by the method described by Schnettler & Suh (1975), introducing necessary modifications (Brzezińska, unpublished data). In preliminary pharmacological tests it acted as tranquilizer and also showed some neuroleptic activity.

Experimental. Colourless needle-shaped crystals (0.3 × 0.5 × 0.8 mm) from ethanol at room temperature. Diffraction data measured on a CAD-4 dif-

Table 1. Final fractional coordinates ($\times 10^4$), and equivalent isotropic temperature factors ($\times 10^4$) with e.s.d.'s in parentheses

For non-H atoms $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.				
	x	y	z	$U_{eq}(\text{\AA}^2)$
Cl(1)	1867 (2)	2826 (1)	818 (3)	508 (10)
N1	3514 (5)	3256 (3)	5138 (10)	571 (34)
N3	4877 (6)	3268 (3)	8137 (11)	651 (39)
N2	4935 (6)	2534 (3)	5452 (13)	667 (41)
C2	4410 (6)	3015 (3)	6196 (12)	530 (39)
C4	4335 (8)	3756 (4)	9461 (14)	643 (47)
C5	4261 (6)	4336 (3)	8167 (11)	540 (38)
C6	3545 (6)	4335 (3)	6170 (11)	530 (37)
C7	2835 (7)	3790 (3)	5681 (15)	570 (42)
C8	4852 (8)	4858 (4)	8718 (14)	672 (52)
C9	4766 (8)	5369 (4)	7430 (17)	755 (56)
C10	4082 (8)	5354 (4)	5439 (16)	752 (57)
C11	3485 (8)	4849 (4)	4889 (14)	647 (47)
C12	4557 (8)	2158 (4)	3524 (14)	579 (47)
C13	3674 (6)	1689 (3)	4131 (14)	579 (39)
C14	3424 (10)	1221 (4)	2635 (15)	784 (60)
C15	2615 (11)	796 (5)	3123 (21)	974 (76)
C16	1969 (11)	817 (5)	5206 (20)	981 (74)
C17	2260 (10)	1266 (5)	6623 (16)	875 (66)
C18	3037 (8)	1695 (4)	6206 (13)	699 (46)

$I > 3\sigma(I)$. The structure was solved by direct methods using *SHELX76* (Sheldrick, 1976), atomic scattering factors (except for Cl ion) from *SHELX76*, for Cl ion from *International Tables for X-ray Crystallography* (1974). Refinement was carried out by full-matrix least squares using F magnitudes, 268 parameters, unit weights. All H atoms located by a difference map. Final $R = 6.15\%$, $S = 1.0082$, max. $(\Delta/\sigma) = 1.772$ (most probably due to short c lattice constant), largest min. and max. $\Delta\rho$ on a difference Fourier map are -0.75 and 0.32 e \AA^{-3} . Torsion angles and the best planes were calculated by our own *GEOM* program. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The benzodiazepine ring has an envelope-like conformation (see Fig. 1), with an angle of

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51406 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$)

N1—C2	1.311 (8)	N1—C7	1.454 (9)
N2—C2	1.301 (8)	N2—C12	1.463 (10)
N3—C2	1.369 (8)	C4—C5	1.494 (10)
C4—N3	1.467 (10)	C5—C8	1.382 (10)
C5—C6	1.421 (8)	C6—C11	1.366 (9)
C6—C7	1.487 (9)	C9—C10	1.398 (11)
C8—C9	1.362 (12)	C12—C13	1.496 (10)
C10—C11	1.352 (11)	C13—C18	1.410 (10)
C13—C14	1.384 (10)	C15—C16	1.420 (14)
C14—C15	1.355 (14)	C17—C18	1.327 (11)
C16—C17	1.336 (13)		
C7—N1—C2	130.6 (6)	C12—N2—C2	125.9 (7)
C4—N3—C2	124.7 (6)	N3—C2—N1	121.7 (6)
N2—C2—N1	122.8 (7)	N2—C2—N3	115.4 (6)
C5—C4—N3	113.4 (6)	C6—C5—C4	116.3 (6)
C8—C5—C4	125.4 (6)	C8—C5—C6	118.3 (6)
C5—C6—C7	118.3 (6)	C11—C6—C5	118.2 (6)
C11—C6—C7	123.4 (6)	C6—C7—N1	114.3 (6)
C9—C8—C5	122.4 (8)	C10—C9—C8	118.4 (8)
C11—C10—C9	120.0 (8)	C10—C11—C6	122.7 (8)
C13—C12—N2	114.7 (6)	C14—C13—C12	121.0 (8)
C18—C13—C12	123.0 (7)	C18—C13—C14	116.0 (8)
C15—C14—C13	122.2 (9)	C14—C15—C16	120.9 (9)
C15—C16—C17	114.8 (10)	C18—C17—C16	126.3 (10)
C17—C18—C13	119.8 (8)		
C13—C12—N2—C2	-84.9 (9)	C2—N3—C4—C5	-65.8 (10)
C12—N2—C2—N1	-6.6 (12)	N3—C4—C5—C6	64.1 (9)
C12—N2—C2—N3	175.3 (7)	C4—C5—C6—C7	6.7 (9)
N2—C2—N1—C7	-178.9 (7)	C5—C6—C7—N1	-66.0 (9)
N2—C2—N3—C4	-170.8 (7)	C6—C7—N1—C2	48.8 (10)
N1—C2—N3—C4	11.1 (11)	C7—N1—C2—N3	-0.9 (12)

fractometer using an ω - 2θ scan, graphite-monochromatized $\text{Cu K}\alpha$, collected to $2\theta_{\text{max}} = 146^\circ$; ranges of hkl : 0 to 14, 0 to 27, 0 to 7 respectively, no absorption correction. Lattice parameters by least squares using 25 reflections with θ range 8.8 – 42.8° . Standard reflection counts variation 1.85%. 1759 independent reflections, 1641 unique accepted as observed by the criterion

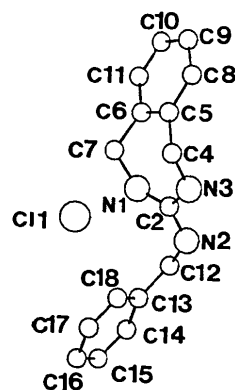


Fig. 1. A view of a molecule of the title compound with atomic numbering scheme.

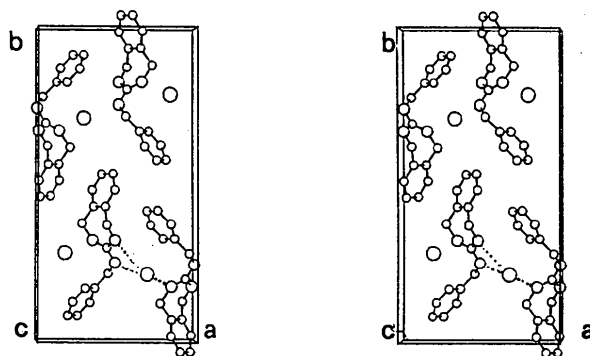


Fig. 2. A stereoview of the molecular packing in the unit cell (hydrogen bonds as dotted lines).

124.7(12)^o between planes C5C6C8C9C10C11 (plane 1) and C4C7N1N3 (plane 2). The small displacements of atoms C4 and C7 from plane 1 [−0.047(10), 0.131(7) Å], C2, N2, C12 atoms from plane 2 [0.052(10), 0.116(10), 0.332(12) Å respectively], and unequal equivalent torsion angles [e.g. C2N3C4C5 = −65.8(10) and C2N1C7C6 = 48.8(10)^o] indicate small distortion of the benzodiazepine ring. Both diazepine N atoms are protonated in the crystal, but the N1–C2 = 1.311(2) and N3–C2 = 1.369(8) Å bonds are not equal; this suggests that N1–C2 has significant double-bond character in solution, consistent with NMR results (Brzezinska, unpublished data). The N2–C2 bond, 1.301(8) Å, is also shorter than a normal single N–C bond, e.g. N2–C12 = 1.463(10) Å. These data indicate the presence of an aminodiazepine ion. The ionic form of the compound is stabilized by hydrogen bonds N1...Cl(1) = 3.284(20) Å [HN1...Cl(1) = 2.93(32) Å, N–HN1...Cl(1) = 112.2(54)^o, N1 from the molecule at *x*, *y*, *z*], N2...Cl(1) = 3.202(24) Å [HN2...Cl(1) = 2.29(20) Å, N2–HN2...Cl(1) = 157.7(46)^o,

N3...Cl(1) = 3.389(24) Å [HN3...Cl(1) = 2.34(17) Å, N3–HN3...Cl(1) = 154.6(57)^o, the N2 and N3 atoms from the molecule at $-x, \frac{1}{2}+y, \frac{1}{2}-z$]. These interactions in the crystal (see Fig. 2) result in the formation of chains of type [molecule 1...Cl(1)...molecule 3]_n and [molecule 2...Cl(2)...molecule 4]_n, which are connected only by van der Waals forces.

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Structure of Y₂BaCuO₇: a Refinement by Single-Crystal X-ray Diffraction

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Abstract. *M_r* = 458.7, orthorhombic, *Pbnm*, *a* = 7.1276(8), *b* = 12.1742(9), *c* = 5.6564(7) Å, *V* = 490.82(9) Å³, *Z* = 4, *D_x* = 6.21 Mg m^{−3}, λ(Ag Kα) = 0.56087 Å, μ = 19.2 mm^{−1}, *F*(000) = 828, *T* = 300 K, *R* = 0.020 for 1661 unique observed reflections. Seven O atoms are bonded similarly to each Y atom, 11 O atoms to the Ba atom. Five O atoms coordinate pyramidally to the Cu atom which is shifted 0.23 Å from the basal plane towards the apex of the coordination pyramid. Bond lengths are: Y–O

2.276(2)–2.378(2), Ba–O 2.609(2)–3.244(2), and Cu–O 1.972(2)–2.205(2) Å.

Experimental. Crystals grown by sintering a mixture of BaCO₃, Y₂O₃ and CuO at 1203 K for 40 h in air. Details of data collection and structure refinement are summarized in Table 1. The structure was refined by full-matrix least squares; the initial values of the positional parameters were those reported by Michel & Raveau (1982).