reduces eclipsing, with destruction of mirror symmetry. The actual deformation is a combination of (1) and (2), and the overall effect is to displace the N atom to one side of the mean plane of the 5-membered ring and the carbonyl C(11) to the other, towards the epoxy ring.

The short O···C(11) distance of 2·86 Å can also be regarded as the expression of an attractive intramolecular O···C=O interaction (Bürgi, Dunitz & Shefter, 1974). Although the lone-pair orbital of the epoxy O cannot point exactly towards C(11), the O···C=O approach angle of 110·6° is nearly optimal. As described above, the approach of C(11) towards O could be driven by factors other than direct attraction, but there is also a significant shear of the entire epoxy ring from its 'normal' position, centred on the mean mirror plane, towards the C(11) side of the molecule. The displacements are 0·055 Å for the midpoint of C(3) and C(4) and 0·065 Å for the O atom. The midpoint of C(11) and C(12) is displaced from the mean mirror plane by 0·014 Å but in the opposite direction.

We thank Professor D. Ginsburg for providing a sample of the compound. This work was supported by the Swiss National Fund for the Advancement of Scientific Research. Microdensitometer measurements were performed at the Science Research Council Atlas Computer Laboratory.

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2,4-Dimethyl-1,5-benzodiazepinium Chloride Dihydrate, and its Isomorphous Bromide

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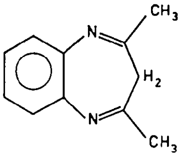
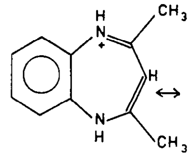
Abstract. $C_{11}H_{13}N_2Cl.2H_2O$, orthorhombic, *Pbca*, $a=19{\cdot}325$ (11), $b=6{\cdot}900$ (4), $c=18{\cdot}734$ (10) Å, $D_m=1{\cdot}29$ g cm^{-3}, $Z=8$, $D_x=1{\cdot}301$. The cation, $C_{11}H_{13}N_2^+$, has all its atoms, except the six methyl H, nearly coplanar, and appears to be stabilized by electron delocalization, which partially accounts for the intense colour. There are various hydrogen bonds involving the NH groups, the Cl^- ion and the H_2O molecules. The bromide, $C_{11}H_{13}N_2Br.2H_2O$, is isomorphous: $a=19{\cdot}60$ (5), $b=6{\cdot}97$ (2), $c=19{\cdot}08$ (5) Å, $D_m=1{\cdot}45$, $D_x=1{\cdot}473$.

Introduction. A base, $C_{11}H_{12}N_2$, to which formula (I) was assigned, was prepared by Thiele & Steimmig (1907) who also described a hydrochloride, $C_{11}H_{13}N_2^+Cl^-.2H_2O$. This salt is the title compound and (II) and (III) would now be used to represent its cation.



(I)



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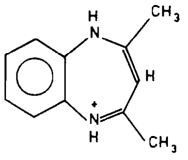

(III)

Though the free base is colourless, the hydrohalides are intensely coloured, deep violet in aqueous solution and almost black in the crystals. Mr D. Lloyd (Lloyd & Marshall, 1956) gave us samples of both chloride and bromide. These crystals being isomorphous, the problem was attractive, in 1963, for X-ray study. Structural analysis would be of interest because of the ring system, and perhaps in connexion with the colour.

Crystals, from aqueous solution containing a trace of excess HCl (or HBr), were fine needles, elongated parallel to **b**, and with (100) as the best developed faces though {102} were also present. Preliminary work was on the bromide (Cu radiation, visual estimates of intensities), approximate positions for most of the atoms (but not H) being found by the heavy-atom method (Wilson, 1971). From this basis a more accurate study of the chloride, for which μ(Mo) = 3·3 cm^{-1}, followed. The crystal habit was unfavourable for precise intensity measurements, but a crystal was found with dimensions $0{\cdot}37\times0{\cdot}14\times0{\cdot}10$ mm; the longest dimension was parallel to **b**, about which the crystal was mounted. Measurements were made on a Hilger–Watts four-circle diffractometer which the ω–θ scan. Of some 1500 reflexions observed out to $\theta=20°$, 1400 were independent;

950 of these with intensities $>\sigma$ (counting statistics) were used in refinement. Absorption errors would be small and were not corrected. The later stages of refinement were done with *CRYLSQ*: full-matrix operation, isotropic vibrational parameters for O, anisotropic for Cl, N and C. At an appropriate stage, the 13 H atoms of the cation, roughly located in difference syntheses, were allowed a cycle of isotropic, full-matrix refinement; but no great accuracy is claimed for their coordinates. The H atoms of the water molecules were not sought. Scattering functions were taken from *International Tables for X-ray Crystallography* (1974), chlorine being supposed to be Cl^-. The weighting scheme was $\sqrt{w}=1\cdot0$ if $|F_o|<20\cdot0$, else $=1/|F_o|$, and analysed satisfactorily. In the last two cycles an isotropic extinction parameter was introduced (Larson, 1967); it converged at $g=0\cdot08$. The final R was 7·6%, $R_w=$ 11·5%.* Parameters are in Table 1 and the numbering of atoms is in Fig. 1. The H atoms, except H(3), are numbered according to the C or N atoms to which they are attached. The numbered set, in Table 1, constitutes the crystal-chemical unit (CCU); other units needed in the paper are coded thus:

	CCU		x, y, z
i	$\frac{1}{2}-x, \frac{1}{2}+y, z$	iii	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
ii	$\frac{1}{2}-x, -y, \frac{1}{2}+z$	iv	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

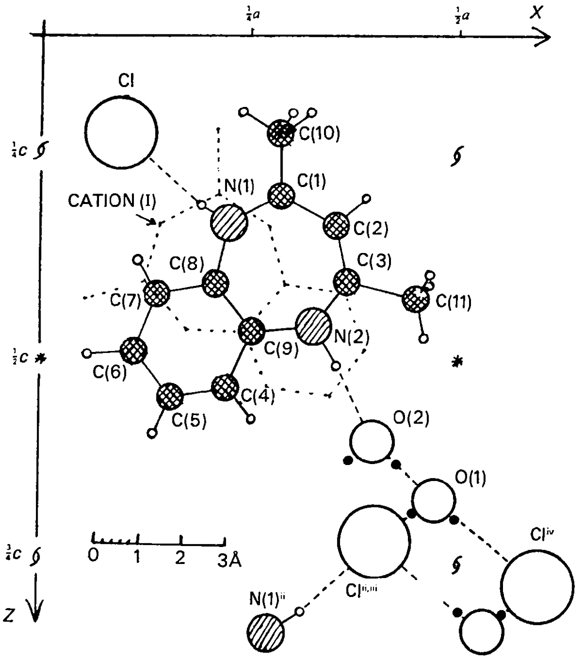

Fig. 1. The crystal structure projected along **b**. (The smallest circles represent hydrogen atoms; the filled circles suggest possible positions for the hydrogens of the water molecules, though these were not definitively located. Centres of inversion are here represented by asterisks.)

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *except* H, $\times 10^3$) *and vibrational parameters* (U_{ij} *or* U_{iso}, Å^2, $\times 10^4$; *except* H, $\times 10^3$), *with standard deviations in parentheses*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	961 (1)	1516 (3)	2248 (1)	508 (17)	754 (17)	475 (15)	2 (11)	−31 (9)	20 (11)
N(1)	2280 (3)	1339 (9)	3334 (3)	304 (42)	597 (42)	408 (39)	81 (30)	32 (31)	−27 (31)
N(2)	3283 (3)	1471 (9)	4614 (3)	331 (48)	557 (40)	445 (40)	−66 (31)	−42 (33)	−14 (32)
C(1)	2886 (4)	1289 (10)	3012 (4)	346 (55)	390 (46)	467 (49)	41 (35)	78 (44)	15 (35)
C(2)	3525 (4)	1342 (12)	3346 (4)	425 (56)	767 (61)	350 (49)	−9 (42)	118 (42)	166 (42)
C(3)	3703 (4)	1402 (10)	4051 (4)	430 (57)	344 (45)	506 (58)	93 (36)	35 (46)	84 (38)
C(4)	2265 (5)	1552 (11)	5327 (4)	742 (75)	525 (49)	260 (45)	38 (42)	10 (40)	−186 (36)
C(5)	1568 (5)	1566 (13)	5445 (4)	514 (64)	816 (63)	445 (52)	51 (44)	269 (48)	83 (45)
C(6)	1128 (4)	1457 (13)	4881 (5)	411 (50)	736 (58)	584 (62)	9 (40)	47 (49)	140 (48)
C(7)	1389 (4)	1410 (11)	4198 (4)	457 (64)	565 (52)	341 (47)	24 (47)	95 (38)	43 (39)
C(8)	2093 (4)	1431 (10)	4069 (4)	463 (58)	334 (43)	361 (48)	20 (37)	128 (42)	−81 (34)
C(9)	2544 (4)	1465 (10)	4646 (3)	355 (55)	345 (41)	345 (47)	−29 (34)	−8 (38)	7 (32)
C(10)	2878 (4)	1221 (13)	2214 (3)	555 (53)	863 (70)	354 (49)	28 (47)	72 (37)	18 (45)
C(11)	4455 (4)	1469 (13)	4255 (5)	368 (58)	797 (64)	824 (64)	32 (45)	12 (45)	180 (54)

Table 1 (*cont.*)

	x	y	z	U_{iso}
O(1)	4718 (3)	4524 (9)	6695 (3)	747 (19)
O(2)	3991 (3)	1586 (8)	5981 (3)	688 (19)
H(1)	194 (3)	153 (8)	311 (3)	0 (14)
H(2)	353 (4)	170 (10)	509 (4)	37 (14)
H(3)	386 (3)	136 (8)	302 (3)	0 (14)
H(4)	255 (3)	174 (8)	569 (3)	0 (14)
H(5)	142 (3)	149 (8)	590 (3)	11 (14)
H(6)	63 (4)	145 (10)	488 (4)	33 (20)
H(7)	118 (3)	130 (8)	378 (3)	0 (14)
H(101)	244 (5)	151 (13)	207 (5)	69 (28)
H(102)	300 (5)	6 (13)	214 (5)	98 (28)
H(103)	320 (5)	219 (14)	202 (5)	45 (27)
H(111)	462 (5)	32 (12)	415 (5)	69 (28)
H(112)	452 (5)	134 (13)	479 (5)	53 (29)
H(113)	461 (5)	255 (13)	407 (5)	47 (27)

Discussion. Methyl atoms apart, the $C_{11}H_{13}N_2^+$ cation is nearly planar. The mean plane through the C and N atoms of the rings is defined by:

$$0\cdot00204X-0\cdot99923Y+0\cdot03931Z=-0\cdot66292\ \text{Å}.$$

Deviations from this plane are recorded in Fig. 2: none of them is significant at the 3σ level ($\chi^2=15\cdot6$ for 8 degrees of freedom).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31426 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *within the cation*

(Standard deviations in parentheses.)

N(1)–C(1)	1·320 (10)	N(2)–C(3)	1·332 (10)
N(1)–C(8)	1·424 (9)	N(2)–C(9)	1·430 (10)
C(1)–C(2)	1·385 (11)	C(2)–C(3)	1·365 (11)
C(7)–C(8)	1·384 (12)	C(4)–C(9)	1·386 (10)
C(6)–C(7)	1·376 (12)	C(4)–C(5)	1·366 (13)
C(1)–C(10)	1·496 (10)	C(3)–C(11)	1·504 (11)
C(5)–C(6)	1·357 (12)	C(8)–C(9)	1·389 (10)
N(1)–H(1)	0·79 (5)	N(2)–H(2)	1·03 (7)
C(7)–H(7)	0·89 (5)	C(4)–H(4)	0·89 (4)
C(6)–H(6)	0·96 (7)	C(5)–H(5)	0·90 (6)
C(2)–H(3)	0·89 (5)		
C(2)–N(1)–C(8)	132·0 (6)	C(3)–N(2)–C(9)	129·9 (6)
N(1)–C(1)–C(2)	125·8 (7)	N(2)–C(3)–C(2)	127·9 (7)
N(1)–C(8)–C(9)	126·5 (7)	N(2)–C(9)–C(8)	126·4 (6)
N(1)–C(8)–C(7)	114·7 (6)	N(2)–C(9)–C(4)	115·2 (6)
C(9)–C(8)–C(7)	118·8 (7)	C(4)–C(9)–C(8)	118·3 (7)
C(8)–C(7)–C(6)	121·5 (7)	C(9)–C(4)–C(5)	122·1 (7)
C(7)–C(6)–C(5)	119·7 (8)	C(4)–C(5)–C(6)	119·5 (8)
N(1)–C(1)–C(10)	116·7 (7)	N(2)–C(2)–C(11)	112·7 (7)
C(2)–C(1)–C(10)	117·5 (7)	C(2)–C(3)–C(11)	119·3 (7)
C(1)–C(2)–C(3)	131·5 (7)		

Table 3. *Geometry of the hydrogen bonds*

(Distances in Å, angles in degrees, standard deviations in parentheses.)

A–H...*B*	*A*...*B*	*A*–H	H...*B*	*A*–H...*B*
N(1)–H(1)...Cl	3·263 (6)	0·79 (5)	2·49 (5)	167 (2)
N(2)–H(2)...O(2)	2·904 (9)	1·03 (7)	1·89 (7)	168 (3)
O(1)...O(2)	2·807 (9)	–	–	–
O(1)...Cl^{iii}	3·203 (7)	–	–	–
O(1)...Cl^{iv}	3·194 (7)	–	–	–
O(2)...Cl^{ii}	3·198 (6)	?	?	?

Further structural details are listed in Table 2, from which the cation evidently has substantial 'chemical' symmetry about the broken line drawn in the diagram through C(2); bond lengths and angles, averaged across this line, are also shown. These dimensions suggest electron delocalization, with consequent distribution of the positive charge. The lengths of N(1)–C(8) and N(2)–C(9) imply that there is only limited cross conjugation between the π-bonded systems to the right and left of the formula. Comparison is of interest with a similar, though homocyclic, ring system (Ibata, Shimanouchi & Sasada, 1975).

The stacking of the flat cations may contribute to the coloration of the crystals. As indicated in Fig. 1, there are infinite columns of cations along **b**, each related to its neighbours by a glide-symmetry element. Their perpendicular separation is 3·45, comparable with 3·35 between the layers in graphite, with 3·41 between pairs of equivalent molecules in quaterrylene (Kerr, Ashmore & Speakman, 1975), and with 3·4–3·5 Å between differing molecules in charge-transfer compounds (Herbstein, 1971).

The structure is stabilized by hydrogen bonds involving the Cl^- ion, the two N atoms and the H_2O molecules. (The loss of water which occasionally causes crystals of the hydrobromide to effloresce may be due to weaker hydrogen bonding at Br^- than at Cl^-.) These bonds are indicated in Fig. 1, with some geometrical details in Table 3. The H atoms of the water molecules were not specifically located, but they may reasonably be disposed as shown, by filled circles, in Fig. 1: the angle at O(1) subtended by Cl^{iii} and Cl^{iv} is 107°, favourable for proton donation by the water; on the other hand, $Cl^{ii}\cdots O(2)\cdots O(1) = 64°$, which – since one proton must be placed on, or near, the short $O(2)\cdots O(1)$ line – is unfavourable for bonding between O(2) and Cl^{ii}. Hence the last item in Table 3 is probably no more than a van der Waals contact.

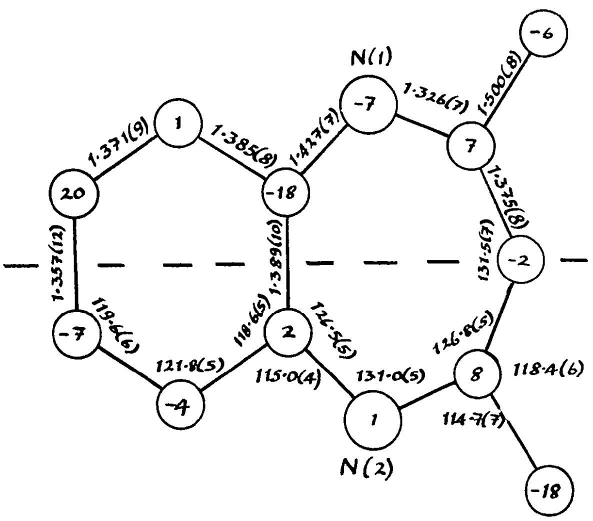

Fig. 2. Some dimensions (distances in Å, angles in degrees) in the cation, averaged across the broken line. Within each circle is shown the deviation (in 10^{-3} Å) of the atom from the mean plane through the eleven atoms of the rings.

Some preliminary work on these compounds was done at Glasgow by Dr Beryl Rimmer during 1964–7. Some of the early refinement used a least-squares program developed by P. D. Cradwick. The X-RAY 70/72 System was used in the definitive stages. Mr D. Lloyd made helpful comments on our results, and will be publishing a fuller discussion of this and related structures.

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