Diazepines, Part 24.[1] Crystal and Molecular Structure of 2,3-Dihydro-5,7-dimethyl-1,4-diazepinium Perchlorate

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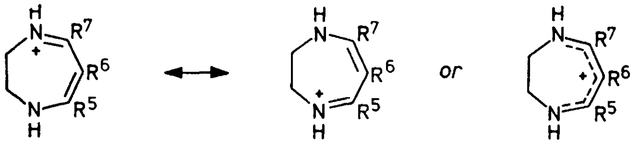
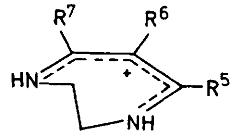
The cation of the title compound (I) contains a five-atom delocalized 1,5-diazapentadienium chain [N(1), N(4), C(5)—(7); mean C–C 1.390, mean C–N 1.318 Å] whose ends are linked by two methylene groups in a staggered conformation. The five atoms are arranged helically, and distances of atoms from the least-squares plane through them are: N(1) −0.22, N(4) 0.21 Å, and methylene carbon atoms C(2) and C(3) −0.48 and 0.51 Å. The crystal structure contains discrete diazepinium cations and perchlorate anions linked in chains by N–H ··· O hydrogen bonds (2.996 and 3.176 Å). Crystals are orthorhombic, space group $Pn2_1a$, with $Z = 4$ in a unit cell of dimensions $a = 9.946(2)$, $b = 11.311(1)$, and $c = 9.276(1)$ Å. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0.027 for 834 observed reflections.

THE 2,3-dihydro-1,4-diazepinium cations (I) are of interest because the unsaturated portion of the molecule [atoms (1), (4)—(7)] shows many resemblances in its chemistry to that of benzene derivatives,[2] earning the system at different times a description as quasi-aromatic [3] or, later, meneidic.[4] From the electronic [5] and n.m.r. spectra [6,7] it was deduced that the unsaturated portion was coplanar or helical, while the dimethylene bridge took up a staggered half-chair form which was rapidly inverting in solution at room temperature but not at lower temperatures. Coupling constants indicated almost complete delocalization of the electrons in the conjugated portion.[6]



(I)



(II)

Until now, evidence for the structure (II) has depended entirely upon spectroscopic and chemical evidence. Very recently a pyrrolo-annellated derivative was identified by X-ray crystallography,[8] which indicated this type of structure. We now report the first X-ray crystallographic study of a simple example of this type of compound, namely the 5,7-dimethyl derivative (I; $R^5 = R^7 = Me$, $R^6 = H$).[9] The results are in complete accord with the previous suppositions, establishing the shape of the molecule and in particular the delocalized nature of the unsaturated system which is responsible for its chemical properties, the C–C and C–N bond lengths averaging respectively 1.390 and 1.318 Å.

EXPERIMENTAL

Crystal Structure Analysis of (I; $R^5 = R^7 = Me$, $R^6 = H$).—Small, needle crystals were obtained by recrystallisation from water. Accurate cell parameters were obtained by a least-squares procedure applied to 12 general reflections measured on a Hilger and Watts diffractometer.

Crystal Data.—$C_7H_{13}ClN_2O_4$, $M = 224.6$. Orthorhombic, $a = 9.946(2)$, $b = 11.311(1)$, $c = 9.276(1)$ Å, $U = 1\,043.5$ Å^3, $Z = 4$, $D_c = 1.43$ g cm^{-3}, $F(000) = 472$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 3.6 cm^{-1}. Space group $Pn2_1a$ (C_{2v}^9) from systematic absences: $hk0$, $h = 2n + 1$, $0kl$, $k + l = 2n + 1$.

The intensities of all reflections with 2θ(Mo-K_α) $< 50°$ were measured on a PDP 81 controlled Hilger and Watts Y290 four-circle diffractometer fitted with a graphite monochromator in a manner similar to that described previously.[10] Lorentz and polarization factors were applied to the intensity data and the structure amplitudes derived. Of the 961 unique data, 834 reflections had intensities $I > 3\sigma(I)$ and were labelled observed; the remaining 127 data were taken as unobserved and given zero weight in refinement calculations.

Space group $Pn2_1a$ was chosen over the alternative $Pnma$ (D_{2h}^{16}) on the basis of E-statistics and because with $Z = 4$ $Pnma$ would have required the cation to have mirror symmetry or an inversion centre. These restrictions were considered unlikely and the choice of $Pn2_1a$ was confirmed by the successful solution and refinement of the structure. The position of the chlorine atom was deduced from a three-dimensional Patterson distribution and the remaining carbon, nitrogen, and oxygen atoms found by application of the heavy-atom method.

Refinement by full-matrix least-squares calculations using weights derived from the counting statistics proceeded smoothly. Isotropic followed by anisotropic least-squares calculations gave R 0.060. At this stage a difference synthesis clearly revealed the positions of all hydrogen atoms and no other significant features. Inclusion of the hydrogen atoms in the refinement with isotropic temperature factors gave a final R of 0.027 for the 834 observed reflections and 0.031 for all 961 reflections. The final weighted factor R' $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.042. A final difference map was featureless. In least-squares calculations scattering curves for carbon, nitrogen, oxygen, and chlorine were taken from ref. 11, those for hydrogen from ref. 12. Atom co-ordinates are given in Table 1 with the standard deviations from the least-squares refinement. Thermal parameters, bond angles involving hydrogens, and final values of measured and calculated structure factors have been deposited as Supplementary Publication No. SUP 22590 (16 pp.).* Table 2 contains details of bond lengths and angles.

TABLE 1

Final atom co-ordinates (Cl, O, N, and C × 10^4, H × 10^3), with estimated standard deviations in parentheses for 2,3-dihydro-5,7-dimethyl-1,4-diazepinium perchlorate

Atom	x/a	y/b	z/c
Cl	1 874(1)	2 500 *	2 183(1)
O(1)	2 294(4)	1 294(3)	2 298(4)
O(2)	506(3)	2 569(4)	1 841(5)
O(3)	2 646(4)	3 077(3)	1 095(4)
O(4)	2 146(3)	3 108(3)	3 500(3)
N(1)	−1 362(3)	1 685(3)	9 295(3)
C(2)	−719(4)	592(4)	9 685(4)
C(3)	672(4)	466(4)	9 030(4)
N(4)	620(3)	118(3)	7 534(3)
C(5)	−80(3)	646(3)	6 519(4)
C(6)	−913(3)	1 612(3)	6 730(4)
C(7)	−1 455(4)	2 115(3)	7 976(4)
Me(5)	101(6)	188(5)	5 022(5)
Me(7)	−2 265(7)	3 223(5)	7 827(6)
H(N1)	−171(4)	203(4)	995(5)
H(21)	−70(4)	51(4)	1 070(5)
H(22)	−131(4)	−10(5)	942(5)
H(31)	109(4)	125(4)	916(4)
H(32)	109(6)	−22(7)	964(6)
H(N4)	94(5)	−45(5)	733(4)
H(6)	−126(4)	200(4)	591(5)
H(Me51)	82(7)	44(6)	464(7)
H(Me52)	26(6)	−52(7)	498(7)
H(Me53)	−60(7)	29(8)	449(8)
H(Me71)	−193(7)	386(7)	811(8)
H(Me72)	−287(6)	325(6)	700(8)
H(Me73)	−296(5)	337(7)	867(7)

* Held constant to fix the origin in $Pn2_1a$.

DISCUSSION

The crystal structure of (I; $R^5 = R^7 =$ Me, $R^6 =$ H) (Figure 1) contains discrete diazepinium cations and perchlorate anions linked in chains *via* N–H · · · O hydrogen bonds (2.996 and 3.176 Å; Table 2). Other inter-ion contacts correspond to normal van der Waals distances.

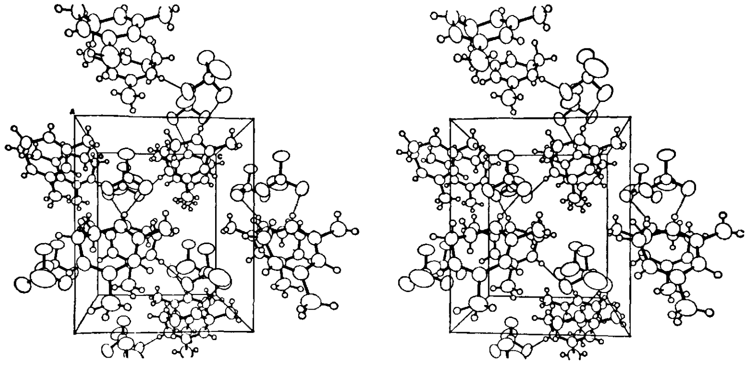


FIGURE 1 Stereoview of the unit cell and environs for 2,3-dihydro-5,7-dimethyl-1,4-diazepinium perchlorate. Thin lines indicate N–H · · · O hydrogen bonds

An ORTEP view of the cation with the chemical (and crystallographic) numbering scheme is shown in Figure 2 together with torsion angle data. Other details of molecular geometry are in Table 2.

TABLE 2

Molecular geometry details for 2,3-dihydro-5,7-dimethyl-1,4-diazepinium perchlorate

(*a*) Bond lengths (Å)

Cl–O(1)	1.431(4)	N(4)–C(5)	1.315(4)
Cl–O(2)	1.399(4)	N(4)–H(N4)	0.74(5)
Cl–O(3)	1.426(4)	C(5)–C(6)	1.385(4)
Cl–O(4)	1.428(3)	C(5)–Me(5)	1.493(6)
N(1)–C(2)	1.438(5)	C(6)–C(7)	1.396(5)
N(1)–C(7)	1.320(5)	C(6)–H(6)	0.95(5)
N(1)–H(N1)	0.80(5)	C(7)–Me(7)	1.496(7)
C(2)–C(3)	1.518(6)	Me(5)–H(Me51)	0.84(7)
C(2)–H(21)	0.95(5)	Me(5)–H(Me52)	0.82(7)
C(2)–H(22)	1.01(5)	Me(5)–H(Me53)	0.86(8)
C(3)–N(4)	1.443(5)	Me(7)–H(Me71)	0.84(8)
C(3)–H(31)	0.99(5)	Me(7)–H(Me72)	0.98(7)
C(3)–H(32)	1.05(6)	Me(7)–H(Me73)	1.06(7)

(*b*) Angles (°) not involving hydrogen

O(1)–Cl–O(2)	110.7(3)	C(3)–N(4)–C(5)	125.7(4)
O(1)–Cl–O(3)	109.4(3)	N(4)–C(5)–C(6)	125.0(4)
O(1)–Cl–O(4)	109.9(3)	N(4)–C(5)–Me(5)	116.4(4)
O(2)–Cl–O(3)	109.7(3)	C(6)–C(5)–Me(5)	118.5(4)
O(2)–Cl–O(4)	110.6(3)	C(5)–C(6)–C(7)	132.0(4)
O(3)–Cl–O(4)	106.4(3)	C(6)–C(7)–N(1)	126.2(4)
C(7)–N(1)–C(2)	125.5(4)	C(6)–C(7)–Me(7)	118.2(4)
N(1)–C(2)–C(3)	112.7(4)	N(1)–C(7)–Me(7)	115.6(4)
C(2)–C(3)–N(4)	112.2(4)		

(*c*) Interatomic distances (Å) and angles (°)

N(1) · · · O(4^{I})	2.996	N(4) · · · O(3^{II})	3.176
H(N1) · · · O(4^{I})	2.20	H(N4) · · · O(3^{II})	2.47
N(1)–H · · · O(4^{I})	172°	N(4)–H · · · O(3^{II})	162°

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I $x, y, 1 + z$; II $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$.

(*d*) Details of mean through delocalized moiety of ring

(*i*) Equation of best plane through N(1), N(4), C(5), C(6) and C(7)

$$0.7871X + 0.6166Y + 0.0119Z = 0.4364$$

(*ii*) Displacements (Å) of the atoms from plane:

N(1) −0.225, C(2) −0.479, C(3) 0.515, N(4) 0.214, C(5) 0.023, C(6) 0.048, C(7) −0.013, Me(5) −0.171, Me(7) 0.124.

In the diazepinium cation all the bond lengths (Table 2) are consistent with the delocalized system implied by formula (I). Atoms N(1), N(4), and C(5)—(7) in the delocalized portion of the ring form a portion of a helix with N(1)-0.22 Å below and N(4) 0.21 Å above the best plane of the five atoms (Table 2); evidence of this helicity is also given by the torsion angles (Figure 2).

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index Issue.

The remaining two atoms [C(2) and C(3)] of the seven-membered ring are -0.48 and 0.51 Å respectively from the plane of the delocalized moiety.

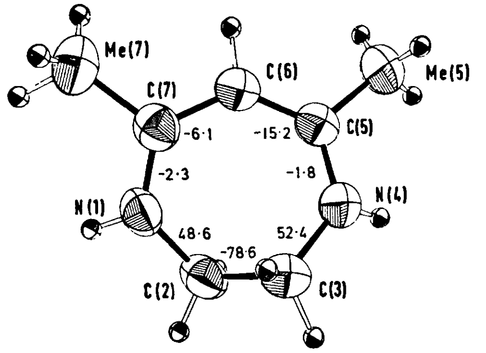

FIGURE 2 The cation showing the atom numbering scheme and torsion angles (°) within the ring

The ring valency angles (mean 126.9°) at the delocalized atoms have been increased markedly from the 120° value expected for sp^2 hybridization to accommodate the almost planar delocalized portion of the seven-membered ring system; by contrast, the sp^3 hybridized carbon atoms have N–C–C bond angles close to normal values (mean 112.4°) but the N–C–C–N torsion angle ($-78.0°$) shows a significant extra twisting from a gauche conformation. There is no evidence from difference maps or thermal parameters of any disorder or flipping associated with atoms C(2) and C(3).

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