Model Compounds for Simple Saturated 7–9 Membered Rings: the *X*-Ray Crystal Structure of Hexa-, Hepta-, and Octa-methyleneammonium Salts

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Summary The structures of the title compounds have been determined by *X*-ray crystallography, and ring torsional angles are given for all three compounds; the conformation of the seven-membered ring is a slightly 'twisted chair' and that of the eight-membered ring a 'boat chair,' while the nine-membered ring does not possess any obvious symmetry.

MUCH information about medium-sized rings has recently become available.[1–3] Since the reactivity and physical properties of cyclic amine derivatives, like the corresponding alicyclic compounds, depend upon ring size,[3–5] it is unfortunate that little is known about the structure and conformation of these amines. This reactivity is thought to be controlled by variations in the *I*-strain, resulting from alterations of the nitrogen hybridisation;[5,6] *e.g.*, there is a wide range of reactivities among the cyclic iminium[7] and amidinium salts.[8] *X*-Ray structural studies of the amidinium salts $\mathrm{HC(\overset{+}{N}[CH_2]_{\mathit{n}})_2\ X^-}$ (n = 6—8) are in progress; reported here are the structures of the cyclic amine salts $\mathrm{H_2N^+[CH_2]_{\mathit{n}}\ X^-}$ (n = 6—8) (I) which provide very close analogues to cycloheptane, cyclo-octane, and cyclononane.[9]

Hexamethyleneammonium chloride (I, n = 6) and heptamethyleneammonium tosylate (I, n = 7) were prepared from the amine and dry hydrochloric acid or dry toluene-*p*-sulphonic acid. Octamethyleneammonium tosylate (I, n = 8) was prepared by refluxing a solution of methylammonium tosylate and octamethyleneamine in acetonitrile, m.p.s.: (I, n = 6, X = Cl), unsharp; (I, n = 7, X = tosyl) 94—95 °C; (I, n = 8, X = tosyl) 118·5—119 °C.

Crystal data: $\mathrm{[CH_2]_6NH_2^+\ Cl^-}$, orthorhombic, $a = 9{\cdot}280$, $b = 10{\cdot}567$, $c = 10{\cdot}050$ Å, space group $Pca2_1$, $Z = 4$, $D_c = 1{\cdot}137$ g cm^{-3}, Cu-$K_{\alpha 1}$, $\lambda = 1{\cdot}54051$ Å, four-circle diffractometry, 561 independent reflections with $I > 3\sigma\ (I)$. $\mathrm{[CH_2]_7NH_2^+\ \mathit{p}\text{-}MeC_6H_4SO_3^-}$, orthorhombic, $a = 9{\cdot}280$, $b = 11{\cdot}855$, $c = 27{\cdot}682$ Å, space group $Pbca$, $Z = 8$, $D_c = 1{\cdot}245$ g cm^{-3}, Cu-$K_{\alpha 1}$, four-circle diffractometry, 1737 independent reflections with $I > 3\sigma(I)$. $[CH_2]_8NH_2^+$ p-$MeC_6H_4SO_3^-$, monoclinic, $a = 12{\cdot}592$, $b = 7{\cdot}855$, $c = 16{\cdot}160$ Å, $\gamma = 96{\cdot}83°$, space group $P2_1/b$, $Z = 4$, $D_c = 1{\cdot}253$ g cm^{-3}, Cu-$K_{\alpha 1}$, four-circle diffractometry, 2256 independent reflections with $I > 3\sigma(I)$.†

The structures of all three compounds were solved by an application of the tangent formula; the positions of the hydrogen atoms were located from difference Fourier syntheses. The structures were refined by 'large-block' least-squares with anisotropic temperature factors for all atoms except hydrogen. Hydrogen atoms were constrained to have chemically reasonable positions. The conventional R-values for all reflections with $I > 3\sigma(I)$ are 0·078, 0·059, and 0·079 for the 7, 8, and 9 membered rings respectively, and the bond lengths and angles within these rings have acceptable values.

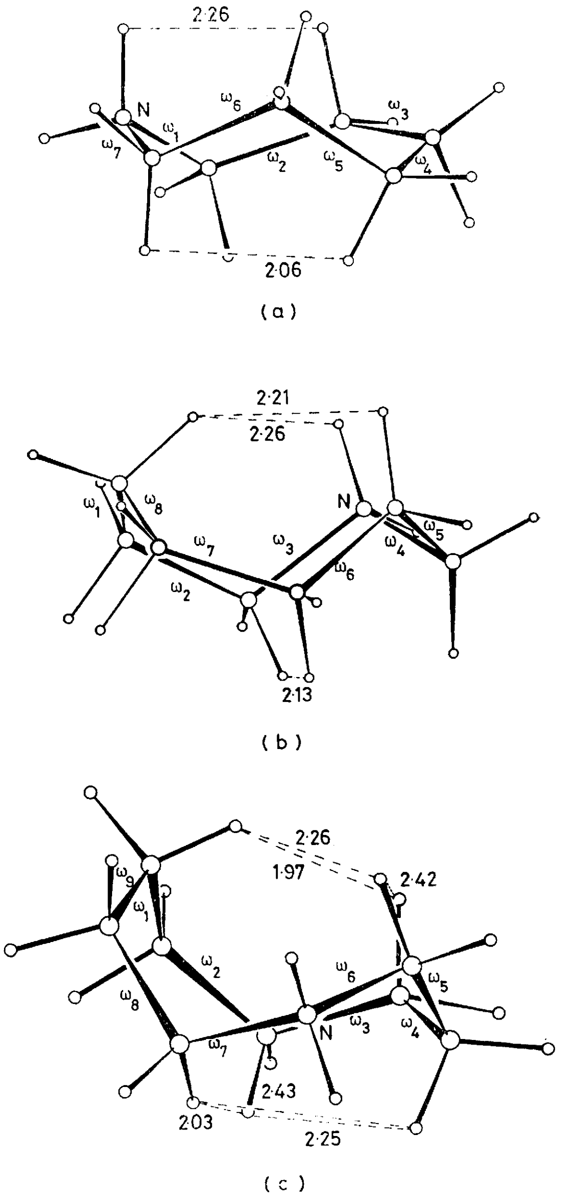
Hexamethyleneammonium chloride. The cyclic ion adopts a slightly twisted chair conformation; torsional angles for the ring are given in the Table and compared to those recently predicted for cycloheptane[1] in the chair and twist-chair conformations. The nitrogen atom was located by the short bonds it formed in the ring and by an anomalously low temperature factor when all the atoms in the ring were refined as carbon, although this was the least definitive assignment of the nitrogen atom in the three structures and there is some evidence of libration within the ion. However the structure could not be satisfactorily refined in any other conformation (see below[10]). The corresponding amidinium salt also has a ring conformation close to the twist-chair.[11]

TABLE. Ring torsional angles (ω) and mean internal ring bond angle (θ) for $NH^+_2[CH_2]_n$ (I)

(1) (I, $n = 6$); (2) expected values for the twist-chair and (3) the chair conformation of cycloheptane (ref. 1); (4) (I, $n = 7$); (5) expected values for the boat-chair conformation of cyclo-octane (ref. 2); (6) (I, $n = 8$).

	(1)	(2)	(3)	(4)	(5)	(6)
ω_1	−68·6°	−73·0	−85·6	55·3	65·0	−76·4
ω_2	58·6	89·4	68·5	50·6	44·7	−39·8
ω_3	−10·2	−40·0	0·02	−106·3	−102·2	99·1
ω_4	−50·7	−40·4	−68·3	69·9	65·0	−84·6
ω_5	87·9	89·4	85·0	−68·0	−65·0	105·3
ω_6	−83·7	−72·7	−63·9	95·7	102·2	−60·3
ω_7	67·1	55·4	63·8	−35·2	−44·7	−63·8
ω_8				−65·4	−65·0	76·5
ω_9						53·2
θ	116·1			117·1		117·6

Heptamethyleneammonium tosylate. The eight-membered ring has the boat-chair conformation;[2] torsional angles are given in the Table and compared with those calculated[2] for cyclo-octane. The three shortest transannular contacts are given in the Figure. There is no evidence of any appreciable libration in the ring; indeed the Weissenberg photographs of this compound are exceptionally sharp. This is in marked contrast to those of the corresponding chloride salt[10,11] and the choice of an irregularly shaped counter-ion may well have avoided the difficulties that were encountered by Dunitz in a previous attempt[10] to refine a structure containing the heptamethyleneammonium ion. In this context, attempts are still being made to prepare a suitable crystal of hexamethyleneammonium tosylate.



(a)

(b)

(c)

FIGURE. Conformations of the cyclic ammonium ions NH_2^+-$[CH_2]_n$; (a) $n = 6$, (b) $n = 7$, (c) $n = 8$.

Octamethyleneammonium tosylate. The nine-membered ring does not adopt any of the symmetric conformations that have been suggested[12] from calculations, inferred[13] from low temperature ^{13}C n.m.r. studies, or observed[14] in the

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

cyclononylammonium ion ($C_9H_{17}NH_3^+$). It is, however, close to the most stable calculated conformation which does not posses any element of symmetry.[15] It has three short transannular contacts above and below the main plane of the ring (see Figure) which are similar to but somewhat longer than those in the cyclononylammonium ion.

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