Crystal and Molecular Structure of 1-Azabicyclo[3.3.3]undecane Hydrochloride. Correlation of Some Molecular Dimensions with Spectroscopic Properties

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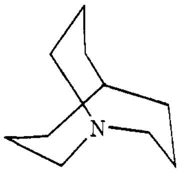
Abstract: The crystal structure of the hydrochloride salt of 1-azabicyclo[3.3.3]undecane has been determined on the basis of 1664 nonzero intensities measured on a diffractometer. The crystals are triclinic with a = 10.830 (8) Å, b = 7.122 (6) Å, c = 7.014 (3) Å, α = 97° 58′ (4′), β = 90° 24′ (4′), and γ = 96° 17′ (4′). The space group is $P\bar{1}$ and there are two molecules of $C_{10}H_{20}NCl$ in the unit cell. The structure, including hydrogen atoms, has been refined by full-matrix least-squares methods to an R factor of 0.047. The cation has effective but noncrystallographic C_3 symmetry. The three constituent eight-membered rings are in the boat–chair (BC) conformation with the detailed geometry being a compromise between torsional, bond angle, and transannular H---H nonbonded effects. The C–C–C, C–N–C, and N–C–C bond angles are all increased above tetrahedral values. The large angles in the cation can be correlated with the uv spectrum and $J_{^{13}C-H}$ coupling constant at the methine carbon atom of the free base. There is an N^+–H---Cl^- hydrogen bond of length 2.978 (3) Å.

Bicyclo[3.3.3]undecane ("manxane") (I)[1–3] and its heterocyclic analog, 1-azabicyclo[3.3.3]undecane ("manxine") (II),[2,3] have recently been synthesized. For the origin of the trivial names, see ref 1 and 3. With a view to investigating the molecular conformation of the 1-azabicyclo[3.3.3]undecane system and to attempt a correlation of some unusual spectral properties of these molecules with detailed geometry, we have undertaken a single-crystal X-ray analysis of the hydrochloride salt of II, 1-azabicyclo[3.3.3]undecane hydrochloride (III). A preliminary report of this study has been published.[4]



II

Experimental Section

A small plate-like crystal of III was shown to be triclinic on the basis of a photographic examination. Cell data were obtained from a least-squares analysis of the settings for the four angles for nine reflections that had been carefully centered on the diffractometer (Cu Kα_1 radiation, λ = 1.5405 Å). Crystal data: $C_{10}H_{20}N^+$-Cl^-; M = 189.73; triclinic; a = 10.830 (8) Å, b = 7.122 (6) Å, c = 7.014 (3) Å; α = 97° 58′ (4′), β = 90° 24′ (4′), γ = 96° 17′ (4′); V = 532.4 Å^3; ρ_{measd} = 1.24 g cm^{-3}; Z = 2; ρ_{calcd} = 1.18 g cm^{-3}; $F(000)$ = 208; μ = 27.5 cm^{-1}; no systematic absences, space group either $P1$ or $P\bar{1}$. The density was measured by flotation in a mixture of carbon tetrachloride and hexane. The density was measured several times, but the discrepancy between the observed and calculated values remained. One possible explanation could be that small amounts of acetone were trapped interstitially, although the microanalytical data would suggest that these amounts were very small.

Intensity data were collected on a Picker FACS-1 computer-controlled diffractometer using Cu Kα radiation. The intensities were measured using a θ–2θ scan technique with a counter scan rate of 1 deg min^{-1}. The base width of the scan was 2° but a dispersion factor was applied to take account of the α_1–α_2 splitting. Background counts for periods of 10 sec were recorded at each limit of the scan range. A hemisphere of data out to 2θ = 130° was measured. The intensities of three standard reflections, 10 0 0, 0 0 7, and 0 $\bar{6}$ 0, were measured after every set of 50 measurements and all three fell amost linearly with time. At the end of the period of data collection (about 1 week) the standards had fallen to about 60% of their original intensity. The data were corrected for Lorentz and polarization factors, and a scale factor was applied to correct for the assumed linear falloff in intensity. No correction was made for absorption. Employing the criteria that the net count be greater than 0.10 × total background count and/or greater than 200 counts, a total of 1644 structure amplitudes was considered to be observed.

Structure Determination. The structure determination was undertaken assuming $P\bar{1}$ to be the correct space group. The structure was solved by Patterson–heavy atom methods and three cycles of full-matrix least-squares refinement on the positional and isotropic thermal parameters of all the nonhydrogen atoms reduced the R factor to 0.14. All nonzero reflections were given unit weight and the quantity minimized was $\Sigma w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2$. A difference map was calculated and had peaks of height 0.4–0.6 electron/Å^3 that corresponded to the positions of all the hydrogen atoms in the structure.

Four cycles of full-matrix least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms reduced the R factor on all observed data to 0.047. In the final cycle of refinement, the largest shift:esd ratio for a parameter was 0.40. A difference map computed at this stage had no maxima or minima outwith the range ±0.2 electron/Å^3.

The final positional and thermal parameters are listed in Tables I and II. The list of h, k, l, $|F_{\text{obsd}}|$, and F_{calcd} values will appear in the microfilm edition.[5] The scattering curves used in the analysis were those for C, N, Cl^- taken from the complication by Cromer and Mann[6] and that for H calculated by Stewart, *et al.*[7]

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[1] M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Lett.*, 3619 (1970).

[2] N. J. Leonard and J. C. Coll, *J. Amer. Chem. Soc.*, **92**, 6685 (1970); **93**, 287 (1971).

[3] J. C. Coll, D. R. Crist, M. d. C. G. Barrio, and N. J. Leonard, *ibid.*, **94**, 7092 (1972).

[4] N. J. Leonard, J. C. Coll, A. H.-J. Wang, R. J. Missavage, and I. C. Paul, *ibid.*, **93**, 4628 (1971).

[5] The list of h, k, l, $|F_{\text{obsd}}|$, and F_{calcd} will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7092. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[6] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table I. Final Atomic Coordinates in Fractions of the Unit Cell Edges. Standard Deviations are Given in Parentheses[a]

Atom	x	y	z
Cl	0.34784 (7)	0.31049 (12)	0.21732 (11)
N	0.6218 (2)	0.2983 (3)	0.2097 (3)
C(2)	0.6326 (3)	0.1723 (5)	0.3656 (5)
C(3)	0.7328 (3)	0.0395 (5)	0.3442 (5)
C(4)	0.8690 (3)	0.1200 (5)	0.3582 (5)
C(5)	0.9217 (3)	0.2344 (5)	0.1993 (5)
C(6)	0.9195 (3)	0.4511 (5)	0.2451 (5)
C(7)	0.8101 (3)	0.5255 (5)	0.3546 (5)
C(8)	0.6842 (3)	0.4997 (4)	0.2585 (5)
C(9)	0.6367 (3)	0.2036 (5)	0.0053 (4)
C(10)	0.7631 (3)	0.2354 (6)	−0.0826 (4)
C(11)	0.8712 (3)	0.1503 (5)	−0.0052 (5)
H(N)	0.526 (3)	0.319 (4)	0.214 (4)
H(2a)	0.542 (3)	0.080 (5)	0.374 (4)
H(2b)	0.643 (3)	0.263 (5)	0.498 (5)
H(3a)	0.712 (3)	−0.052 (5)	0.449 (5)
H(3b)	0.717 (3)	−0.057 (4)	0.220 (5)
H(4a)	0.919 (3)	−0.006 (5)	0.353 (5)
H(4b)	0.893 (3)	0.203 (5)	0.495 (5)
H(5)	1.010 (3)	0.220 (4)	0.194 (4)
H(6a)	0.934 (3)	0.517 (5)	0.133 (5)
H(6b)	0.993 (3)	0.511 (4)	0.317 (4)
H(7a)	0.799 (3)	0.466 (5)	0.471 (5)
H(7b)	0.841 (3)	0.675 (5)	0.385 (5)
H(8a)	0.619 (3)	0.559 (5)	0.343 (5)
H(8b)	0.693 (3)	0.564 (5)	0.140 (5)
H(9a)	0.603 (3)	0.054 (5)	0.000 (4)
H(9b)	0.575 (3)	0.261 (4)	−0.066 (5)
H(10a)	0.790 (3)	0.375 (5)	−0.087 (4)
H(10b)	0.749 (3)	0.173 (5)	−0.209 (5)
H(11a)	0.843 (3)	0.002 (5)	−0.013 (5)
H(11b)	0.953 (3)	0.178 (5)	−0.102 (5)

[a] Hydrogen atoms are given the number of atom to which they are bonded.

Table II. Final Thermal Parameters[a,b] with Standard Deviations in Parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.00783 (7)	0.0294 (2)	0.0210 (2)	0.00530 (9)	0.00097 (8)	0.0019 (2)
N	0.0073 (2)	0.0210 (6)	0.0157 (5)	0.0035 (3)	0.0006 (3)	0.0022 (4)
C(2)	0.0095 (3)	0.0230 (8)	0.0193 (7)	0.0021 (4)	0.0015 (4)	0.0067 (6)
C(3)	0.0108 (3)	0.0205 (8)	0.0231 (8)	0.0032 (4)	0.0004 (4)	0.0058 (7)
C(4)	0.0104 (3)	0.0237 (8)	0.0227 (8)	0.0052 (4)	−0.0014 (4)	0.0030 (7)
C(5)	0.0068 (3)	0.0236 (8)	0.0234 (8)	0.0030 (4)	0.0010 (4)	−0.0012 (6)
C(6)	0.0081 (3)	0.0232 (8)	0.0239 (8)	−0.0006 (4)	0.0024 (4)	−0.0015 (7)
C(7)	0.0099 (3)	0.0186 (7)	0.0217 (8)	0.0014 (4)	0.0025 (4)	−0.0018 (6)
C(8)	0.0097 (3)	0.0177 (7)	0.0201 (7)	0.0039 (4)	0.0028 (4)	0.0014 (6)
C(9)	0.0089 (3)	0.0259 (9)	0.0159 (7)	0.0041 (4)	−0.0019 (4)	−0.0017 (6)
C(10)	0.0109 (4)	0.0277 (9)	0.0146 (7)	0.0043 (5)	0.0013 (4)	−0.0007 (6)
C(11)	0.0092 (3)	0.0239 (8)	0.0200 (7)	0.0037 (4)	0.0024 (4)	−0.0025 (6)

	B_θ		B_θ		B_θ		B_θ
H (N)	5.1 (7)	H (4a)	5.8 (8)	H (7a)	5.1 (8)	H (9b)	5.0 (7)
H (2a)	5.0 (8)	H (4b)	5.2 (8)	H (7b)	6.6 (9)	H (10a)	4.8 (7)
H (2b)	5.7 (8)	H (5)	4.1 (7)	H (8a)	5.8 (8)	H (10b)	6.6 (10)
H (3a)	5.4 (8)	H (6a)	5.7 (9)	H (8b)	6.1 (9)	H (11a)	5.8 (9)
H (3b)	4.5 (7)	H (6b)	5.4 (8)	H (9a)	4.8 (7)	H (11b)	6.6 (9)

[a] Anisotropic thermal parameters are expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Isotropic thermal parameters as $\exp[-B_\theta \sin^2 \theta/\lambda^2]$.

Results and Discussion

Views of the structure are shown in Figures 1 and 2. Bond lengths and angles are listed in Tables III and IV. The packing of molecules in the crystal is shown in Figure 3. As there were several somewhat disquieting features about the behavior of the crystal during data collection, such as the loss of intensity and the discrepancy between measured and calculated densities, the results of the analysis are surprisingly good. The difference map showed no unusual features, the internal consistency in the bond lengths and angles (including those involving hydrogen) was good, and the thermal parameters of the hydrogen atoms were refined to reasonable values. There was no evidence to indicate that the loss of intensity was caused by other than a uniform decomposition of the crystal.

The cation has effective but noncrystallographic C_3 symmetry about the N---C(5) axis. Each of three constituent eight-membered rings (N, C(2), C(3), C(4), C(5), C(6), C(7), C(8); N, C(9), C(10), C(11), C(5), C(4), C(3), C(2); and N, C(8), C(7), C(6), C(5), C(11), C(10), and C(9)) is in the boat–chair (BC) conformation (see IV in Table V), and there is no evidence from the X-ray study to indicate that inversion of the conformation of the cation (see formulas **2a** and **b** in ref 3) takes place in the crystal.

The crystals consist of individual rows containing an essentially linear arrangement of alternating cations and hydrogen-bonded chloride anions, with adjacent rows containing all P or all M cations (see footnote 7 in ref 3).

The values for the bond lengths and angles related by the noncrystallographic C_3 axis are quite consistent. The lengths of the bonds involving the three central methylene carbon atoms (C(3), C(7), and C(10)) may be slightly artificially short due to thermal motion,[8] although the thermal ellipsoids of these atoms are not particularly unusual. The fact that the N–C–C, C–N–C, and C–C–C bond angles are all substantially greater than tetrahedral gives rise to some interesting spectroscopic properties.[3,4] Bond angles greater than tetrahedral are commonly found in carbocyclic eight-membered rings[9] and also in heterocyclic analogs.[10,11] However, the N–CH_2–CH_2, CH_2–CH_2–CH_2, and CH_2–

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[8] See, for example, M. Bixon, H. Dekker, J. D. Dunitz, H. Eser, S. Lifson, C. Mosselman, J. Sicher, and M. Svoboda, *Chem. Commun.*, 360 (1967).

[9] J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. 2, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1968, pp 35–39.

[10] I. C. Paul and K. T. Go, *J. Chem. Soc. B*, 33 (1969).

[11] S. M. Johnson, C. A. Maier, and I. C. Paul, *ibid.*, 1603 (1970).

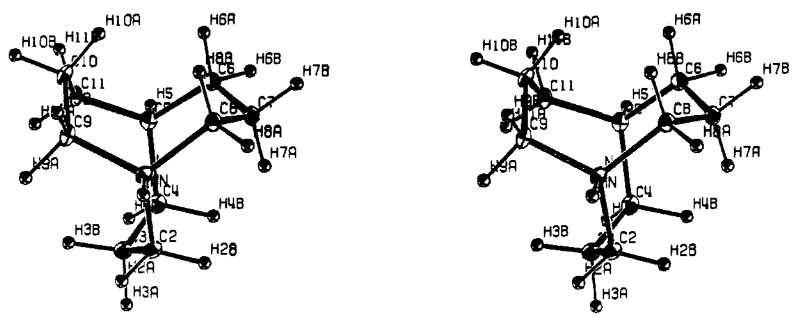


Figure 1. Stereoscopic view of the cation of III looking nearly along the N---C(5) (approximate C_3) axis.

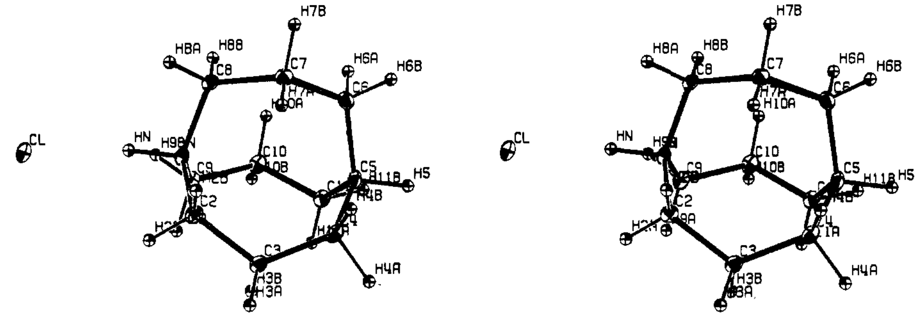


Figure 2. Stereoscopic view of III looking along the c axis.

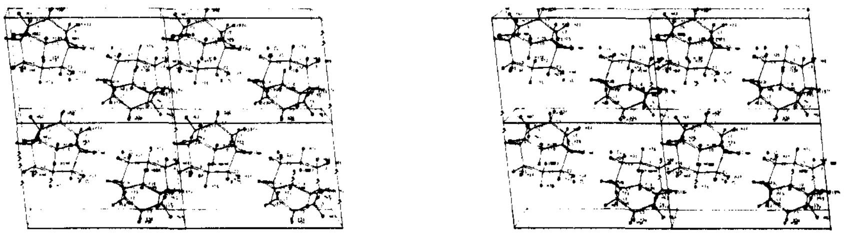


Figure 3. Stereoscopic view of the packing in four unit cells looking nearly along the c axis. The a axis is horizontal and the b axis is nearly vertical.

Table III. Bond Lengths (Å) Grouped According to Molecular C_3 Symmetry

N-C(2)	1.519 (4)	C(3)-C(4)	1.522 (5)
N-C(8)	1.511 (4)	C(6)-C(7)	1.521 (5)
N-C(9)	1.515 (4)	C(10)-C(11)	1.504 (5)
C(2)-C(3)	1.509 (5)	C(4)-C(5)	1.549 (5)
C(7)-C(8)	1.497 (5)	C(5)-C(6)	1.535 (5)
C(9)-C(10)	1.515 (5)	C(5)-C(11)	1.546 (5)
N-H(N)	1.07 (3)	C(7)-H(7a)	0.98 (3)
C(2)-H(2a)	1.13 (3)	C(7)-H(7b)	1.07 (4)
C(2)-H(2b)	1.05 (4)	C(8)-H(8a)	1.01 (3)
C(3)-H(3a)	1.06 (3)	C(8)-H(8b)	1.00 (4)
C(3)-H(3b)	1.03 (3)	C(9)-H(9a)	1.08 (3)
C(4)-H(4a)	1.09 (3)	C(9)-H(9b)	0.98 (3)
C(4)-H(4b)	1.07 (4)	C(10)-H(10a)	1.01 (3)
C(5)-H(5)	0.98 (3)	C(10)-H(10b)	0.94 (4)
C(6)-H(6a)	0.98 (3)	C(11)-H(11a)	1.06 (4)
C(6)-H(6b)	0.97 (4)	C(11)-H(11b)	1.14 (4)
N---Cl	2.978 (3)		
H(N)---Cl	1.92 (3)		

Table IV. Bond Angles[a] (deg) Grouped According to Molecular C_3 Symmetry

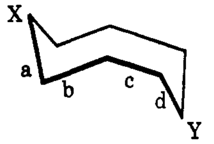
C(2)-N-C(8)	115.0 (2)	C(3)-C(4)-C(5)	118.7 (2)
C(2)-N-C(9)	115.6 (2)	C(5)-C(6)-C(7)	118.3 (2)
C(8)-N-C(9)	115.9 (2)	C(5)-C(11)-C(10)	117.4 (3)
N-C(2)-C(3)	117.0 (3)	C(4)-C(5)-C(6)	114.8 (3)
N-C(8)-C(7)	117.4 (3)	C(4)-C(5)-C(11)	113.5 (2)
N-C(9)-C(10)	117.4 (3)	C(6)-C(5)-C(11)	113.5 (2)
C(2)-C(3)-C(4)	120.1 (2)		
C(6)-C(7)-C(8)	119.6 (2)		
C(9)-C(10)-C(11)	119.5 (2)		
C(2)-N-H(N)	102 (2)	C(4)-C(5)-H(5)	106 (2)
C(8)-N-H(N)	102 (2)	C(6)-C(5)-H(5)	103 (2)
C(9)-N-H(N)	103 (2)	C(11)-C(5)-H(5)	104 (2)

[a] The N-C-H, C-C-H, and H-C-H angles range from 96 to 113°, esd 2-3°.

CH_2-CH angles are 2-3° greater than those found in unconstrained carbocyclic eight-membered rings in the BC conformation.[9] If one makes the rather crude assumption of C_s symmetry in the BC conformation of the constituent eight-membered rings (this assumption implies C(5) and N are related by mirror symmetry), the resulting symmetry-averaged torsion angles in the three constituent eight-membered rings are compared in Table V with the torsion angles found in some other BC eight-membered rings.[10,12] In general, the agreement among the torsion angles of the three constituent rings

(12) H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 51, 1514 (1968).

Table V. Torsion Angles[a] Averaged Across the Assumed C_s Symmetry in Each of the Three Constituent BC Rings in Cation IV



IV, Eight-membered ring in III

Torsion angle	C(3)–C(7)[b]	C(7)–C(10)	C(10)–C(3)	Cyclooctane-*cis*-1,2-dicarboxylic acid[c]	Thiaazacyclooctane derivative (α form)[d]
a	66.5	67.9	68.7	67	67
b	−95.9	−96.5	−97.3	−101	−104
c	39.5	38.9	40.1	43	48
d	67.9	68.7	66.5	65	64

[a] The signs for the torsion angles given in the table correspond to one-half of the molecule and would all be reversed when the other half is generated by mirror reflection. [b] Named according to atoms X and Y in IV. [c] Reference 12. [d] Reference 10.

in III is better than that between those in III and those in unconstrained cyclooctane derivatives. The principal difference between the structure for the cation found in this study and that represented by a Dreiding model involves a repulsive interaction of the *endo*-hydrogen atom, *e.g.*, H(7a), with the intraannular hydrogen atoms on the γ-carbon atoms, *i.e.*, H(2b) and H(4b) (Figure 1). These 1,4 H---H distances are listed in Table VI and range from 2.12 (5) to 2.28 (5) Å as compared with a value of 2.4 Å for twice the van der Waals radius for hydrogen.[13] The intraannular 1,3 H---H distances, *e.g.*, H(2b)---H(4b), are sufficiently long (2.67 (5)–2.78 (5) Å) as to imply no repulsive interactions.[14] The 1,4 H---H interactions have the result that the torsion angles around the two bonds involving the central methylene carbon atom and which would be greater than 90° in a Dreiding model are reduced to the range 66.5–68.7°, giving rise to a more perfectly staggered arrangement. The torsional energy thus gained and the overcrowding relief afforded by the pushing apart of the hydrogen atoms presumably compensate for the increase in the bond angles above tetrahedral values.

Table VI. Nonbonded Intramolecular H---H Contacts (Å)

	1,4 Contacts		
H(7a)---H(2b)	2.12 (5)	H(3b)---H(9a)	2.24 (4)
H(7a)---H(4b)	2.25 (5)	H(3b)---H(11a)	2.20 (4)
H(10a)---H(8b)	2.28 (5)		
H(10a)---H(6a)	2.24 (5)		
	1,3 Contacts		
H(2b)---H(4b)	2.78 (5)	H(9a)---H(11a)	2.67 (4)
H(8b)---H(6a)	2.67 (5)		

The C–C–C valency angles at the C(5) (methine) atom (113.5–114.8 (3)°) are also much greater than tetrahedral values; consequently, the C–C(5)–H(5) angles are reduced to 103–106°. C(5) and H(5) lie 0.387 and 1.36 Å, respectively, from the plane defined by the three carbon atoms, C(4), C(6), and C(11). For C–C bond lengths of 1.54 Å and tetrahedral bond angles, a carbon atom would lie 0.513 Å above the plane defined by its three bonded neighboring carbon atoms. A flattening of the bridgehead carbon atom will lead to greater p character in the C(5)–H(5) bond; this should in turn reduce the $J_{^{13}C-H}$ coupling constant,[15,16] which was estimated as 121 ± 5 Hz for III.[3,4] This value agrees well with that (119.5 Hz) reported for a sterically crowded triphenylmethane derivative where the average C–C(H)–C bond angle was 115.3°[16] and would support a $J_{^{13}C-H}$ bond angle correlation of the general type proposed by Mislow and by Foote.[15] The $J_{^{13}C-H}$ value for the methine C–H group in quinuclidine hydrochloride was estimated as ≥140 Hz,[3] and as the C–C–C bond angles in quinuclidine are virtually tetrahedral,[17] presumably some "through-space" influence, not present in III, of the nitrogen atom is responsible. The N---C(H) distance in quinuclidine is estimated as 2.5 Å from a Dreiding model and measured as 2.54 Å in an X-ray study of quinuclidine benzilate hydrobromide,[17] whereas the N---C(H) distance in III is 3.328 (4) Å.

The enlarged bond angles in the bicyclo[3.3.3]undecane ring system are in marked contrast to those found in the bicyclo[2.2.2]octane system, where geometric constraints among the various C–C–C angles exist.[18] In bicyclo[2.2.2]octane-1,4-dicarboxylic acid,[18] the in-internal C–C–C angles range from 108.4 to 110.6 (5)°, in 1-*p*-bromobenzenesulfonyloxymethylbicyclo[2.2.2]octane,[19] the range is 106.6–113.3 (8)°, while in quinuclidine benzilate hydrobromide,[17] the C–C–C angles in the quinuclidine portion range from 103.0 to 112.0 (9)°. These differences are manifested in very different nmr spectral properties for III than for the bicyclo[2.2.2]octane systems.[3,4] The phenomenon of increase of C–C–C bond angles to relieve nonbonded H---H overcrowding in fused systems has been observed previously in two bicyclo[3.3.1]nonane derivatives with the "boat-boat"[20] conformation V,[21,22] where the average bond angles are 114°, and in similar

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(13) L. Pauling in "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 257–264.

(14) These 1,3 H---H distances should not be greatly affected by the well-known tendency for hydrogen atoms to be located too near their covalently bonded atoms in an X-ray analysis.

(15) K. Mislow, *Tetrahedron Lett.*, 1415 (1964); C. S. Foote, *ibid.*, 579 (1963).

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(20) The "boat-boat" conformation in bicyclo[3.3.1]nonane derivatives as used here refers to the conformation of the "cyclooctane" moiety and does not involve the single methylene bridge. This convention is not always used, however: see P. D. Cradwick and G. A. Sim, *J. Chem. Soc. B*, 2218 (1971).

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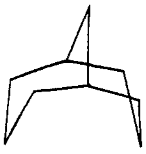
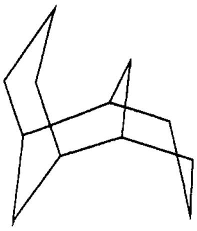
moieties in the tricyclo[5.3.1.1^{2,6}]dodecane system VI,[23] where the internal angles at the nonbridgehead positions are 116°. If equivalence is assumed between N and C(5), the cation III has almost exact C_{3h} symmetry; the projection angles C(2)–N–C(5)–C(4), C(8)–N–C(5)–C(6), and C(9)–N–C(5)–C(11) being 0.3, −1.5, and −0.6°, respectively. The question as to whether there was a mirror plane, horizontal to the C_3 axis, in the bicyclo[2.2.2]octane system has been investigated with somewhat differing conclusions.[18,19]


V


VI

The C–N–C bond angles (115.0–115.9°) are also considerably greater than 109° 28′, resulting in a flattening at the bridgehead nitrogen atom, with the result that N and H(N) lie 0.326 and 1.39 Å, respectively, out of the plane defined by C(2), C(8), and C(9), and the C–N–H(N) angles are 102–103 (2)°. In the ideal case with N–C lengths of 1.515 Å and tetrahedral angles, the distance of nitrogen from the plane of its three bonded carbon atoms would be 0.505 Å. The uv absorptions in manxine[3,4] and quinuclidine[24] correspond to an n → p transition, and these molecules may approach planarity at nitrogen in the excited (p) state.[24] In view of the significantly smaller deviation of nitrogen from the plane of the three bonded carbon atoms in the hydrochloride *salt* of II, it seems quite reasonable to assume that *less energy* would be required to produce a planar nitrogen arrangement in the excited state of II than in quinuclidine where the bond angles at nitrogen are nearly tetrahedral.[17] Our X-ray results are, therefore, in accord with the n → p transition in II occurring at a longer wavelength than that in quinuclidine. A Dreiding model of II can readily be constructed with a planar nitrogen atom although considerable strain is introduced when the configuration at nitrogen is inverted as in the case of the "nitrogen-in" amines prepared by Simmons and Park.[25]

The principal feature of the packing in the crystal is the N$^+$–H---Cl$^-$ hydrogen bond (see Figure 3). The N$^+$---Cl$^-$ and H---Cl$^-$ distances are 2.978 (3) and 1.92 (3) Å, while the N$^+$–H---Cl$^-$ angle is 170 (1)°. The anions and cations alternate in rows along the *a* axis, and the C(5)---Cl$^-$ and H(5)---Cl$^-$ distances are 4.587 (3) and 3.64 (3) Å, and the C(5)–H(5)---Cl$^-$ angle is 164 (1)°. The overall packing is presumably a compromise in energy between the tendency for the small chloride anions to fill the spaces left by close packing of the much larger cations and the directional properties of the hydrogen bond. Other important intermolecular contacts are listed in Table VII.

Table VII. Some Intermolecular Contacts (≤2.60 Å)

H(4b)---H(6b)^{I}	2.47	H(3a)---H(7b)^{IV}	2.51
H(6b)---H(6b)^{I}	2.60	H(4a)---H(7b)^{IV}	2.38
H(6a)---H(6a)^{II}	2.36	H(9a)---H(9a)^{V}	2.28
H(6a)---H(11b)^{II}	2.41	H(4a)---H(11b)^{VI}	2.52
H(2a)---H(2a)^{III}	2.37	H(5)---H(11a)^{VI}	2.58

I refers to molecule at $2 - x, 1 - y, 1 - z$
II refers to molecule at $2 - x, 1 - y, -z$
III refers to molecule at $1 - x, -y, 1 - z$
IV refers to molecule at $x, -1 + y, z$
V refers to molecule at $1 - x, -y, -z$
VI refers to molecule at $2 - x, -y, -z$

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