David Smith and Charles N. Caughlan for their help in the X-ray analysis.

Registry No.—**1**, 1469-48-3; **2**, 2144-87-8; **3**, 49558-71-6; **4**, 935-79-5; **6**, 49558-73-8; **7**, 43208-79-3; **7** (a)-CD_3 analog, 49558-75-0; **7** (e)-CD_3 analog, 49558-76-1; **8**, 49559-22-0; **9**, 49559-23-1.

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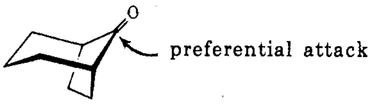
(11) (a) For a recent review of some problems in the tropane series, see G. Fodor, D. Frehel, M. J. Cooper, and N. Mandavar in "Conformational Analysis—Scope and Present Limitations," G. Chirudoglu, Ed., Academic Press, New York, N. Y., 1971, pp 73-92. (b) A recent X-ray analysis demonstrates the propensity of tropanes toward equatorial alkylation. See V. O. de la Camp, A. T. Bottini, C. C. Thut, J. Gal, and A. G. Bellettini, *J. Org. Chem.*, **37**, 324 (1972), and leading references.

(12) This suggestion is compatible with the observed dominating effect of the cyclopentane ring in controlling the course of reduction of bicyclo[3.2.1]octan-8-one.[15]



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Crystal and Molecular Structure of *cis*-8-Azabicyclo[4.3.0]non-3-ene Methiodide Quaternary Salt, $C_{10}H_{18}NI$

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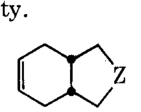
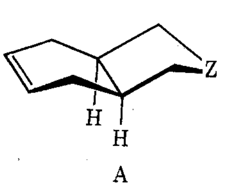
The crystal and molecular structure of the methiodide quaternary salt of *cis*-8-azabicyclo[4.3.0]non-3-ene has been determined by X-ray analysis. The crystals are orthorhombic, space group *Pbca*, with $a = 11.673$ (6), $b = 11.718$ (4), and $c = 17.142$ (12) Å. The structure was solved from the Patterson and refined by full-matrix least squares to $R = 3.7\%$ for 616 observed reflections. Owing to distortions in the five-membered heterocyclic ring, one of the methyl groups is in a pseudo-axial position while the other methyl group is in a pseudo-equatorial position. Bond distances around nitrogen range from 1.48 (2) to 1.52 (2) Å while angles range from 100.0 (1) to 112.0 (1)°.

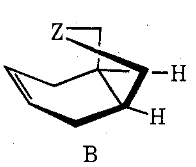
There is a paucity of data relating to structural analysis in the *cis*-bicyclo[4.3.0]non-3-ene series (I). Examination of Drieding models suggests two major conformational types (Ia and Ib), both possessing a boat cyclohexene moiety.



Ia, Z = CH_3
b, Z = O
c, Z = NCH_3



A



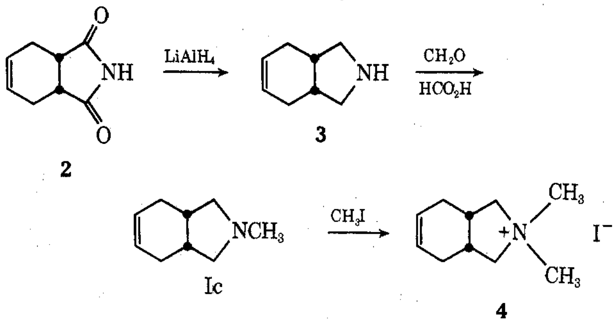
B

By indirect chemical methods alone, Ia was suggested to possess conformation B.[1] Using the same tests, and buttressed by nmr data, Ib was shown to exist as A.[2] Additional evidence supporting product assignments in chemical studies with Ib has recently been reported.[3]

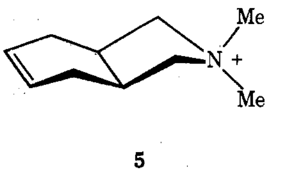
The difficulty in obtaining solid derivatives of Ia and Ib has precluded the use of X-ray analysis for these systems. However, the potential for preparing quaternary salts of Ic makes this more amenable to scrutiny by X-ray methods.

As part of a continuing study on the effects of heteroatoms in determining conformation and reactivity,[4] the preparation of the methiodide salt of *cis*-8-methyl-8-azabicyclo[4.3.0]non-3-ene (4) was undertaken (Scheme I).

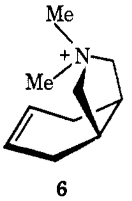
Scheme I
Synthesis of the Methiodide Salt of *cis*-8-Methyl-8-azabicyclo[4.3.0]non-3-ene



The nmr spectra of 4 exhibited two distinct methyl signals at δ 3.52 and 3.60.[5] Consideration of the two most likely conformations, 5 and 6, prompted us to suggest 6 as the more likely. A conformation of this type would be con-



5



6

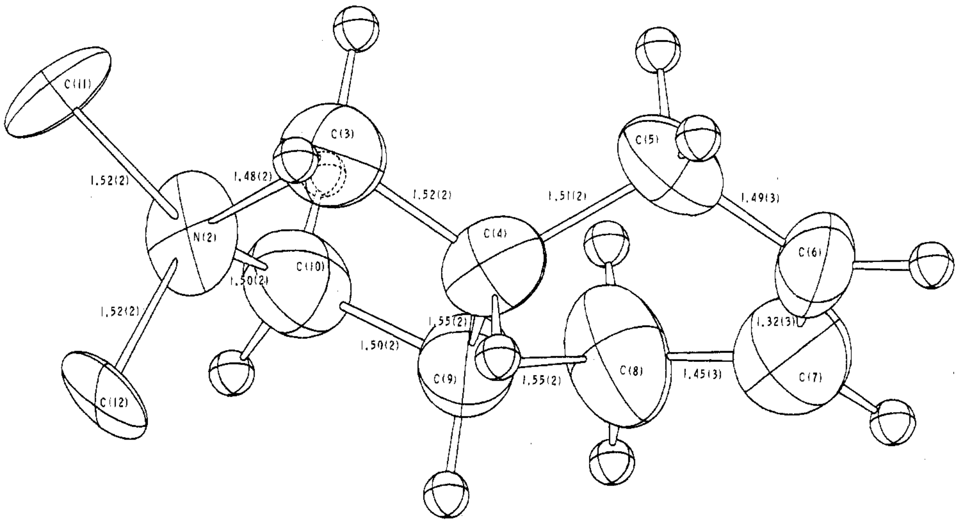


Figure 1. ORTEP drawing of the molecule illustrating bond distances and standard deviations for the nonhydrogen atoms. All hydrogen-carbon bond distances are 1.00 Å. Thermal ellipsoids are scaled to include 50% probability; for clarity, hydrogen atoms have been assigned an isotropic temperature factor of 1.0.

sistent with the different chemical shifts for the two methyl groups and might explain the observation that the vinyl protons of Ic (349 Hz) were shifted downfield in 4 (359 Hz). However, an unambiguous assignment of 5 could be made, based upon the X-ray results reported in this paper.

Experimental Section

Clear, colorless crystals of the methiodide salt of *cis*-8-azabicyclo[4.3.0]non-3-ene were obtained by recrystallization from a mixture of methylene chloride and diethyl ether. Preliminary Weissenberg photographs of a small single crystal mounted on a glass fiber indicated an orthorhombic space group. Systematic absences were $hk0$, $h \neq 2n$; $h0l$, $l \neq 2n$; and $0kl$, $k \neq 2n$, uniquely defining the space group as *Pbca*.

Precise unit cell dimensions were obtained by a least-square refinement of 13 independent 2θ values obtained on a manual G.E. XRD-5 equipped with a scintillation counter as a detector using Mo Kα radiation. These results, as well as other pertinent crystal data, are given in Table I.

Data were collected out to a 2θ of 35° using 60-sec θ–2θ scans at a scan rate of 2° min^{-1} and counting backgrounds for 10 sec on either side of the peak. Three standard reflections were measured every 2 hr and showed no significant change throughout the course of the data collection. The crystal which was used for both the intensity data collection and determination of the unit cell parameters was mounted along the b axis and was bound by {1.0.0}, {0.0.1}, {0.1.1}, (1.0.2), and (1.0.2). The approximate dimensions of the crystal were 0.27 × 0.18 × 0.37 mm. A total of 746 reflections were collected with 616 considered observed based on the criteria $I > 3\sigma(I)$. Unobserved data were given zero weight and not included in the refinement.

Backgrounds were corrected for counting times and Lorentz and polarization factors were applied in the normal manner.[6] The data were corrected for absorption using Tompa's method;[7] transmission factors varied from 0.85 to 0.89. Weights were calculated according to the method of Stout and Jensen;[8] $\omega(F) = [k/4LpI(\sigma^2(I) + (0.06I)^2)]^{-1}$. Scattering factors for nonhydrogen atoms were taken from the literature;[9] both real and imaginary terms were applied to the iodide ion.[10] The scattering factor curve for hydrogen was that of Stewart, Davidson, and Simpson.[11] No correction was made for extinction.

Structure Analysis and Refinement. The iodide ion was located from a three-dimensional Patterson function. The position of this atom was refined using full-matrix least squares minimizing $\Sigma\omega\Delta F^2$; the subsequent Fourier map revealed the positions of the rest of the heavy atoms. The structure was refined isotropically to an R factor of 5.6% ($R = \Sigma|F_o - F_c|/\Sigma|F_o|$). Further refinement, treating the vibration of all atoms anisotropically, reduced the R to 4.8%. An attempt was made to locate hydrogens from a difference Fourier, but the positions and temperature factors would not refine to reasonable values. The positions of the 12 hydrogens attached to ring carbon atoms were calculated; methyl hydrogen positions were not included because of the ambiguity of their position. Hydrogen atoms were arbitrarily assigned an isotropic temperature factor of 4.0. Further refinement of heavy-atom positions and temperature factors reduced the R factor to 3.7% for the observed data only; the R factor for both the observed and unobserved data was 6.3%. The weighted R $([\Sigma\omega\Delta F^2]/\Sigma\omega F_o^2)^{1/2}$, was 6.4% while S, the standard deviation of an observation of unit weight $[\Sigma\omega\Delta F^2/m - n]^{1/2}$, where m is the number of observations and n is the number of parameters, was 1.72. A $\delta(R)$ normal probability plot[12] was calculated and was linear; the equation of the least-squares straight line had a slope of 1.70 and an intercept of −0.02. The slope of this line, along with the value of S, indicates that the $\sigma(F)$ are underestimated by a factor of about 1.7.

Table I
Crystal Data for $C_{10}H_{18}NI$

$a = 11.673\ (6)$
$b = 11.718\ (4)$ $\alpha = \beta = \gamma = 90°$
$c = 17.142\ (12)$
Space group *Pbca* $Z = 8$
$\rho_c = 1.581$ g cm^{-3} $\rho_{meas} = 1.572$ g cm^{-3}
μ (Mo Kα) = 27.20 cm^{-1}

Discussion

Figure 1 is an ORTEP drawing of the molecule illustrating bond distances.[13] It is felt that no real significance can be attached to the thermal ellipsoids because of the influence of the heavy iodide ion on the refinement as well as the limited amount of data which were available. This may also account for the results which were obtained when hydrogen positions were refined. Also, because of the presence of the iodide ion, the standard deviations of the bond distances and angles are consideraly larger than one would expect for a structure which has refined to an R factor of 3.7%.

Bond angles are listed in Table II. To within three standard deviations, both bond distances and angles are related by a pseudo-mirror plane in the molecule which passes through the nitrogen and the midpoint of the double bond. It is interesting to note that three of the bond angles in the five-membered ring have decreased from the normally expected values. This is particularly true for the angle at nitrogen. This produces a very important effect on the two methyl groups. C(12) is significantly closer (5.52 Å) to the double bond in the cyclohexene ring than is C(11) (5.97 Å). Thus, C(12) could be considered to be to an axial position while C(11) might be considered to be equatorial.

Table II
Bond Angles with Standard Deviations in Parentheses

C(3)–N–C(10)	100 (1)	C(5)–C(6)–C(7)	120 (2)
C(3)–N–C(11)	110 (1)	C(5)–C(6)–HC6(1)	120
C(3)–N–C(12)	112 (1)	C(7)–C(6)–HC6(1)	120
C(10)–N–C(11)	111 (1)	C(6)–C(7)–C(8)	120 (2)
C(10)–N–C(12)	112 (1)	C(6)–C(7)–HC7(1)	120
C(11)–N–C(12)	111 (1)	C(8)–C(7)–HC7(1)	120
N–C(3)–C(4)	107 (1)	C(7)–C(8)–C(9)	114 (1)
N–C(3)–HC3(1)	110	C(7)–C(8)–HC8(1)	108
N–C(3)–HC3(2)	110	C(7)–C(8)–HC8(2)	108
C(4)–C(3)–HC3(1)	110	C(9)–C(8)–HC8(1)	108
C(4)–C(3)–HC3(2)	110	C(9)–C(8)–HC8(2)	108
HC3(1)–C(3)–HC3(2)	109	HC8(1)–C(8)–HC8(2)	109
C(3)–C(4)–C(5)	115 (1)	C(4)–C(9)–C(8)	112 (1)
C(3)–C(4)–C(9)	102 (1)	C(4)–C(9)–C(10)	105 (1)
C(3)–C(4)–HC4(1)	109	C(4)–C(9)–HC9(1)	109
C(5)–C(4)–C(9)	115 (1)	C(8)–C(9)–C(10)	116 (1)
C(5)–C(4)–HC4(1)	106	C(8)–C(9)–HC9(1)	106
C(9)–C(4)–HC4(1)	109	C(10)–C(9)–HC9(1)	108
C(4)–C(5)–C(6)	114 (1)	N–C(10)–C(9)	108 (1)
C(4)–C(5)–HC5(1)	108	N–C(10)–HC10(1)	110
C(4)–C(5)–HC5(2)	108	N–C(10)–HC10(2)	110
C(6)–C(5)–HC5(1)	108	C(9)–C(10)–HC10(1)	110
C(6)–C(5)–HC5(2)	108	C(9)–C(10)–HC10(2)	110
HC5(1)–C(5)–HC5(2)	109	HC10(1)–C(10)–HC10(2)	110

Table III
Equations of Planes and Dihedral Angles

	A^a	B	C	D	Σ
(1) N(2), C(11), C(12)	0.6973	0.7167	−0.0022	1.814	
(2) N(2), C(3), C(10)	0.0747	−0.0842	0.9936	5.696	
(3) C(3), C(4), C(9), C(10)	−0.3648	0.3944	0.8434	6.563	3.6×10^{-3}
(4) C(4), C(5), C(8), C(9)	0.3040	−0.2028	0.9309	5.974	1.1×10^{-3}
(5) C(5), C(6), C(7), C(8)	−0.1569	0.3094	0.9379	6.161	4.4×10^{-5}

Dihedral Angles

(1)–(2)	89.6°	(3)–(4)	53.5°
(2)–(3)	39.0°	(3)–(5)	14.0°
(2)–(4)	15.3°	(4)–(5)	40.3°

[a] The equation of the plane is $Ax + By + Cz - D = 0$, where A, B, and C are direction cosines, D is the perpendicular distance from the plane to the origin, and Σ is the sum of the squares of the deviations of the atoms from the least-square plane. The coordinate system is described by x along a, y along b, and z along the c axis.

Table III contains the equations of various planes in the molecule as well as the dihedral angles between these planes. The plane containing C(5), C(6), C(7), and C(8) is the most nearly planar four-membered carbon chain in the molecule; C(6) and C(7) are the atoms farthest from this plane, the distance being plus and minus 0.004 Å.

The closest contact to the iodide ion is to HC3(2) at a distance of 3.11 Å.

This structural analysis, resulting in a definitive answer to the question of conformation, is also important in that it gives much-needed data regarding quaternary salts of the pyrrolidine series. The preceding paper in this series[5] utilizes this information to discuss the stereochemistry of quaternization.

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Registry No. 4, 43208-79-3.

Supplementary Material Available. Table IV, positional and thermal parameters along with their standard deviations, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-321.

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(5) For details regarding the preparation and steric course of quaternization of Ic, and the nmr analyses of the N-alkyl groups, see ref 4d.

(6) Computer programs used were by F. R. Ahmed and coworkers (NRC-2, Data Reduction; NRC-8, Fourier for Distorted and Undistorted Nets; and NRC-12, Scan of Interatomic Distances and Angles, National Research Council, Ottawa, Ontario, Canada), Busing and Levy (ORFLS), and Carrol K. Johnson (ORTEP). These programs were locally modified for use with the XDS Sigma 7 computer. Other programs were written locally by G. D. Smith, E. L. Enwall, and C. N. Caughlan.

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(13) See paragraph at end of paper regarding supplementary material.