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Crystal and Molecular Structure of 8,8-Dimethyl-8-Azoniabicyclo [5.1.0] Octane Iodide

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The crystal and molecular structure of 8, 8-dimethyl-8-azoniabicyclo[5. 1. 0]octane iodide has been elucidated. The aziridine ring is bridged *cis* to the cycloheptane ring. The cycloheptane ring has been shown to have a distorted chair conformation. No close transannular hydrogen distances have been observed. The compound crystallizes in the space group $Pna2_1$ with unit cell dimensions a = 17.31, b = 8.58 and c = 7.56Å. The final value of $R = \Sigma || F_o | - | F_c || / \Sigma | F_o |$ is 0.145 for the 734 observed reflections.

INTRODUCTION

The study of *cis*-8,8-dimethyl-8-azoniabicyclo[5.1.0]-octane iodide ($C_9H_{18}NI$) was undertaken as part of a continuing study of polycyclic compounds with at least one small-ring system containing nitrogen. It is of interest to see how the fusion of these two-ring systems affects the conformations, structures, and molecular parameters which have been found (1) or postulated (2) for each of these ring systems separately. Of particular interest are the closest approach distances of transannular hydrogen atoms in the cycloheptane portion of the molecule. Close contacts have been previously reported (3, 4) in such distances when one deals with bicyclic ring systems in which the larger ring can legitimately be classified as a "medium-sized" ring. Whether such close contacts persist when one is dealing with a cycloheptane ring in such a bicyclic system has not been previously reported.

The sample was kindly furnished to us by Professor P. E. Fanta (5).

CRYSTAL DATA

The white sample was recrystallized from a solution of ethyl alcohol and ethyl acetate and grew in flat plates perpendicular to the [010] axis. The space group ($Pna2_1$) and cell dimensions (a = 17.31, b = 8.58, c = 7.56Å) were determined from precession photographs taken with filtered Mo-K_α radiation. The density of 1.58 gms per cm^3 calculated by assuming four formula weights per unit cell agrees with the observed density of 1.57 gms per cm^3 obtained by flotation methods.

Intensity data were collected from the zero and first four levels about the [010] axis, the zero and first three levels about the [100] axis, the h,h,l, zero level and the $2k,k,l$ zero level. Intensities were estimated visually using a scale made from timed exposures of a selected "typical" reflection. Lorentz and polarization corrections were made in the usual manner (6). Reflections common to more than one film were used to correlate the corrected intensities and a list of 734 independent reflections, all on the same relative scale, was finally obtained.

Extinction of all $0kl$ where $k+l$ was odd and $h0l$ where h was odd led to the space groups $Pna2_1$ and Pnam as possibilities. However, with four molecules per unit cell, the latter choice would imply a mirror plane in the molecule. To avoid any assumptions about the molecular symmetry, $Pna2_1$ was assumed initially.

The iodine position was determined from the Patterson projections. Using these coordinates and an initial isotropic temperature factor of 4.0Å^2, structure factor calculations gave a reliability index (R) of 0.31. Two cycles of least squares refinement were then carried out resulting in values of r^7, R = 0.92, 0.29. A three-dimensional difference Fourier map was calculated based on the observed data and the results of the last least squares cycle. A composite drawing of the region from x = 0 to x = 1/2, projected down the x-axis given in Figure I. Because of the special position of the iodine

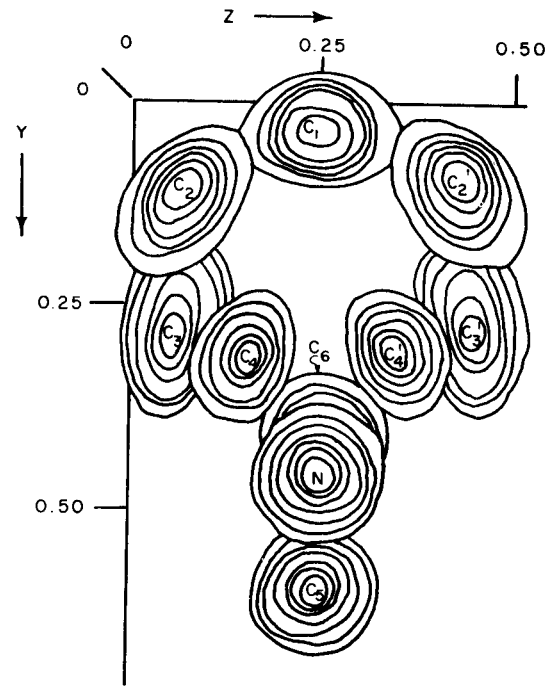

Figure I

Composite drawing of the original difference Fourier map from x = 0 to x = 1/2 (iodine omitted). Contours drawn in arbitrary units.

atom, mirror planes were generated at z = 1/4 and z = 3/4 whether the structure in fact, had these mirror planes or not. It is interesting to note that one cannot disregard these mirror related peaks, because only if one includes them can one obtain sufficient peaks to coincide with the number of atoms - other than hydrogen - which are in the unit cell. The peaks assumed to be

atomic peaks appeared with heights ranging from 3.0 to 4.6 e/Å^3. All other peaks on the maps, except for a residual peak about the iodine position, had heights less than 1.3 e/Å^3.

Although the nitrogen peak could be assigned with some certainty on the basis of chemical evidence, all peak positions other than iodine, were assigned carbon scattering factor curves and in addition, only those atoms either on the mirror plane or only on one side of the mirror plane were included in the initial refinements. In this way an attempt was made to identify the nitrogen atom and also to prove (or disprove) the actual existence of a mirror plane in the molecule on the basis of the observed crystallographic data.

Three additional cycles of least squares lowered the r, R values to 0.28, 0.22. The peak, previously suspected on chemical grounds of being the nitrogen atom peak had a rapidly declining temperature factor which had already dropped to 3.2Å^2, whereas the other peaks had relatively stable temperature factors in the range 3.8-4.3Å^2 thus justifying the choice, on crystallographic grounds, for the nitrogen peak. The results of this cycle were used in calculating a new three-dimensional difference Fourier map in which the three previously mirror-plane related peaks again appeared although their positions had shifted somewhat; that of carbon C_2' with a shift of 0.25Å being shifted the most. These maps also indicated a pronounced anisotropy in the iodine atom and were suggestive of anisotropic motions in the other atoms.

Seven cycles of least squares refinements were carried out, assuming an anisotropic temperature factor for the iodine atom only, assigning a nitrogen scattering factor to the peak identified as the nitrogen atom and including all of the atom positions in the structure. The resulting r, R values of 0.18, 0.16 confirmed the correctness of the structure. At this stage, anisotropic temperature factors were assigned to all atoms and six additional cycles of least squares resulted in final r, R values of 0.117, 0.145 for the observed reflections and maximum shifts of less than 0.006Å in coordinate positions. The final positions in the unit cell, the last isotropic temperature factors obtained and the final anisotropic temperature factors are given in Table I. Figure II shows the bond distances and bond angles within the molecule.

DISCUSSION

The standard deviations, as estimated from the standard deviations in positional parameters by the usual formulae (8) for the propagation of errors, were about 0.03Å for all bond lengths and 2.5° for all bond angles. The average bond length for carbon-carbon bonds in the cycloheptane portion of the molecule was 1.52Å with all but one bond length lying within one standard deviation of the average bond length. In the aziridine portion of the molecule, the carbon-carbon bond is discreetly smaller than the carbon-nitrogen average distance and although the difference is not statistically significant, in the light of the previous study on aziridine itself (1), the result is reasonable. Of more significance is the general increase observed in all of the bond lengths in the aziridine ring in this and other studies (3,4) in systems resulting from the fusion of an aziridine ring to a second ring system.

The molecule itself does not have a mirror plane.

Table I

Coordinates and Temperature Factors

	x	y	z	B*	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
Iodine	.13433	.17207	.25227	anisot.	.0037	.0213	.0208	-.0052	.0042	0
Nitrogen	.35910	.49067	.25356	3.29	.0036	.0135	.0120	-.0098	0	0
Carbon - C_1	.42638	.03763	.24881	4.93	.0045	.0176	.0262	.0078	0	0
Carbon - C_2	.39489	.09544	.06796	5.99	.0071	.0128	.0205	.0020	0	0
Carbon - C_3	.39903	.27299	.04682	4.55	.0042	.0182	.0149	-.0007	-.0105	.0007
Carbon - C_4	.33576	.34215	.15424	5.78	.0032	.0200	.0374	.0098	.0120	.0101
Carbon - C'_2	.40018	.09718	.42563	6.16	.0070	.0139	.0299	.0002	.0123	-.0065
Carbon - C'_3	.39830	.27680	.46052	6.11	.0058	.0213	.0178	-.0102	0	.0020
Carbon - C'_4	.33375	.34178	.35203	6.26	.0052	.0248	.0408	.0017	0	-.0118
Carbon - C_5	.29324	.61368	.27175	4.40	.0055	.0170	.0229	-.0128	0	-.0028
Carbon - C_6	.44194	.43270	.23325	6.15	.0062	.0492	.0269	-.0061	-.0187	-.0058

*Taken from last isotropic cycle.

B (isotropic) and B_{ij} (anisotropic) are both given in Å^2.

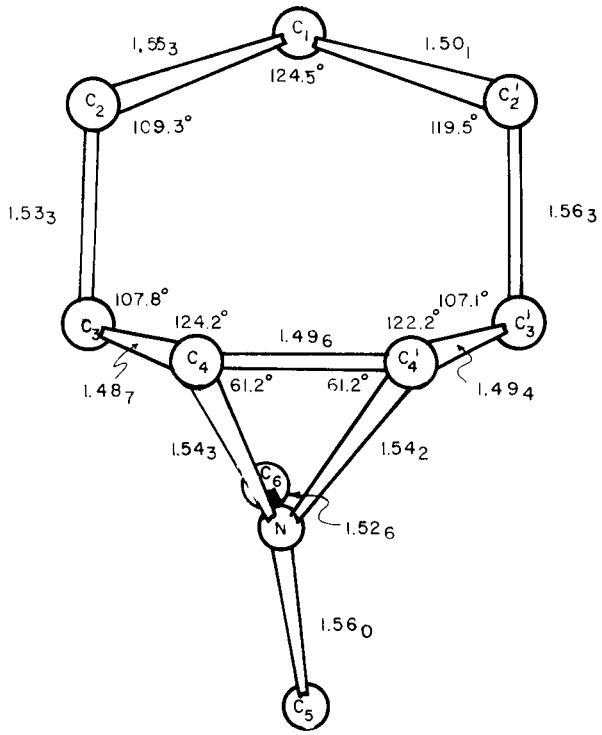

Figure II

Perspective drawing of molecule (iodine omitted). Bond distances and bond angles within the molecule indicated.

The major distortion from C_s-m symmetry being greatest (about 0.25Å) in the positions of atoms C_2 and C_2'. In all probability, the refinement could have been carried out in the space group Pnam by first assuming the mirror plane and then assuming disorder in the crystal in order to adjust the positions of these atoms. However, the choice of $Pna2_1$ obviates the necessity of making these assumptions. These distortions from C_s-m symmetry are most likely due to the packing of the molecules within the unit cell (Figure III) in which distances as close as 3.96Å are observed between carbon atoms of different molecules.

The cycloheptane ring has a distorted chair conformation and is fused *cis* to the aziridine ring. The angles at the fusion points average to 123.2 ± 1° in agreement with the values for the fusion angles observed when an aziridine ring is fused *cis* to a cyclooctane (3) ring (122.7°), but both values are somewhat smaller than the value observed (4) for the *trans* fusion of an aziridine ring to a cyclododecane ring (126.6°).

Since the compound included iodine, the locations of the hydrogens were chosen by assuming C-H distances of 1.10Å, HCH angles of 109° and HCC angles as close to 109° as possible. The positions chosen (Table II)

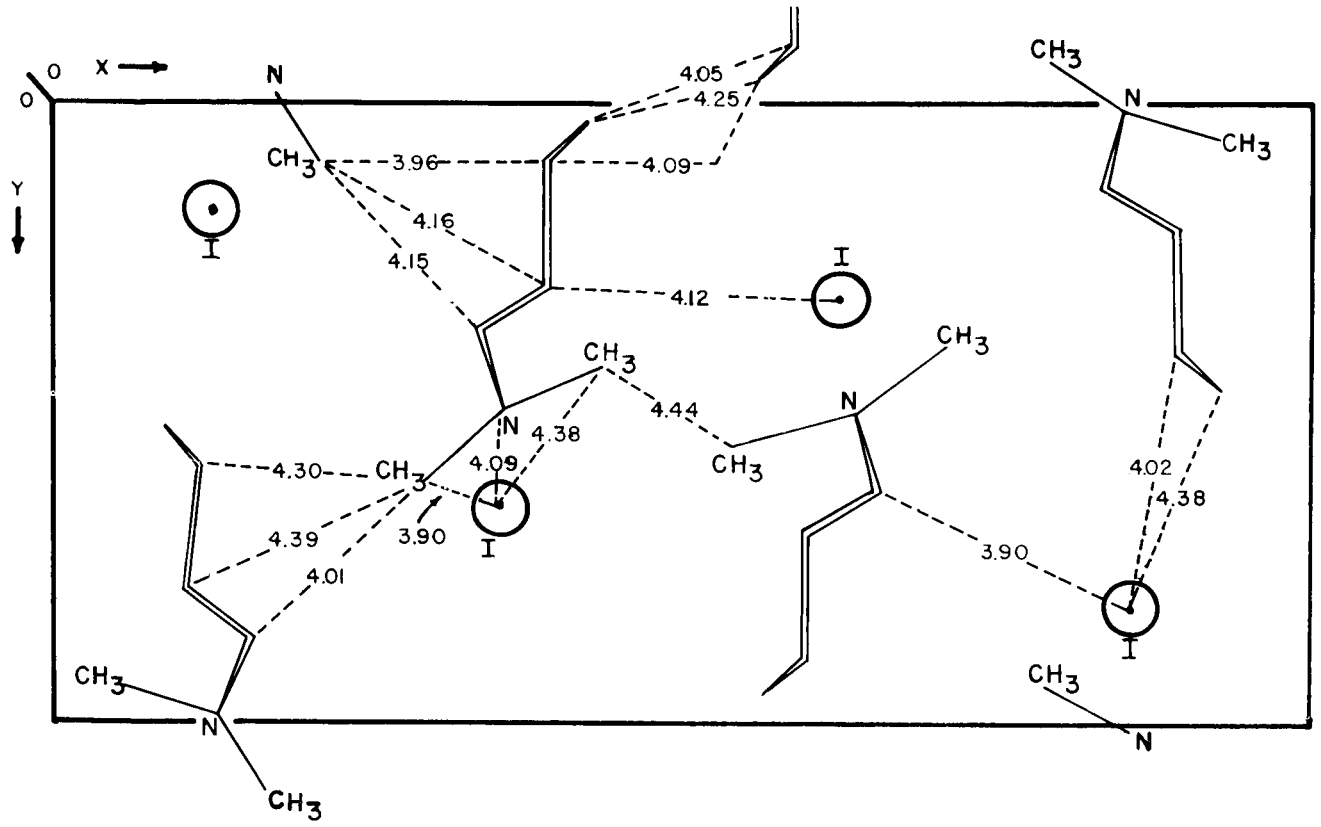

Figure III

Contents of unit cell projected down the z-axis. Closest intermolecular contacts and iodine distances indicated.

Table II

Hydrogen Atom Coordinates

		x	y	z
Atom C_1	H_1	0.489	0.057	0.245
	H_2	0.414	0.912	0.254
Atom C_2	H_1	0.334	0.060	0.057
	H_2	0.429	0.043	0.961
Atom C'_2	H_1	0.341	0.053	0.449
	H_2	0.438	0.043	0.527
Atom C_3	H_1	0.455	0.313	0.095
	H_2	0.393	0.300	0.906
Atom C'_3	H_1	0.453	0.328	0.415
	H_2	0.392	0.302	0.601
Atom C_4	H_1	0.279	0.315	0.098
Atom C'_4	H_1	0.277	0.308	0.400

were then compared to the final difference Fourier map and all fell in positive regions ranging in height from 0.4-0.9 e/Å^3. No other regions with heights greater than 0.4 e/Å^3 were found in the vicinities of the atom positions. Figure IV shows the molecule, excluding iodine, and lists the closest contacts between hydrogen atoms. As can be seen from Figure IV, no close transannular distances comparable to the 1.98-2.05Å values found in previous studies for medium-sized rings (3,4, 9, 10) were obtained.

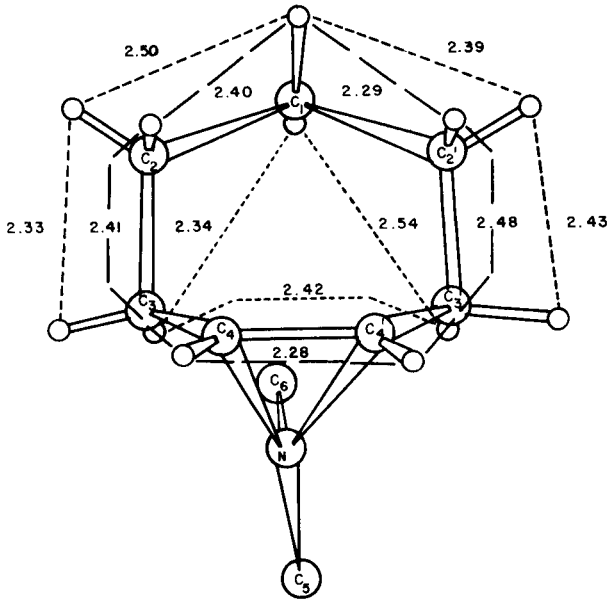

Figure IV

Perspective drawing of molecule including hydrogen atoms. Closest transannular hydrogen distances indicated. (Iodine omitted.)

Thus, although this compound forms a stable methiodide (in agreement with the properties found (5) for such bicyclic systems containing a medium-sized ring and contrary to those found in the fusion of an aziridine ring to a cyclohexane ring), the close transannular hydrogen distances characteristic of medium-sized rings are absent. Conformations previously postulated for cycloheptane, (2, 11) were based upon energetic considerations and tacitly assumed some degree of transannular contacts to exist. The resulting conformations consequently differ from the results obtained in this study. Whether this difference is due primarily to the *cis* fusion of the aziridine ring in this case or whether, in fact, the cycloheptane molecule itself has a conformation similar to that obtained in this study can be settled only by a structure determination of cycloheptane itself.

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REFERENCES

(1) T. E. Turner, V. C. Fiora and W. M. Kendrick, *J. Chem. Phys.*, 23, 1966 (1955).
(2) James B. Hendrickson, *J. Am. Chem. Soc.*, 83, 4537 (1961).
(3) L. M. Trefonas and Richard Majeste, *Tetrahedron*, 19, 929 (1963).
(4) L. M. Trefonas and John Couvillion, *J. Am. Chem. Soc.*, 85, 3184 (1963).
(5) P. E. Fanta, H. J. Hsu and R. Golden, *J. Chem. Eng. Data*, in press (1964).
(6) J. Waser, *Rev. Sci. Instr.*, 22, 567 (1951).
(7) R. E. Dickerson, P. J. Wheatley, P. A. Howell and W. N. Lipscomb, *J. Chem. Phys.*, 27, 200 (1957). The least squares routine employs the diagonal approximation with an appropriate damping factor. Weighting factors used were $w = (4F_{min}/F^o)^4$ for $F^o \geq 4F_{min}$ and $w = 1$ for $F^o < 4F_{min}$.

The weighted residual factor (r) is then defined as follows:
$r = \Sigma w (k^2F_o^2 - F_o^2)^2 / \Sigma w^4 (kF_o)^4$

The value of this function is invariably large during the initial refinements (particularly if the heavy atom technique is used where all of the atoms are not included in the initial refinements). It then drops very rapidly ending at values appreciably below that of R, the usual residual factor, provided that the structure determination is correct. A comparison of the relative behavior of r and R during the process of refinement is given in the following paper: Louis Trefonas and W. N. Lipscomb, *J. Chem. Phys.*, 28, 54 (1958).
(8) E. W. Hughes and W. N. Lipscomb, *J. Am. Chem. Soc.*, 68, 1970 (1946).
(9) R. F. Bryan and J. D. Dunitz, *Helv. Chim. Acta.*, 43, 3, (1960).
(10) J. D. Dunitz and H. M. Shearer, *ibid.*, 43, 18 (1960).
(11) Norman L. Allinger, *J. Am. Chem. Soc.*, 81, 5727 (1959).

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