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The Crystal Molecular Structure of *cis*-13,13-Dimethyl-13-azoniabicyclo[10.1.0]tridecane Iodide

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The crystal and molecular structure of *cis*-13,13-dimethyl-13-azoniabicyclo[10.1.0]tridecane iodide has been determined by a three-dimensional, single-crystal, x-ray diffraction study. The compound crystallizes in the orthorhombic space group *Pnam* with cell dimensions $a_0 = 21.36 \pm .01$, $b_0 = 9.07$, $c_0 = 8.29$ Å. The aziridine ring is fused to the cyclododecane ring with fusion angles of 123.5° . The molecule is bisected by a mirror plane with the cyclododecane portion distorted from its anticipated square conformation. Transannular hydrogen interactions are estimated on the basis of geometric considerations. A final value of $R = 0.112$ was obtained for the 557 non-equivalent reflections which were observed.

INTRODUCTION

The study of *cis*-13,13-dimethyl-13-azoniabicyclo[10.1.0]tridecane iodide (Figure I) was undertaken as part of a more general study of aziridinium-bicyclic compounds.

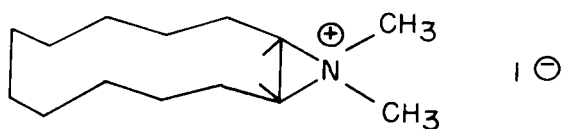


Figure I

In all of the previously studied bicyclic systems in which an aziridine ring is fused *cis* and in which the alicyclic ring contains at least six carbon atoms (2-4), the fusion angles have turned out to be $123 \pm 1^\circ$ whereas in the only *trans*-fused compound studied (5) the fusion angle was 127° . The only conclusive way, however, of showing whether this variation in fusion angle is really a function of the type of fusion is to obtain analogous derivatives of the same compound, one *cis*-fused and the other *trans*-fused, and to then do complete structure determinations of both compounds. This has now been accomplished for the case of an aziridine ring fused to a cyclododecane ring.

It can further be expected that the fusion of these two rings will cause conformational changes in the larger ring to accommodate these fusion angles. In the case of the *trans*-fused compound, the conformation of the cyclododecane ring is altered substantially near the fusion points from that found for cyclododecane itself (6) although the conformation of the remainder of the ring is unchanged. If

one attempts to construct models of both the *cis* and *trans*-fused systems, it is relatively simple (at least after the fact) to predict the conformation obtained for the *trans*-fused system. On the other hand, objections can easily be raised towards any of the models constructed for the *cis*-fused compounds.

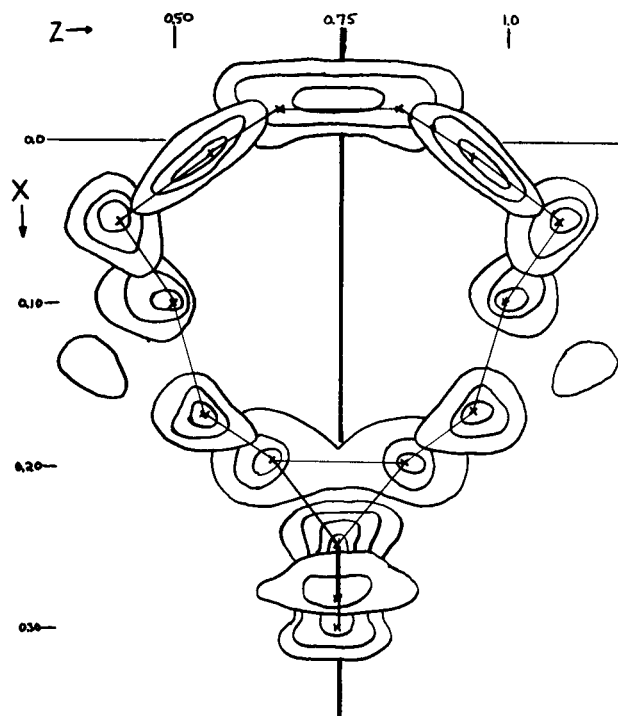


Figure II. Original Difference Fourier based on iodine parameters only. Contours in arbitrary units.

TABLE I

Coordinates and Temperature Factors (Pnam)

Atom	X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Iodine	0.3230	0.1604	0.2500	0.0029	0.0066	0.0182	0.0003	0	0
Nitrogen	0.2516	0.1430	0.7500	0.0035	0.0104	0.0566	0.0020	0	0
Methyl-A	0.2816	0.2980	0.7500	0.0024	0.0035	0.0139	-0.0029	0	0
Methyl-B	0.3010	0.0183	0.7500	0.0024	0.0303	0.0538	0.0069	0	0
Carbon-A	0.1946	0.0912	0.6580	0.0012	0.0187	0.0254	-0.0026	0.0034	0.0056
Carbon-B	0.1650	0.2145	0.5552	0.0046	0.0192	0.0438	0.0031	-0.0011	0.0093
Carbon-C	0.0975	0.1527	0.5283	0.0102	0.0245	0.0478	0.0051	-0.0058	-0.0063
Carbon-D	0.0550	0.2627	0.4400	0.0043	0.0891	0.0510	-0.0114	0.0002	-0.0315
Carbon-E	0.0101	0.3275	0.5650	0.0133	0.0431	0.1505	0.0049	0.0040	0.0690
Carbon-F	0.9750	0.2050	0.6580	0.0030	0.0747	0.1300	-0.0052	0.0035	-0.0418

Transannular close-contacts among the hydrogen atoms have been observed in alicyclic ring systems containing eight or more carbon atoms and also in the analogous bicyclic systems (4-7). Whether this compound would also have such close-contacts would be of major interest.

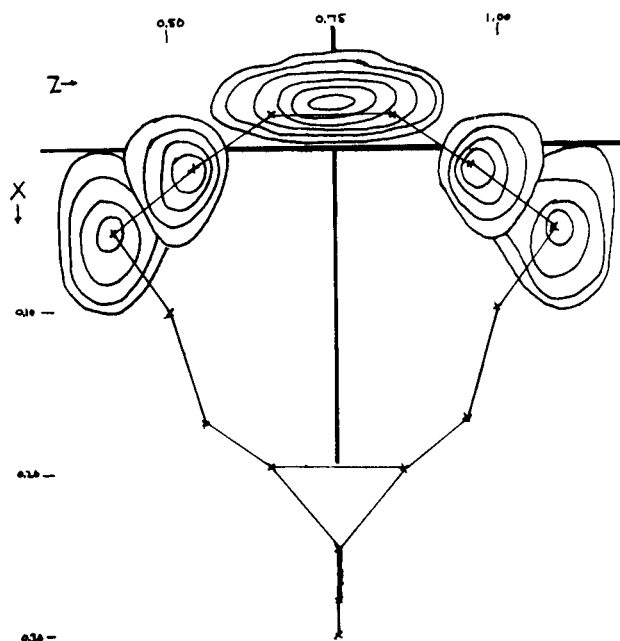


Figure III. Difference Fourier based on all atoms except D,E,F, in space group Pnam. Contours drawn at one electron per cubic angstrom beginning with one.

Lastly, medium-sized rings have been shown generally to be disordered in the crystalline state. Such orientational disorder is relatively rare in most crystalline compounds.

Samples of this compound were kindly furnished to us by Professor P. E. Fanta (8).

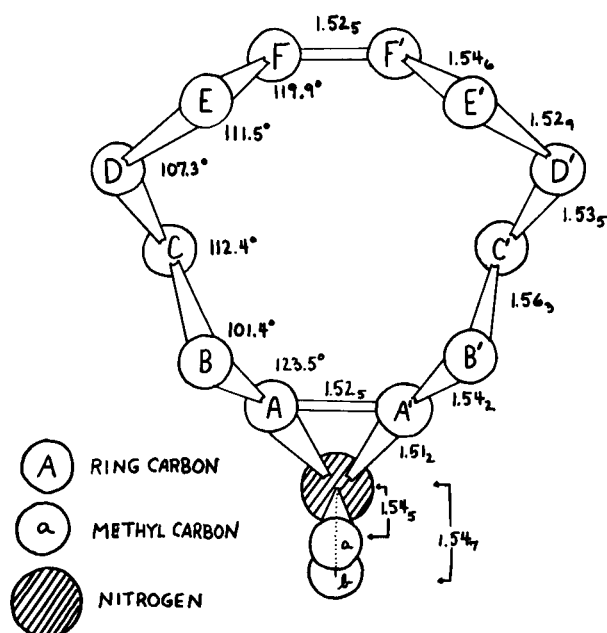


Figure IV. Conformation and molecular parameters for ring system.

TABLE II

Bond Distances and Bond Angles (by Types)

Atoms Involved	Bond Distances (Å)	Atoms Involved	Angles	Atoms Involved	Non-bonded Distances Å
N-C (Methyl)	1.54 ₆	CNC (Dimethyl)	112.5°	C _D ···C _D	3.15
N-C (Aziridine)	1.51 ₂	NCC (Aziridine)	59.7°	C _E ···C _E	3.34
C-C (Aziridine)	1.52 ₅	CNC (Aziridine)	123.5°	C _B ···Methyl (B)	3.81
C-C (Cyclododecane)	1.54 ₀	CCC (Fusion)	123.5°	C _C ···C _F	3.91
		CCC (Back end of ring)	119.9°	I···C _A	4.00
		CCC (Cyclododecane)	108.2°	I···Methyl (A)	3.98
		(Excluding above angles)		I···Methyl (B)	4.19
				I···C _B	4.36
				I···N	4.96

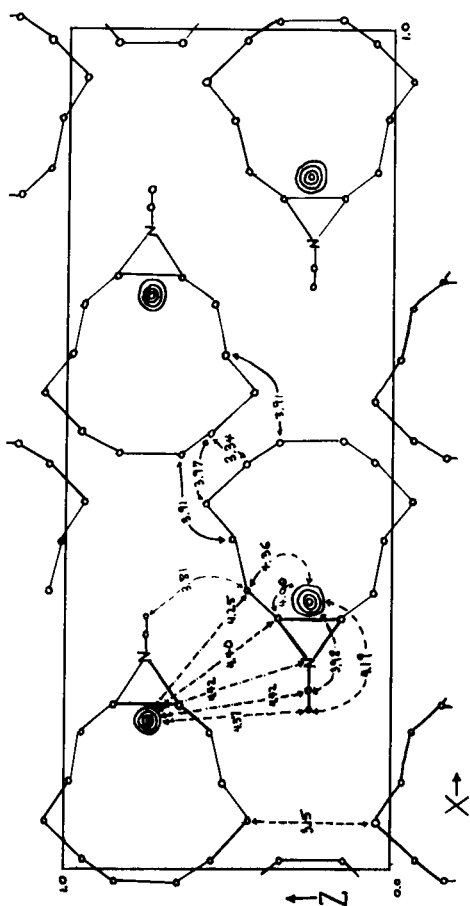


Figure V. Contents of unit cell (in space group Pnam). All non-iodine contact distances under 4.0 Å indicated. Closest iodine contact distances indicated.

CRYSTAL DATA

The compound was recrystallized from a solution of ethyl alcohol and ethyl acetate and formed transparent plate-like crystals.

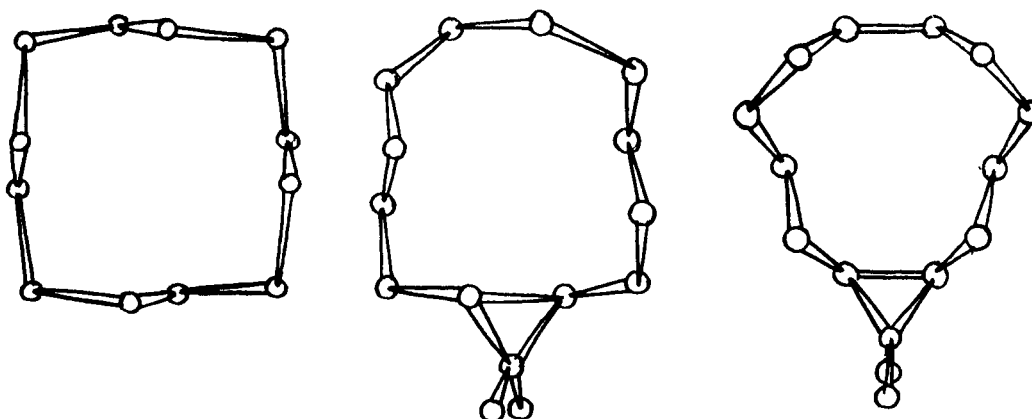
Intensity data of the zero and first five levels about the [001] axis, the zero and first four levels about the [100] axis and the $h, k, 2h$ zero level were collected using a precession camera and filtered Mo-K α radiation. Extinctions for $k + l$ odd in the $Ok\bar{l}$ zone and h odd in the $hk0$ zone indicated either space group Pna2₁ or Pnam.

The cell dimensions of this crystal were $a = 21.36$, $b = 9.07$ and $c = 8.29 \pm .01$ Å. The assumption of four molecules per unit cell led to a calculated density of 1.395 gms. per c.c. which was in agreement with the measured density (by flotation techniques) of $1.40 \pm .01$ gms. per c.c. The space group Pna2₁ was chosen originally for the refinements. However, the structure was later refined in both space groups, Pna2₁ and Pnam.

The intensities were estimated visually using timed exposures of a selected typical reflection from this crystal. Lorentz and polarization corrections were made in the usual way (9) and then reflections common to more than one zone were utilized in putting all intensities on the same relative scale. A total of 557 non-equivalent reflections were observed.

STRUCTURE DETERMINATION

The iodine position was determined from Patterson projections and refined on the basis of the complete three dimensional data. Initial refinements in the acentric space



J. D. Dunitz and H. M. Shearer
Helv. Chim. Acta 43 18 (1960)

L. M. Trefonas and J. Couvillion
J. Am. Chem. Soc. 85 3184 (1963)

L. M. Trefonas, R. Towns and
R. Majeste (This Study)

Figure VI. Comparison of known ring structures containing the cyclododecane moiety.

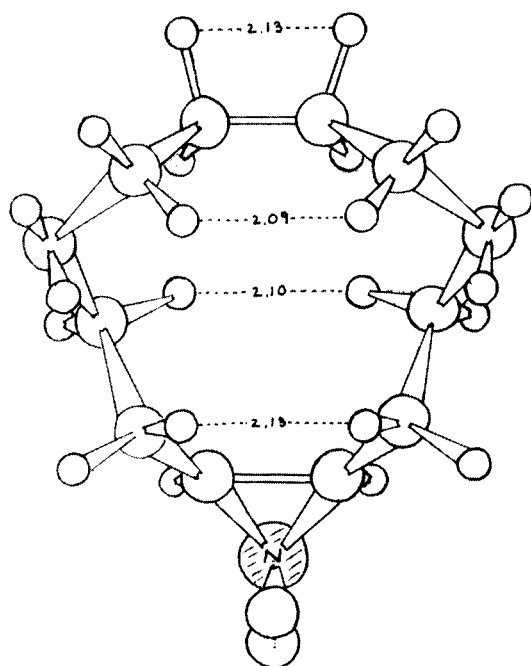


Figure VII. Suggested locations (and resulting transannular interactions) for hydrogens in the molecule based on geometric considerations.

group ($Pna2_1$) led to r_1 , R values of .45, .27 (10). An initial difference Fourier map (Figure II) utilizing the phases obtained from the iodine coordinates and the magnitudes from the observed structure factors was

calculated. The structure was evident in sufficient detail so that by alternating cycles of least squares and additional difference Fourier maps, the entire structure was eventually determined.

As an intermediate check during the least squares refinement, a difference Fourier (Figure III) was calculated after all atoms but D, E, F (and their related atoms D', E', F') had been placed. At this point, it seemed reasonable to continue the refinements in the higher space-group ($Pnam$) since the fragment previously placed and the only new peaks observed (Figure III) all were, in fact, related by a mirror plane.

Refinements in $Pnam$, assuming an ordered molecule bisected by a mirror plane, led to final r_2 , R values = 0.13₀, 0.11₆ for all reflections. If one excludes those minimal structure factors for which only an upper limit to the intensity can be estimated (47 structure-factors) the final value of the reliability index is $R = 0.11_1$. However, the conformation of the molecule thus obtained (Figure IV) does not easily fit within the general structural framework of other medium-sized ring systems determined either in this laboratory (2-5) or by other investigators (6,7,11). Consequently, two alternative approaches towards checking the refinement of the structure were attempted.

If one assumes that the higher space group ($Pnam$) is correct, but that the crystal is disordered, then the positions obtained above represent an average position for each of the pairs of atoms. This concept would then fit the trend observed in previous structural studies on medium-sized rings--namely, the existence of orientational disorder. Unfortunately, attempts to refine in $Pnam$, assuming a disordered structure, led at first to unrealistic distances and

angles and, upon further refinement, to parameters which began oscillating wildly. Thus this approach was abandoned.

In refining the structure in the lower space group ($Pna2_1$), the final coordinates from the refinement in space group $Pnam$ were used as initial coordinates in these refinements. Five cycles of refinement led to only negligible shifts in the final coordinates obtained above and the structure retained its mirror plane well within the estimated standard deviations. The r_2 , R values remained as before. At this point, refinement was terminated and the centric structure accepted as correct.

DISCUSSION

Standard deviations for the various atoms (based on the last cycle of least squares in space-group $Pnam$) were estimated as 0.01 Å for the iodine atom and less than 0.03 Å for each of the lighter elements. E. S. D. for the bond angles were 3.0° or less. Table I lists the final coordinates and anisotropic temperature factors in space group $Pnam$. Table II lists the final bond distances, bond angles and average values for different groups of atoms.

If one considers the aziridine ring first, both its C-N distance (1.51₂ Å) and its C-C distance (1.52₅ Å) are in conformity with the trends observed in these bicyclic systems. Namely, there is a lengthening of both bond types from the values found in the free aziridine molecule (C-C = 1.48₀ Å and C-N = 1.48₈ Å) (12) as one increases the size of the second ring from cyclohexane through cyclododecane. The N-CH₃ distances (1.54₆ Å) and the H₃C-N-CH₃ angle (112.5°) are in good agreement with the same distances in analogous compounds (3-5).

In aziridine itself, (12) the dihedral angle between the HCH plane and the C-C bond is 159.4°. In order that one may fuse a second ring to an aziridine ring at the C-C positions, this dihedral angle must be drastically reduced and the bond angle in the second ring increased. If the second ring is sufficiently large so that this fusion angle can be opened up, the best apparent compromise occurs at 123° for a *cis*-fused compound and 127° for a *trans*-fused compound. This is the situation found in those cases where the second ring contains six or more atoms (2-5) and verified in this study. If, on the other hand, the second ring is sufficiently small (five atoms or less) the fusion angle is opened up only to 112° as evidenced in the bicyclic aziridinium system containing an oxacyclopentane ring (13).

The cyclododecane portion of the molecule has average C-C bond distances of 1.54 Å. The bond angles vary from 101.4° to the large compensating angles at the back of the ring (angles EFF' and FF'E) of 120°. The large deviations in the bond angles undoubtedly results from the relatively

close intermolecular contact distances between the molecules in the solid. In Figure V, which shows the packing in the crystal, all closest contact distances under 4.0 Å are indicated with the closest distance being 3.15 Å. The cations pack in layers separated by the iodide ion with the closest iodide-cation contact distances occurring between the iodide ion and the cyclododecane portion of the cation. This packing is common to those bicyclic aziridinium systems where the second ring contains eight or more atoms (2,5).

The conformation of the cyclododecane moiety differs greatly from that obtained in other studies (Figure VI). In the structural determination of cyclododecane itself (5) the most reasonable structure was built up of four nearly planar units of four atoms each arrayed in an approximately square conformation, the resulting unit having approximate $D_4(422)$ symmetry. In forming the *trans*-fused aziridinium bicyclic compound (5), the cyclododecane unit retains its approximately square conformation since no really large distortion is necessary to accommodate the *trans*-fusion. However, the large dihedral angles in aziridine do cause sufficient distortion so that the symmetry of the cyclododecane moiety is reduced to $D_2(222)$.

However, when one attempts to make a *cis*-fusion of these two ring systems, it can be easily shown with models that the conformation of the cyclododecane moiety will be altered greatly. It is not obvious from the models exactly what the final conformation of this distorted cyclododecane moiety will be. The resulting structure determined by this study indicates that the primary accommodation occurs at the back end of the ring with the angles there (EFF' and FF'E) opening up to 120°. One can thus visualize the structure as consisting of two parallel but distorted *n*-hexyl chains joined by a common bond at the A,A' positions and the F,F' positions. The remaining deviations of bond angles with the cyclododecane moiety are a compromise between an attempt of the ring to retain angles near the expected 112° and at the same time to maintain reasonable intramolecular contact distances (distances as close as 3.15 and 3.34 Å are observed).

Because of the lack of resolution in the Fourier maps, the presence of the iodide ion and the large distortions observed in the ring system, no serious attempt has been made to place the hydrogen atoms by difference Fourier techniques. A suggested arrangement based on geometric considerations is indicated in Figure VII.

Acknowledgments.

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- (10) The initial least-squares were carried out on a Remington-Rand 1103A Computer at S. M. U. in Dallas, Texas. The program employed the diagonal approximation with an appropriate damping factor. R is the usual reliability index and

$$r_1 = \frac{\sum w | |F_o|^2 - |F_e|^2 |^2}{w |F_o|^4} \text{ where } w = \begin{cases} \left(\frac{4F_{\min}}{F_o} \right)^4 & \text{for } F_o > 4|F_{\min}| \\ 1 & \text{for } |F_o| < 4|F_{\min}| \end{cases}$$

For various non-chemical reasons, midway through the structure determination this crystallographic group began utilizing the I. B. M. 32K 7040 at L. S. U. in Baton Rouge, La. A modified version of ORFLS by Busing, Martin and Levy, using the full matrix was employed. R is again defined as the usual reliability index and

$$r_2 = \left[\frac{w(F_o - kF_o)^2}{wF_o^2} \right]^{1/2} \text{ with } w = 1$$

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