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CRYSTAL AND MOLECULAR STRUCTURE OF 9,9-DIMETHYL-9-AZONIA-BICYCLO [6.1.0] NONANE IODIDE

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Abstract—The molecular and crystal structure of 9,9-Dimethyl-9-azoniabicyclo [6.1.0] nonane iodide has been elucidated. The aziridine ring is bridged *cis* to the cyclo-octane ring. The cyclo-octane ring has been shown to have a skewed conformation. Transannular hydrogen distances as short as 1·98 A have been postulated. The crystal is disordered with two formula weights in a unit cell of dimensions a = 7·58, b = 9·02, c = 8·98 A, and the space group is $Pmn2_1$. The final value of $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$ is 0·13 for the 554 observed reflections.

INTRODUCTION

THE study of 9,9-dimethyl-9-azoniabicyclo [6.1.0] nonane iodide was undertaken as part of a more general study of polycyclic compounds with at least one small-ring system containing nitrogen. Of particular interest is what effect the presence of a bridged aziridine ring will have on the conformation and molecular parameters of the cyclo-octane ring. The compound also affords an opportunity to compare the closest approach distances of *trans*-annular hydrogen atoms in a bicyclic system to those found for the cyclononane[1] and cyclododecane[2] rings. The final molecular parameters should aid in deciding whether the cyclo-octane ring in the compound has any significant negative Baeyer strain or any Pitzer strain.

The sample was kindly furnished by P. E. Fanta and is a previously unreported compound. Details of the chemistry of the compound will appear in a forthcoming publication by P. E. Fanta and H. J. Su.

Crystal data

The sample was crystallized from ethanol and grew in flat plates perpendicular to the [010] axis. The space group ($Pmn2_1$) and cell dimensions (a = 7·58, b = 9·02, c = 8·98 A) were determined from precession photographs taken with filtered Mo–K_α radiation. The observed density was 1·53 gm per cm^3 compared to a density of 1·52 gm per cm^3 calculated for a unit cell containing two formula weights. Abnormal streaking of the spots and the rapid decline of their intensities with increasing angle of scattering for pictures taken about the [100] axis suggested some orientational disorder in the crystal. This was subsequently confirmed in the course of the structure determination.

Structure determination

Intensity data were collected of the zero and first three upper levels about the [010] axis, the zero and first two levels about the [100] axis, and the (h,h,l) and (2k,k,l) zero levels. Intensities were estimated visually using two scales of timed

[1] R. F. Bryan and J. D. Dunitz, *Helv. Chim. Acta* **43**, 3 (1960).
[2] J. D. Dunitz and H. M. Shearer, *Helv. Chim. Acta* **43**, 18 (1960).

exposures of selected typical "reflections" from the (h0l) and (0kl) films. This was done to allow a better comparison of the shapes and sizes of the spots appearing in films taken both perpendicular and parallel to the plates. Reflections common to both sets of films were then utilized in putting all intensities on the same relative scale. A total of 554 independent reflections were observed. Lorentz and polarization corrections were made in the usual manner.[3]

Extinction of all h0l where h + l were odd led to the space groups $Pmn2_1$ and Pmnm as possibilities. However the density measurements indicated only two

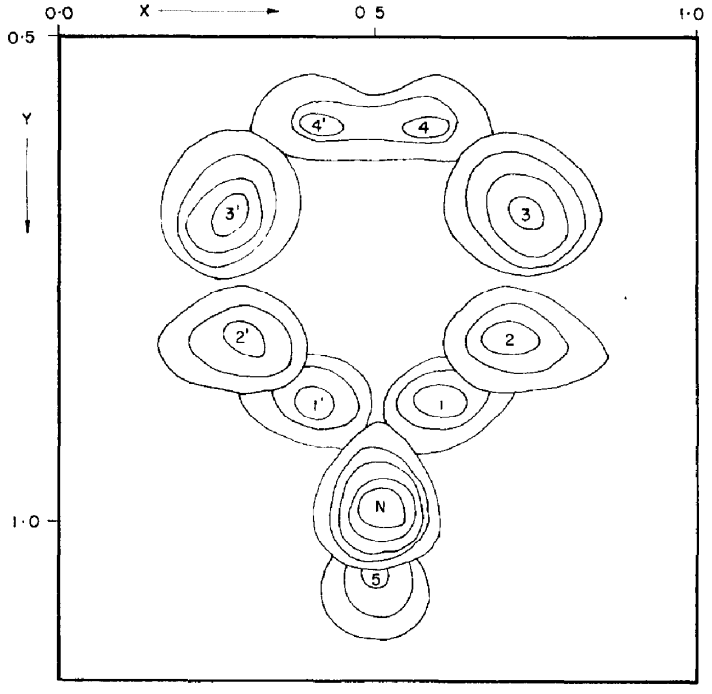

FIG. 1. Composite drawing of difference Fourier map from $z = 0$ to $z = \frac{1}{4}$ (iodine omitted). Contours at 1·0 e/A³ with first contour at 1·0 e/A³.

molecules per unit cell and so space group Pmnm would be satisfied only if the molecule as a whole contained two perpendicular mirror planes. Since this is not possible only $Pmn2_1$ was considered. Based upon the density measurements and the space group $Pmn2_1$, the iodine and the nitrogen atoms were required to lie on the crystallographic mirror planes at $x = 0, \frac{1}{2}$ and the molecule itself would have a mirror plane for any ordered structure assumed.

The iodine position was determined from the three Patterson projections. Structure factors using iodine only and assuming an isotropic temperature factor, $B = 4{\cdot}5$ A², led to $r^4 = 0{\cdot}44$ and $R = 0{\cdot}26$. A three dimensional difference Fourier map was then calculated on the Remington Rand 1103 digital computer using the phases obtained from the iodine position. Figure 1 is a composite drawing of the

[3] J. Waser, *Rev. Sci. Instr.* **22**, 567 (1951).
[4] R. E. Dickerson, P. J. Wheatley, P. A. Howell and W. N. Lipscomb, *J. Chem. Phys.* **27**, 200 (1957).

region from $z = 0$ to $z = \frac{1}{4}$, projected down the z-axis. Because of the special position of the iodine atom, mirror planes were generated at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, which led to all the peaks which appear in Fig. 1 being reflected across these additional mirror planes. The light atom peaks showed up with heights ranging from 3·1–4·3 e/A^3 with the exception of one peak whose height was 5·2 e/A^3 and whose position corresponded to that anticipated on chemical grounds for the nitrogen atom. Except for a residual positive peak at the iodine position indicating a decrease in the value of the temperature factor for iodine, no other peak of height greater than 1·4 e/A^3 appeared on the map. N and C_3 were situated on the mirror planes at $z = \frac{1}{4}, \frac{3}{4}$ and elongated in the z-direction and all other light atom peaks (excluding the methyl carbon atoms) were within 0·35 A of these mirror planes.

If the crystal was ordered then only two reasonable possibilities (or their respective enantiomorphs) would exist. One of these would be with the eight membered ring in the boat form and the other with the eight membered ring in the chair form. Since C_3 and C_3' are located on the false mirror planes at $z = \frac{1}{4}, \frac{3}{4}$, the two models would differ by the choice of C_4 and C_4' being at z, z′ (boat form) or at $\frac{1}{2}$–z, $\frac{1}{2}$–z′ (chair form).

Both of these models were tested by a least squares routine[4] employing the diagonal approximation with an appropriate damping factor. The weighting factors used were $w = (4F_{min}/F^\circ)^4$ for $F^\circ \geq 4F_{min}$ and $w = 1$ for $F^\circ < 4F_{min}$. The "chair form" essentially stopped refining at $r = 0{\cdot}09$, $R = 0{\cdot}165$ and led to some bond distances greater than 2·0 A and consequently was not considered further. The "boat form" (referred to as "Model A") will be discussed below in further detail.

Finally, the possibility of disorder in the crystal was considered. If one assumes the crystal is disordered, a multiplicity of choices arises. For example, starting at C_3 which is located at $z = \frac{1}{4}$, does one pick the C_2 peak with $z = 0{\cdot}30$ (above the mirror plane) or $z = 0{\cdot}20$ (below the mirror plane)? Once one has chosen atom C_2, the same question arises with respect to each of the other atoms around the eight-membered ring. The number of choices can be narrowed to only two possibilities (enantiomers of each other) if one eliminates all structures as improbable which do not contain reasonable bond distances and bond angles throughout the eight-membered ring. This second possibility (Model B) differs from Model A only in the staggering of atoms C_4 and C_4' such that C_4 has $z = 0{\cdot}31$ and C_4' has $z = 0{\cdot}19$.

Model A was chosen so that all of its atoms were located on the same side of the mirror plane at $z = \frac{1}{4}$ and since it is the ordered structure, the individual molecule retains the mirror plane required by the crystal symmetry. It was carried through six cycles of least squares refinement resulting in values of $r = 0{\cdot}08$, $R = 0{\cdot}15$. The bond angles and bond distances which were obtained are listed in Table 1. It is not too surprising that the only results which are suspicious are the C_4–C_4' distance and the angles 4′43 and 44′3. These results strengthened our earlier convictions from the films that the crystal was in fact disordered. The disorder is apparently due to an equal distribution of pairs of enantiomorphs about the statistical mirror planes at $z = \frac{1}{4}, \frac{3}{4}$ in analogy with previous studies done on medium-sized rings.[1,2]

The molecular structure chosen as Model B, does not by itself satisfy the requirement of the crystal symmetry of a mirror plane bisecting the molecule through the nitrogen and the methyl carbon atoms. However, if the molecules are assumed to be statistically distributed in enantiomorphic pairs about $z = \frac{1}{4}$ and $z = \frac{3}{4}$, then the enantiomorphic pair preserves the crystal symmetry.

The subsequent least squares refinements of Model B were carried out in two ways. In one set of refinements, all atoms except C_4 and C_4' were given the same initial coordinates as in Model A. Atoms C_4 and C_4' were included with z coordinates of 0·31 and 0·19 respectively, and with statistical weight equal to half that of the other carbon atoms. Anisotropic temperature factors were assumed for all atoms. After four cycles of refinement, the values r = 0·06 and R = 0·13 were attained with the largest coordinate shift being less than 0·008 A. The bond distances and bond angles resulting from this set of refinements is listed as Model B_1, in Table 1.

TABLE 1. BOND DISTANCES AND BOND ANGLES

	Model A	Model B_1	Model B_2
C_4–C_4'	1·19 A	1·55 A	1·63 A
C_3–C_4	1·58	1·58	1·46 (1·66)*
C_2–C_3	1·57	1·57	1·51
C_1–C_2	1·49	1·49	1.54
C_1–C_1'	1·54	1·54	1·48
N–C_1	1·52	1·52	1·56 (1·49)*
N–C_5	1·50	1·50	1·35
N–C_6	1·53	1·53	1·60
$\angle 4'43$	117·8°	113·0°	121·3° (106·4°)*
$\angle 432$	103·0	103·0	107·0°
$\angle 4'3'2'$	113·5	113·5	113·0
$\angle 321$	111·5	111·5	108·3
$\angle 211'$	122·7	122·7	122·7
$\angle 1N1$	61·0	61·0	59·0
$\angle 11_1N$	59·5	59·5	60·5
$\angle 5N6$	107·1	107·0	104·7

* Non-equivalence of distances and angles resulting in Model B_2.

In the other set of refinements, Model B_2, all of the observed light atoms from both enantiomorphs were included, with each atom, being given a statistical weight equal to half of its normal weight. In the case of N and C_3 which had been at $z = \frac{1}{4}$, initial z coordinates of 0·24 and 0·26 were chosen. It was felt that with the assumption of half-atoms for each atom it would not be necessary to carry out this set of refinements anisotropically. Values of r = 0·07 and R = 0·14 resulted.

One unexpected result of this last set of refinements was the shift of the two half-nitrogens 0·11 Å apart rather than towards each other. An even greater divergence was observed for the two-half-carbons (C_3) which ended up 0·35 A apart. This divergence was assumed not to be real and probably could be attributed to the very close overlap of each of these peaks with their mirror image atoms. Furthermore, these shifts would imply the non-equivalence of the following bond distances: N–C_1 vs. N–C_1' in the aziridine ring; C_2–C_3 vs. C_2'–C_3' and C_3–C_4 vs. C_3'–C_4' in the cyclo-octane ring; and the N–C_5 and N–C_6 for the dimethyl groups.

It is usual in the process of crystallization for the crystal to distinguish between a molecule and its mirror image and consequently to crystallize in one enantiomorphic form. However, if the enantiomorphic pair is able to occupy almost exactly the same available space without any crowding resulting, then the possibility of orientational

disorder is enhanced. In order to examine this condition, three dimensional packing models of both the disordered and the ordered forms were constructed, each encompassing a given molecule and all of its surrounding molecules. Both models were equally compatible with the space available and conformed closely to similar packing requirements. That disordering may instead be the usual case for medium-sized rings makes an interesting conjecture based upon this study and other studies on medium-sized rings previously published.[1,2]

DISCUSSION

Model A can be discounted on the basis of the unreasonably short C_4–C_4' distance. The non-equivalence of distances which are chemically equivalent is reason enough for discarding Model B_2.

The standard deviations in the bond lengths, as estimated from the standard deviations in the positional parameters by the usual formulas for the propagation of errors were about 0·035 A for all the bonds. If one compares the bond distances in each of the models to the normal carbon–carbon single bond distance of 1·54 A, keeping in mind the estimated standard deviations, the evidence for retaining Model B_1 is strengthened. In Model A, the C_4C_4' distance is completely out of line with these values. In Model B_2, five of the bond distances differ by more than the estimated standard deviation from 1·54 A and three of these differ by more than twice the estimated standard deviation. In Model B_1 on the other hand, only the distance C_1–C_2 differs by more than the standard deviation from 1·54 A. The coordinates and anisotropic temperature factors obtained from Model B_1 (Fig. 2), are listed in Table 2. Closest contacts in the unit cell are given in Fig. 3. Final R values of 0·160, 0·139 and 0·151 for the 0kl, h0l, hk0 projections respectively and a R value of 0·130 for all 554 reflections were obtained.

TABLE 2. COORDINATES AND TEMPERATURE FACTORS MODEL B_1

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
I	0	0·18613	0·25003	0·0185	0·0135	0·0135	0	0·0023	0
N	0·50000	0·98332	0·25000	0·0206	0·0131	0·0176	0	0	0
C_1	0·39813	0·85638	0·18470	0·0103	0·0077	0·0097	0	0·0022	−0·0005
C_2	0·29049	0·77411	0·29844	0·0335	0·0180	0·0298	0	0·0055	0·0072
C_3	0·25440	0·61005	0·25000	0·0204	0·0156	0·0194	0	0	0
C_4*	0·42281	0·52316	0·30678	0·0185	0·0121	0·0145	0	0·0060	−0·0014
C_4'*	0·57719	0·52316	0·19322	0·0183	0·0120	0·0151	0	−0·0005	0
C_5	0·50000	0·08433	0·38649	0·0247	0·0283	0·0127	0	0·0093	0
C_6	0·50000	0·08170	0·11609	0·0226	0·0277	0·0122	0	−0.0114	0

* Atoms C_4 and C_4' were put in as "Half-atoms".

Using the coordinates from Model B_1, and assuming C—H = 1·10 A and angles CCH and HCH as close to 109° as possible, positions for each of the hydrogen atoms in the eight-membered ring were calculated. These positions were then compared to a difference Fourier map calculated by using the phases obtained from the positions in Model B_1. The hydrogen atoms all fell in positive regions ranging in height from 0·3–0·7 e/A^3. No other region of height greater than 0·4 e/A^3 was observed. Figure 2 shows the contact distances between the nearest hydrogen atoms.

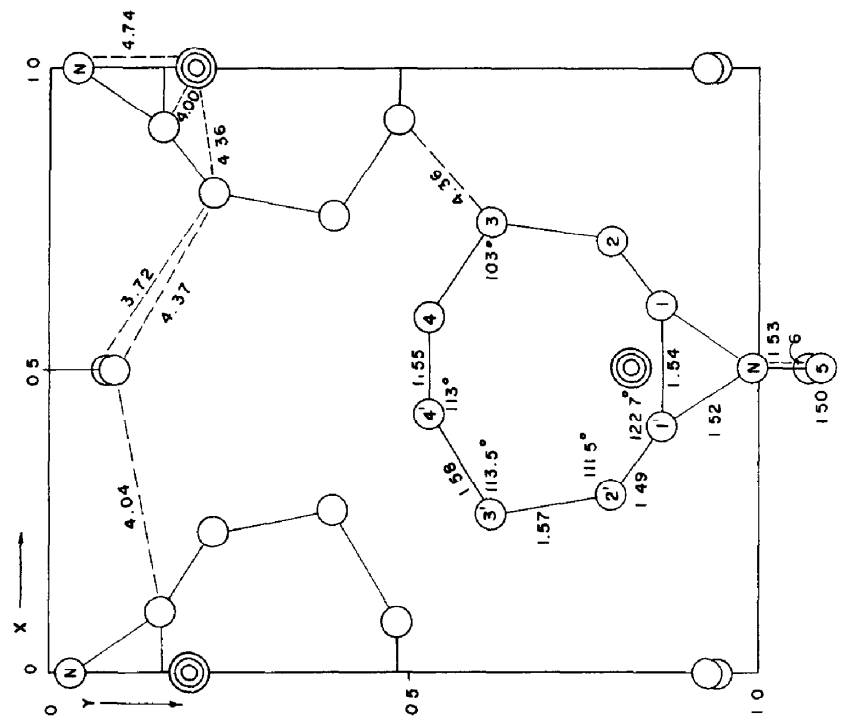

FIG. 3. Contents of unit cell. Bond distances, bond angles and closest contacts indicated.

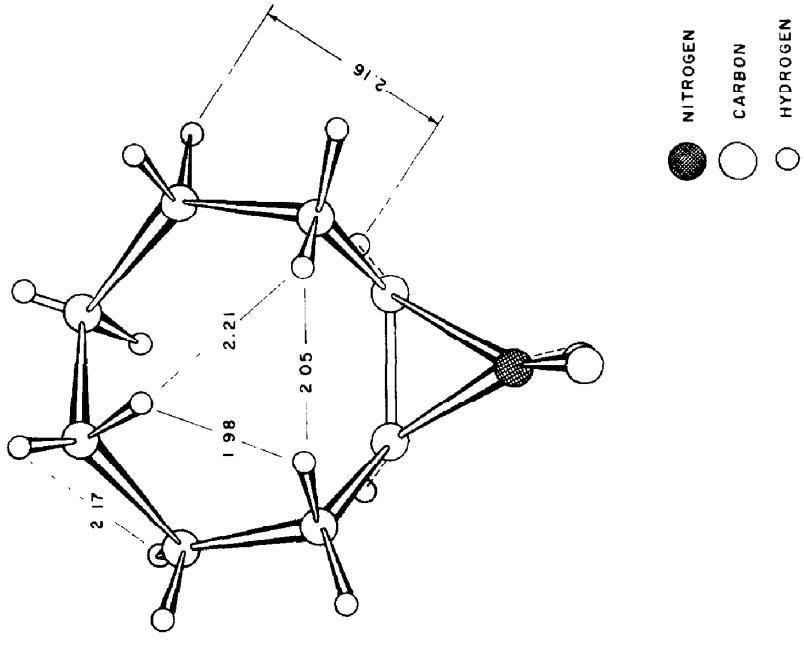

FIG. 2. Perspective drawing of molecule (omitting iodine). Closest H . . . H contact distances indicated.

If one assumes that the eight-membered ring existing alone would have tetrahedral angles throughout, then the angles 211′ and 11′2′ have been forced to open up to 122·7° to accommodate the 2,2′ hydrogen atoms. The resulting positions are then a compromise between the negative Baeyer strain induced by this widening and the repulsions of the hydrogen atoms 2,2′ which are still relatively close at 2·05 A.

Alternately, one can look at the molecule from the view-point of the aziridine ring. In the free aziridine molecule (Gas Phase, C_2H_4ND),[5] the dihedral angle between the HCH plane and the C—C bond is 159·4°. In order to fuse an eight-membered ring to the aziridine ring at the C—C positions, this dihedral angle must be drastically reduced, or the bond angle in the eight-membered ring drastically increased, or both should change somewhat to accommodate each other The results of the structure determination show that the compromise choice prevails. The bond angles each open up to 122·7° and the dihedral angles are decreased to 139°.

The closest transannular distances between the hydrogen atoms in the ring as a whole are found in the 3 hydrogens above the ring 2,2′ and 4 which approach each other as closely as 1·98 A and 2·05 A (Fig. 2). Of the hydrogens located below the ring, the closest approaches are 2·15 A and 2·17 A. The net effect of these interactions also increases the valence angles. Taking the carbon–carbon bonding-force constant as $0{\cdot}8 \times 10^{-11}$ erg-radians^{-2}, the energy required to deform a bond angle is given[6] by $E = 0{\cdot}0175\ X^2$ where E is the deformation energy in Kcal per mole and X is the deformation angle in degrees. The average value of the angles in the cyclo-octane ring is 113° which would be an average deformation of 4° in each bond angle and require only 0·28 Kcal per mole per bond angle.

Due to the fusion of the aziridine ring, the crown conformation postulated for cyclo-octane[7] cannot be assumed by the eight-membered ring in this compound. Instead, the ring assumes a conformation intermediate between the boat and chair form due to the disymmetry of atoms 4,4′. Model A for example, would be in the boat conformation, whereas if the peaks mirrored across $z = \frac{1}{4}, \frac{3}{4}$ were chosen instead for atoms 4,4′ then one would obtain the chair form. Either conformation however, would then have a bond distance of 1·19 Å for the single bond C_4–C_4'. Consequently, only by assuming the skewed positions can one arrive at a chemically reasonable structure.

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[5] T. E. Turner, V. C. Fiora and W. M. Kendrick, *J. Chem. Phys.* **23,** 1966 (1955).
[6] E. L. Eliel, *Stereochemistry of Carbon Compounds* P. 252, McGraw-Hill Series in Advanced Chemistry (1962).
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