Crystal and Molecular Structure of *trans*-13,13-Dimethyl-13-azoniabicyclo[10.1.0]tridecane Iodide

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The molecular and crystal structure of 13,13-dimethyl-13-azoniabicyclo[10.1.0]tridecane iodide has been elucidated. The aziridine ring is bridged *trans* to the cyclododecane ring. The cyclododecane ring is built of four nearly planar atoms with an atom shared in common between the successive units. Transannular hydrogen distances of 2.05 Å. have been postulated. The crystal is disordered with two formula weights in a unit cell of dimensions $a = 8.26$, $b = 11.00$, $c = 8.70$ Å. and the space group of the orthorhombic crystal is Pmn2$_1$. The final value of $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ is 0.13 for the 440 observed reflections.

Introduction

The study of *trans*-13,13-dimethyl-13-azoniabicyclo[10.1.0]tridecane iodide ($C_{14}H_{28}NI$) was undertaken as part of a continuing study of polycyclic compounds with at least one small-ring system containing nitrogen. It is of particular interest to study the effects of a bridged aziridine ring on the conformation and molecular parameters of the cyclododecane ring and, conversely, to see what effect the fusion of a cyclododecane ring will have on the large exterior dihedral angles found in aziridine.[1] Further, one can also look at the closest approach distances of the transannular hydrogen atoms in the cyclododecane portion of the molecule. Lastly, it is of interest to note whether the general trend of orientational disorder in the solid state, emerging from other studies on medium-sized rings,[2-4] is further verified.

The sample was kindly furnished to us by Professor P. E. Fanta and is a previously unreported compound. Details of the chemistry of this compound will appear in a forthcoming publication.

Crystal Data

The sample was recrystallized from a mixture of ethyl alcohol and ethyl acetate and grew in flat plates perpendicular to the [010] axis. The space group (Pmn2$_1$) and cell dimensions ($a = 8.26$, $b = 11.00$, $c = 8.70 \pm 0.01$ Å.) were determined from precession photographs taken with filtered Mo Kα radiation. The calculated density of 1.42 g. per cm.^{3} for a unit cell containing two formula weights seems reasonable by comparison to the value found for 9,9-dimethyl-9-azoniabicyclo[6.1.0]nonane iodide, a compound of similar structure which crystallizes in the space group Pmn2$_1$ and has a unit cell of comparable cell dimensions.[2] The subsequent determination of the structure confirmed this estimation of the density of the crystal. Streaking of the spots and the rapid decline of their intensities with increasing angle of scattering led to a strong suspicion of orientational disorder in the crystal.

Structure Determination

Intensity data were collected of the zero and first three levels about the [100] axis, the zero and first four levels about the [010] axis, and the (h,h,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.[5] Reflections common to more than one film were then used to correlate the corrected intensities and a list of 440 independent reflections, all on the same relative scale, was finally obtained. Extinctions of all $(h0l)$ where $h + l$ was odd led to the space groups

Pmn2$_1$ and Pmnm as possibilities. However, the assumption of two molecules per unit cell would imply that for space group Pmnm each molecule must contain two perpendicular mirror planes which is not possible. Consequently, only space group Pmn2$_1$ was considered in the determination of the structure.

Based upon the density measurements and the space group Pmn2$_1$, the iodine and nitrogen atoms were required to occupy special positions on the crystallographic mirror planes at $x = 0$, $^1/_2$. The iodine position was determined from the three Patterson projections. Using the iodine position only, and assuming an initial isotropic temperature factor, $B = 4.5$ Å.^{2}, least-squares refinements were carried out. The least-squares routine[6] used in this and in all subsequent refinements employed the diagonal approximation with an appropriate damping factor. The weighting factors used were $w = (4|F_{min}|/|F^°|)^4$ for $|F^°| \geq 4|F_{min}|$ and $w = 1$ for $|F^°| < 4|F_{min}|$.

After three cycles of refinement using only the iodine position, values of $r = 0.61$ and $R = 0.31$ were obtained. The phases of the structure factors from the last cycle of these refinements were used to calculate a three-dimensional difference Fourier map. A composite drawing of the significant region from $z = 0$ to $z = ^1/_4$, projected down the z-axis is given in Fig. 1. Because of the special position of the iodine atom, mirror planes were generated at $z = ^1/_4$ and $z = ^3/_4$ and consequently the region from $z = ^1/_4$ to $z = ^1/_2$ is a mirror image of Fig. 1.

The peaks assumed to be carbon atom peaks appeared with heights ranging from 2.2 to 4.2 e/Å.^{3} whereas the one assumed to be the nitrogen peak had a height of 5.8 e/Å.^{3}. Except for a residual positive peak at the iodine position indicating a decrease in the value of the temperature factor, no other peak of height greater than 1.1 e/Å.^{3} appeared on the maps.

Although at first glance it appears that all of the peaks are well enough resolved so that the structure of the molecule is essentially determined at this stage, one major difficulty presents itself. For all of the peaks except those located on the false mirror planes at $z = ^1/_4$, $^3/_4$, two choices for each atom appear. For the molecule located near $z = ^1/_4$, one could choose either z or $^1/_2 - z$, equally well for the z-coordinate of each atom.

If one assumes the crystal is ordered and that the crystal symmetry is obeyed by each molecule individually, the molecule would then have a mirror plane bisecting it at $x = ^1/_2$. However, this would immediately cause some serious difficulties. The C_1–C_1' and C_6–C_6' single bond distances would have maximum lengths of 1.45 and 1.15 Å., respectively. The methyl carbon atoms C_7 and C_7' would have to be in the mirror plane at at $x = ^1/_2$ which would make the fusion *cis* rather than *trans* contrary to the chemical evidence.[7] Also, placing

(1) T. E. Turner, V. C. Fiora, and W. M. Kendrick, *J. Chem. Phys.*, **23**, 1966 (1955).

(2) L. M. Trefonas and R. Majeste, *Tetrahedron*, **19**, 929 (1963).

(3) R. F. Bryan and J. D. Dunitz, *Helv. Chim. Acta*, **43**, 3 (1960).

(4) J. D. Dunitz and H. M. Shearer, *ibid.*, **43**, 18 (1960).

(5) J. Waser, *Rev. Sci. Instr.*, **22**, 567 (1951).

(6) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).
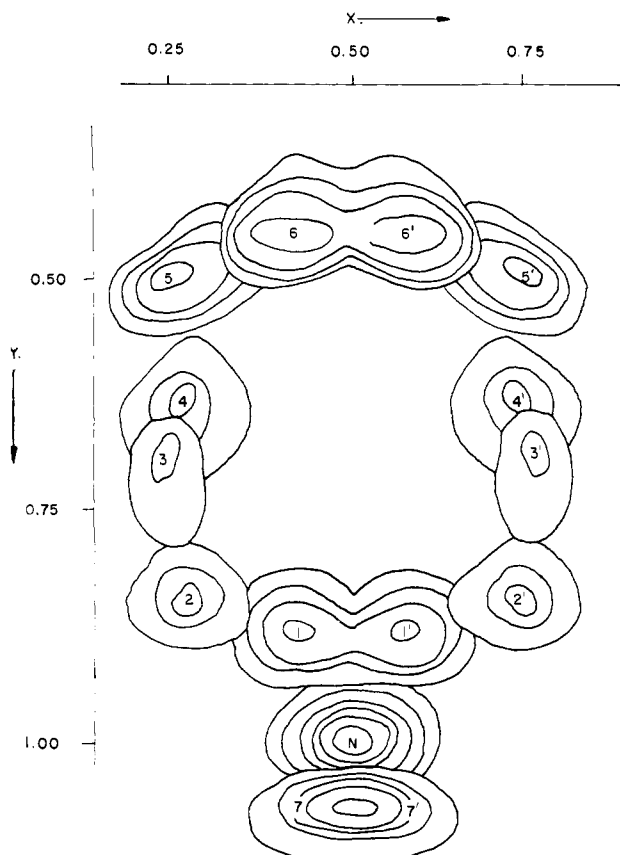
Fig. 1.—Composite drawing of difference Fourier map from $z = 0$ to $z = \frac{1}{4}$ (iodine omitted). Contours at approximately 1.0 e/Å.[3] with the first contour at approximately 1.0 e/Å.[3]

Fig. 2.—Perspective drawings of the four possible molecular configurations.

atoms C_7 and C_7' on the mirror plane would be in very poor agreement with the elongated peaks found in the difference Fourier maps for these atoms since each appears to be greater than 0.30 Å. from the mirror plane at $x = \frac{1}{2}$. Lastly, the appearance of the spots on the films is strongly suggestive of disorder within the crystal.

Consequently, the investigation proceeded on the assumption that orientational disorder exists in the crystal. If one makes this assumption, a multiplicity of choices arises. For example, starting with C_5 which is at $z = 0.25$, one can choose C_4 with a z-coordinate of 0.29 or 0.21. Once one has made a choice for C_4, a similar choice arises for C_3 and so forth for all of the other atoms of the molecule which do not coincidentally lie on the false mirror plane at $z = \frac{1}{4}$. Fortunately, the situation is not quite as unresolvable as it appears at first. If one eliminates all structures which do not contain "reasonable" bond distances and bond angles throughout the molecule, one is left with only four possibilities. For each of these configurations it is assumed that the disorder is due to an equal distribution of pairs of enantiomorphs about the statistical mirror planes at $z = \frac{1}{4}$, $\frac{3}{4}$. Three-dimensional packing models of each of these configurations were studied to see if any of these possibilities could be eliminated on purely packing considerations. Unfortunately, all of the models were reasonably compatible with the available space.

One can most easily visualize the differences between these configurations if one recognizes that the atoms in

(7) P. E. Fanta, private communication (December, 1962): " . . . The *trans* structure assigned to this compound is deduced from the fact that it was prepared by ring closure of the *cis*-2-aminocyclododecyl hydrogen sulfate, a type of reaction which consistently has been found to occur with inversion of configuration . . . . "
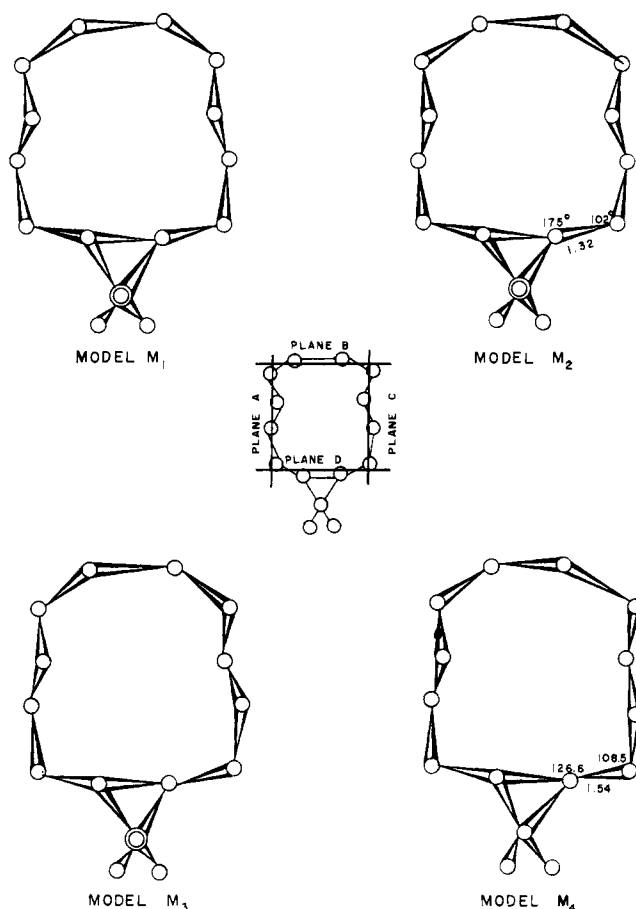
the cyclododecane portion of the molecule, if taken in groups of four, essentially lie in four planes (Fig. 2)

atoms C_2, C_3, C_4, and C_5 lie in plane A (within 0.16 Å.)
atoms C_5, C_6, C_6', and C_5' lie in plane B (within 0.26 Å.)
atoms C_5', C_4', C_3', and C_2' lie in plane C (within 0.16 Å.)
atoms C_2', C_1', C_1, and C_2 lie in plane D (within 0.14 Å.)

If atom by atom, the atoms in plane A lie on the same side of $z = \frac{1}{4}$ as their related member in plane C, let us call this "parallel AC." If, on the other hand, C_2 and C_2', C_3 and C_3', C_4 and C_4', taken in pairs have z-coordinates related by z, $\frac{1}{2} - z$, let us call this "opposed AC." Similarly if C_1 and C_6, and C_1' and C_6', taken in pairs, lie on the same side of $z = \frac{1}{4}$, call this "parallel BD"; otherwise call it "opposed BD." Then, quite simply, the four models (Fig. 2) can be classified as

model M_1, parallel AC, parallel BD
model M_2, parallel AC, opposed BD
model M_3, opposed AC, parallel BD
model M_4, opposed AC, opposed BD

The question then becomes one of finding a technique which will allow a choice between these four models. If one uses Fourier techniques all of the peaks of both enantiomers of any one model appear with equal heights. If one assumes "half-atoms" at each of the enantiomorphic positions and then proceeds with least-squares refinements, again no choice can be made. However, if one includes in the least-squares refinements the light atom coordinates for only one of the enantiomers, adjusts the scale factor accordingly, and then carries out the refinements, the results will differ for those models having a "parallel BD" configuration (models M_1 and M_3) and those having an "opposed BD" configuration (models M_2 and M_4) because the
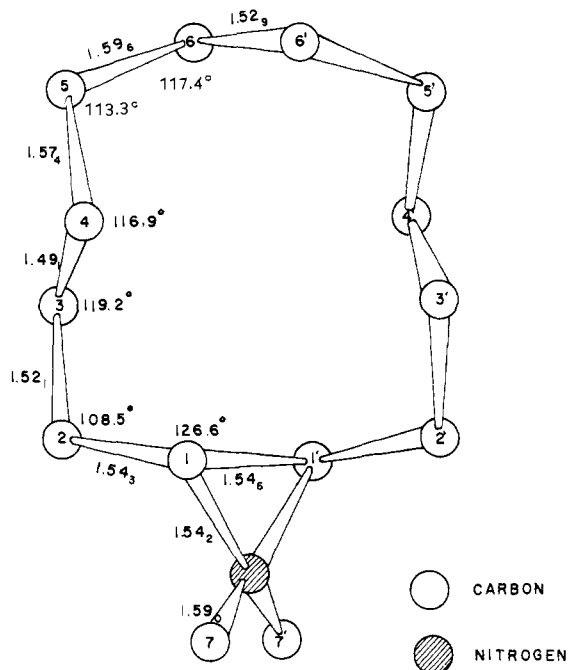
Fig. 3.—Perspective drawing of the final molecular structure with bond distances and bond angles indicated (iodine omitted.)

Fig. 4.—Contents of one unit cell; closest interatomic distances indicated.

coordinates relative to the iodine atom coordinate will differ.

Two cycles of least-squares were carried out on the "parallel BD" configuration resulting in values of $r,R = 0.59$, 0.27 with average shifts of 0.04 Å. in coordinate positions and 2.8 in the temperature factors. On the other hand, two cycles of least-squares on the "opposed BD" configuration resulted in values of $r,R = 0.31$, 0.23 with average shifts of 0.02 Å. in coordinate positions and 0.8 in the temperature factors. The results are thus indicative of a strong preference by the data for an "opposed BD" configuration eliminating models M_1 and M_3.

As a check on this technique, two cycles of least-squares were run on the enantiomer of the "opposed BD" configuration (by changing each of the z-coordinates to $^1/_2 - z$ coordinates). This refinement gave results identical with those in the previous refinement indicating no preference of the data for either member of the enantiomeric pair of a given configuration as was expected. A three-dimensional difference Fourier map was calculated using the phases resulting from the refinement of the "opposed BD" configuration. The peaks from both enantiomers were found to have been subtracted out equally, indicating that this technique of refining the positions of only one member of an enantiomeric pair would lead to the correct final positions for the atoms.

This difference Fourier map also indicated pronounced anisotropy for each of the atoms. It was decided therefore to use anisotropic temperature factors in the subsequent refinements. Seven additional cycles of refinement resulted in coordinate shifts all less than 0.005 Å. and so the refinement of the positions was essentially complete. Final values of $r,R = 0.08$, 0.13 and R-values of 0.14, 0.11, and 0.14 for the $0kl$, $h0l$, and $hk0$ projections, respectively, were obtained.

One must keep in mind that since the refinements have been carried out in space group Pmn2₁, no distinction has yet been drawn between models M_2 and M_4. Both models are compatible with the crystallographic data and the assumption of orientational disorder in the space group Pmn2₁. However, since atoms C_1 and
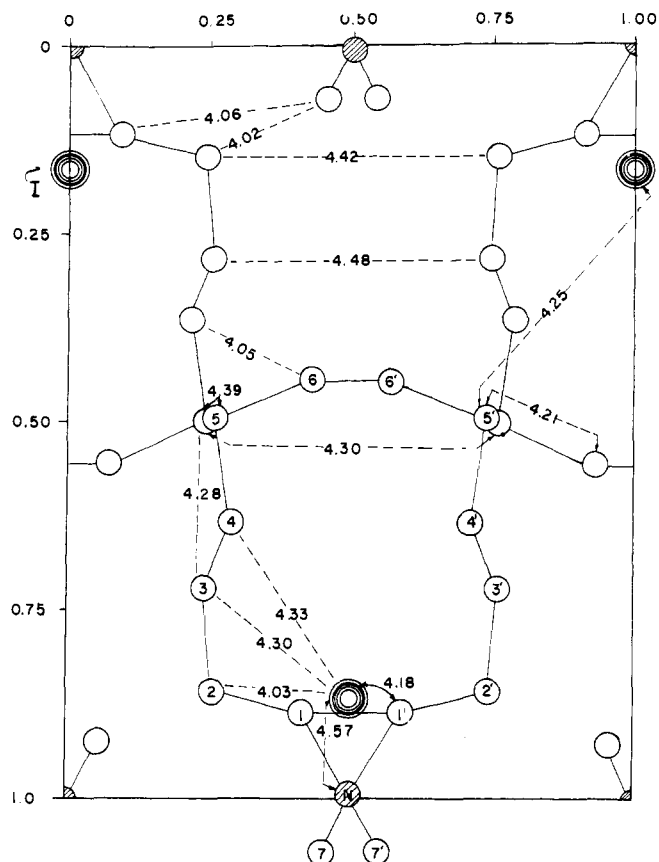
C_1' are located on opposite sides of the false mirror planes at $z = ^1/_4$, $^3/_4$ and atoms C_2 and C_2' are not on these false mirror planes, the refined coordinates of models M_2 and M_4 will result in different bond distances and bond angles about these atoms. The particular distances and angles which differ are shown in Fig. 2 for models M_2 and M_4 and one quite easily sees that model M_4 (opposed AC, opposed BD) is the only configuration which is both chemically reasonable and consistent with the crystallographic data.

Discussion

The coordinates and anisotropic temperature factors obtained for model M_4 are given in Table I. The bond distances and bond angles for the molecule are given in Fig. 3, and the closest contacts between molecules in the unit cell are shown in Fig. 4.

The standard deviations, as estimated from the standard deviations in the positional parameters by the usual formulas[8] for the propagation of errors, were about 0.03 Å. for all the bond lengths and $3°$ for all the bond angles. The average bond length for the carbon–carbon bonds was 1.54 Å., with only two bond distances differing by more than the estimated standard deviation from the average bond distance and both of these are well within two standard deviations of that value. The average of the bond angles (excluding the angles at the fusion of the two rings) in the cyclododecane ring was $112°$.

Using the coordinates from model M_4, and assuming C–H 1.10 Å. and angles HCH and CCH as close to $109°$ as possible, positions for each of the hydrogen atoms in the twelve-membered ring were calculated. A final three-dimensional difference Fourier map was then calculated and the hydrogen positions previously de-

(8) E. W. Hughes and W. N. Lipscomb, *J. Am. Chem. Soc.*, **68**, 1970 (1946).

Coordinates and Temperature Factors in Model M_4

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
I	0	0.1626	0.2500	0.0268	0.0110	0.0195	0	−0.0001	0
N	0.5000	.0038	.2500	.0291	.0113	.0068	0	.0015	0
C_1	.4120	.8825	.2802	.0311	.0106	.0007	−0.0021	.0024	0.0012
C_2	.2584	.8565	.1847	.0248	.0118	.0166	.0042	.0022	.0148
C_3	.2456	.7200	.1595	.0272	.0179	.0147	− .0053	.0056	− .0080
C_4	.2867	.6350	.2870	.0360	.0129	.0119	− .0026	.0085	− .0246
C_5	.2601	.4962	.2500	.0310	.0128	.0218	− .0150	0	0
C_6	.4305	.4455	.1920	.0426	.0178	.0069	− .0069	−0.0006	0.0101
C_7	.4532	.0700	.4064	.0442	.0384	.0167	− .0019	−0.0010	0.0002

rived strictly from geometric considerations were compared to these maps. All of the hydrogen atom positions calculated fell in positive regions ranging in height from 0.2–0.8 e/Å.^{3}. The only other positive region higher than 0.4 e/Å.^{3} was around the iodine position.

As can be seen from Fig. 5 (which shows closest contact distances within the molecule for the hydrogen atoms), not all of the transannular interactions observed in the cyclodedecane molecule are repeated in this molecule. Contacts as close as 2.05 Å. are observed between the hydrogens on atoms C_4 and C_6' and their analogs on C_6 and C_4'. But the anticipated close contacts between the hydrogen atoms on the other half of the cyclododecane ring are not observed because of two related effects. The separation of these hydrogens is greatly increased by the large angles of 126.6° at the fusion points of these two rings and the *trans* fusion of the two rings staggers the hydrogens on opposite sides of the ring making such close contacts highly improbable. It will be of interest in the investigation now under way of the *cis*-fused analog of this compound to see how much of a difference the type of juncture (*cis* or *trans*) makes to these contact distances. In a previous study^2 in which an aziridine ring was fused *cis* to a cyclooctane ring, transannular hydrogen close contacts of 1.98 and 2.05 Å. were observed for hydrogen atoms on a carbon atom adjacent to the ring fusion atoms.

If one excludes the angles at the fusion point of the two rings, the bond angles and bond distances for the cyclododecane portion of this molecule average out to the same values, as those found for the cyclododecane^4 ring itself. The ring skeleton of the cyclododecane molecule by itself has $D_2(222)$ symmetry and, in fact, variations from $D_4(422)$ symmetry are barely significant. However, the fusion of the aziridine ring to the cyclododecane ring in this molecule distorts the cyclododecane ring sufficiently so that its symmetry is lowered. It is actually $C_2(2)$, differing from $D_2(222)$ symmetry primarily in the positions of atoms C_1 and C_2 around the points of fusion of the two rings.

The angles at the points of fusion of the two rings (angles 211' and 11'2') have values of 126.6°. In the free aziridine molecule (gas phase, C_2H_4ND)^9 the dihedral angle between the HCH plane and the C–C bond is 159.4°. In order that one may fuse a twelve-membered ring to the aziridine ring, this dihedral angle must be drastically reduced, or the bond angle in the cyclododecane ring drastically increased, or, lastly, both should change sufficiently to accommodate each other. The results of the structure determination show that the compromise choice prevails. The bond angles each open up to 126.6° and the dihedral angles are decreased to 140°. Taking the carbon–carbon bending-force constant as 0.8×10^{-11} erg-radian^{-2}, the energy required to deform

a bond angle is given^{10} by $E = 0.0175X^2$ 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 cyclododecane ring is 112° which would lead to an average deformation of 14.6° in each of the
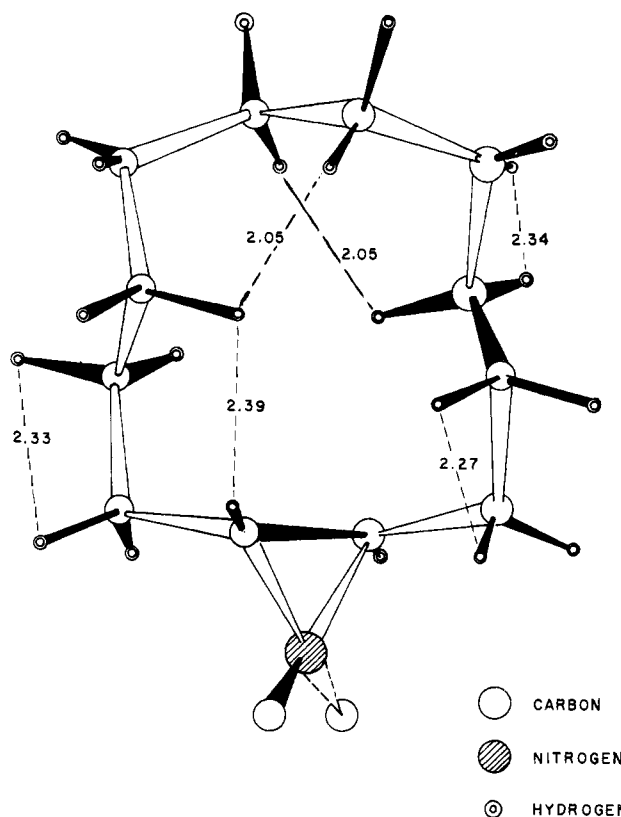

Fig. 5.—Perspective drawing of the final molecular structure with postulated hydrogen positions included; closest H···H contact distances indicated.

angles at the fusion point and require 3.73 kcal. per mole per bond angle. However, this energy loss is in great part compensated for by the elimination of the close-contact repulsions of the transannular hydrogens in this portion of the ring.

(9) T. E. Turner, V. C. Fiora, and W. M. Kendrick, *J. Chem. Phys.*, **23**, 1966 (1955).

(10) E. L. Eliel, "Stereochemistry of Carbon Compounds," P-252. McGraw–Hill Series in Advanced Chemistry (1962).