Table VII. Observed and Calculated Rate Constants for Me_2NH_2Cl in the Presence of Et_4NCl

Soln[a]	$10^{-6} \cdot k'_2\eta/\eta_0$	$10^{-6} \cdot \alpha k_0$[b]	$10^{-6} \cdot \Delta$[c]	$10^{-6}k'$
1	34.4[d]	34.4[d]	...	...
2	27.0	24.9	2.1	5.6
3	24.7	17.4	7.3	13.0
4	20.4	9.90	10.2	13.5
5	16.9	5.27	11.6	13.4
6	14.8	2.95	11.9	12.7

[a] For the salt concentrations and the values of k'_2 see Table III. [b] $k_0 = \alpha^{-1}k'_2\eta/\eta_0$; k'_2 is obtained from the solution containing no Et_4NCl; $k'_2 = 3.13 \times 10^7\ M^{-1}\ sec^{-1}$. [c] $\Delta = k'_2\eta/\eta_0 - k_0\alpha$. [d] No Et_4NCl present.

analysis could not be performed on them. However, it seems likely that their salt effects can be explained by the same theory.

As shown in Table I, the value of k'_2 for trimethylammonium salts does not decrease significantly when tetraethylammonium salts are added. The freezing point data given in Table V for trimethylammonium chloride clearly indicate that this salt is complexing with tetraethylammonium chloride. Therefore, one may conclude that the complexed and uncomplexed trimethylammonium chloride undergo proton exchange at about the same rate.

The fact that added Et_4NCl does not affect the value of k'_2 for Me_3NHCl and decreases it for Me_2NH_2Cl is not unreasonable. Since the sole NH proton of Me_3NHCl is already strongly interacting with the chloride ion,[1] complexing with Et_4NCl need not affect significantly the reactivity of this proton. On the other hand, in addition to an NH proton hydrogen bonded to the anion, Me_2NH_2Cl has one which is hydrogen bonded to solvent and is much more reactive.[1] Consequently, complexing with Et_4NCl can reduce the reactivity of this "free" NH proton.

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The Crystal and Molecular Structure of 1-Methyl-6-[5-(1-methyl-1H-1-pyrindinyl)]-1-azoniaindan Iodide

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Contribution from the Department of Biological Structure, University of Washington, Seattle, Washington. *Received August 2, 1965*

Abstract: The crystal structure of an unknown material has been solved by the heavy-atom method using three-dimensional X-ray diffraction data. The compound consists of 1-methyl-1H-1-pyrindine and 1-methyl-1-azoniaindan iodide groups joined by their respective 5- and 6-positions. Location of the two nitrogen atoms within the carbon skeleton was not possible using limited Cu data. This difficulty was subsequently resolved with a larger set of Mo data. Structural parameters, including those describing thermal anisotropy, were refined by the technique of least squares. The 1,5-disubstituted 1H-1-pyrindine half of the molecule is iso-π-electronic with azulene. Bond lengths, angles, and planarity are in agreement with postulated aromatic character for such a moiety. The structure is layered with the organic residues forming well-defined rectangular "rods" parallel to *a*. The iodide ions are located in spaces between the "rods."

Demonstrations of aromatic character in azulene[2] have stimulated study of similar iso-π-electronic structures in which heteroatoms have replaced one or more carbon atoms. These compounds can be classified as either (1) π-equivalent, in which one or more heteroatoms (=X–; X = N, S^+, O^+) replace an equal number of carbon atoms (=C–) in the 5- and 7-rings or (2) π-excessive,[3] in which a heteroatom (–X–; X = NR, S, O) replaces an ethylenic group (–C=C–) in the 7-ring. Early examples of the π-excessive heterocycles were either highly substituted, fused to other benzenoid nuclei, or both, and as such were too complex to permit significant comparisons with the azulenes. Only very recently have certain of the parent heterocycles been synthesized (cyclopenta[*c*]thiapyran,[4,5] cyclopenta[*b*]thiapyran[6]).

The compound 5H- and 7H-pyrindine (**1**; these two isomers are probably in tautomeric equilibrium), first prepared by Robison,[7] provides a ready entry (see Figure 1) into the 1H-1-pyrindine system. Anderson, *et al.*,[4] had even postulated that the slight orange color of **1** was due to the presence of a small amount of a

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(1) Cowell College, University of California at Santa Cruz, Santa Cruz, Calif.

(2) A review of azulene aromaticity is given by E. Heilbronner, "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter V.

(3) The terms "π-equivalent" and "π-excessive"[4] are used to denote relative numbers of π-electrons and ring atoms. Examples of π-equivalent and π-excessive derivatives of benzene are pyridine and pyrrole, respectively.

(4) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson, and A. G. Osborne, *J. Am. Chem. Soc.*, **81**, 1255 (1959).

(5) A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *ibid.*, **85**, 3448 (1963).

(6) R. Mayer, J. Franke, V. Horák, I. Hanker, and R. Zahradník, *Tetrahedron Letters*, 289 (1961).

(7) M. M. Robison, *J. Am. Chem. Soc.*, **80**, 6255 (1958).

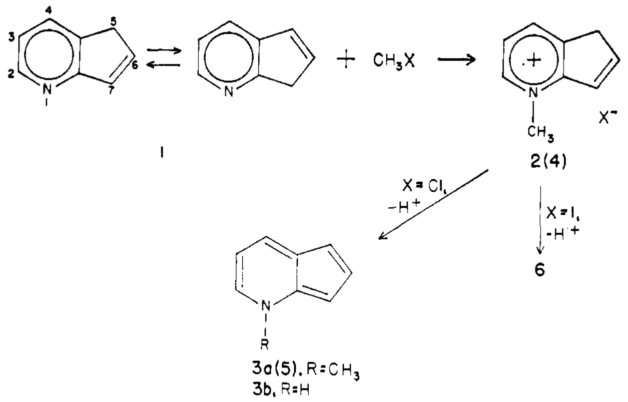

Figure 1. Proposed reaction sequence for the synthesis of 1-methyl-1H-1-pyrindine from 5H- and 7H-1-pyrindine.

third tautomer, 1H-1-pyrindine (**3b**; 2- and 3-vinylpyridines are colorless). Reese[8] allowed **1** and a large excess of methyl iodide to react and identified the resulting solid (**4**) as 1-methyl-5H-1-azoniaindene iodide (**2**, X = I). Removal of a proton from **2** should give the desired 1-methyl-1H-1-pyrindine (**3a**). He was, however, unable to isolate and characterize a compound corresponding to **3a** and only reported the spectrum of the chloride of **2** (**4**, X = Cl)[9] in basic solution (**5**).[10]

Studies by Ammon and Anderson[11] on the 1H-1-pyrindine system resulted in the isolation of a crystalline solid (**6**) from the reaction of base with **4** (X = I). This is a report of an X-ray diffraction study of **6** and the determination casts doubt on the structural assignments of Reese (*i.e.*, the identity of **5** and **3a** and of **4** and **2** are in question).

Experimental Section

Compound **6**, recrystallized from an acetonitrile–benzene solvent mixture, was obtained as beautiful, deep purple needles elongated along *a* with a rectangular cross section. A preponderance of multiple crystals, joined along the needle axis, made location of a usable diffraction sample difficult. Density measurements were made in a *sym*-tetrabromoethane–benzene mixture and preliminary unit cell dimensions and space group extinctions were determined from oscillation, Weissenberg (Cu Kα), and precession (Mo Kα) photographs.

More accurate cell dimensions were obtained from a least-squares fit of data collected in the following manner. The 2θ values (Cu Kα radiation, ranging from 27 to 50°) for twelve general reflections were carefully measured on a Picker X-ray diffractometer (General Electric quarter-circle goniostat). An average of two determinations on each side of $2\theta = 0°$ (at constant ϕ and χ) yielded 2θ's independent of settings in ϕ and χ and required no knowledge of the true zero point in 2θ. The parameters and their estimated standard deviations are reported below ($^1/_{12}\Sigma|2\theta_o - 2\theta_c| = 0.0037°$).

The crystal data (Cu Kα, $\lambda = 1.5418$ Å) for 1-methyl-6-[5-(1-methyl-1H-1-pyrindinyl)]-1-azoniaindan iodide ($C_{18}H_{19}N_2I$), mol wt 390.3, mp 230–231°, are: monoclinic, $a = 7.476 \pm 0.001$, $b = 14.547 \pm 0.002$, $c = 14.712 \pm 0.004$ Å, $\beta = 90° 31.2' \pm 0.6'$; $D_{\text{measd}} = 1.605$ g cm^{-3}, $Z = 4$, $D_{\text{calcd}} = 1.620$ g cm^{-3}; $V = 1600$ Å^3; $F(000) = 776$; absent spectra, $h0l$ for $h + l$ odd, $0k0$ for k odd; space group $P2_1/n$.

All intensity measurements were made on the same crystal mounted along *a* with a cross section of *ca.* 0.1 × 0.1 mm and a length of 0.2 mm. In a preliminary study Ni-filtered Cu Kα radiation and the multiple-film technique were employed to take equi-inclination Weissenberg photographs. The spots were integrated (0.9 mm) at right angles to the rotation axis and measured by scanning with a microdensitometer (logarithmic slide wire) in a direction parallel to the rotation axis. Intensities were taken as proportional to the areas under the photometer tracings as obtained with a planimeter. A constant exposure time of 24 hr was used to collect each of the levels ($0kl$–$5kl$). Of the 568 reflections examined (out to sin θ of *ca.* 0.6), 369 (65%) were observed. No data were taken for level-to-level scaling.

Subsequently, intensity data ($0kl$–$4kl$) were re-collected on the Weissenberg camera using Zr-filtered Mo Kα ($\lambda = 0.7107$ Å) radiation and exposure times of 150 hr. In both the Cu and Mo data, unobserved reflections were coded as such and assigned an intensity equal to the minimum observed value on the appropriate level. The overlap of some reflections with the white radiation streaks of nearby intense reflections made accurate film measurement of the affected data difficult. All of the questionable data were later re-collected on a diffractometer. In addition, the diffractometer was used to collect all intense reflections and data for level-to-level scaling of the films and to extend the limit of observation to $2\theta \sim 45°$.

Measurements on the diffractometer (with the crystal aligned about a^*) were made using Mo Kα radiation, Zr–Y balanced filters, potassium iodide scintillation detector, pulse height analysis, and the 2θ scan technique. The 2θ scan ranges were calculated as a function of tan θ according to Alexander and Smith.[12] Some equations pertinent to the data work-up follow (the C's are intensities in counts).

$$C_{P,Y} = C_{T,Y} - C_{B,Y} \tag{1}$$

if $C_{T,Y} - C_{B,Y} < 0$

$$C_{P,Y} = 0 \tag{2}$$

$$C_P = C_{T,Zr} - C_{B,Zr} - C_{P,Y} \tag{3}$$

if $C_{T,Zr} - C_{B,Zr} - C_{P,Y} < \sigma$

$$C_P = \sigma \tag{4}$$

$$\sigma = (C_{T,Zr} + C_{B,Zr} + C_{T,Y} + C_{B,Y})^{1/2} \tag{5}$$

C_T is the scan count with the appropriate filter (Zr or Y); C_B is the sum of the two stationary background determinations made at the upper and lower (2θ) sides of the expected peak position, each taken for half of the reflection scan time; C_P is the corrected net intensity. The observed–unobserved cutoff for data taken on the diffractometer was placed (after some experimentation) at σ (the inclusion of $C_{P,Y}$ and $C_{B,Y}$ makes σ a little larger than it would be for Zr-filter measurements alone). A comparison of the final F_o and F_c lists[13] for these data indicates that this was a realistic level ($F_c > F_o$ for a few cases). However, use of *ca.* 1.5σ would have made $F_c < F_o$ for all of these reflections.

Of the 1538 reflections (*ca.* $^2/_3$ film and $^1/_3$ diffractometer) examined, 1114 (72%) were considered as observed. Structure factors were calculated from the I's in the normal fashion. No absorption corrections were made.

Solution of the Structure and Refinement. Preliminary work was done with the Cu film data. A three-dimensional Patterson synthesis, calculated using $E^2_{hkl} - 1$[14] as the Fourier coefficients, readily revealed the iodine–iodine vectors. The R factor ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) for a structure factor calculation (F_c) based solely

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[8] C. B. Reese, *J. Am. Chem. Soc.*, **84**, 3979 (1962).

[9] The chloride was obtained by passage of a solution of the iodide through an ion-exchange column.

[10] Reese assumed that **5** and **3a** were the same. Absorption was exhibited in the visible region.

[11] H. L. Ammon and A. G. Anderson, Jr., paper in preparation.

[12] L. E. Alexander and G. S. Smith, *Acta Cryst.*, **17**, 1195 (1964).

[13] These data have been deposited as Document No. 8583 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[14] This produces a sharpened, origin-removed vector map. The relative F values were placed on an absolute basis and converted into normalized structure factors (E's: H. Hauptman and J. Karle, "Solution of the Phase Problem I. The Centrosymmetric Crystal," American Crystallographic Association Monograph No. 3, Polycrystal Book Service, Brooklyn, N. Y., 1953) with the program DATFIX (a link of X-RAY 63[15]). The program utilizes the fact that $\langle E^2 \rangle$ is 1 to obtain a scale and over-all temperature factor.

[15] "Crystal Structure Calculations System, X-RAY 63", TR-64-6(NSG-398), Computer Science Center, University of Maryland, and Research Computer Center, University of Washington.

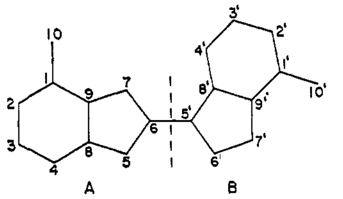

Figure 2. The skeleton of the organic part of the molecule obtained from the Cu data. The numbering scheme and designation of the A and B rings are shown.

on the iodine was 0.24. A few Fourier synthesis-F_c cycles were sufficient to locate the rest of the atoms. The molecular skeleton was unexpectedly revealed as two 1-methyl-1-pyrindine moieties joined through their respective 5- and 6-positions (see Figure 2).[16] For convenience in discussion, the molecule has been divided across the 5′–6 bond and the two "halves" designated A and B.

Table I. Individual Isotropic Temperature Factors before (B_i) and after (B_f) Location of the Two Nitrogen Atoms

Atom	B_i, Å^2	B_f,[a] Å^2
I	3.87	4.15
C(1), N(1)	2.10	2.78
C(2)	4.68	4.88
C(3)	4.49	4.58
C(4)	5.06	5.58
C(5)	4.83	3.99
C(6)	4.14	4.31
C(7)	3.65	3.52
C(8)	3.76	3.45
C(9)	4.38	3.86
C(10)	4.58	4.72
C(1′), N(1′)	2.18	3.17
C(2′)	4.41	3.93
C(3′)	3.97	3.86
C(4′)	3.12	2.89
C(5′)	3.65	3.91
C(6′)	4.20	4.14
C(7′)	3.95	3.90
C(8′)	3.05	3.18
C(9′)	4.22	4.40
C(10′)	4.73	5.46
F_o scale	1.002	0.996
R factor	0.128	0.118

[a] These parameters were obtained after two further cycles of isotropic refinement.

It now became necessary to identify the two nitrogen atoms. Chemical and spectral data available at this time were interpretable on the basis that methylation of 1-pyrindine (to form **2**) did not occur exclusively on nitrogen. Therefore, the nitrogen atom sites could not be inferred from the methyl group positions. The locations of the methyls, however, were good evidence that the nitrogen atoms occupied either the 1- or 4-positions (and 1′- or 4′-positions) of their respective rings giving four possible combinations. Subsequently, several cycles of least squares were calculated using individual isotropic temperature factors and coding all atoms (except, of course, the iodine) as carbon. It was hoped that the nitrogens could be pinpointed as those atoms with lower than average B's. Unfortunately, this approach was not successful. Several of the B's became negative in the following refinements, and in most instances the associated atoms could not possibly have been nitrogens (unless gross rearrangement of the 1-pyrindine skeleton had occurred either prior to or as a result of methylation). When this line of investigation was finally abandoned, R was 0.09 and two of the atoms (C(7′) and C(8′) in the final structure) had negative B's. The four combinations of nitrogen–carbon atom positions discussed above were also examined without success.

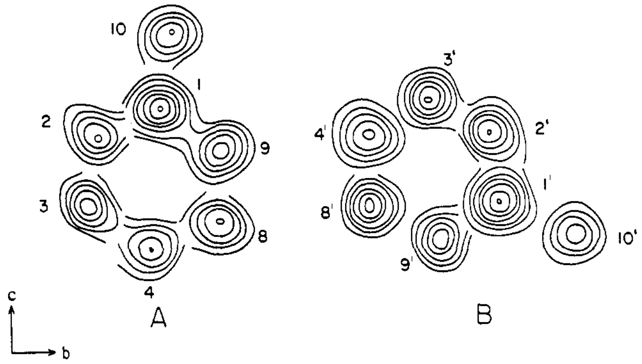

Figure 3. Fourier composite of the 6-rings of A and B viewed on a section parallel to the *bc* plane. Calculations were done with all atoms as carbons. Contours are at intervals of 1 e Å^{-3}, beginning at 2 e Å^{-3}.

These problems were, to a large extent, attributable to the small amount and poor quality of the Cu data. A satisfactory solution seemed to be the collection of a reasonably extensive set of data with Mo Kα radiation. The remeasurement of the intensities has been described in the previous section. A structure factor calculation using the positional parameters output from the final cycle of refinement of the Cu data (all B's = 3.0 Å^2 and all atoms, except iodine, coded as carbon) gave an R factor of 0.18. Two cycles of least squares with individual isotropic temperature factors dropped the R factor to 0.13. Examination of the B's revealed that two were *ca.* 2.1 Å^2 while all the others were 3 Å^2 or greater. A Fourier synthesis, calculated at this point (see Figure 3), showed these same two atoms to have the highest electron density (*ca.* 8 *vs.* 6–7 e Å^{-3} for the others). The atoms in question were also bonded to the methyls giving additional support to their identification as nitrogens. The temperature factors of these two atoms, when coded as nitrogens, increased to *ca.* 3 Å^2 during subsequent refinement. Table I gives the isotropic temperature factor data before and after selection of the atoms at the 1- and 1′-positions as nitrogens. Several following cycles of refinement with individual atom anisotropic temperature factors gave an R of 0.070.

Many large discrepancies existed between F_o and F_c and in a number of cases unobserved reflections from films had F_c's which were appreciably greater than the corresponding F_o's. All of those observed data for which $|F_o| - |F_c| \geqslant 10$ and all unobserved data for which $||F_c| - |F_o'|| \geqslant 2$ were recollected on the diffractometer. Some obvious errors were found in the observed data, but, in general, the corrections were few. However, in almost all cases in which an unobserved reflection from film was examined, an intensity equal to at least 4σ of the measurement was obtained and a peak was clearly discernible on the strip chart recorder tracing. This is practical evidence, obtained in a routine data collection, for the significantly greater recording efficiency of a scintillation detector over film (150-hr exposures) for Mo radiation. These corrections dropped R to 0.057 and another cycle of anisotropic refinement gave an R of 0.055.

A ΔF synthesis ($F_o - F_c$) was then calculated in an attempt to locate the hydrogen atoms. The map was quite poor and possessed many positive and negative regions equal, in absolute magnitude, to *ca.* 0.3 e Å^{-3}. Maxima ranging from 0.4 to 0.6 e Å^{-3} were found in the general areas[17] expected for fourteen of the nineteen hydrogens. Three cycles of least squares on the hydrogens, with individual isotropic temperature factors, gave an R of 0.047. C–H bond lengths ranged from 0.65 to 1.18 Å and the associated angles were in a few cases quite erratic. The remaining five hydrogen positions were calculated assuming a C–H bond length of 1.02 Å and tetrahedral angles. The position for H(6) was obtained as an average from calculations using C(5′)–C(6)–C(5), C(5′)–C(6)–C(7), and C(7)–C(6)–C(5) to define the positions of two methylene hydrogens.

Storage limitations of the least-squares program did not permit the simultaneous refinement of all carbon, nitrogen, and iodine parameters (190 variables with anisotropic temperature factors and an F_o scale factor) using the full matrix of the normal equations.

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[16] The locations of the nitrogens and sites of unsaturation were unknown at this point.

[17] An examination of the heavy-atom bond lengths and angles had revealed the points of unsaturation in the molecule.

Table II. Iodide Ion, Carbon, and Nitrogen Atom Positional and Anisotropic Thermal Parameters ($B_{ij}{}^{a} \times 10^4$)

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	0.6709 (01)	−0.0221 (01)	−0.2902 (01)	276 (2)	48 (0)	45 (0)	−5 (1)	−14 (1)	4 (0)
N(1)	0.2091 (11)	−0.2197 (07)	0.0347 (06)	160 (21)	50 (7)	35 (5)	−5 (9)	7 (9)	−8 (4)
C(2)	0.1577 (17)	−0.3040 (09)	0.0042 (08)	252 (31)	53 (9)	57 (8)	−16 (13)	35 (13)	−23 (6)
C(3)	0.0947 (16)	−0.3134 (08)	−0.0822 (07)	254 (29)	37 (7)	40 (6)	−26 (11)	9 (11)	−26 (5)
C(4)	0.0842 (16)	−0.2390 (10)	−0.1386 (09)	186 (29)	75 (11)	47 (8)	−40 (14)	34 (13)	−14 (7)
C(5)	0.1447 (15)	−0.0620 (09)	−0.1540 (08)	180 (26)	56 (8)	51 (7)	35 (12)	−22 (11)	−9 (6)
C(6)	0.2604 (17)	−0.0036 (07)	−0.0897 (08)	275 (29)	35 (7)	47 (6)	7 (10)	−28 (11)	15 (5)
C(7)	0.2531 (15)	−0.0485 (07)	0.0042 (07)	198 (24)	38 (7)	40 (6)	4 (10)	−18 (10)	1 (5)
C(8)	0.1391 (14)	−0.1519 (09)	−0.1080 (07)	132 (24)	60 (8)	37 (6)	5 (11)	−14 (10)	−2 (6)
C(9)	0.2024 (13)	−0.1456 (07)	−0.0221 (08)	122 (22)	30 (6)	46 (8)	−8 (9)	19 (10)	10 (5)
C(10)	0.2783 (17)	−0.2107 (09)	0.1266 (09)	234 (30)	67 (9)	52 (8)	−27 (13)	19 (13)	1 (7)
N(1′)	0.3061 (12)	0.3314 (06)	−0.0162 (06)	193 (21)	30 (5)	49 (5)	10 (8)	−8 (9)	14 (4)
C(2′)	0.3678 (14)	0.3227 (08)	0.0700 (08)	151 (24)	35 (7)	58 (8)	25 (10)	9 (11)	−9 (6)
C(3′)	0.3905 (15)	0.2415 (08)	0.1117 (08)	176 (26)	42 (7)	42 (6)	9 (11)	−6 (10)	3 (5)
C(4′)	0.3452 (14)	0.1607 (08)	0.0647 (06)	162 (23)	68 (8)	21 (5)	29 (11)	4 (9)	−6 (5)
C(5′)	0.2314 (14)	0.0985 (07)	−0.0932 (08)	162 (24)	26 (6)	52 (7)	1 (10)	−10 (10)	−13 (5)
C(6′)	0.1801 (14)	0.1504 (09)	−0.1673 (07)	198 (25)	52 (8)	21 (5)	10 (11)	3 (9)	15 (5)
C(7′)	0.1929 (15)	0.2459 (08)	−0.1533 (07)	224 (27)	48 (7)	34 (6)	−16 (11)	22 (10)	4 (5)
C(8′)	0.2865 (14)	0.1649 (08)	−0.0250 (07)	156 (23)	46 (7)	29 (5)	20 (10)	−11 (9)	−12 (5)
C(9′)	0.2611 (15)	0.2573 (08)	−0.0657 (08)	185 (26)	34 (7)	45 (7)	17 (11)	16 (11)	−3 (6)
C(10′)	0.2875 (18)	0.4226 (09)	−0.0591 (10)	313 (35)	36 (7)	83 (9)	−20 (13)	−11 (14)	14 (7)

[a] The B_{ij}'s are the thermal parameters in the expression: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. Estimated standard deviations are given in parentheses.

Table III. Hydrogen Atom Positional and Temperature Parameters and Carbon–Hydrogen Bond Lengths

Atom[a]	x/a	y/b	z/c	B, Å^2	C–H distance, Å
H(2)	0.1887	−0.3510	0.0643	9.3	1.14
H(3)	0.0663	−0.3720	−0.1112	2.3	0.98
H(4)	0.0518	−0.2112	−0.1880	5.2	0.87[b]
H(7a)	0.3972	−0.0797	0.0332	3.6	1.24
H(7b)	0.2064	−0.0325	0.0572	4.5	0.89
H(10a)	0.3605	−0.1936	0.1224	9.3	0.67
H(2′)	0.4067	0.3766	0.1075	2.2	1.00
H(3′)	0.4639	0.2357	0.1792	4.1	1.13
H(4′)	0.3544	0.0916	0.0930	9.9	1.09
H(6′)	0.1339	0.1088	−0.2272	9.2	1.12
H(7′)	0.1940	0.2773	−0.1953	9.5	0.77
H(10′a)	0.2924	0.4712	−0.0207	6.4	0.91
H(10′b)	0.1720	0.4176	−0.0897	4.0	0.97
H(10′c)	0.3857	0.4267	−0.1059	4.0	1.01
H(5a)[c]	0.1966	−0.0683	−0.2180	7.0	
H(5b)[c]	0.0174	−0.0347	−0.1602	7.0	
H(6)[c]	0.3929	−0.0114	−0.1119	7.0	
H(10b)[c]	0.2896	−0.2709	0.1613	7.0	
H(10c)[c]	0.2015	−0.1658	0.1662	7.0	

[a] The σ ranges for the refined H atoms were $x/a = 0.0113 - 0.0201$, $y/b = 0.0064 - 0.0119$, $z/c = 0.0061 - 0.0110$, $B = 2.2$–4.4 Å^2, and C–H distance = 0.09 − 0.17 Å. [b] The C(3)–C(4)–H(4) and C(8)–C(4)–H(4) angles were 153.6 ($\sigma = 7.5°$) and 85.8° ($\sigma = 10.1°$). [c] Calculated hydrogen positions assuming tetrahedral angles and a C–H distance of 1.02 Å.

Therefore, the molecule had been "separated" across the C(6)–C(5′) bond and the two halves refined independently and consecutively. For example, one "cycle" of refinement consisted of a cycle on iodine + A with B fixed, followed by refinement of B with the parameters output from the preceding cycle (on iodine + A) fixed. A few of the bond lengths were inconsistent (*e.g.*, the N(1)–C(9) bond was 1.31 Å) and deviated from accepted values (they were, however, within 3σ of these values). Two more complete cycles of refinement (hydrogens included as fixed atoms), in which *ca.* 75% of the parameters were varied in each cycle, produced a marked change in some bond lengths (up to *ca.* 0.03 Å). All significant parameter changes were made in the first cycle and in all cases the final shifts were less than the respective standard deviations.[18] The final R factor was 0.044. Two further cycles of isotropic refinement on the fourteen hydrogens[19] produced no change in R. Coordinates and temperature factor data for the nonhydrogen atoms are given in Table II. The hydrogen parameters are shown in Table III.

All refinement was done by least squares using the full matrix of the normal equations and a weighting scheme patterned after that suggested by Hughes.[20] A value of 50.0 chosen for $4F_{\min}$ (the F_o scale factor was at the time 6% larger than that finally obtained) gave weights ranging from 0.22 to 1.0. All reflections for which $w||F_o| - |F_c|| \geqslant 5.0$ were automatically weighted zero by the least-squares program. This amounted to 48 data on calculations using the final atomic parameters. Unobserved reflections were given $w = 1.0$ if $|F_c| \geqslant |F_o|$ and $w = 0$ if $|F_c| < |F_o|$. Forty-two of the 424 unobserved data had $|F_c| \geqslant |F_o|$. Surprisingly, there was no tendency for F_o to be consistently smaller than F_c for large values of the structure factors and this may be interpreted as evidence for the absence of secondary extinction effects. Such effects would be expected to be less important for Mo Kα than for Cu Kα radiation. The final R factor was 0.044 for 1114 observed data.

The scattering factors used were the following: C and N, Berghius, *et al.*[21]; H, Stewart, *et al.*[22]; I, Cromer.[23] All calculations were done using scattering curves appropriate for iodine (53 electrons). Two further cycles of anisotropic refinement using those for iodide ion (54 electrons) produced only negligible parameter changes. No corrections for dispersion were applied.

All calculations were performed on an IBM 7094 computer using programs which are part of X-RAY 63.[15]

Results and Discussion

In most structural determinations by X-ray diffraction, the molecular skeleton, atom types, and single and multiple bond positions are known beforehand. A comparison of observed bond lengths and angles with representative values from known compounds is standard procedure. However, we shall have to follow a reverse path and use measured bond lengths and angles and molecular geometry to deduce bond types. Bond length and angle data are given in Figure 4.

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(18) The minimum, average, and maximum shift/σ ratios were 0.0016, 0.1628, and 0.6479, respectively.

(19) These were the hydrogens located from the difference map. The remaining five calculated hydrogen positions were not refined.

(20) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(21) J. Berghius, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(22) R. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(23) D. T. Cromer, *Acta Cryst.*, 18, 17 (1965).

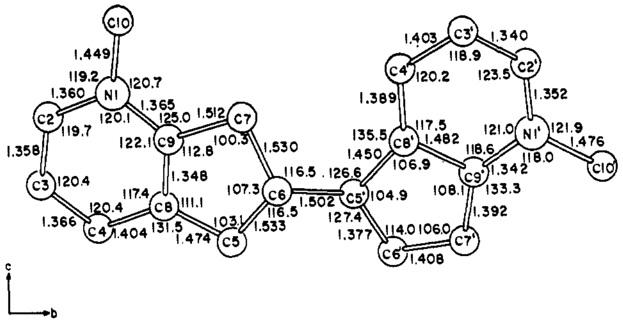

Figure 4. View of a molecule down the *a* axis showing bond lengths (Å) and angles (°). Estimated standard deviations in the bond lengths and angles are 0.014–0.019 Å. and 0.6–1.0°, respectively.

The positions of the two nitrogen atoms have been previously discussed and are well established. Planarity of the 6-ring of A and its three substituents (C(5), C(7), and C(10); see Table IV) and bond lengths in the ring (average 1.367 Å, range 1.348–1.404 Å) are evidence for sp^2 hybridization of the 6-ring atoms and electron delocalization. The N(1)–C(2) and N(1)–C(9) bond lengths (1.360 and 1.365 Å), C–C distances (average 1.369 Å), and associated angles (average 120.0°, range 117.4–122.1°) are in good agreement with similar parameters in heterocyclic molecules. These values may be compared with C–N bond lengths of 1.352 (average of several compounds)[24] and 1.37 Å (pyridine[25] and pyridinium dicyanomethylide[26]), C–C lengths of 1.39 (pyridine[25] and pyridinium reineckate[27]) and 1.38 Å (picolinic acid hydrochloride[28]), and angles of 120° in cyclic aromatic systems.

Table IV. Least-Squares Plane[a] of Nine Atoms in A
$6.9635x - 2.6794y - 4.7427z = 2.1849$

Atom	Deviation, Å
N(1)	−0.010
C(2)	0.002
C(3)	−0.001
C(4)	−0.007
C(5)	0.014
C(7)	−0.018
C(8)	−0.003
C(9)	0.014
C(10)	0.011
C(6)[b]	0.358

[a] The plane was calculated according to the method of V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959). [b] Not included in the plane calculation.

The 5-ring of A can be best described as "cyclopentenyl." The four bonds not in common with the 6-ring (C(5)–C(8), 1.474 Å; C(5)–C(6), 1.533 Å; C(6)–C(7), 1.530 Å; C(7)–C(9), 1.512 Å) are definitely single in agreement with this designation. In addition, the assignment is supported by the observed 0.36-Å deviation of C(6) from the least-squares plane[29] through the four other atoms in the ring. A puckering of this magnitude would be unlikely in a five-atom ring having more than one double bond. The C(5)–C(8) and C(7)–C(9) distances are a little shorter than the other two as would be expected for C(sp^3)–C(sp^2) bonds (1.510, 1.505 Å)[30] when compared to C(sp^3)–C(sp^3) bonds (1.533 Å).[31] Pauling[32] has predicted a shortening for the C–N$^+$ distance of *ca.* 0.03 Å from that of a similar, neutral C–N bond. The C(10)–N(1) distance (1.449 Å) is in good agreement with the prediction (the normal C–N(sp^2) distance is *ca.* 1.47 Å).[33]

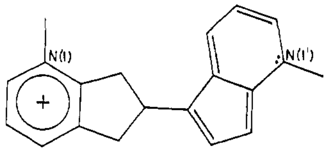

Figure 5. The organic skeleton showing the nitrogen atoms and the pattern of unsaturation.

The three main structural features of A can be summarized as (1) an aromatic 6-ring containing one nitrogen; (2) a cyclopentenyl ring fused to the 6-ring; (3) a methyl substituent attached to the nitrogen atom. On this basis, the 6-ring is pyridinium (positively charged) and A is a 6-substituted 1-methyl-1-azoniaindan ion (see Figure 5).

The empirical formula of the compound ($C_{18}H_{19}N_2I$) deduced by Ammon and Anderson[11] minus the elemental composition of A ($C_9H_{11}N$) leaves C_9H_8N for B. This information, coupled with the observed molecular skeleton, provides evidence that B is a 5-substituted 1-methyl-1H-1-pyrindine (see Figure 5). The hypothesis is adequately substantiated by bond lengths and angles and group planarity.

The bonds in B, divided into four groups, are shown in Table VI. Bond lengths in groups 1 (C–N) and 2 (C–C) are characteristic of aromatic systems, and the latter agree well with those found in azulenes. Robertson, Shearer, Sim, and Watson[34] obtained peripheral C–C lengths of 1.382–1.413 Å for azulene, a 1.37–1.41-Å range was observed for similar bonds in 2-aminoazulene by Takaki, Sasada, and Nitta,[35] and a mean of 1.395 Å was found for these distances in a 1:1 azulene-*sym*-trinitrobenzene complex by Hanson.[36]

The extremes shown by the two distances in group 3 are a cause for concern (even though their average is 1.395 Å). However, two points should be taken into consideration: (1) errors in these lengths make differences from some of those in group 2 barely significant; (2) the formally written structure for a 1H-1-pyrindine (see **3**) makes the 2–3 and 5–8 bonds double and single, respectively.

The bond shown in group 4 is perhaps the most interesting of all. It is the transannular bond between

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(24) "Tables of Interatomic Atomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958, p S17.

(25) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).

(26) C. Bugg and R. L. Sass, *Acta Cryst.*, **18**, 591 (1965).

(27) Y. Takeuchi and R. Pepinsky, *Z. Krist.*, **109**, 29 (1957).

(28) A. Laurent, *Acta Cryst.*, **18**, 799 (1965).

(29) The equation of the plane is $6.9868x - 2.5947y - 4.6555z = 0.1825$. Deviations (Å) of the four atoms from the plane are 0.01 (C(5)), −0.01 (C(7)), −0.01 (C(8)), and 0.01 (C(9)).

(30) "Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement 1956–1959," The Chemical Society, London, 1965, p S15s.

(31) L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3497 (1959).

(32) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1945, p 170.

(33) Reference 30, p S19s.

(34) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).

(35) Two-dimensional work: Y. Takaki, Y. Sasada, and I. Nitta, *J. Phys. Soc. Japan*, **14**, 771 (1959).

(36) A. W. Hanson, Abstracts, American Crystallographic Association Meeting, June 1965, p. 65.

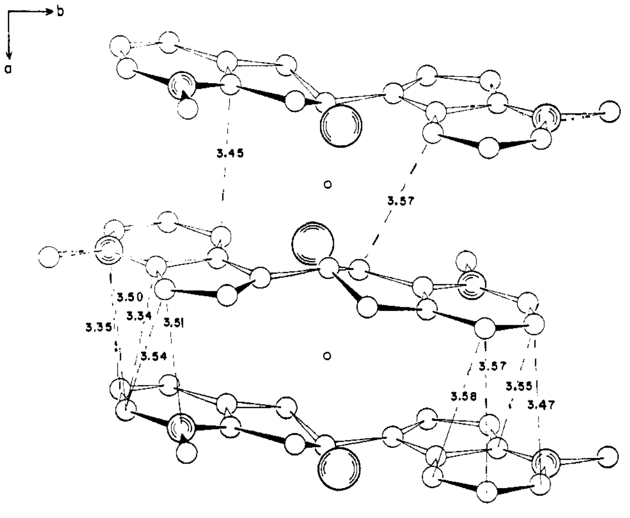

Figure 6. View of three molecules in a direction perpendicular to the *ab* plane. Some of the shorter distances (Å) between enantiomorphs are shown.

the 5- and 6-rings and is significantly longer than the peripheral bonds. A close agreement is found with the same bond in azulene[34] (1.483 Å), azulene-*sym*-trinitrobenzene complex[36] (1.498 Å), and 2-aminoazulene[35] (1.52 Å) and with C(sp^2)-C(sp^2) single bonds (1.477 Å).[37] The length of this bond is important experimental support for the hypothesized similarity between azulene and its π-excessive heterologs.

Table V. Least-Squares Plane of the Ten Atoms in B
$7.0271x - 0.6794y - 5.1010z = 1.7878$

Atom	Deviation, Å
N(1′)	−0.001
C(2′)	−0.001
C(3′)	0.001
C(4′)	−0.022
C(5′)	0.025
C(6′)	0.007
C(7′)	−0.039
C(8′)	0.020
C(9′)	−0.014
C(10′)	0.025

Table VI. Four Groups of Bond Lengths in the Two Rings of A[a]

Group	Bond	Length, Å	
1	C(2′)-N(1′)	1.352	
	C(9′)-N(1′)	1.342	Av 1.347
2	C(3′)-C(4′)	1.403	
	C(4′)-C(8′)	1.389	
	C(5′)-C(6′)	1.377	Av 1.394
	C(6′)-C(7′)	1.408	
	C(7′)-C(9′)	1.392	
3	C(2′)-C(3′)	1.340	
	C(8′)-C(5′)	1.450	
4	C(8′)-C(9′)	1.482	

[a] The N-CH$_3$ bond, N(1′)-C(10′), is not included.

Additional evidence for the aromaticity of B is the planarity of all ten atoms (see Table V). Special emphasis should be given to the planarity (see Table VII) of N(1′) and its three substituents (C(2′), C(9′), C(10′)) as evidence for sp^2 hybridization of the nitrogen. As a result, the N lone pair (in a p-orbital) may strongly interact with the C p-orbitals, making a $4n + 2$ π-electron system possible.

Table VII. Least-Squares Planes of the Two Nitrogens and Their Respective Substituents

Atom	Deviation, Å
Ring A	
$6.9541x - 2.7526y - 4.7532z =$	-0.0837
N(1)	−0.015
C(2)	0.005
C(9)	0.005
C(10)	0.005
Ring B	
$7.0241x - 0.9200y - 5.0776z =$	1.6354
N(1′)	−0.003
C(2′)	0.001
C(9′)	0.001
C(10′)	0.001

The C(5′)-C(6) bond (1.502 Å, C(sp^2)-C(sp^3)) is normal for this bond type (1.510, 1.505 Å[30]). Surprisingly, C(6) is 0.28 Å out of the least-squares plane of B. C(5′) should have sp^2 hybridization and on this basis C(6) would also be expected to lie in the plane of B. Packing of the molecules, to be discussed later, along the *a* axis is undoubtedly responsible for this distortion. The nonplanarity of the three bonds to C(5′) could possibly be used as an indication of increased p-character in C(5′) and this may be, in part, responsible for the lengthening of C(5′)-C(8′). The N(1′)-C(10′) (N-CH$_3$) bond is normal.

The 5-ring of A is considerably puckered with C(6) 0.36 Å out of the least-squares plane of the other nine atoms. Nonbonded interactions between substituents on adjacent carbons are generally thought to be responsible for the deviations from planarity of cyclopentane and cyclopentene. Calculations of the C–C–C angle strain energy for a planar model of cyclopentene have been done by Bartlett and Rice[38] using fixed bond lengths of 1.34 (C(1)-C(2)), 1.50 (C(2)-C(3)), and 1.54 Å (C(3)-C(4)). A strain energy minimum of 3.2 kcal mole^{-1} was obtained for angles of 112.25° (C(1)-C(2)-C(3)), 104.25° (C(2)-C(3)-C(4)), and 107° (C(3)-C(4)-C(5)). It is interesting to note the similarity of these lengths and angles with those in the 5-ring of A.

The combination of a compound possessing an asymmetric atom (C(6)) and a centrosymmetric space group requires that the crystal structure contain both members of the enantiomorphic pair and that they be related by a center of symmetry. Each of the "halves" is internally planar (with the exception of C(6) in A) and the two are joined by the C(6)-C(5′) bond to form a molecule which is almost flat (the acute angle between the A and B planes is 8°). These crude planes are stacked approximately perpendicular to the *a* axis with the C(6)-C(5′) bond (the "long axis" of the molecule) in the direction of the *b* axis. The closest intermolecular approaches (for nonhydrogen atoms) are between enantiomorphs whose respective C(6)'s point away from the intervening center of symmetry (4.73

(37) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(38) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

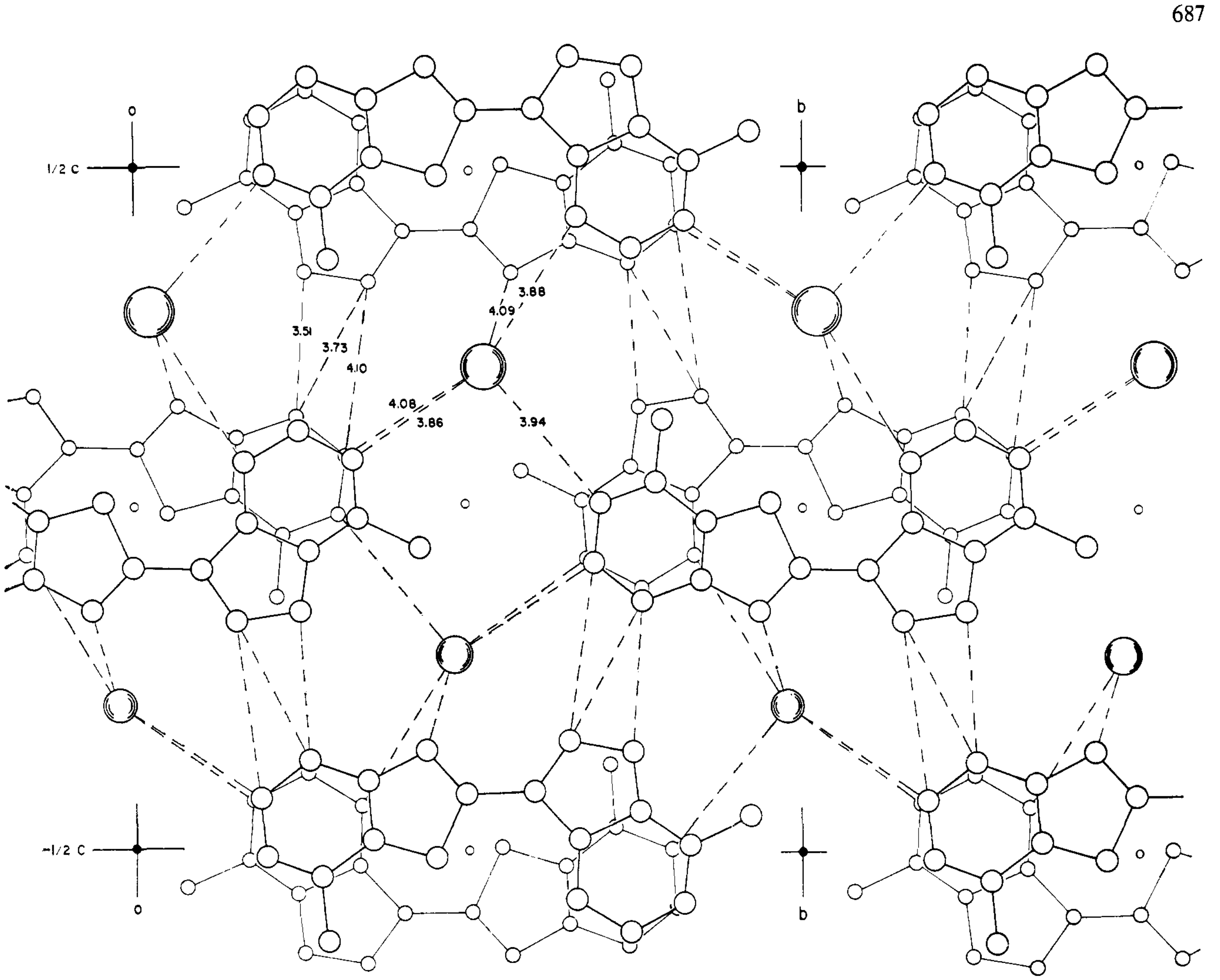

Figure 7. View of sections parallel to the *bc* plane showing some intermolecular distances (Å).

Å between these two atoms).[39] As might be expected, the enantiomorphs are arranged so that the positively charged 6-ring of A and neutral π-cloud of B in one are nearest respectively to the π-cloud of B and positively charged A in the other. The shortest approaches between the enantiomorphs are 3.35 ($C(3)_1$–$N(1')_2$[40]) and 3.34 Å ($C(2)_1$–$C(9')_2$) (and, of course, $C(3)_2$–$N(1')_1$ and $C(2)_2$–$C(9')_1$), the rest being normal for van der Waals separation between aromatic rings ("half-thickness" of 1.70 Å[41]).

As previously mentioned, C(6) is 0.28 Å out of the plane of B. If C(6) were to lie in the plane of B (to agree with the anticipated sp^2 hybridization of C(5′)), a molecule would result in which the A and B halves would be tilted (to form a "V") with respect to each other (even though the observed amount of pucker in the 5-ring of A would tend to make the halves parallel but offset). In such an arrangement, the rings in the respective enantiomorphs would no longer be parallel, causing a larger average intermolecular separation, and a good deal of electrostatic attraction, in the *x* direction, would be forfeited. Presumably the desirability of having an almost flat molecule to favor this interaction overshadows the strain introduced by deformation of the C(5′)–C(6) bond.

Operation of the unit translation along the relatively short *a* axis (7.476 Å) places another molecule so that the respective C(6)'s now point toward the intervening center of symmetry (4.43 Å between the two atoms). The shortest distance between molecules at $-x, -y, -z$ and $-1 + x, y, z$ is 3.45 Å (C(4′)–C(9)). The net effect of the center of symmetry and unit translation is to place a neutral 6-ring of B above and below each positively charged 6-ring of A and a + 6-ring of A above and below each 6-ring of B. The usual van der Waals forces between aromatic groups, augmented by additional electrostatic forces due to interaction of the + 6-ring in A with the π-cloud of B, are presumably responsible for this mode of packing along *a*. Figure 6 shows this interesting arrangement.

Operation of the 2_1 screw or *n* glide on the "original enantiomorphic pair" at $\pm(x, y, z)$ places another pair about the center at $^1/_2, ^1/_2, ^1/_2$. The members of the original pair are located at *ca.* $x = \pm ^1/_4$, and the net three-dimensional result of these symmetry elements is to place other molecules (related by a twofold axis (parallel to *b*) to the originals) in the same approximate planes as the originals but translated *ca.* $^1/_2$ in the *y* and *z* directions. The length of a molecule is such that the +6-ring of A in the molecule at $^1/_2 - x, ^1/_2 + y,$

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[39] The origin has been chosen so that the molecules at $\pm$ (x, y, z) are in this relationship.

[40] The subscripts refer to the different molecules.

[41] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

$^1/_2 - z$ is close to the 5-ring of B at x, y, z,[42] and symmetry requires that the 5-ring of B at $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$ have an identical, but opposite, relationship to the + 6-ring of A at x, $1 + y$, z. This arrangement forms zig-zag "ribbons," approximately perpendicular to a and in the direction of b (see Figure 7). They cut a at *ca.* $\pm ^1/_4$ and their widths extend from *ca.* 0 to $+^1/_2c$ ($-^1/_4a$) and 0 to $-^1/_2c$ ($+^1/_4a$). The "edges" of the "ribbons" are held together by van der Waals forces between molecules stacked along a.

The A and B "halves" are oriented so that C(5)–C(6′) and C(7)–C(8′) are *cis* to each other with respect to the C(6)–C(5′) bond. An equally good arrangement for electrostatic interaction in the x direction could be achieved by rotation of A 180° about the C(6)–C(5′) bond. C(5)–C(6′) and C(7)–C(8′) would then be *trans* to each other. The effect of such a rotation would be to maintain the same configuration but to exchange the position of C(4) and N(1)–C(10). In this arrangement, the overlap of the two nitrogens (N(1)$_1$ and N(1)$_2$) in the A's of an enantiomorphic pair with the 6-rings of the respective B's would be somewhat less than that observed. Increase of the overlap of the positive N's with the neutral 6-rings in this new arrangement may involve a decrease in the distances (and subsequent increase in nonbonded interactions) between C(5)$_1$–C(5′)$_2$ and C(5)$_1$–C(6)$_2$ (and, of course, C(5)$_2$–C(5′)$_1$ and C(5)$_2$–C(6)$_1$). Distances for the observed orientation in this area are 4.12 (C(6)$_1$–C(7)$_2$), 3.93 (C(5′)$_1$–C(7)$_2$), 3.17 (C(6)$_1$–H(7a)$_2$[43]), and 3.18 Å (C(5′)$_1$–H(7a)$_2$[43]). The position of C(10), however, would be quite different in the alternate configuration. Reference to Figure 7 shows that it is above (or below) the 5-ring of B in the enantiomorphic molecule and as such does not increase the "width" of the molecule in the z direction. In the new position, the methyl group would protrude in the opposite direction from that observed and would no longer be "under" or "over" the 5-ring of B. The effective width of an enantiomorphic pair in the z direction would thereby increase by an amount approximately equal to twice the length of the C(10)–N(1) bond. Strong nonbonded interactions resulting from this new position of C(10) would undoubtedly prevent the observed intermolecular arrangement along z and would require the molecules to pack in some more undesirable (energetically) manner.

The iodide ions are located in the relatively empty spaces (at *ca.* 0, $^1/_4$; $^1/_2$, $^1/_4$; 0, $^3/_4$ and $^1/_2$, $^3/_4$ in y and z) created by the zig-zag placing of the molecules in each of the ribbons. Some of the shorter intermolecular C–I contacts are shown in Figure 7. van der Waals forces between an iodide ion and atoms in each of the layers probably have little influence on the observed mode of packing. It would be interesting to examine the crystal structures with other anions. For example, chloride ion (smaller than iodide) would undoubtedly behave similarly, but the size of a perchlorate ion would either require a different arrangement of cations or a similar arrangement but with more intermolecular separation in the y and z directions.

The similar methods of preparation of **5** and **6** would suggest that the organic parts are the same and, therefore, the species observed by Reese[8] in solution is probably not **3a** but **6** (with Cl^- in place of I^-). In addition, it would seem unlikely that the "dimerization" to form **6** occurred in the basic treatment of **2** (**4**). Therefore, the material obtained by treatment of **1** with methyl iodide is probably not **2** but **6** plus the elements of HI (such a compound would have the identical empirical formula as **2**). These matters will be more fully discussed by Ammon and Anderson.[11]

Acknowledgment. We are indebted to Professor A. G. Anderson, Jr., for his constant interest and to Dr. M. Sundaralingam for much valuable discussion. We gratefully acknowledge support under USPHS Grant GM 10828 from the National Institutes of Health and wish to thank the University of Washington Computer Laboratory for a generous gift of machine time.

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[42] The three shortest distances are 3.51 (C(7′)$_1$–C(4)$_2$), 3.73 (C(6′)$_1$–C(4)$_2$), and 4.10 Å (C(6′)$_1$–C(3)$_2$).

[43] The H positions were calculated using 1.09 Å for the C–H distance.