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The Structure of *N*-Methylpyridinium Iodide

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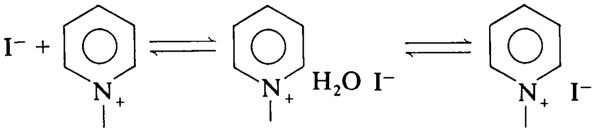
Abstract. C_6H_8IN, orthorhombic, $P2_12_12_1$, a = 7·744 (3), b = 8·541 (3), c = 12·045 (4) Å, V = 796·7 (5) $Å^3$. 1057 unique reflections were measured on an automatic diffractometer. The crystal structure was solved by the heavy-atom technique and Fourier maps, and refined by full-matrix least-squares methods to R = 0·066. The *N*-methylpyridinium ring is very planar with a N—I distance of 3·76 Å (out of plane) and C—I distances of 3·90 and 3·98 Å (in plane).

Introduction. *N*-Methylpyridinium iodide (NMPI) is a compound of which the long-wavelength UV spectral behavior in solution has been interpreted as arising from the formation of a charge-transfer complex (Kosower, 1955; Kosower & Burbach, 1956). In these laboratories we have conducted both experimental (Hemmes, Costanzo & Jordan, 1973, 1978) and theoretical studies (Jordan, 1975) aimed at the elucidation of the types of forces responsible for the complex formed. We have interpreted the experimental data (both thermodynamic and ultrasonic relaxation kinetic) to mean that there are two types of ion pairs present in solution:



solvent-separated and intimate ion pairs. The thermodynamic data collected on ionic association in this system as a function of solvent dielectric constant, as well as the results of the theoretical calculations, strongly suggested that the association process is driven predominantly by electrostatic forces. In addition, however, the theory employed (both STO-3G minimal basis set *ab initio* and CNDO/2) suggested that in the intimate ion-pair structure the Cl ion (employed instead of the I^- on account of the intractability of the *ab initio* approach on I^-) is not located on the twofold symmetry axis of the *N*-methylpyridinium ion, rather it is nearer to a C atom (the one adjacent to the N) with a very short C—Cl nonbonding contact of 2·3–2·5 Å. In order to better understand the system we resorted to a single-crystal X-ray determination of NMPI and here report the results of our studies.

A slightly elongated colorless crystal was selected from a batch of NPMI prepared by mixing equimolar amounts of methyl iodide and dry pyridine in an excess of dry acetone. Both the pyridine and acetone were dried over molecular sieves, as the NPMI is extremely hygroscopic. To prevent later absorption of water the crystal was immediately sealed in a glass capillary with epoxy cement. Preliminary Weissenberg and precession photograhs indicated an orthorhombic system. Examination of the $h0l$ and the $0kl$ layers taken with Cu $K\alpha$ radiation (Ni-filtered) produced the following systematic absences: in $h00$, $h = 2n + 1$; in $0k0$, $k = 2n + 1$; in $00l$, $l = 2n + 1$. These conditions uniquely determine the space group to be $P2_12_12_1$ and successful solution and refinement of the structure confirm this assignment.

A new crystal of dimensions 0·45 × 0·25 × 0·20 mm was sealed in a capillary with epoxy cement and was placed on a Syntex $P2_1$ computer-controlled automatic diffractometer where the cell parameters were obtained using 15 accurately centered reflections and Mo $K\alpha$ radiation (graphite-monochromatized). The temperature was 24 (1)°C. The calculated density assuming four molecules of molecular weight 221·04 per unit cell is 1·85 g cm^{-3}. Because of the extremely hygroscopic nature of the crystal an observed density was not obtained; however, a final difference map after refinement of the structure based on the four molecules described above indicated that all scattering matter in the cell had been accounted for.

Assuming the crystal to be a cylinder of radius 0·011 cm and $\mu = 39{\cdot}9$ cm^{-1} the absorption factor for $0 < \theta < 30°$ ranges from 1·95 to 1·92, a change of 1·5%; thus absorption corrections were considered unnecessary and were not applied. Intensity data were collected at 24 °C by the θ–2θ scan technique out to a maximum 2θ value of 60°. Three standard reflections were collected every 47 reflections throughout the data collection and showed variations of ±2·3% but no significant trends. All intensities collected were corrected for any variations by applying decay factors calculated from the standard-reflection intensities. A total of 1057 unique reflections with $I \geq 3\sigma(I)$ were collected out of a possible 1378. Thirty-one reflections were rejected on the basis of a profile scan (Glick, 1975). All reflections were then placed on an arbitrary scale by applying Lorentz and polarization corrections, and estimates of the overall scale and temperature factors were obtained by Wilson's method (Wilson, 1942).

The presence of an I atom (or I^- ion) prompted the use of the Patterson function (Patterson, 1935) as a means of obtaining initial phases for the subsequent electron density synthesis. Interpretation of the Patterson map by Harker analysis (Harker, 1936) produced coordinates for the I atom which produced an R_F value of 0·13 ($R_F = \sum||F_o| - |F_c||/\sum|F_o|$), indicating that the I itself is responsible for most of the structure factor magnitudes as well as their phases. This implied that the light atoms would be difficult to find and also to refine, because their contributions to the structure factors are minimal. This was not altogether unexpected since the ratio of the sum of the squares of the light-atom atomic numbers to the square of the I atomic number is 0·097 which is a full order of magnitude less than the optimum value of 1·00 for successful solution by the heavy-atom method (Woolfson, 1970). The situation was further complicated by the fact that the space group is noncentrosymmetric and therefore the inclusion of only one atom in a structure factor calculation would lead to phases which would reflect two images of the molecule: the correct image and the enantiomorph, with the two images intermixed, thus decreasing the probability of correctly identifying atoms which belong to only one enantiomorph.

Eventually a series of Fourier electron density maps revealed the structure of only one enantiomorph, but only after many false indications. After several cycles of full-matrix refinement (Busing, Martin & Levy, 1962), a difference map was calculated in an attempt to reveal hydrogen atom coordinates, but only one hydrogen atom could be located with reasonable certainty, thus the other seven hydrogen positions were calculated.

A weighting scheme was then determined by an analysis of variance (Lalancette, Cefola, Hamilton & La Placa, 1967) which set the $\sigma(i)$ values according to the following conditions: if $|F| < 22$, $\sigma(i) = -0{\cdot}1111|F| + 5{\cdot}43$; if $22 \leq |F| < 38$, $\sigma(i) = 0{\cdot}0261|F| + 2{\cdot}42$; if $38 \leq |F| < 54$, $\sigma(i) = -0{\cdot}0408|F| + 5{\cdot}03$; if $|F| \geq 54$, $\sigma(i) = 0{\cdot}043|F| + 0{\cdot}53$. The quantity minimized was $\sum_i w_i(|F_{oi}| - |F_{ci}|)^2$ where $w_i = 1/\sigma^2(i)$, F_{oi} = observed structure factor magnitude and F_{ci} = the calculated structure factor magnitude.

With the hydrogen atoms held invariant and assigned isotropic temperature factors of 4·0 Å^2, and all other atoms allowed anisotropic thermal motion, the refinement converged to values of $R_F = 0{\cdot}066$, $R_w = 0{\cdot}086$ $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$; the estimated standard deviation of an observation of unit weight = 1·44, and the scale factor = 2·78. The scale factor was found to be highly correlated with the I diagonal thermal parameters as evidenced by correlation coefficients of 0·614, 0·573 and 0·588 between the scale factor and $\beta_{11}, \beta_{22}, \beta_{33}$, respectively.

The atomic scattering factors for all non-hydrogen atoms were taken from the Dirac–Slater calculations of Cromer & Waber (1965); I ion scattering factors were used for the heavy atom. Hydrogen scattering factors as well as the anomalous scattering factors for I were obtained from *International Tables for X-ray Crystallography* (1962). Table 1 lists the final parameters from the least-squares refinement along with their estimated standard deviations.* A final difference Fourier map produced no peak larger than 0·76 e Å^{-3} near the site of the I atom.

Discussion. The structure was found to consist of an ionic network with each *N*-methylpyridinium ion interacting with two symmetry-related I ions. The two iodides form contact distances with the associated cation of 3·76 (1) and 3·90 (1) Å and lie approximately perpendicular to and in the plane of the cation respectively. All other iodide–cation interactions are greater than 4·0 Å (neglecting ring hydrogens). Bond distances and angles, along with their estimated standard deviations are provided in Table 2. Fig. 1 indicates the numbering sequence as well as illustrating the two close contacts. The equation of the best least-squares plane along with the atoms defining it and their respective distances from the plane are presented in Table 3. Distances are also given for the halogen positions relative to the plane of the cation.

Table 1. *Positional parameters* (× 10^4)

	x	*y*	*z*
I	2320 (1)	609 (1)	4470 (1)
N	4222 (15)	3139 (15)	8164 (9)
C(1)	3297 (24)	2801 (20)	7238 (14)
C(2)	1704 (27)	3376 (25)	7104 (18)
C(3)	978 (22)	4358 (24)	7927 (16)
C(4)	1962 (25)	4702 (24)	8853 (17)
C(5)	3577 (22)	4073 (21)	8961 (14)
C(6)	5944 (21)	2468 (22)	8313 (16)
H1(C6)	5900	1400	8750
H2(C6)	6541	2310	7586
H3(C6)	6692	3228	8771
H(C1)	3804	2131	6655
H(C2)	1018	3062	6437
H(C3)	−224	4816	7828
H(C4)	1479	5372	9437
H(C5)	4294	4353	9615

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33577 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *and angles* (°), *with their associated estimated standard deviations in parentheses*

N–C(1)	1·36 (2)	C(1) N C(5)	121 (1)
N–C(5)	1·34 (2)	C(1)–N–C(6)	120 (1)
N–C(6)	1·46 (2)	C(5)–N–C(6)	119 (1)
C(1)–C(2)	1·34 (3)	N–C(1)–C(2)	121 (2)
C(2)–C(3)	1·42 (3)	C(1)–C(2)–C(3)	120 (2)
C(3)–C(4)	1·38 (3)	C(2)–C(3)–C(4)	118 (2)
C(4)–C(5)	1·37 (3)	C(3)–C(4)–C(5)	120 (2)
		C(4)–C(5)–N	120 (2)

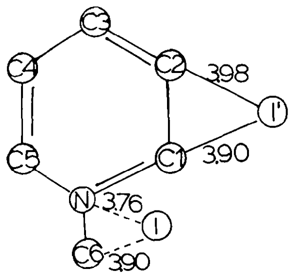

Fig. 1. Labelling scheme for NMPI. I′ (in the plane of the ring shown) and I (above the plane of the ring shown) are related by a screw axis. Distances indicated are in ångströms.

Table 3. *Equation of the plane*

Equation is of the form $AX + BY + CZ - D = 0$ where X, Y and Z refer to triclinic crystal coordinates.

A	B	C	D
3·0200	6·8053	−5·5598	−1·1344

Atoms defining the plane	Distance from plane (Å)	Atoms defining the plane	Distance from the plane (Å)
N	0·007	C(4)	0·004
C(1)	0·012	C(5)	0·005
C(2)	−0·003	C(6)	−0·012
C(3)	−0·012		

Distances of I′ and I to the pyridinium plane shown in Fig. 1 are 0·235 and 3·74 Å respectively.

It is found that the closest halide–ring atom distance is 3·76 (1) Å and is between an iodide ion (I) and the N atom. The halide is nearly perpendicular to the C_2 axis in the cation and is 3·73 Å above the plane of the ring approximately above the N but closer to C(1) than C(5). Secondary contacts involving this I^- are 3·90 (2) Å to C(6), and 3·99 (2) Å to C(1).

A symmetry-related iodide ion (I′) is found to make contacts of 3·90 (2) and 3·98 (2) Å with C(1) and C(2) respectively. This second I^- ion is found to lie 0·24 Å above the plane of the ring. Secondary contacts involving this I^- are 3·15 and 3·32 Å with H(C1) and H(C2) respectively. An alternative description of the cation–anion relationship in terms of the anion geometry requires each I ion to form short contacts of 3·76 and 3·90 Å with two symmetry-related pyridinium rings respectively. One of the rings would resemble a stacked configuration with respect to the halide, and the other would more resemble a planar system. The interactions are illustrated in Fig. 2 by way of a packing diagram.

With the comparable values of 3·76 and 3·90 Å, it is not clear which site on the ring bears the larger positive charge, the N atom or C(1); however, when one considers the standard deviations associated with each length, a difference of 14σ between the two candidates can only be interpreted one way: with the N more positive. On the other hand the extent of I^-—I^- repulsion in determining cation position relative to the anions is unknown. It may well be that I^-—I^- repulsion positions the iodides in the cell with cation rings merely filling in the gaps. Jordan (1975) pointed out that two negative charges at a distance of 12 Å from each other with −0·7 charge each (calculated by theory for the anion) would yield 6 kcal mol^{-1} repulsion.

CNDO/2 calculations (Pople & Segal, 1966) on *N*-methylpyridinium chloride (Jordan, 1975) indicate a halide position near C(1). Although the complex is still considered stacked, it is not believed to possess integral

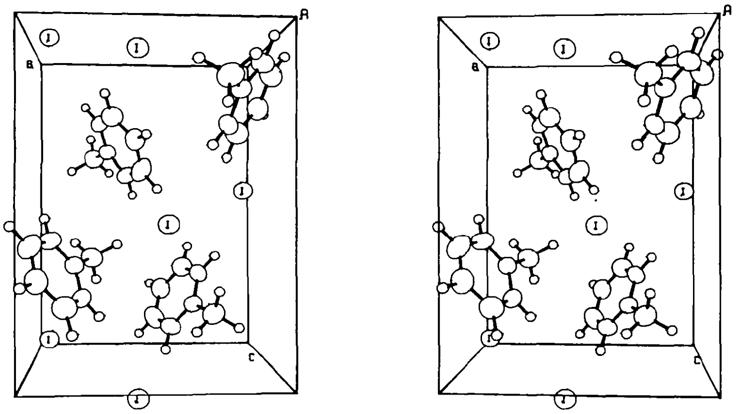

Fig. 2. *ORTEP* stereoscopic view of the unit cell and packing pattern; thermal ellipsoids are plotted at the 50% probability level except those for hydrogen atoms which are drawn as spheres of arbitrary radius.

charges as the minimum energy calculated corresponds to a structure some 100 kcal mol^{-1} more stable than the separated ions. The addition of the methyl group has the effect of making most atoms less positively charged, except at C(1) where the atom becomes more positively charged. This conceivably accounts for the short halide–C(1) distance as the attractive force is intensified.

The X-ray result is somewhat in agreement with the calculation in that a short halide–C(1) distance was obtained; however, this distance was not the shortest halide–ring contact. The current investigation is more in accord with the findings of Rérat (1962) on pyridine hydrochloride, with halide–N distances representing short contacts. It should be pointed out that the distances of 3·76 and 3·90 Å, while significantly different, are not different enough to conclude that any single interaction dictates the cation–anion relationship. The I^- to ring distances correspond approximately to the mean ionic radius calculated from the thermodynamic data (*ca* 4–5 Å, Hemmes *et al.*, 1978). As nucleophilic substitution in the gas phase is more favored than in solution, the short Cl^- to ring distances found by theory (Jordan, 1975) perhaps approximate the structure of an intermediate for nucleophilic substitution rather than a ground-state ion pair.

Programs used were of local origin and also included the following: refinement of cell dimensions, Syntex program; Fourier synthesis, Zalkin's (1962) *FORDAP*; hydrogen calculations, Shiono's *GENATM*; lengths and angles, the Busing, Martin & Levy (1964) program *ORFFE*; plotting, Johnston's (1970) *ORTEP* II thermal ellipsoid plotting program.

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6,7-Dihydro-6,6-dimethylbenzofurazan-4(5*H*)-one Oxime

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Abstract. $C_8H_{11}N_3O_2$, monoclinic, $P2_1/n$, $a = 6{\cdot}048$ (2), $b = 12{\cdot}934$ (1), $c = 11{\cdot}565$ (1) Å, $\beta = 92{\cdot}59$ (2)°, $Z = 4$, $D_c = 1{\cdot}33$ g cm^{-3}, m.p. 193–194 °C. The furazan ring is planar and nearly coplanar with the oxime group which is *anti* to the ring, as in the two related furoxan isomers.