An Ionic Organic Charge-transfer Complex, 1-Ethyl-2-methylquinolinium Iodide, and its Structure

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IN connection with studies on charge-transfer complexes in general,[1] and 1-ethyl-2-methylquinolinium iodide in particular, the crystal structure of the latter compound has been determined by means of X-ray crystallography.

The crystal is monoclinic, with unit cell dimensions $a = 7{\cdot}18_7$, $b = 15{\cdot}91_4$, $c = 10{\cdot}33_1$ Å, and $\beta = 94{\cdot}6_7°$; $Z = 4$, $D_c = 1{\cdot}68_7$ g. cm.$^{-3}$, and space group: $P2_1/c$. The three-dimensional intensity data were collected by a Rigaku computer-controlled four-circle single-crystal X-ray diffractometer with Mo-K_α radiation. The crystal structure

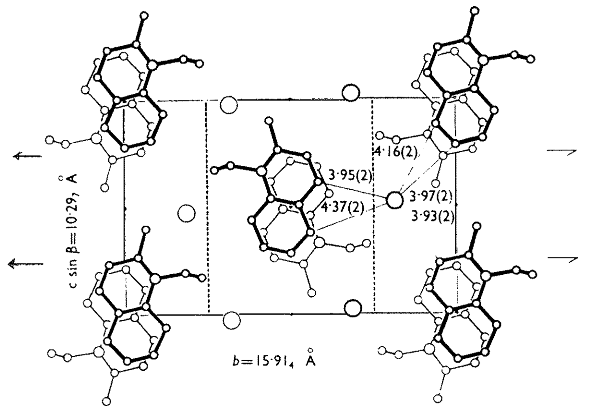

FIGURE 1. *Crystal structure of* 1-*ethyl*-2-*methylquinolinium iodide.* (*Projected along the* a *axis. Estimated standard deviations are given in parentheses.*)

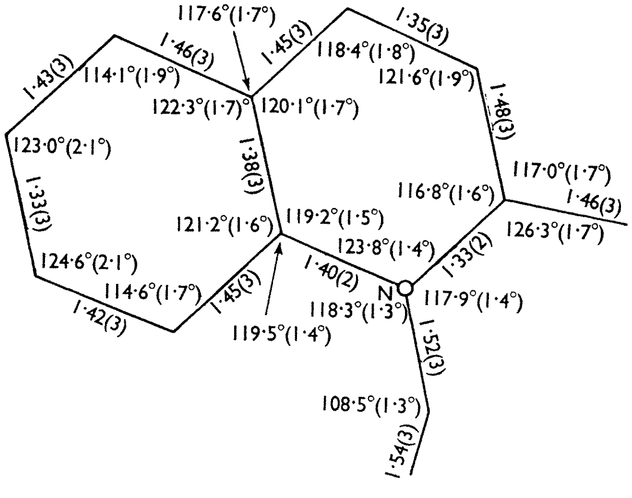

FIGURE 2. *Bond lengths and angles* (*and e.s.d.*) *in the* 1-*ethyl*-2-*methylquinolinium cation.*

was solved by the heavy-atom method, from 1841 observed reflections. The position, and thermal parameters, of each atom except hydrogen were refined by the block-diagonal least-squares method ($R = 0{\cdot}074$, 5 cycles).

The view along the *a* axis of the structure is shown in Figure 1. In non-polar solvents, such complexes presumably exist in the form of ion pairs, with an iodide ion in the plane of the *N*-hetero-aromatic ring cation.[2] In the crystal, however, anions and cations lie roughly in a plane. Each iodide ion is surrounded by three cations. The planar 1-ethyl-2-methylquinolinium cations are stacked approximately parallel to the *a* axis, forming an endless column. Interplanar spacings of these cations along the column are alternately 3·4 and 3·6 Å, which seem to be usual van der Waals contacts. Iodide ions are located in the spaces between these columns and the ethyl groups of the cations. The shortest distance between an iodide ion and carbon atoms of an 1-ethyl-2-methylquinolinium ring is 3·93 Å (Figure 1).

The absorption spectrum ($CHCl_3$) showed a new shoulder band ($\lambda_{max} = 365$ nm., $\epsilon = 2450$) in addition to the absorption of component ions. This is attributed to charge transfer from the iodide ion to the 1-ethyl-2-methylquinolinium cation, since it disappears in polar solvents such as water or ethanol at the same concentration; this behaviour was also observed with *N*-hetero-aromatic iodides.[3] The yellowish green colour of this complex in the solid state seems to be related to the charge transfer. The wavelength dependence of photo-conduction in this complex (single crystal) showed that the peak of the response is located at the long-wavelength tail of the charge-transfer band.[4]

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[4] H. Mikawa, S. Kusabayashi, and R. Matsuyama,, unpublished data.