An Organic Charge-transfer Salt, *N*-Methylacridinium Iodide: Crystal and Molecular Structure

By KEN'ICHI NAKAMURA, NORITAKE YASUOKA, NOBUTAMI KASAI,* and HIROSHI MIKAWA
(*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka*, 564, *Japan*)

and MASAO KAKUDO
(*Institute for Protein Research, Osaka University, Joancho, Kita-ku, Osaka*, 530, *Japan*)

Summary The crystal structure of an organic charge-transfer salt, *N*-methylacridinium iodide has been determined by *X*-ray structure analysis.

MANY N-heteroaromatic iodides, when dissolved in non-polar solvents, give new absorption bands which are attributed to electronic charge-transfer from the iodide anion to the N-heteroaromatic cation within an ion-pair.[1,2]

We have already reported preliminary results of *X*-ray analyses of 1-ethyl-2-methylquinolinium iodide (EMQI)[3] and quinolinium 2-dicyanomethylene-1,1,3,3-tetracyanopropanedi-ide.[4] We report here the structure of a compound similar to EMQI, *N*-methylacridinium iodide (NMAI), determined by means of an *X*-ray diffraction study, in which an iodide anion and an *N*-methylacridinium (NMA) cation form an ion-pair. The structure of the ion pair in the crystal is of particular interest in connection with that in solution.

The red crystals of NMAI, recrystallized from an ethanol solution, are triclinic, space group $P\bar{1}$; $a = 8{\cdot}38(1)$, $b = 10{\cdot}34(2)$, $c = 7{\cdot}47(1)$ Å, $\alpha = 91{\cdot}27(1)$, $\beta = 99{\cdot}01(1)$, and $\gamma = 105{\cdot}26(1)^\circ$, $V = 618{\cdot}93$ Å^3; $D_m = 1{\cdot}74$, $D_c = 1{\cdot}72$ g cm^{-3} for $Z = 2$. The three-dimensional intensity data were collected by the multi-film equi-inclination Weissenberg method using Cu-K_α radiation, and estimated visually. The structure was solved by the use of the Patterson function, and refined by the Fourier and least-squares procedures ($R = 0{\cdot}085$ for 1692 non-zero reflections).

The NMAI crystal consists of ion pairs, and the structure of the ion pair projected on the ring plane is shown in the Figure. Some short interatomic distances between an iodide anion and the NMA ring are 3·75(2) [I–C(1)] and

3·78(2) Å (I–N). The iodide anion is located approximately above the mid-point of the C(1)–N bond. Such ion-pairs are stacked parallel along the *c* axis to form a crystal.

In the crystal of tropylium iodide, which also gives a charge-transfer band in solution,[5] the iodide anion is located above the centre of the tropylium ring.[6] For 1-alkylpyridinium iodide, Kosower[1] suggested the existence of a structure similar to that of tropylium iodide, where the iodide anion is in contact with a 1-alkylpyridinium ion, with the line joining the centres of charge perpendicular to the plane of the ring. In NMAI, the iodide anion is above the C–N bond. This fact may support Kosower's suggestion, and such a structural feature may be explained as due to the polarity of the C–N bond and also to an effect of the methyl group bonded to the nitrogen atom in the NMA cation.

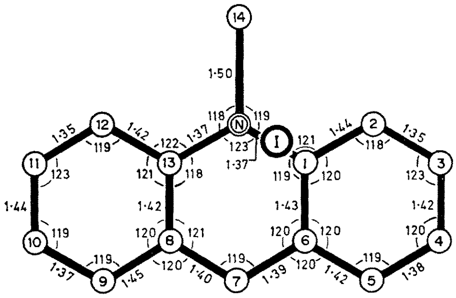

FIGURE. *Structure of the ion pair. E.s.d.'s in bond distances and bond angles are* 0·03 Å *amd* 2°, *respectively.*

The red colour of the NMAI crystal seems to be related to charge transfer, while EMQI has a yellowish-green colour. EMQI does not have an ion-pair structure; planar cations are stacked parallel, forming an endless column, along the *a* axis and the iodide anions occupy the interstices between these columns. The shortest interatomic contact between anions and cations in EMQI is 3·93(2) Å (I–C). Such differences between structural features of NMAI and EMQI, which suggest a stronger charge-transfer interaction in NMAI than in EMQI, probably depend upon the difference in electron affinity between these two kinds of N-heteroaromatic cations.

(*Received, July* 6*th*, 1970; *Com.* 1082.)

---

[1] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261, 3267.

[2] S. F. Mason, *J. Chem. Soc.*, 1960, 2437.

[3] S. Sakanoue, Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, and H. Mikawa, *Chem. Comm.*, 1969, 176; *Bull. Chem. Soc. Japan*, 1970, **43**, 1306.

[4] S. Sakanoue, N. Yasuoka, N. Kasai, M. Kakudo, S. Kusabayashi, H. Mikawa, and H. Kuroda, *Bull. Chem. Soc. Japan*, 1969, **42**, 2408.

[5] K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Amer. Chem. Soc.*, 1962, **84**, 3349.

[6] A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin, and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, 32.