The Crystal Structure of an Organic Charge Transfer Salt, $[2(C_9H_8N)^+ \cdot (C_{10}N_6)^{2-}]$

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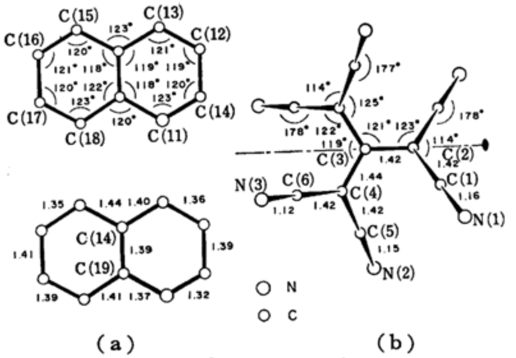
The crystal of quinolinium 2-dicyanomethylene-1,1,3,3-tatracyanopropanediide, $[2(C_9H_8N)^+ \cdot (C_{10}N_6)^{2-}]$, is orthorhombic with the unit cell dimensions of $a=13.18$, $b=15.40$, $c=11.56$ Å; $Z=4$, $D_m=1.31_8$, and $D_c=1.31_4$ g/cm^3, and with the space group *Pbcn*. The intensities of 2003 reflections were measured visually from the multiple-film equi-inclination Weissenberg photographs taken with nickel-filtered Cu*Kα* radiation around the *a* and *c* axes. The structure was solved by the symbolic addition, phase-determining procedure developed by Karle and Karle.1) The $\sum_2$ formula was applied to 247 reflections with $|E| \geqq 1.60$. After six cycles, the signs of 161 reflections were determined; the *E*-map based on these signs allowed us to locate all the non-hydrogen atoms. The positional and thermal parameters of each atom were refined by the block-diagonal least-squares method ($R=15.2\%$).

Figure 1 shows the structures of the anion and the cation. The $(C_{10}N_6)^{2-}$ anion in this crystal has a C_2-2 symmetry instead of the C_3-3 symmetry (or approximately D_3-32) found in crystals of the hexahydrated calcium salt.2) The four central carbon atoms are exactly co-planar. The three cyano-substituents, $-C(CN)_2$ are, however, tilted out of this plane, and the anion takes a propeller-shape. The one arm which lies on the 2-fold axis is rotated by 13° from the completely planar conformation, the other two being 24°. On the other hand, in the calcium salt2) the three angles of tilt are all 24°. The decrease in the angle from 24° to 13° may be due to weak interaction between the anion and the cation. The bond distances and angles in the anion are similar to those found in the calcium salt. The quinolinium cation is co-planar within the limits of experimental error.



(a) (b)

Fig. 1. Structure of component ions.
(a) Quinolinium cation, $(C_9H_8N)^+$
(b) 2-Dicyanomethylene-1,1,3,3-tetracyanopropane anion, $(C_{10}N_6)^{2-}$
(Estimated standard deviations in distances are 0.013−0.02Å, and those in angles are 0.83−1.4°.)

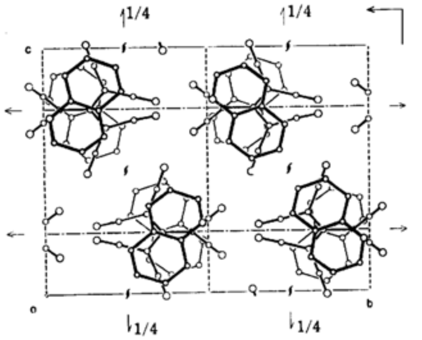


Fig. 2. Crystal structure of $[2(C_9H_8N)^+ \cdot (C_{10}N_6)^{2-}]$ projected onto the (010) plane.

Figure 2 shows the projectional view along the *a* axis. The packing unit consists of one di-anion and two mono-cations, and the anion lies on a 2-fold axis between two identical cations forming a sandwich. The N(1)–N(11) distance is 3.00 Å, which is the closest atomic contact between ions in this unit. These units stack infinitely along the *a* axis. In the contacts between these stacks along the *b* axis, a hydrogen bond exists between the N(3) of one unit and the N(11) of the other unit; the distance is 2.84 Å. The other intermolecular contacts are almost comparable with the sum of the van der Waals radii.

These results are interesting compared with the structures of other charge-transfer salts, 1-ethyl-2-methylquinolinium iodide3) and tropylium iodide.4)

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1) For example, J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849, (1966).

2) D. A. Bekoe, P. K. Gantzel and K. N. Trueblood, *ibid.*, **22**, 657, (1967).

3) S. Sakanoue, Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo and H. Mikawa, *Chem. Commun.*, **1969**, 176.

4) A. I. Kitaigorodskii, Yr. T. Struchlov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **1**, 32, (1960).