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The Electronic Spectra of the Anion Radical Salts Derived from 2,3-Dicyano-1,4-naphthoquinone

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Much attention has been paid to solid-ion-radical salts,[1-3] because the ion-radical molecules form, in themselves, a plane-to-plane stacking into columns so as to make a large overlap between their half-filled molecular orbitals.[4] In this case, since any individual radical molecule interacts through charge transfer most strongly with one or two other radicals, the electronic spectrum of the solid salt was found to be different from the monomer spectrum of the radical anion in solution and to show an intermolecular charge-transfer band in the low-energy region.[2,3] In this respect, it was interesting to examine the solid-state spectra of the anion-radical salts of 2,3-dicyano-1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[3]

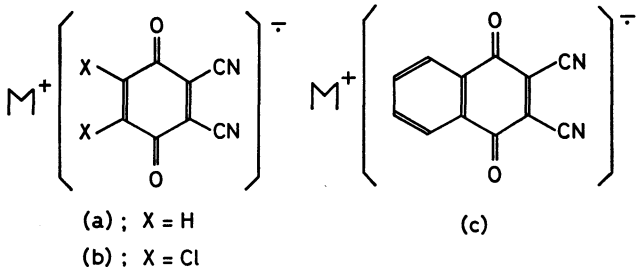

Fig. 1. The anion radical salts of (a) 2,3-dicyano-1,4-benzoquinone, (b) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and (c) 2,3-dicyano-1,4-naphthoquinone (DCNQ). M^+ represents a diamagnetic counter cation.

The present paper will describe the solid-state spectra, as well as the absorption spectra in solution, of some stable anion-radical salts derived from 2,3-dicyano-1,4-naphthoquinone (DCNQ). The following anion-radical salts were prepared according to the method of Reynolds and VanAllan[5]: Na^+ $DCNQ^-$, K^+ $DCNQ^-$, Rb^+ $DCNQ^-$, and Cs^+ $DCNQ^-$. The purpose of this paper is to show that the charge-transfer interaction between the DCNQ anion radicals also takes place in these solid anion-radical salts. It is interesting that the data indicate that the manner of the charge-transfer interaction is similar to those in the 2,3-dicyano-1,4-benzoquinone anion-radical salts.[3]

The Absorption Spectra in Solution

The absorption spectra of the anion-radical salts in an acetonitrile solution were measured at room temperature. The measurements were made at concentrations of the order of 1×10^{-4} mol/*l*, using a Beckman DK-2A spectrophotometer.

All of the DCNQ anion-radical salts dissolved in an acetonitrile solution appear red, and are quite

1) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963); R. G. Kepler, *ibid.*, **39**, 3528 (1963).

2) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968); Y. Iida, *ibid.*, **42**, 71, 637 (1969); Y. Iida, *ibid.*, **43**, 2772 (1970); Y. Iida, *ibid.*, **44**, 663 (1971); Y. Iida, *ibid.*, **45**, 105 (1972).

3) Y. Iida, *ibid.*, **44**. 1777 (1971).

4) C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 892 (1966); C. J. Fritchie, Jr., and P. Arthur, Jr., *ibid.*, **21**, 139 (1966); P. Goldstein, K. Seff, and K. N. Trueblood, *ibid.*, **B24**, 778 (1968); J. Tanaka and N. Sakabe, *ibid.*, **B24**, 1345 (1968); H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, *ibid.*, **B26**, 459 (1970).

5) G. A. Reynolds and J. A. VanAllan, *J. Org. Chem.*, **29**, 3591 (1964).

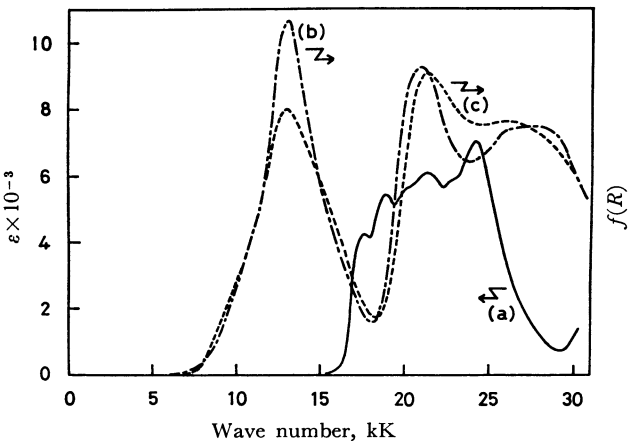

Fig. 2. The electronic spectra of the 2,3-dicyano-1,4-naphthoquinone (DCNQ) anion radical salts; (a) the absorption spectrum of K^+ $DCNQ^-$ in an acetonitrile solution, (b) the solid-state spectrum of Na^+ $DCNQ^-$ and (c) the solid-state spectrum of K^+ $DCNQ^-$.

stable at room temperature. As an example, the absorption spectrum of K^+ $DCNQ^-$ in an acetonitrile solution is reproduced in Fig. 2, Curve (a). It has absorption peaks at 17.6 kK and 18.8 kK, a peak at 21.3 kK with a shoulder around 20.3 kK, and a high-energy band at 24.1 kK with a slight shoulder around 22.7 kK. The spectrum does not change even when the counter cation of the salt is replaced. Since the concentrations are so dilute, the salts seem to be completely dissociated. The obtained spectrum is that of the DCNQ anion radical monomer, because the counter cations of the salts are simple alkali-metal cations.

The Solid-state Spectra

The electronic spectra of the solid DCNQ anion-radical salts were measured by the diffuse-reflection technique. The diffuse-reflection spectra were recorded on a Beckman DK-2A spectroreflectometer in the range from 4.0 kK to 30.8 kK at room temperature. The solid-state spectra were then obtained by plotting the diffuse-reflection spectra using the Kubelka-Munk equation, $f(R)=(1-R)^2/2R$, in which R is the reflectance. The experimental details were the same as those presented in previous papers.[2,3]

All of the DCNQ anion-radical salts were obtained as dark green polycrystals, and all were quite stable at room temperature.

The solid-state spectrum of Na^+ $DCNQ^-$ (Fig. 2, Curve (b)) shows a strong absorption at 13.1 kK, a band at 20.9 kK, and a broad high-energy band around 27.8 kK. This spectrum was found to be quite different from the monomer spectrum of the DCNQ anion radical in solution. The band at 13.1 kK characteristic of the solid salt appears in the low-energy region, where the anion-radical monomer does not absorb. This band has no vibrational structures, and its intensity is remarkably strong. It cannot be assigned to the charge-transfer transition from the anion radical to the counter cation, since its maximum position is scarcely shifted when the counter cation of the salt is replaced (see below). Although, at present, no experimental data on the charge-transfer absorption in the dimer of the DCNQ anion radicals are available for purposes of comparison, the low-energy band at 13.1 kK seems to be attributable to the charge-transfer transition between the DCNQ anion radicals in the solid state. This assignment is analogous to those for the anion-radical salts of the cyano-substituted *p*-benzoquinones,[3] where the charge-transfer band of Na^+ 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone$^-$ has been reported to be located at 12.6 kK, while that of Na^+ 2,3-Dicyano-1,4-benzoquinone$^-$ is located at 10.7 kK with a shoulder around 14.3 kK.

The appearance of the strong charge-transfer band in Na^+ $DCNQ^-$ means that, in the solid state, the DCNQ anion radicals are stacked closely enough together for the half-filled molecular orbitals to make a large overlap. The DCNQ anion radicals seem to form, in themselves, a plane-to-plane stacking into columns; this feature of the crystal structure has also been found in a number of other ion-radical salts.[4] The charge-transfer absorption characteristic of the solid salt should be ascribed to the transition of the $\langle\cdots Q^-Q^-Q^-Q^-\cdots\rangle \rightarrow \langle\cdots Q^-Q^0Q^{2-}Q^-\cdots\rangle$ type, where Q denotes a quinone molecule. In this case, the π–π transitions of the DCNQ anion radical monomer will be perturbed in the field of the other anion radicals. This is shown as appreciable blue-shifts of the high-energy bands at 20.9 kK and 27.8 kK for the solid-state spectrum of Na^+ $DCNQ^-$, compared to the monomer absorptions of the DCNQ anion radical, shown in Fig. 2, Curve (a).

The solid-state spectra of K^+ $DCNQ^-$, Rb^+ $DCNQ^-$, and Cs^+ $DCNQ^-$, although the intensities of the low-energy charge-transfer bands depend slightly on the species of the counter cations, were found to be very similar to that of Na^+ $DCNQ^-$. As an example, the solid-state spectrum of K^+ $DCNQ^-$ is given in Fig. 2, Curve (c). Hence, the electronic structure in the solid DCNQ anion radical salts and the charge-transfer interaction between the DCNQ anion radicals are scarcely affected even though the counter cations of the salts are replaced in the present investigation. It is interesting to note that this situation coincides well with that previously reported for the cyano-substituted *p*-benzoquinone anion-radical salts.[3]