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Complex Anion Radical Salts Derived from Dicyanomethylenetrinitrofluorene

Yoshio MATSUNAGA and Yuji YOSHIDA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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Synopsis. Four anion radical salts of the 2 : 3 type were derived from 9-dicyanomethylene-2,4,7-trinitrofluorene. Their electronic spectra, the ESR spectra characteristic of triplet excitons, and the electrical properties were measured.

9-Dicyanomethylene-2,4,7-trinitrofluorene (DTF) has been known to form anion radical salts with a number of onium cations.[1,2] All the cations so far examined have given salts of the 1:1 type. However, Dupuis and Néel have reported the isolation of 1,2,3-trimethylbenzimidazolium salts not only of the 1:1 type, but also of the 1:2 type.[2] In addition, they have noted that the salts prepared by the reduction of DTF with onium iodides tend to include an excess of DTF, which could be eliminated by repeated recrystallizations from acetonitrile. Consequently, it seemed highly likely that some complex anion radical salts could be obtained if the preparation conditions and the cations were appropriately selected.

As has been described by Mukherjee and Levasseur,[1] DTF was prepared by a condensation reaction between 2,4,7-trinitrofluorenone, Eastman reagent-grade, and malononitrile in methanol, and was then recrystallized from acetonitrile. The anion radical salts were obtained by mixing DTF and the onium iodide, separately dissolved in hot acetonitrile, in a mole ratio of 3:2 under a nitrogen atmosphere. The mole ratio employed by Dupuis and Néel was reversed here in order to attempt the isolation of possible complex salts. The greenish-black products were recrystallized two or three times from acetonitrile. Although we examined a number of cations, only the following four complex salts could be isolated (two independent preparations were analysed for each salt). With tetrapropylammonium, Found: C, 59.19, 58.93; H, 4.90, 4.91; N, 16.18, 15.85%. Calcd for $[(C_3H_7)_4N]_2(DTF)_3$: C, 59.13; H, 4.89; N, 16.28%. With tetrabutylammonium, Found: C, 60.81, 60.68; H, 5.89, 5.77; N, 14.28, 13.63%. Calcd for $[(C_4H_9)_4N]_2(DTF)_3$: C, 61.02; H, 5.57; N, 15.12%. With propyltriphenylphosphonium, Found: C, 62.28, 63.68; H, 3.51, 3.45; N, 11.83, 12.19%. With isopropyltriphenylphosphonium, Found: C, 63.07, 63.26; H, 3.56, 3.48; N, 11.89, 12.03%. Calcd for $[C_3H_7(C_6H_5)_3P]_2(DTF)_3$: C, 63.57; H, 3.50; N, 12.36%. The composition was checked by measuring the ratio of optical density at 515 nm to that at 380 nm, following Dupuis and Néel. The optical density at the former wavelength arises solely from the anion, but that at the latter, from both the anionic and neutral species. Dupuis and Néel have found that the ratio is about 0.64 in the 1 : 1 salt and 0.34 in the 1 : 2 salt. The values observed with our salts were in the range from 0.42 to 0.48, and so seemed to be consistent with the proposed composition.

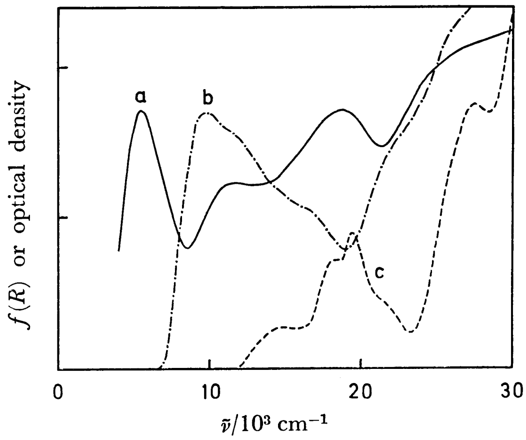

Fig. 1. Diffuse reflection spectra of (a) isopropyltriphenylphosphonium-DTF(2 : 3), (b) lithium-DTF (1 : 1), and (c) absorption spectrum of the DTF$^-$ ion in acetone.

The solid-state spectra of the four salts, as recorded on a Beckman DK-2A spectroreflectometer, are similar to each other. In Fig. 1, the spectra of the isopropyltriphenylphosphonium salt and the simple lithium salt, plotted using the Kubelka-Munk function, are compared with the absorption spectrum of the latter dissolved in acetone. The band around 5.5×10^3 cm^{-1} appears in all the solid complex salts and may be assigned to the charge-transfer transition from the highest occupied level of the DTF anion to the lowest vacant level of the DTF molecule. The second band, located near 11×10^3 cm^{-1}, observable also with the simple salt, may arise from the charge-transfer interaction between the anions.

In the ESR spectra of the present salts taken at the X-band, the appearance of three pairs of resonance lines characteristic of triplet-spin excitons was noted in the temperature range from 30 to 120 °C. No change in the separation of the pair was detected in the measured range; however, the collapse of the inner two pairs by broadening was observed at the highest temperature employed. For the sake of simplicity, an isotropic g value was assumed to be equal to the free electron value; then, the principal axis splittings are related to the zero-field splitting parameters, D and E, by the following equations:

$$d_1 = 2|D/g\beta|,$$
$$d_2 = |D/g\beta| + 3|E/g\beta|,$$
$$d_3 = |D/g\beta| - 3|E/g\beta|,$$

where d_i is the measured separation and β is the Bohr magneton. The numbering, i, is given starting from

Table 1. Zero-field splitting parameters and singlet-triplet separation energies of the complex anion radical salts derived from dicyanomethylenetrinitrofluorene

Cation	$\lvert D/g\beta \rvert$ /G	$\lvert E/g\beta \rvert$ /G	J/eV
Tetrapropylammonium	99.5	2.2	0.31
Tetrabutylammonium	97.8	3.9	0.42
Propyltriphenylphosphonium	98.3	3.7	0.28
Isopropyltriphenylphosphonium	95.2	3.4	0.32

the outermost pair of resonance lines. The estimated parameters are summarized in Table 1. The magnitude depends on the average spatial distribution of the correlated spins of the exciton. When the spins interact strongly, the parameters may be expected to increase. The values of $|D/g\beta|$ in our salts, 95—99 G, are close to those in the complex TCNQ salts of the 2:3 type, 100 G, while the simple TCNQ salts are known to give values of 140—170 G, and the complex salts of the 1:2 type, about 70 G.³⁾ Thus, one may be led to the conclusion that the spins in the DTF salts are as delocalized as those in the TCNQ salts and are more delocalized than those in the anion radical salts derived from 2,3-dicyano-1,4-naphthoquinone studied earlier.⁴⁾ Taking the peak height or the peak-to-peak intensity on the first derivative curve as a measure of the relative intensity of the ESR absorption for a triplet state, I, the following approximation was found to be well-obeyed;

$$I \times T \propto \exp(-J/kT),$$

where J is the energy for the singlet-triplet separation. The energies listed in Table 1 are comparable with the values for the dicyanonaphthoquinone salts. The absence of any appreciable exciton-exciton exchange in the DTF salts is consistent with such large separation energies.

The electrical resistivities, ρ, observed with polycrystalline compactions were in the order of 10^4 or 10^5 ohm cm at room temperature. These values are close to those reported by Dupuis and Néel for their simple DTF salts containing aromatic counter ions with large polarizabilities.⁵⁾ The temperature-dependence recorded employing the potential-probe method described before⁶⁾ does not fit in with the usual exponential law, $\rho=\rho_0 \exp(E/kT)$. The increase at high temperatures was found for the tetrabutylammonium and propyltriphenylphosphonium salts. Such behavior is not unexpected when the conduction is extrinsic in the measured range, but the impurity concentration is low. The intrinsic resistivities of the present complex anion radical salts at room temperature may be higher by a factor of tens or hundreds than the observed values.

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