# Simple and Complex Anion-radical Salts Derived from 2,3-Dicyano-1,4-naphthoquinone

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Simple and complex anion-radical salts were prepared by the reduction of 2,3-dicyano-1,4-naphthoquinone with a number of onium iodides. The simple salts are green-colored, and the complex salts, with a composition of 1 : 2, are dark green or brown. The latter salts show electronic absorptions extending into the near-infrared region. The electrical resistivities are rather high—— $10^7$—$10^{12}$ ohm cm in the simple salts and $10^3$—$10^7$ ohm cm in the complex salts. The ESR spectra characteristic of triplet excitons were observed with polycrystalline samples, and the zero-field splitting parameters and the singlet-triplet separation energies were estimated for most of the salts. The anion-radicals appeared to be in strong pair-by-pair interactions in these salts.

Extensive studies have been carried out on the synthesis and physical properties of the anion-radical salts derived from 7,7,8,8-tetracyanoquinodimethane (TCNQ); however, little attention has been paid to the possibility of finding new series derived from compounds other than TCNQ. So far, only the following compounds have been reported to form series of the onium salts: 9-dicyanomethylene-2,4,7-trinitrofluorene and -2,4,5,7-tetranitrofluorene,[1,2] 3,3′,5,5′-tetrachloro-4,4′-diphenoquinone (TCDQ), its bromo analogue (TBDQ),[3] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[4] Continuing our search for highly-conducting anion-radical salts,[3] we worked on the preparation of a new series based on 2,3-dicyano-1,4-naphthoquinone, hereafter abbreviated as DCNQ. This quinone has an electron-acceptor strength comparable with that of *o*-bromanil in terms of their complexing properties,[5,6] and it is readily reduced to the semiquinone anion by the use of the iodide ion. The solid-state spectra of some alkali salts have been described by Iida of our laboratory.[7] The anion-radical salts formed with most of the onium ions were of a 1 : 1 composition, and the complex salts, when available, were not always well-defined. Moreover, the electrical resistivities of this series were found to be discouragingly high. Nevertheless, the recent report by Gordon and Hove on triplet excitons in the four tetraalkylammonium salts of the DDQ anion-radical, which is the only other anion-radical after TCNQ which exhibits this behavior, prompted us to do a little more work and to publish the results.

## Experimental

*Materials.* 2,3-Dicyano-1,4-naphthoquinone was prepared by the procedures reported by Reynolds and VanAllan or by Wallenfels *et al.* starting from 2,3-dichloro-1,4-naphthoquinone,[8,9] Eastman yellow label. The crude product was purified by recrystallization from toluene and then by sublimation *in vacuo*. The anion-radical salts were obtained by the reduction of the quinone dissolved in acetone with an appropriate onium iodide. All the cations employed were diamagnetic, and their iodides were taken from the stock prepared for our earlier work.[3] The precipitated salt was filtered and washed with a small amount of acetone. The salts are fairly soluble in this solvent. The composition was determined by microanalysis.

*Measurements.* The electrical resistivities of compressed polycrystalline samples were examined by means of a Wheatstone bridge (Yokogawa Electric Works, Type 2768) employing a cell similar to that designed by LaFlamme.[10] The electronic spectra of the solid salts in the region from 325 to 25000 nm were measured with a Beckman DK-2A spectroreflectometer. The pulverized sample was diluted with sodium chloride in concentrations of the order of 1 weight percent in order to obtain a reasonable reflectance. The spectra were recorded as the difference in reflectance between the mixture and pure sodium chloride and were plotted using the Kubelka-Munk function $f(R)=(1-R)^2/2R$, where $R$ is the reflectance. The ESR measurements were carried out by means of a JEOL model JES-ME-3X spectrometer in the temperature range from room temperature to 100 °C. The magnetic field scan was calibrated with $Mn^{2+}$-doped MgO powder (86.9 G).

## Results and Discussion

The twenty-five DCNQ anion-radical salts for which the compositions could be established by microanalysis are listed in Table 1. They are of a 1 : 1 composition unless otherwise stated. The onium cations employed in the present series include ammonium, phosphonium, arsonium, quinolinium, and acridinium. The resistivities of the simple salts range from $10^7$ to $10^{12}$ ohm cm, and those of the complex salts, from $10^3$ to $10^7$ ohm cm. Thus, complex salts are apparently more conducting than the simple salts, in agreement with the tendency well-established for TCNQ anion-radical salts.[11,12] However, the resistivity values, especially those of the complex salts, are appreciably greater than those of TCNQ salts and also those of the TCDQ and TBDQ salts prepared by us.

All the simple DCNQ salts are dark green, and the solid-state spectra are similar to each other. For example, Fig. 1 presents the spectra of the morpholinium and methyltriphenylphosphonium salts. They consist of three bands, located at 12.9, 20.4, and $26.3\times10^3$ cm$^{-1}$, and at 14.8, 20.0, and $27.6\times10^3$ cm$^{-1}$, respectively. Although the locations are somewhat different, the other salts including the sodium salt show essentially the same pattern. The band maxima are listed in Table 1. The low-energy bands are found in the region from 12.9 to $15.1\times10^3$ cm$^{-1}$; the middle bands, in the

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Table 1. Electrical resistivities and electronic absorption bands of the anion-radical salts derived from dicyanonaphthoquinone

| Cation | Resistivity (ohm cm) | Band maxima ($10^3$ cm$^{-1}$) |
|---|---|---|
| Sodium | $7\times10^7$ | 13.3, 22.8, 26.3 |
| Dibenzylammonium | $3\times10^{11}$ | 13.3, 21.1, 25.7 |
| Ethyldibenzylammonium | $1\times10^{10}$ | 13.2, 22.2, 25.3 |
| *n*-Propyl-dibenzylammonium | $1\times10^{10}$ | 13.5, 21.5, 25.0 |
| Morpholinium | $1\times10^9$ | 12.9, 20.4, 26.3 |
| *N*-Methylmorpholinium | $4\times10^9$ | 13.1, 21.1, 25.3 |
| *N*-Ethylmorpholinium | $4\times10^9$ | 13.2, 20.8, 26.3 |
| *N*-*n*-Propylmorpholinium | $4\times10^9$ | 13.1, 20.8, 26.3 |
| Methyltriphenyl-phosphonium | $1\times10^{10}$ | 14.8, 20.0, 27.6 |
| Ethyltriphenylphosphonium | $1\times10^{10}$ | 14.8, 20.0, 27.5 |
| *n*-Propyltriphenyl-phosphonium | $3\times10^{10}$ | 14.8, 20.0, 26.3 |
| Methyltriphenylarsonium | $2\times10^{12}$ | 14.7, 19.8, 27.0 |
| Ethyltriphenylarsonium | $1\times10^{10}$ | 15.1, 19.5, 27.0 |
| 4-Methylquinolinium | $2\times10^{10}$ | 13.7, 20.4, 27.4 |
| *N*-Ethyl-4-methyl-quinolinium | $4\times10^{10}$ | 12.9, 21.0, 26.0 |
| *N*-*n*-Propyl-4-methyl-quinolinium | $1\times10^8$ | 13.5, 20.0, 26.7 |
| *N*-*n*-Propylisoquinolinium | $6\times10^8$ | 13.8, 20.5, 29.3 |
| Acridinium | $4\times10^9$ | 12.9, 22.2, 28.6 |
| *N*-Ethylacridinium | $8\times10^8$ | 14.0, ——, 28.2 |
| Di-*n*-propylammonium (1:2) | $5\times10^7$ | 8.9, 14.1, 20.7, 24.4 |
| Methyldi-*n*-propyl-ammonium (1:2) | $2\times10^7$ | 8.7, 14.1, 22.2, 25.0 |
| Ethyldi-*n*-propyl-ammonium (1:2) | $1\times10^7$ | 8.8, 13.5, 22.0, 24.1 |
| Tri-*n*-propylammonium (1:2) | $1\times10^7$ | 9.1, 13.8, ——, —— |
| *N*-Ethylquinolinium (1:2) | $7\times10^3$ | $<$4.0, —, 21.1, $>$30.0 |
| Isoquinolinium (1:2) | $1\times10^4$ | 4.8, 14.3, 20.5, 29.0 |

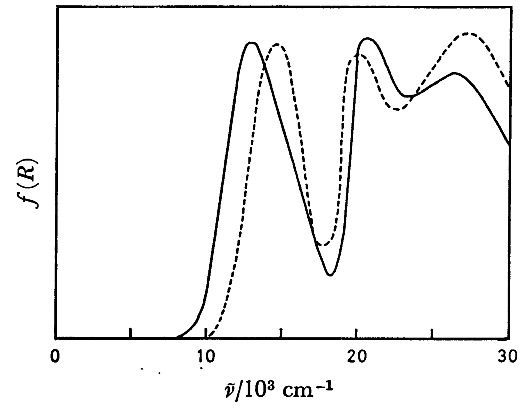

Fig. 1. Diffuse reflection spectra of the simple DCNQ salts containing morpholinium ion (——) and methyltriphenylphosphonium ion (------).

region from 19.5 to $22.8\times10^3$ cm$^{-1}$, and the high-energy bands, in the region from 25.0 to $29.3\times10^3$ cm$^{-1}$. The last location may be affected by the absorption due to the counter ion. In the case of the *N*-ethylacridinium salt, the middle band could not be determined clearly because of its breadth. These radical salts are supposed to contain columns of the semiquinone ions, which may be in an essentially pair-by-pair or more-than-by-pairs interaction. Although Iida did not identify the type of interaction in the alkali salts,$^{7)}$ the observation of the triplet exciton ESR to be described later indicates that the pattern in Fig. 1 arises from the former interaction.

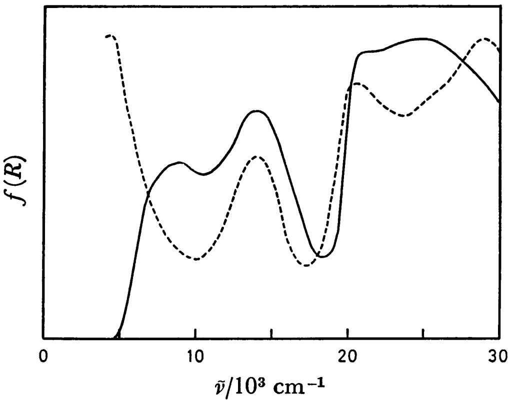

Fig. 2. Diffuse reflection spectra of the complex DCNQ salts containing tri-*n*-propylammonium ion (——) and isoquinolinium ion (------).

The complex ammonium salts are dark green, and the quinolinium salts are brown. As is shown in Fig. 2, the spectra of the complex tri-*n*-propylammonium and isoquinolinium salts consist of four bands; therefore, the whole pattern looks like the pattern of the simple salts, with an "additional" band in the near-infrared region. The location of this band depends greatly upon the kind of the onium ion. The bands in the four ammonium salts are located at energy values nearly twice as high as those in the *N*-ethylquinolinium and isoquinolinium salts. In accordance with LeBlanc's postulate that aromatic counter ions with large polarizabilities are effective in producing low resistivities of anion-radical salts,$^{13)}$ the latter two may be said to be about one thousand times more conducting than the former four. The tendency for the energy of the lowest-energy band to be less as the resistivity is lower is also roughly observed in the TCDQ and TBDQ anion-radical salts studied earlier.$^{3)}$ When the band shifts to a lower energy, the intensity becomes relatively higher than that of the second low-energy band. Thus, the maximum of the latter band in the most conducting *N*-ethylquinolinium salt is not observed in the spectrum. The lowest-energy absorption may be ascribed to the interaction between the DCNQ anion-radical and the neighboring DCNQ molecule, which are possibly stacked together to form a column. However, the correlation between the location of the absorption band and the resistivity suggests that the interaction is not strictly limited within such a pair.

Although the results of microanalysis were far from the values calculated for any composition, the DCNQ salts with the following cations appeared to be not simple: methyldibenzylammonium, isopropyltriphenylphosphonium, *N*-methylquinolinium, *N*-methyl-4-methylquinolinium, *N*-methylisoquinolinium, *N*-ethylisoquinolinium, and *N*-methylacridinium. The resistivity values of the first two are of the orders of $10^6$ and $10^4$ ohm cm respectively, while those of the rest of the order of $10^3$ ohm cm. These values are too low to be considered as those of the simple salts, but they fit into the range shown by the six complex salts given in Table 1. All the salts except the methyldibenzylammonium salt are dark brown in color. The spectral patterns are also characteristic of the complex salts mentioned above. The lowest-energy band in the ammonium salt is located at $7.7\times10^3$ cm$^{-1}$, and that of the phosphonium salt, at $5.8\times10^3$ cm$^{-1}$. The absorption maxima in the other salts are beyond the limits of the spectrophotometer employed—namely, below $4\times10^3$ cm$^{-1}$.

Würster's blue perchlorate and various TCNQ anion-radical salts have been known to exhibit ESR spectra from triplet spin excitons.[14–19] When a polycrystalline sample is employed for the measurement, the triplet character of the paramagnetic excitations is best manifested by the appearance of three pairs of resonance lines.[4,19] They correspond to the three principal axis splittings, which result from an anisotropic zero-field splitting of the triplet levels caused by the dipole-dipole interaction of the two electrons. All the above-mentioned salts are apparently of the class in which each radical interacts strongly with only one other free radical,[20] and they are known to exhibit rather high electrical resistivities.[16] It seems very likely that the DCNQ anion-radical salts belong mostly to such a class also. Indeed, the ESR spectra characteristic of triplet excitons could be observed with all the salts having resistivity values of $10^7$ ohm cm or higher.

TABLE 2. ZERO-FIELD SPLITTING PARAMETERS AND SINGLET-TRIPLET SEPARATION ENERGIES OF THE ANION-RADICAL SALTS DERIVED FROM DICYANONAPHTHOQUINONE

| Cation | $\|D\|$ (gauss) | $\|E\|$ (gauss) | $\Delta E$ (eV) |
|---|---|---|---|
| Sodium | 111 | 8 | 0.20 |
| Dibenzylammonium | 236 | 19 | 0.35 |
| Ethyldibenzylammonium | 222 | 23 | 0.41 |
| *n*-Propyldibenzylammonium | 225 | 21 | 0.33 |
| Morpholinium | 238 | 20 | 0.44 |
| *N*-Ethylmorpholinium | 232 | 20 | 0.43 |
| Methyltriphenylphosphonium | 239 | 22 | 0.41 |
| Ethyltriphenylphosphonium | 234 | 19 | 0.45 |
| *n*-Propyltriphenylphosphonium | 231 | 21 | 0.41 |
| Methyltriphenylarsonium | 238 | 23 | 0.47 |
| *N*-Ethyl-4-methylquinolinium | 211 | 18 | 0.33 |
| *N*-*n*-Propyl-4-methylquinolinium | 241 | 25 | 0.37 |
| *N*-Ethylacridinium | 226 | 20 | 0.41 |
| Di-*n*-propylammonium (1: 2) | 206 | 18 | 0.43 |
| Methyldi-*n*-propylammonium (1: 2) | 165 | 13 | 0.14 |
| Ethyldi-*n*-propylammonium (1: 2) | 203 | 17 | 0.47 |
| Tri-*n*-propylammonium (1: 2) | 207 | 18 | 0.38 |

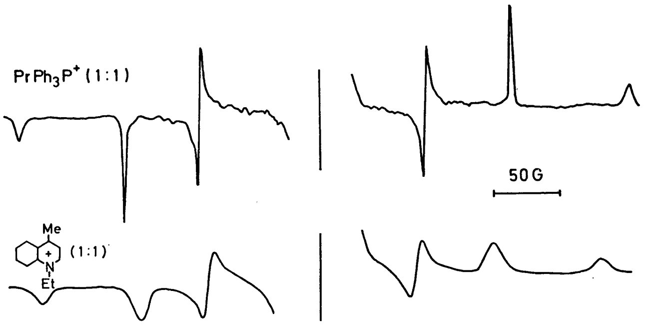

Fig. 3. First derivatives of ESR absorption spectra of the simple *n*-propyltriphenylphosphonium and *N*-ethyl-4-methylquinolinium DCNQ salts.

The triplet spectrum, particularly the outermost pair, is very weak at room temperature, and the salt starts to decompose between 80 and 110 °C; therefore, the measurements could be made only in a limited temperature range. No change in the shape and separation of the pair was detected in such a narrow range. For example, Fig. 3 shows the polycrystalline powder spectra of the *n*-propyltriphenylphosphonium and *N*-ethyl-4-methylquinolinium salts. The former spectrum was recorded at 80 °C, and the latter, at 70 °C. The central line, which may be attributed to impurities or lattice imperfections, is several orders of magnitude stronger than the triplet spectrum and becomes broader as the temperature is raised. Assuming, for the sake of simplicity, an isotropic $g$ value equal to the free electron value, the principal axis splittings are related to the zero-field splitting parameters, $D$ and $E$, by the following equations:[20]

$$d_1 = 2|D|$$
$$d_2 = |D| + 3|E|$$
$$d_3 = |D| - 3|E|,$$

where $d_i$ is the measured separation. The numbering is given starting from the outermost pair of resonance lines. The parameters may be expressed in terms of the spatial distribution of the correlated spins of the triplet excitons. The values of $D$ and $E$ for seventeen salts, including four complex ones, are summarized in Table 2. Among the salts here, the outermost pairs in the ethyl- and *n*-propyl-dibenzylammonium salts were too weak to be accurately located, even at the highest temperature examined, 90 °C. Consequently, only the values of $d_2$ and $d_3$ were used to estimate the parameters. In addition to the salts given in Table 2, we observed the triplet spectra with the *N*-methyl- and *N*-propylmorpholinium and acridinium salts; however, these spectra were so poor that no assignment of the resonance lines could be made with confidence.

The spectra of the complex salts are exemplified by the methyldi-*n*-propylammonium and tri-*n*-propylammonium salts presented in Fig. 4. They were recorded at 30 and 80 °C respectively. The magnitude of the parameters depends on the size of exciton, which in turn may be expected to depend on the composition of the salt. As a matter of fact, both the zero-field splitting parameters in the simple TCNQ salts are about twice as large as those of the complex salts of a 1: 2 composition, while those of a 2: 3 composition come between them.[19] Nevertheless, the difference found with the DCNQ salts is not appreciable at all. We can see that the parameters in the complex salts are

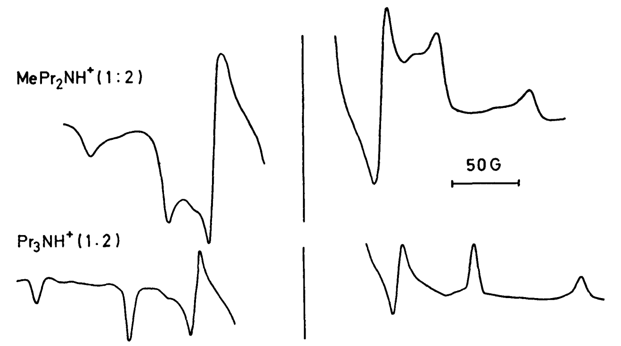

Fig. 4. First derivatives of ESR absorption spectra of the complex methyl di-*n*-propylammonium and tri-*n*-propylammonium DCNQ salts.

only slightly less than those in the simple salts. This observation may imply that the DCNQ anion-radicals in a column do not alternate with the molecules. The repeating unit might be approximated by $(DCNQ)^0$-$(DCNQ)^-$$(DCNQ)^-$$(DCNQ)^0$, which is analogous to a tetrad of TCNQ established by the structural analysis of triethylammonium $(TCNQ)_2$.[21] Except for the sodium and methyldi-*n*-propylammonium salts, all the salts have $D$ values over 200 gauss and $E$ values of about 20 gauss. Gordon and Hove have reported that the $D$ parameter of their tetrapropylammonium DDQ salt, 231 gauss, exceeds the largest value ever recorded for the linear-chain radical salts, that is, 215 gauss for $[TMPD^+]_2[Ni(nmt)_2]^{2-}$, where TMPD is *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine and where nmt is the dinegative *cis*-1,2-dicyanoethylene-1,2-dithiolate anion, studied earlier by the same author.[20] The $D$ parameter in many of the DCNQ salts matches the value in the DDQ salts or is even larger. Both the simple and complex DCNQ salts undoubtedly belong to the class of ion-radical salts with strong pair-by-pair interactions.

The integrated intensity of the ESR absorption for a triplet state is given by:

$$I \propto T^{-1}[\exp(\Delta E/kT)+3]^{-1},$$

where $\Delta E$ is the energy for the singlet-triplet separation. As the shape remains the same through the measured temperature range, the peak-to-peak intensity on the first derivative curve was taken as a measure of $I$. Because the separation energy was expected to be larger than $kT$, the following approximation was employed in the present work:

$$I \times T \propto \exp(-\Delta E/kT).$$

Plots of log $IT$ in arbitrary unit *versus* $1/T$ give straight lines, as is demonstrated by the five salts shown in Fig. 5. The open and shaded circles represent the data taken from different pairs. The separation energies of the DCNQ salts also listed in Table 2 are generally larger than those observed with the four DDQ salts (0.19—0.30 eV) and are comparable with the value for the simple morpholinium TCNQ salt reported by Jones and Chesnut (0.41 eV) and also with that reported by Bailey and Chesnut (0.36 eV).[17,18] In this TCNQ salt, the exciton creation energy is so high that, at accessible temperatures, the exciton concentration is too low to enable one to observe any appreciable exciton-exciton exchange.[15,17] Moreover, the resistivity at room temperature has been reported to be as high as $10^9$ ohm cm.[11,12] This feature is quite similar to that of most of the DCNQ salts.

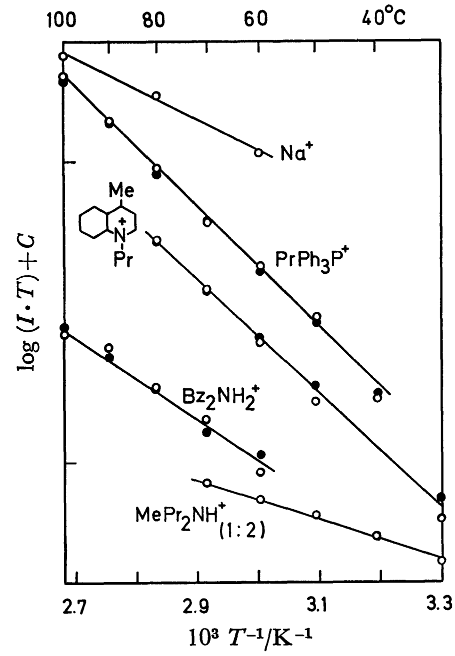

Fig. 5. Temperature dependence of ESR absorption characteristic of triplet excitons in the simple sodium, *n*-propyltriphenylphosphonium, *N*-propyl-4-methyl quinolinium, and dibenzylammonium DCNQ salts and in the complex methyldi-*n*-propylammonium DCNQ salt.

In conclusion, all the properties studied here seem to indicate that 2,3-dicyano-1,4-naphthoquinone was not a good choice for our original purpose of finding a new series of highly-conducting anion-radical salts. However, the salts may be worthwhile for a detailed study of the behavior of the triplet exciton.

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