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Syntheses and Electrical Properties of *α,α,α′,α′*-Tetracyanodiphenoquinodimethane Complexes

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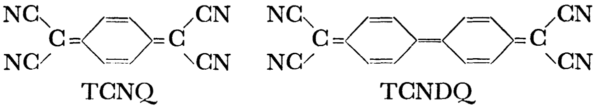
Synopsis. Two charge-transfer complexes of α,α,α′,α′-tetracyanodiphenoquinodimethane (TCNDQ), *i.e.*, *N*-methylphenazinium (NMP)-TCNDQ and *N*-methylquinolinium (NMQ)-TCNDQ, were synthesized. The electrical resistivities with pressed pellet samples were 7.1×10^8 Ω cm for $\mathrm{NMP^+TCNDQ^-}$ and 6.9×10^7 Ω cm for $\mathrm{NMQ^+TCNDQ^-}$; they are thus much less conductive than the corresponding TCNQ complexes.

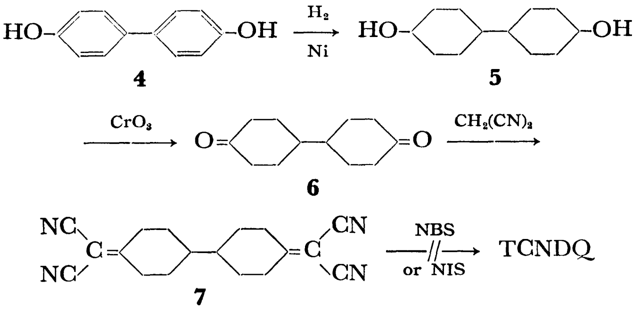
Great attention has been paid to the high electrical conductivities of tetracyanoquinodimethane (TCNQ) complexes.[1] The highly conductive properties of TCNQ complexes were analysed by means of the Hubbard model.[2] It was suggested that a large transfer integral (t) and a small Coulomb repulsion energy (U_{eff}) are needed for high conductivity. The large t is realized by the large overlap of the π-electron cloud between adjacent TCNQ anion radicals, and the small U_{eff} by the distant location of cyano groups in TCNQ and also by the polarization stabilization caused by the donor cation.



The separation of cyano groups in tetracyanodiphenoquinodimethane (TCNDQ) is greater than in TCNQ, thereby possibly resulting in a smaller U_{eff} than in TCNQ. Thus, the TCNDQ complexes are expected to be good candidates for highly conductive organic materials. However, no electrical property is known for TCNDQ.[3] We have synthesized two complexes, *N*-methylphenazinium (NMP)-TCNDQ and *N*-methylquinolium (NMQ)-TCNDQ, and measured their electrical resistivities, electronic absorption spectra, and ESR spectra.

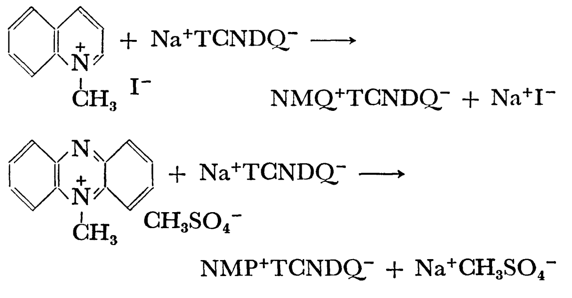
Results and Discussion

Synthesis of $\mathit{Na^+TCNDQ^-}$*.* $\mathrm{Na^+TCNDQ^-}$ has usually been synthesized through several step-reactions starting from 4,4′-bis(bromomethyl)biphenyl (**1**).[3] However, the yield of **1** was low (4%),[4] thus limiting the total yield of $\mathrm{Na^+TCNDQ^-}$. On the other hand, the yield of 4,4′-bis(chloromethyl)biphenyl (**2**)[5] was much higher (60%).[4] We succeeded in obtaining 4,4′-bis(cyanomethyl)biphenyl (**3**) (the second step material for the synthesis of $\mathrm{Na^+TCNDQ^-}$) from **2** (50% yield). Thus, **2** should be used as a starting material for the synthesis of $\mathrm{Na^+TCNDQ^-}$. We also tried another route for the synthesis of TCNDQ:

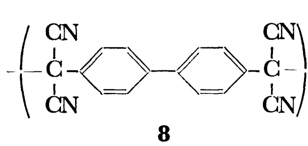


However, the attempted dehydrogenation of 4,4′-bis(dicyanomethylene)-1,1′-bicyclohexane (**7**) by *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS) was unsuccessful, recovering only **7**.

Syntheses of $\mathit{NMP^+TCNDQ^-}$ *and* $\mathit{NMQ^+TCNDQ^-}$ *Complexes.* We have succeeded in obtaining $\mathrm{NMP^+TCNDQ^-}$ and $\mathrm{NMQ^+TCNDQ^-}$ by the following ion-exchange reactions:



We also tried other ion-exchange reactions of several systems, *i.e.*, the tetrabutylammonium iodide-$\mathrm{Na^+TCNDQ^-}$, quinolinium iodide-$\mathrm{Na^+TCNDQ^-}$, and *N,N,N′,N′*-tetramethylbenzidinebromide-$\mathrm{Na^+TCNDQ^-}$ systems. However, all these systems gave polymer **8**:



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The attempt to obtain the complex salt $\mathrm{Na^+TCNDQ^-}$-TCNQ by mixing the methanol solutions of $\mathrm{Na^+TCNDQ^-}$ and TCNQ also gave polymer **8**.

Table 1. Electrical resistivities of the pressed pellet samples of TCNDQ and TCNQ complexes

	TCNDQ[a)]	TCNQ[a)]
Na	3.3×10^{3} [b)]	3.0×10^{4} [d)]
NMP	7.1×10^{8}	5.0×10^{-1} [c)]
NMQ	6.9×10^{7}	1.0×10^{7} [d)]

a) Ω cm. b) Ref. 3. c) Ref. 10. d) Ref. 11.

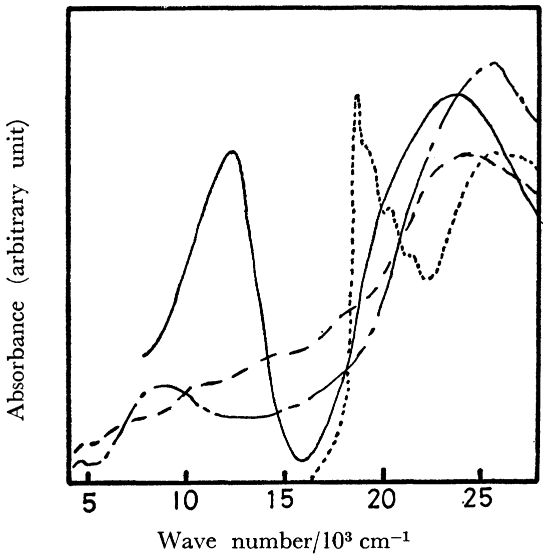

Fig. 1. Electronic absorption spectra of TCNDQ complexes. ······Na$^+$TCNDQ$^-$ (in acetonitrile solution); ——Na$^+$TCNDQ$^-$ (KBr); —·—NMP$^+$TCNDQ$^-$ (KBr); - - - -NMQ$^+$TCNDQ$^-$ (KBr).

Properties of NMP$^+$TCNDQ$^-$ and NMQ$^+$TCNDQ$^-$ Complexes. Table 1 shows the electrical resistivities of the pressed pellet samples of Na$^+$TCNDQ$^-$, NMP$^+$TCNDQ$^-$, and NMQ$^+$TCNDQ$^-$, together with those of the TCNQ complexes for the sake of comparison. Na$^+$TCNDQ$^-$ is one order of magnitude more conductive than Na$^+$TCNQ$^-$. However, NMP$^+$TCNDQ$^-$ and NMQ$^+$TCNDQ$^-$ are much less conductive than the corresponding TCNQ complexes. Although we have no crystallographic data of TCNDQ complexes, one possibility is that the six-membered rings in TCNDQ may not be co-planar, thus leading to the poor conductivity.

The electronic absorption spectra of Na$^+$TCNDQ$^-$, NMP$^+$TCNDQ$^-$, and NMQ$^+$TCNDQ$^-$, as measured by the KBr disk method, are shown in Fig. 1. The spectrum of Na$^+$TCNDQ$^-$ in an acetonitrile solution is also shown in this figure. The solid-state spectrum of Na$^+$TCNDQ$^-$ shows a broad absorption band peaking at 23.5×10^3 cm^{-1} possibly ascribable to the local excitation band of TCNDQ$^-$. The 12000 cm^{-1} band may be a charge-transfer band between adjacent TCNDQ anion radicals in the crystal. Thus, the interaction between TCNDQ anion radicals in Na$^+$TCNDQ$^-$ is expected to be large, suggesting the stacking structure of the anion site. NMP$^+$TCNDQ$^-$ and NMQ$^+$TCNDQ$^-$ also have two absorption bands in the IR and VIS regions, although in the latter spectrum the peak position of the lower energy band is not clear.

The ESR spectra of the powdered Na$^+$TCNDQ$^-$, NMP$^+$TCNDQ$^-$ and NMQ$^+$TCNDQ$^-$ showed strong single-line signals, with *g*-values of 2.003.

Experimental

Measurements. The electrical resistivity of the compaction sample was measured by means of a Takeda-Riken 8651 electrometer. The details of the measurements have been described before.[6] The electronic absorption spectra were measured by means of a Shimadzu MPS 50 L apparatus. The ESR spectra were measured by means of a Japan Electric Optics Laboratory Co., Ltd., JES-ME 2X apparatus.

Materials. *4,4′-Bis(cyanomethyl)biphenyl (**3**)*: The title compound was synthesized by the same procedure as that used in the synthesis of 1,4-bis(cyanomethyl)-2,5-diisopropylbenzene.[7]

*4,4′-Bis(dicyanomethylene)-1,1′-bicyclohexane (**7**)*: The starting material, 1,1′-bicyclohexane-4,4′-dione was synthesized according to the literature.[8] 1,1′-Bicyclohexane-4,4′-dione (6 g), malononitrile (11.5 g), ammonium acetate (0.8 g), and acetic acid (2.4 ml) were added to benzene (80 ml) in a reaction vessel, and then the mixture was refluxed using a water separator until no water came out. The precipitate was collected, washed several times with water, and finally washed with ethyl acetate. The white powder product was dried under a vacuum to obtain 4,4′-bis(dicyanomethylene)-1,1′-bicyclohexane (**7**) (6 g, 67%); mp 229—231 °C; Found: C, 74.55; H, 6.17; N, 19.29%. Calcd for $C_{18}H_{18}N_4$: C, 74.49; H, 6.20; N, 19.31%. IR (KBr) 2200 (C≡N), 1580 cm^{-1} (C=C).

NMP$^+$TCNDQ$^-$ and NMQ$^+$TCNDQ$^-$. Na$^+$TCNDQ$^-$ (100 mg)[3] was dissolved in methanol (100 ml), and the solution was filtered. To the filtrate we then added a methanol solution of *N*-methylphenazinium methylsulfate or *N*-methylquinolinium iodide (50% excess molar ratio) from the dropping funnel under a nitrogen atmosphere and at the room temperature. The solution was then stirred for an additional 2 h under a nitrogen atmosphere. The precipitate (powder) was collected and washed with diethyl ether. NMP$^+$TCNDQ$^-$: Found:[9] C, 76.32; H, 3.85; N, 17.15%. Calcd for $C_{31}H_{19}N_6$: C, 78.32; H, 4.00; N, 17.68%. NMQ$^+$TCNDQ$^-$: Found:[9] C, 78.04; H, 4.22; N, 16.51%. Calcd for $C_{28}H_{18}N_5$: C, 79.25; H, 4.25; N, 16.13%.

References

1) For example, "Organic Conductors and Semiconductors," ed by L. Pal, G. Grüner, A. Janossy, and J. Solyom, Springer-Verlag, Berlin (1977); "Synthesis and Properties of Low-Dimensional Materials," ed by J. S. Miller, Annals of New York Academy of Science, Vol. 313 (1978).

2) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).

3) Two papers have appeared on TCNDQ: W. R. Hertler, US Patent, 3153658 (1964); A. R. Addison, N. S. Dalal, Y. Hoyano, S. Huizinga, and L. Weiler, *Can. J. Chem.*, **55**, 4191 (1977).

4) Our result.

5) J. T. Massengale, W. Chester, and F. C. Bender, US Patent, 3042655 (1962).

6) T. Nogami, M. Morinaga, Y. Kanda, and H. Mikawa, *Chem. Lett.*, **1979**, 111.

7) R. C. Wheland and E. L. Martin, *J. Org. Chem.*, **40**, 3101 (1975).

8) A. L. Wilds, C. H. Shunk, and C. H. Hoffman, *J. Org. Chem.*, **76**, 1733 (1954).

9) We tried to purify the product of each step for the synthesis of Na$^+$TCNDQ$^-$ in order to obtain a good analytical agreement of this complex. However, no good analytical agreement was obtained.

10) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).

11) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).