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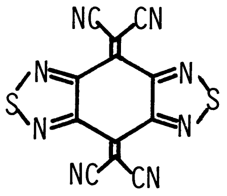
HIGHLY CONDUCTIVE COMPLEXES OF BIS-1,2,5-THIADIAZOLO-TETRACYANOQUINODIMETHAN (BTDA-TCNQ) WITH AMINES

Yoshiro YAMASHITA, Takanori SUZUKI, Gunzi SAITO,† and Toshio MUKAI
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980
†Institute for Solid State Physics, The University of Tokyo, Roppongi, Tokyo 106

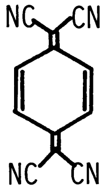
Charge-transfer complexes of bis-1,2,5-thiadiazolo-tetracyanoquinodimethan (BTDA-TCNQ) with various donors were prepared. The 1:1 complex of dimethyldihydrophenazine with BTDA-TCNQ was found to be highly conductive. Factors governing the conductivities were investigated.

Bis-1,2,5-thiadiazolo-tetracyanoquinodimethan (BTDA-TCNQ) (**1**) which we prepared recently1) is a promising electron acceptor to form conductive complexes with electron donors. The charge-transfer complex of **1** with tetrathiatetracene (TTT) (**2s**) was indeed found to exhibit high electrical conductivity.1) In order to search for other highly conductive complexes as well as clarify the factors governing the conductivities, we have prepared the charge transfer complexes of **1** with various donors and examined the electrical properties. This report describes the intriguing properties of BTDA-TCNQ affording highly conductive complexes with some tertiary amines.

Charge-transfer complexes were prepared by direct combination of **1** with donors. The complex of tetramethylphenylenediamine (**2b**) was also obtained by the reaction of Wurster's Blue perchlorate2) with the lithium salt of **1**. Based on elemental analyses, the mole ratios of donor to acceptor were determined to be 1:1 except for **2b**, **2c**, and **2k**.3) The 1:2 complexes of **2a** and **2b** could not be obtained although TCNQ easily forms 1:2 complexes with these amines.4,5) The electrical resistivities of the complexes were measured as compressed pellets at room temperature. These data are summarized in Table 1. It is noteworthy that besides TTT-**1** complex, the complex of dimethyldihydrophenazine (**2a**) exhibits high conductivity. To our knowledge, this is the most highly conducting 1:1 complex of amines with electron acceptors. The complexes of **2b** and **2c** show higher conductivities than their TCNQ complexes.5,6) The conductivity of the complex of **2d** with **1** is also higher than the corresponding TCNQ complex.7) As shown in Table 1, the first half-wave oxidation potentials (E_1^{ox}) of those amines which form highly conductive complexes are relatively low (below 0.3 V vs. SCE), while other amines having E_1^{ox}>0.4 V afford poorly conductive complexes. This finding indicates that the



BTDA-TCNQ **1**

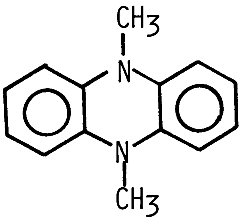


TCNQ

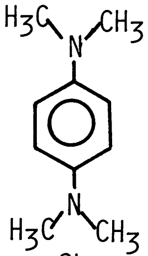
Table 1. First half-wave oxidation potentials of donors, and decomposition points, electrical resistivities, and CN stretching frequencies of the complexes of BTDA-TCNQ with donors

Donor	E_1^{ox}/V vs. SCE[a)]	Decomp./°C	ρ/Ωcm	ν/cm^{-1}
2a	0.14	238-240	0.29	2173
2b	0.10	225-230	8.7	2171
2c	-0.22	232-240	5.1×10	2166
2d	0.30[b)]	240-248	5.1×10	2172
2e	0.13	252-254	3.4×10^4	2214
2f	0.41	225-226	7.1×10^{10}	2215
2g	0.43	313-315	2.7×10^7	2218
2h	0.46[b)]	305-308	1.6×10^9	2220
2i	0.47[b)]	235-245	1.9×10^8	2216
2j	1.12[b)]	265-310	4.1×10^6	2218
2k	-0.01	220-221	4.1×10^4	2184
2l	0.58	288-290	$> 10^{12}$	2226
2m	0.70	197-200	$> 10^{12}$	2218
2n	0.31	247-248	2.5×10^7	2215
2o	0.24	245-246	2.0×10^7	2216
2p	0.25	288-289	3.9×10^9	2212
2q	0.45	270-271	1.2×10^9	2218
2r	0.41	253-259	7.3×10^8	2218
2s	__c)	>400	0.14-0.15[d)]	2173

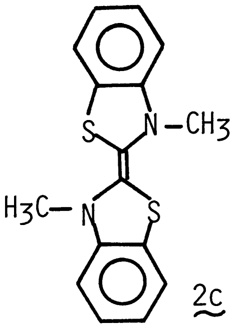
a) These values were measured under the same conditions. 0.1 mol dm^{-3}, Et_4NClO_4 in CH_3CN, platinum electrode, scan rate 100 mV s^{-1}.
b) Irreversible. Calculated as E_{pa} - 0.03 V. c) Insoluble in CH_3CN. E_1^{ox} of **2s** measured in CH_2Cl_2 was almost the same as that of **2p** in CH_2Cl_2.
d) Four-probe technique. Others were measured by two-probe technique. The electrical resistivities of the TCNQ-TTF complex measured for comparisons under the conditions used here were 0.37 (two-probe technique) and 0.19 (four-probe technique).



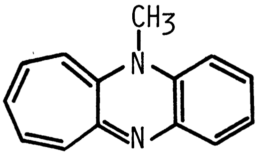
2a



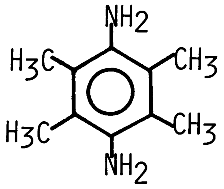
2b



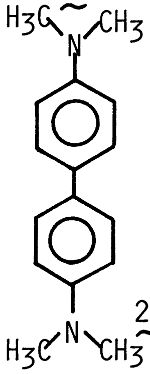
2c



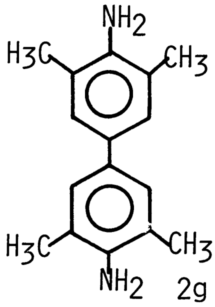
2d



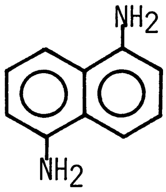
2e



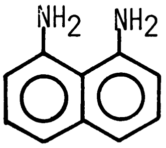
2f



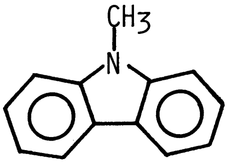
2g



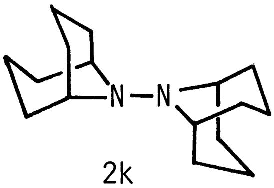
2h



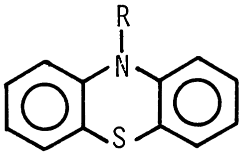
2i



2j

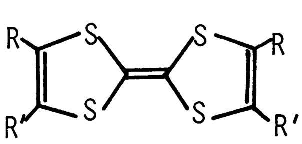


2k



2l; R=H

2m; R=CH_3

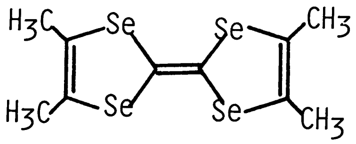


2n; R=R'=H (TTF)

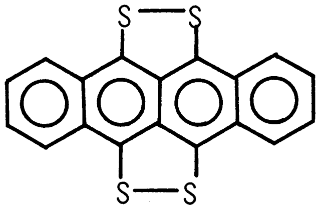
2o; R=R'=CH_3

2p; R,R'=-$(CH_2)_3$-

2q; R,R'=-$S(CH_2)_2S$-



2r



2s (TTT)

conductivities are correlated with the redox potentials as found in TTF (Tetrathiafulvalene)-TCNQ series.[6,8] In the case of BTDA-TCNQ, however, donors having lower oxidation potentials are needed to form highly conductive complexes since the first reduction potential of **1** (-0.02 V vs. SCE) is lower than that of TCNQ (+0.18 V vs. SCE).[1] On the other hand, **1** did not afford highly conductive complexes with TTF and its analogues even if they have lower oxidation potentials than amine **2d**.[9]

Another interesting feature is that nitrile streching frequencies of the highly conductive complexes (2166-2173 cm^{-1}) are lower than those of the metal salts of **1** (Li salt; 2195 cm^{-1}, Na salt; 2185 cm^{-1}, K salt; 2183 cm^{-1}).[10] Other complexes except for **2k**[11] showing low conductivities have comparable values to that of **1** (2225 cm^{-1}). This characteristic is very different from those of TCNQ series in which nitrile stretching frequencies are linearly correlated with the degree of charge transfer, and those of TCNQ complexes or salts exhibiting high conductivities are between TCNQ itself and metal salts due to the partial electron transfer.[12] What makes this difference is still ambiguous. We are attempting to prepare single crystals of the highly conductive complexes of **1** to investigate more detailed properties and crystal structures.

References

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2) L. Michaelis and S. Granic, J. Am. Chem. Soc., 65, 1747 (1943).
3) Amines **2b** and **2k** form 2:3 and 1:2 complexes with BTDA-TCNQ, respectively. On the contrary, **2c** forms a complex including water (**2c**:**1**:H_2O=1:3:1).
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6) R. C. Wheland, J. Am. Chem. Soc., 98, 3926 (1976).
7) The electrical resistivity of the **2d**-TCNQ complex was 1.57 x 10^8 Ω cm for two-probe room-temperature compaction.
8) G. Saito and J. P. Ferraris, Bull. Chem. Soc. Jpn., 53, 2141 (1980).
9) The complex of TTF-**1** was revealed to have a mixed stack structure by the X-ray analysis. This result will be soon reported elsewhere. Other complexes with TTF analogues may also have mixed stack structures resulting in the low conductivities.
10) The IR spectra were measured in KBr disks with a Shimadzu IR-435 spectrometer and a Shimadzu DR-1 data recorder.
11) The nitrile streching frequency of diamine **2k** is almost the same as that of the K salt. Full electron transfer seems to take place in this complex as in the metal salts.
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