

Preparation and Properties of Electron Donor Acceptor Complexes of the Compounds having Capto-dative Substituents

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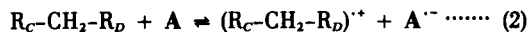
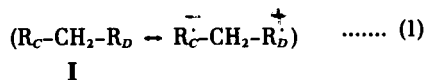
In order to examine the "capto-dative" substitution-effect on the electrical conductivity, five compounds which have capto-dative substituents were prepared. Electron withdrawing (capto) group was nitro- or cyano-substituted phenyl and electron donating (dative) one was 5-methyl-5,10-dihydrophenaziny moiety. The character of intramolecular electron donor acceptor complex of the five compounds were demonstrated by their uv spectra. Electron donor acceptor complexes of them with tetracyanoquinodimethane were prepared and their electrical resistivities were measured.

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The stabilization of a radical due to conjugation with both electron donating and electron withdrawing substituents on the radical center is well known in terms of "Capto-dative" effect or "mero-stabilization" [1]. We have been interested in this effect on the electrical conductivities of organic compounds [2]. This paper describes the attempt on the preparations of the compounds having capto-dative substituents and their properties.

If the compound **I** which has capto-dative substituents (R_C , R_D) forms an electron donor acceptor (EDA) complex with a suitable acceptor molecule **A**, some parts of the mass of the complex change into cation- and anion-radicals mixture and then form the radicals which are expected to contribute to the electrical conduction [equations (1) - (3)].

On the basis of this anticipation, we prepared the complexes of the type **I** compounds, **1-6**, with some acceptors and investigated their properties especially electrical conductivities.

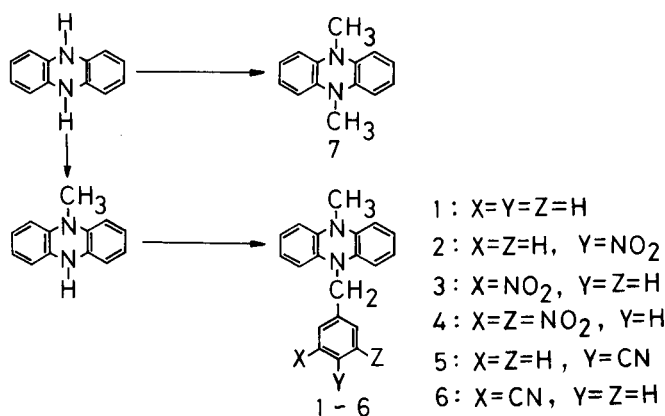


5,10-Dimethyl-5,10-dihydrophenazine **7** has low ionization potential [3] and so the dihydrophenaziny moiety is predicted to be a good electron donor group (R_D). On the other hand, the nitro- or cyano-substituted phenyl group should be useful as an electron withdrawing one (R_C).

Preparation and Properties of **1-6**.

Seven, 5,10-dihydrophenazine derivatives, **1-7**, were prepared according to the route shown in Scheme 1. They were characterized by spectroscopic data and elemental analyses. The relevant properties of them are shown in Table 1. All of the compounds **1-7** showed absorption maxima at 340-355 nm in benzene. Moreover, **2**, **3**, and **4** show-

Scheme 1



ed additional absorption bands at 430, 430, and 516 nm, respectively, which were assigned to the intramolecular EDA absorption bands by comparing the absorption of **1** and that of the mixture of **7** and an electron acceptor (intermolecular EDA absorption) (Table 2). Although **5** and **6** have no remarkable additional absorption bands, both of them showed long-tailed absorption bands [not observed for **1**] which may be assigned to the intramolecular EDA ones. These results show that each of **2-6** has intramolecular EDA complex character. This character is one requirement for the sample compounds as shown in equation 1. Electrical resistivities of **1-6** were in the order of 10⁹ ohm cm which were as high as that of the EDA complex of **7** with 1,3,5-trinitrobenzene (TNB). These values corresponded to those of non-ionic class complexes (see below). The ir spectra of **1-6** also suggested the non-ionic characters of them.

Properties of the Intermolecular EDA Complexes of **1-6** with Electron Acceptors.

A series of preliminary investigations on **7** was carried out to find a suitable electron acceptor. Compound **7**, which is a representative of **1-6**, formed EDA complexes

Table 1
Melting Points, Color of Solid, Absorption maximum [a] and Resistivity of 1-6.

Compound	Mp °C	Color of solid	λ max (log ϵ) nm	Resistivity ρ /Ohm cm
1	126-128	colorless	353 (3.94)	—
2	148-149	violet	351 (3.99), 430 (sh, 2.16)	3×10^9
3	145-147	purple	345 (4.10), 430 (sh, 2.26)	3×10^9
4	197-198	violet	432 (3.89), 516 (2.18)	3×10^9
5	159-162	yellow	350 (3.98)	$> 10^{10}$
6	170-173	yellow	345 (3.92)	$> 10^{10}$

[a] Benzene solution.

Table 2
Molar Absorptivities (ϵ_c) and Equilibrium Constants (K) of Intermolecular EDA Complexes of 7 with Acceptors [a]

Acceptor	ϵ_c (N/nm)	K/mol ⁻¹
1,3,5-Trinitrobenzene	750 (713)	3.76
1,4-Dinitrobenzene	200 (660)	1.56
1,3-Dinitrobenzene	900 (530)	0.43
<i>p</i> -Benzoquinone	133 (700)	1.63

[a] Estimated by the method of Lang [9].

with various acceptors [4]. Elemental analyses suggested their formulation of (Donor)₁(Acceptor)₁. According to the method which was pointed out by Matsunaga [5] for the quinone-containing EDA complexes, the present complexes were possible to be classified as non-ionic or ionic

according as their ir spectra which are similar or dissimilar to the combined spectrum of that of each component molecules. The EDA complexes of 7 with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), with tetracyanoethene (TCNE), with 7,7,8,8-tetracyanoquinodimethane (TCNQ), with tetrachloro-*p*-benzoquinone (TCBQ), and with 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF), were ionic and those with TNB, with 2,4,7-trinitrofluorenone (TNF), and with 1,2,4,5-tetracyanobenzene (TCNB) were non-ionic. The electrical resistivities of ionic complexes were, in general, lower than those of non-ionic complexes (Table 3).

Among the complexes, complexes with DDQ, with TCNE [6], and with TCBQ were unstable at room temperature. Their ir spectra gradually changed with the passage of time. Other complexes did not change for over several weeks. On the basis of these results, the acceptor species were chosen; TCNQ, TNF, TNB, and DTF.

Table 3
Properties and Analytical Data for the EDA Complexes of 7 with Acceptor

Acceptor	Mp °C	Color of crystals	Resistivity ρ /Ohm cm	Found/(Calcd) % [a]		
				C	H	N
DDQ	200 [b]	dark green	1×10^6	60.17 (60.43)	2.74 (3.23)	12.80 (12.81)
TCNE	137-139	greenish black	4×10^6	71.09 (70.99)	3.74 (4.17)	24.92 (24.84)
TCNQ	202-205 [b]	purplish black	8×10^3	75.67 (75.35)	3.92 (4.38)	20.56 (20.28)
TCBQ	310 [b]	black	4×10^5	53.04 (52.66)	2.60 (3.09)	5.72 (6.14)
DTF	188-189	violet	4×10^5	62.99 (62.83)	2.99 (3.34)	17.38 (17.10)
TNF	181-182	black	8×10^9	61.99 (61.71)	3.34 (3.64)	13.56 (13.33)
TCNB	185-186	black	6×10^9	73.99 (74.21)	3.77 (4.15)	21.55 (21.64)
TNB	167-168	dark green	3×10^9	56.46 (56.74)	3.65 (4.05)	16.82 (16.54)

[a] Calculated values for the complex of 1:1 donor acceptor ratio. [b] Decomposition.

Table 4
Properties and Analytical Data for the EDA Complexes of TCNQ

Donor	Mp °C Dec	Color of Crystals	λ max [a] nm	Resistivity ρ /Ohm cm	Found/(Calcd.) % [b]		
					C	H	N
1	158-159	Black	615	1×10^5	78.38 (78.35)	4.25 (4.52)	17.06 (17.13)
2	161-164	Black	618	2×10^5	71.80 (71.77)	3.54 (3.95)	18.31 (18.31)
3	173-175	Black	590	1×10^6	72.12 (71.77)	3.57 (3.95)	18.58 (18.31)
4	168-169	Purplish black	620	2×10^4	66.17 (66.20)	3.09 (3.47)	19.50 (19.30)
5	161-162	Black	650	3×10^5	77.13 (76.88)	3.60 (4.11)	19.04 (19.02)
6	162-162.5	Black	630	1×10^6	77.26 (76.88)	3.83 (4.11)	18.91 (19.02)

[a] In potassium bromide. [b] Calculated for the EDA complexes of 1:1 donor acceptor ratio.

Compounds **1-6** formed intermolecular EDA complexes with the acceptors: each of **1**, **2**, **3**, **5**, and **6** gave the solid EDA complexes with TNF, TNB, and TCNQ, while **4** formed solid EDA complex with only TCNQ. These results mean that the electron donating properties of **1-6** are more or less influenced by the electron withdrawing substituent. Properties and elemental analyses of these intermolecular EDA complexes with TCNQ are shown in Table 4. The elemental analyses led to our conclusion that each of the complexes contained equimolar donor and acceptor molecules. In the ir spectra, the complexes did not resemble the component molecules. This suggested their ionic character and, in fact, their electrical resistivities were as low as those of the ionic complexes (Table 3). The strength of electron withdrawing character of the group R_c seemed to be reflected on the electrical resistivities: The magnitude of the resistivity of the **4**-TCNQ complex (dinitro substituted) is smaller than that of the **2**-TCNQ or the **3**-TCNQ complex (mononitro substituted), while that of the **2**-TCNQ or the **5**-TCNQ complex (*p*-substituted) is smaller than that of the **3**-TCNQ or the **6**-TCNQ complex (*m*-substituted). Needless to mention, steric factors must have an influence on the resistivity. Thus, the resistivity of the **7**-TCNQ complex is smaller than that of the **1**-TCNQ complex which has a larger group (benzyl). However, the conductivity of the **4**-TCNQ complex is higher than that of the **1**-TCNQ complex over the steric disadvantage of two nitro groups. These results may be a contribution of the "capto-dative" substitution as expected in equations (1) - (3).

EXPERIMENTAL

All melting points were uncorrected. Spectra were recorded on Hitachi 215-type spectrophotometer (ir), Hitachi R-24A type spec-

trometer (60 MHz, ^1H nmr), and Hitachi EPS-3T type spectrophotometer (uv). The d.c. electrical resistivities were measured by a Matsushita VP-911C type vacuum tube voltmeter on the polycrystalline compacted substance under 200 kg/cm² at 20° [7].

Materials: 5,10-Dimethyl-5,10-dihydrophenazine (**7**).

To a boiling solution of phenazine (2 g, 11 mmoles) in ethanol (50 ml) was added a solution of sodium dithionite (20 g, 0.11 mole) in water (200 ml). The resulting solid immediately precipitated was collected by filtration and dried over phosphorus pentoxide under reduced pressure to give 5,10-dihydrophenazine (1.8 g, 10 mmoles). To a solution of 5,10-dihydrophenazine (2.5 g, 14 mmoles) in 1,2-dimethoxyethane (30 ml), butyl-lithium in hexane (25 ml of 15% w/w solution, 40 mmoles) was added dropwise over a period of 20 minutes, and then methyl iodide (6.3 ml, *ca.* 0.1 mole) was added at room temperature. After 30 minutes, the reaction mixture was poured into water (200 ml) and extracted with benzene. The extract was dried (sodium sulfate) and evaporated under reduced pressure to afford a yellowish solid, which was purified by chromatography on alumina with benzene. Recrystallization from hexane gave colorless crystals of **7** (2.1 g, 10 mmoles), mp 152-153° (lit [8], 151-152°); ^1H nmr (deuteriochloroform): δ 3.00 (6 H, s, CH₃) and 6.20-6.75 (8 H, m, ArH).

Compounds **1-6** were prepared from 5,10-dihydrophenazine in the same manner. The sample procedure will be described for the preparation of **2**.

5-Methyl-10-(4-nitrobenzyl)-5,10-dihydrophenazine (**2**).

To a solution of 5,10-dihydrophenazine (2.8 g, 15 mmoles) in dimethoxyethane (20 ml), butyl-lithium in hexane (20 ml of 15% w/w solution, 32 mmoles) was added dropwise and then methyl iodide (1.0 ml, *ca.* 16 mmoles) was added at room temperature. After 30 minutes stirring, the reaction mixture was poured into aqueous sodium dithionite, filtered by suction and dried over phosphorus pentoxide. Crude 5-methyl-5,10-dihydrophenazine was obtained (2.4 g, 12 mmoles). To a solution of this (1.2 g, 6 mmoles) in 1,2-dimethoxyethane (15 ml), butyl-lithium in hexane (11 ml, 18 mmoles) was added and then a solution of *p*-nitrobenzyl chloride (1.6 g, 9 mmoles) in 1,2-dimethoxyethane (5 ml) was add-

ed at room temperature. After 2 hours, the reaction mixture was poured into water and extracted with benzene. The extract was dried (sodium sulfate) and evaporated to give a black solid. The purification was carried out by chromatography. Violet solid **2** (0.6 g, 1.8 mmoles, 25% yield based on 5,10-dihydrophenazine) was obtained; ir (potassium bromide): 1525 (NO₂) and 1340 cm⁻¹ (NO₂); ¹H nmr (deuteriochloroform): δ 2.95 (3 H, s, CH₃), 4.74 (2 H, s, CH₂), and 5.8-6.8 (8 H, m) and 7.2-8.1 (4 H, q) (together 12 ArH); ms: m/z 331 (M⁺, 13%) and 195 (M - CH₂C₆H₄NO₂, 100).

Anal. Calcd. for C₂₀H₁₇N₃O₂: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.36; H, 5.02; N, 12.57.

5-Methyl-10-benzyl-5,10-dihydrophenazine (1).

The yield was 40% based on 5,10-dihydrophenazine; ¹H nmr (deuteriochloroform): δ 2.48 (3 H, s, CH₃), 4.38 (2 H, s, CH₂), and 5.9-6.8 (8 H, m) and 6.91 (5 H, s) (together 13 ArH); ms: m/z 286 (M⁺, 14%) and 195 (M - CH₂C₆H₅, 100).

Anal. Calcd. for C₂₀H₁₈N₂: C, 83.88; H, 6.34; N, 9.78. Found: C, 84.11; H, 6.07; N, 9.65.

5-Methyl-10-(3-nitrobenzyl)-5,10-dihydrophenazine (3).

The yield was 11%; ir (potassium bromide): 1530 (NO₂) and 1345 cm⁻¹ (NO₂); ¹H nmr (deuteriochloroform): δ 3.00 (3 H, s, CH₃), 4.78 (2 H, s, CH₂), and 5.8-6.8 (8 H, m) and 7.2-8.1 (4 H, m) (together 12 ArH); ms: m/z 331 (M⁺, 11%) and 195 (M - CH₂C₆H₄NO₂, 100).

Anal. Calcd. for C₂₀H₁₇N₃O₂: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.51; H, 5.16; N, 12.43.

5-Methyl-10-(3,5-dinitrobenzyl)-5,10-dihydrophenazine (4).

The yield was 26%; ir (potassium bromide): 1540 (NO₂) and 1345 cm⁻¹ (NO₂); ¹H nmr (deuteriochloroform): δ 3.00 (3 H, s, CH₃), 4.86 (2 H, s, CH₂), and 5.8-6.8 (8 H, m), 8.35 (2 H, m), and 8.73 (1 H, m) (together 11 ArH); ms: m/z 376 (M⁺, 9%) and 195 [M - CH₂C₆H₃(NO₂)₂, 100].

Anal. Calcd. for C₂₀H₁₆N₄O₄: C, 63.83; H, 4.28; N, 14.89. Found: C, 64.01; H, 4.36; N, 14.69.

5-Methyl-10-(4-cyanobenzyl)-5,10-dihydrophenazine (5).

The yield was 33%; ir (potassium bromide): 2230 cm⁻¹ (CN); ¹H nmr (benzene-d₆): δ 2.47 (3 H, s, CH₃), 4.10 (2 H, s, CH₂), and 5.6-7.0 (12 H, m, ArH); ms: m/z 311 (M⁺, 17%) and 195 (M -

CH₂C₆H₄CN, 100).

Anal. Calcd. for C₂₁H₁₇N₃: C, 81.00; H, 5.50; N, 13.49. Found: C, 81.31; H, 5.41; N, 13.55.

5-Methyl-10-(3-cyanobenzyl)-5,10-dihydrophenazine (6).

The yield was 34%; ir (potassium bromide): 2230 cm⁻¹ (CN); ¹H nmr (benzene-d₆): δ 2.46 (3 H, s, CH₃), 4.07 (2 H, s, CH₂), and 5.6-7.0 (12 H, m, ArH); ms: m/z 311 (M⁺, 13%) and 195 (M - CH₂-C₆H₄CN, 100).

Anal. Calcd. for C₂₁H₁₇N₃: C, 81.00; H, 5.50; N, 13.49. Found: C, 81.09; H, 5.39; N, 13.44.

Preparation of EDA Complexes.

The EDA complexes were prepared by mixing the donor and acceptor solutions which were previously prepared in hot acetonitrile separately. On cooling, the resulting solids were collected by filtration and dried *in vacuo*.

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