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Synthesis and Properties of 1,6-Diazaphenalenes and their Charge-Transfer Complexes with Tetracyanoquinodimethane

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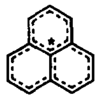
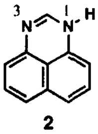
Abstract: 1,6-Diazaphenalene and its derivatives containing methyl, bromo, chloro, phenyl, and 2-pyridyl substituents form charge-transfer complexes with TCNQ. Relatively highly electrical conductive complexes (0.1 Scm^{-1}) with small activation energy around 0.05 eV was obtained.

The neutral states of 1,3- and 1,6-diazaphenalene (**2**[1] and **3**[2]) are isoelectronic with phenalenyl anion ($\mathbf{1}^-$) and electron-rich systems. In addition, these systems have proton-donor and acceptor moieties like the imidazole skeleton.[3] In order to explore a variety of hydrogen-bonded charge-transfer complexes,[4] we have utilized the 1,6-diazaphenalene system as a donor component for charge-transfer complexes with tetracyanoquinodimethane (TCNQ), which showed relatively highly electrical conductivities with small activation energies.



$\mathbf{1}\ast$ = +, •, −



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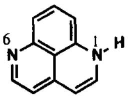

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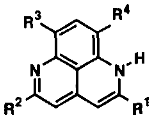

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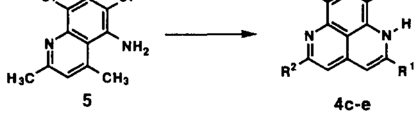
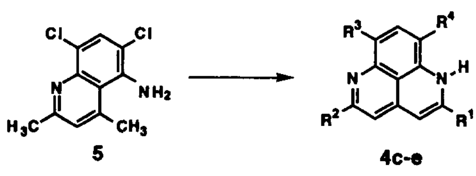
	R^1	R^2	R^3	R^4
a	H	H	Br	H
b	Cl	Cl	H	H
c	CH_3	CH_3	Cl	Cl
d	C_6H_5	CH_3	Cl	Cl
e	2-Py	CH_3	Cl	Cl

According to the procedure reported by Cook, we prepared 1,6-diazaphenalene (**3**)[2d] and its derivatives, **4a**,[2f] and **4b**.[2d] Furthermore, the tetra-substituted derivatives **4c** ($R^1 = CH_3$), **4d** ($R^1 = C_6H_6$), and **4e** (R^1 = 2-pyridyl) were newly synthesized by employing one-carbon elongation and cyclization reaction of 5-amino-4-methylquinoline **5**[5] as a key step. Thus, **5** was treated with 2 equiv of LDA in THF, and then added 2 equiv of the corresponding ethyl ester to give the desired tetra-substituted 1,6-diazaphenalenes **4c–e** in 19, 18, and 41% yield, respectively.[6]



Scheme 1. *Reagents and conditions*: 2 equiv LDA, THF, −78 °C, 1 h, then 2 equiv RCOOEt, −78~0 °C, 4 h.



Scheme 1. *Reagents and conditions*: 2 equiv LDA, THF, –78 °C, 1 h, then 2 equiv RCOOEt, –78~0 °C, 4 h.

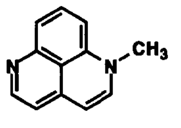
In the proton NMR spectrum in CD_3OD or DMSO-d_6 at room temperature, **4c** shows only four C-H signals, which indicates a C_{2v} symmetric nature in solution and a rapid reversible exchange of the NH proton between the two nitrogen atoms. Such a tautomeric behavior was reported for the parent diazaphenalenes, **2**[3] and **3**.[4d] Comparison of the N-H stretching frequencies between those in the solid (KBr) and in a dilute solution (CCl_2CCl_2, 1 x 10^{-3} M) reveals that the tetra-substituted derivatives **4c–e** show no lower frequency shifts in the solid state in contrast to **2**[3], **3**, **4a**, and **4b** (Table 1). This apparently indicates that in the solid state the four substituents inhibit intermolecular hydrogen-bonding interactions.

Table 1 Frequencies of N-H Stretching of 1,6-diazaphenalenes (cm^{-1})

	2	**3**	**4a**	**4b**	**4c**	**4d**	**4e**
solid[a]	2794	2649	2806	2942	3415	3405	3316
solution[b]	3442	3450	3416	3431	3419	3418	3341, 3418

[a] KBr pellet. [b] CCl_2CCl_2 solution, 1 x 10^{-3} M.

In order to estimate the electron donor ability of 1,6-diazaphenalene systems by cyclic voltammetry, N-methyl-1,6-diazaphenalene (**6**) was prepared.[9] The oxidation potential of **6** was 0.60 V vs SCE in CH_3CN which indicates the weak electron-donor nature of the 1,6-diazaphenalene system. The value is comparable with that of phenothiazine (0.58 V).



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The CT complexes of the diazaphenalenes with TCNQ were prepared by slow evaporation of a THF solution of the donor and acceptor components or by mixing of a hot $CHCl_3$ solution in 33-87% yields. The 1,6-diazaphenalenes, **3**, **4a**, and **4c–e** gave CT complexes, although no CT complexes of **4b** and 1,3-diazaphenalene (**2**) were obtained.

Some selected physical properties of the CT complexes are summarized in Table 2. The degree of CT (Z) is estimated to be 0.55–0.98 by using the CN stretching frequencies of the nitrile group (ν_{CN}).[10] Electronic absorption spectrum in the solid state for each complex shows a low-energy absorption band ($h\nu_{CT}$) at near 3000 cm^{-1}. These two features of the degree of CT and the CT transition energy suggest that these complexes possess a segregated TCNQ stacking with a partial ionicity.[11] The low-energy absorption band prevents the characterization of the stretching vibration of NH···N type hydrogen-bond expected to appear in the region of around 3000 cm^{-1}.

The electrical conductivities (σ_{RT}) of these complexes measured by four-probe method on the compressed pellets show semiconducting behavior with relatively highly electrical conductivities of 0.01–0.1 Scm^{-1} and low activation energies (E_a) of around 0.05 eV. Interestingly, not only the unsubstituted and the bromo-substituted 1,6-diazaphenalene, but also the tetra-substituted derivatives also gave relatively highly conducting CT complexes.

Table 2 Physical Properties of TCNQ Complexes

	3	**4a**	**4c**	**4d**	**4e**
D/A[a]	1/1	1/1	2/1	5/6	2/3
ν_{CN}, cm^{-1}	2197	2196	2203	2184	2200
Z^b	0.68	0.70	0.55	0.98	0.61
$h\nu_{CT}$, cm^{-1}	2900	2900	2600	2600	2600
σ_{RT}, Scm^{-1} [c]	2.9×10^{-2}	2.9×10^{-2}	4.3×10^{-2}	1.9×10^{-2}	1.6×10^{-1}
E_a, eV	0.072	0.078	0.040	0.058	0.052

[a] Determined by the elemental analysis. [b] Degree of CT was calculated from the ν_{CN}.
[c] Compressed pellet measurement using four-probe method.

At this stage we have not succeeded in confirming the hydrogen bonding interaction by the crystal structure analysis of the CT complexes. In order to examine the H-bonding ability of the diazaphenalenyl skeleton, we tried to crystallize the diazaphenalenuim ions. The single crystals of HBr salt of **4b** were obtained as reddish-orange plates. Thus, although **4b** contains two bulky chlorine atoms positioned adjacent to the nitrogen atom, the crystal structure of the salt, $(\mathbf{4b}H)^+ Br^-$, shows the presence of the NH···Br type H-bonding between the N–H group and the counter anion, Br^-, as shown in Figure 1.[12] This is an important finding for further study to obtain H-bonded CT complexes with the diazphenalenyl skeleton.

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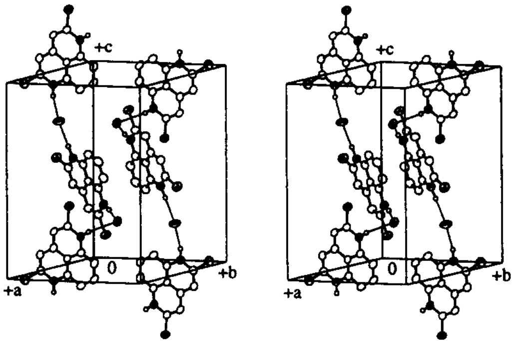

Figure 1. NH···Br type H-bonding interaction of $(\mathbf{4b}H)^+ Br^-$.

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8 All new compounds described here gave satisfactory elemental analyses and spectroscopic data. Selected physical data:

(**5**) yellow gray needle; mp 204–205 °C[7]; ^{1}H NMR ($CDCl_3$), δ 2.69 (3H, s), 2.95 (3H, d, *J* 0.8 Hz), 4.82 (2H, br s), 7.03 (1H, d, *J* 0.8 Hz), 7.69 (1H, s); MS (EI) *m/z* 242 (M^+, 68%), 240 (M^+, 100%).

(**4c**) bright yellow powder; mp 229.5–231 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.21 (3H, br s), 2.54 (3H, br s), 5.72 (1H, br s), 6.40 (1H, br s), 7.21 (1H, br s), 7.54 (1H, s); ^{1}H NMR (DMSO-d_6) δ 2.28 (6H, s), 6.13 (2H, br s), 7.61 (1H, s), 9.85 (1H, br s); ^{1}H NMR (CD_3OD), δ 2.33 (6H, s), 6.15 (2H, br s), 7.57 (1H, s); MS (EI) *m/z* 266 (M^+, 65%), 264 (M^+, 100%).

(**4d**) bright yellow powder; m.p. 212–214 °C; ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s), 5.99 (1H, br s), 6.80 (1H, br s), 7.42–7.54 (4H, m), 7.59 (1H, s), 8.01 (2H, br s); MS (EI) *m/z* 328 (M^+, 65%), 326 (M^+, 100%).

(**4e**) vivid reddish orange powder; mp 220–222 °C; ^{1}H NMR ($CDCl_3$) δ 2.54 (3H, s), 6.42 (1H, br s), 6.77 (1H, br s), 7.39 (1H, dd, *J* 5.0, 8.1 Hz), 7.60 (1H, s), 7.85 (1H, ddd, *J* 1.5, 7.4, and 8.1 Hz), 8.02 (1H, br s), 8.68 (1H, dd, *J* 1.5, 5.0 Hz), 9.41 (1H, br s); MS (EI) *m/z* 329 (M^+, 65%), 327 (M^+, 100%).

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12 Crystal data: for (**4b**H)$^+$Br$^-$, $C_{11}H_7N_2Cl_2Br$, FW = 318.00, deep reddish orange crystal, monoclinic, C_2/c (#15), a = 10.338(4) Å, b = 14.469(2) Å, c = 15.665(2) Å, β = 97.85(2)°, V = 2321.2(7) Å^3, Z = 8, R = 0.046, R_w = 0.046, Goodness of Fit Indicator = 1.46, D(calcd) = 1.820 Mg m^{-3}, μ(MoKα) = 39.82 cm^{-1}, 1789 observed reflections ($Io > 3\sigma(Io)$), T = 296.2 K, ω–2θ scan, maximum $2\theta_{max}$ = 60.0°. Scan Rate = 16.0 °/min (in ω) – up to 5 scans, Scan Width = (1.63 + 0.35 tan θ).

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