N,N'-Dicyano-*p*-acepleiadylenequinonediimine and Its 1,2-Dibromo Derivative: New DCNQI Type Acceptors and Their Conducting Complexes

Ohki Sato, Yuji Okada, Takashi Shirahata,[†] Kazuko Takahashi,*[††] and Josuke Tsunetsugu*
Department of Chemistry, Faculty of Science, Saitama University, Saitama 338-8570
[†]*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578*
[††]*Center for Interdisciplinary Research (CIR), Tohoku University, Sendai 980-8578*

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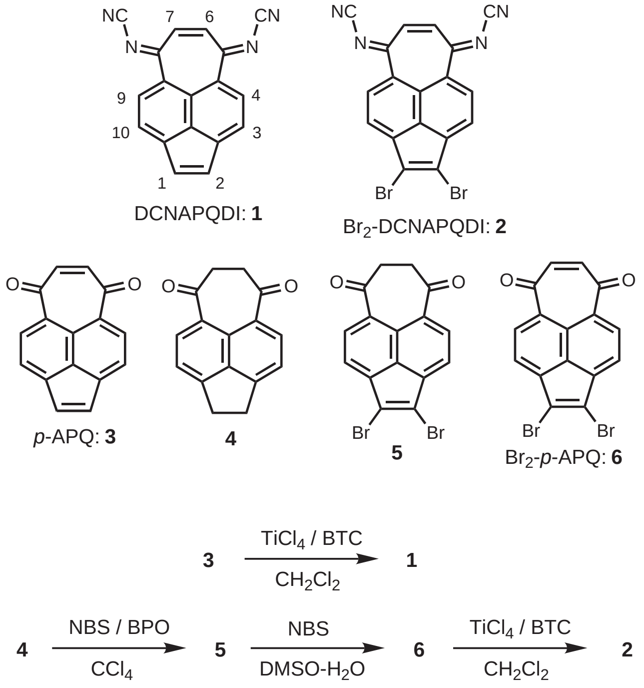
N,N'-Dicyano-*p*-acepleiadylenequinonediimine (DCNAPQ-DI) and its 1,2-dibromo derivative (Br_2-DCNAPQ-DI), a new family of acepleiadylene-based DCNQI type electron acceptors have been synthesized. Br_2-DCNAPQDI exhibiting the first half-wave reduction potential of −0.03 V vs SCE afforded a fairly high conducting Cu salt.

Tetracyanoquinodimethane (TCNQ),[1] N,N'-dicyanoquinonediimine (DCNQI),[2] and their derivatives have been proved to be the most important π-acceptor molecules for organic conductors. However, much effort has been devoted to the synthesis of modified TCNQ and DCNQI to provide superior π-acceptor components. To decrease on-site Coulomb repulsion in the dianion state and to increase intermolecular interactions by means of S···S contacts, oligothiophene-TCNQs have been synthesized.[3] More recently, 4-oxo-2,6-bis(dicyanomethyl-ene)-2,6-dihydrocyclopentadithiophene (CPDT) incorporating three terminal electron accepting groups and giving one-dimensional metallic anion radical salts has been synthesized.[4] As for the nonbezenenoid system, the synthesis of 2,4,6,8-tetracyanoazulene,[5] tetracyanoazulenequinodimethanes,[6] and [3]radialene type acceptors[7] have been reported so far. Recently, many interesting solid state properties have been discovered for the Cu salts of DCNQI derivatives in which 3d electrons in Cu interact with pπ-electrons in the DCNQI near the Fermi level.[8] In this context, we are interested in new nonbenzenoid DCNQI type acceptors, and have now synthesized N,N'-dicyano-*p*-acepleiadylenequinonediimine (DCNAPQDI: **1**) and its 1,2-dibromo derivative (Br_2-DCNAPQDI: **2**), and have clarified their electron accepting abilities as well as conducting properties of their CT and Cu complexes, which are reported herein.

The new acceptors DCNAPQDI (**1**) and Br_2-DCNAPQDI (**2**) have been synthesized according to the routes shown in Scheme 1. *p*-Acepleiadylenequinone (*p*-APQ: **3**)[9] was allowed to react with bis(trimethylsilyl)carbodiimide (BTC) in the presence of $TiCl_4$[2a] to give DCNAPQDI (**1**) in 45% yield.[10,11] The dibromodione **5** was synthesized in 56% yield by the reaction of the dione **4**[9] with NBS (5 mol *eq.*) in the presence of catalytic amount of dibenzoyl peroxide (BPO) in CCl_4. Treatment of **5** with NBS in DMSO-H_2O at 40 °C afforded **6**, the dibromo derivative of *p*-APQ (**3**), in 83% yield as reddish brown needles. Cyanoimination of **6** with BTC in the presence of $TiCl_4$ proceeded smoothly, giving Br_2-DCNAPQDI (**2**) in 51% yield.[10]

The ν_{CN} frequencies in the IR spectra of **1** (2176 cm^{-1}) and **2** (2172 cm^{-1}) are almost the same as that of DCNQI (2175 cm^{-1}).[2a] The ^1H NMR resonances of H-6,7 of **1** (δ 7.50) and **2** (δ 7.52) are found at down field by more than 0.5 ppm from those of **3** (δ 6.94) and **6** (δ 6.97), revealing the strong electron accepting ability of the cyanoimine groups. The electronic spectra of **1** and **2** in dichloromethane showed a characteristic 1st excitation band at ca 430 nm which is more bathochromic by 50 nm than those of **3** and **6** (ca. 380 nm). The cyano groups of **1** and **2** may occupy in the opposite positions to the peri-protons of the naphthalene ring due to the steric repulsion, so that the *syn* isomers would be preferable.



Scheme 1.

Both of DCNAPQDI (**1**) and Br_2-DCNAPQDI (**2**) display two pairs of reversible one-electron redox waves in their cyclic voltammograms. The electrochemical parameters obtained by the cyclic voltammetry are summarized in Table 1 along with those of **3**, **6** and DCNQI. The electron-accepting abilities of **1** and **2** are much higher than those of **3** and **6**, since the first half-wave reduction potentials ($E_1{}^{1/2}$) of **1** and **2** are more positive by 0.51 and 0.45 V than those of **3** and **6**, respectively. The introduction of two bromine atoms at C-1 and C-2 positions is very effective to increase in the electron-accepting ability in this system, since $E_1{}^{1/2}$ of **2** is more positive by 0.09 V than that of **1**. The ΔE values of diimines **1** and **2** are smaller than those of **3** and **6** reflecting the diminished on-site Coulomb repulsion in the dianions of **1** and **2**, in which the negative charge would mainly localize on the nitrogen atoms of the CN groups.

Table 1. Electrochemical data[a] and ν_{CN} (ν_{CO}) bands[b] of DCNAPQDI, Br_2-DCNAPQDI, *p*-APQ, and Br_2-*p*-APQ

Compound	$E_1{}^{1/2}$/V	$E_2{}^{1/2}$/V	ΔE/V	ν_{CN} (ν_{CO})/cm^{-1}
DCNAPQDI (**1**)	-0.12	-0.41	0.29	2176
Br_2-DCNAPQDI (**2**)	-0.03	-0.33	0.30	2172
p-APQ (**3**)	-0.63	-0.97	0.34	1633
Br_2-*p*-APQ (**6**)	-0.48	-0.83	0.35	1634
DCNQI	$+0.13^{c}$	-0.29^{c}	0.42^{c}	2175^{c}

[a]Obtained by cyclic voltammetly: 10^{-3} mol·dm^{-3} in CH_3CN with 0.1 mol·dm^{-3} $Et_4N{\cdot}ClO_4$, scan rate: 100 mV·s^{-1}, reference electrode: SCE. [b]Measured with FTIR using KBr disk. [c]Reference 2a.

Attempted preparation of the CT complexes of DCNAPQDI (**1**) and Br_2-DCNAPQDI (**2**) with TTF was unsuccessful. Although DCNAPQDI (**1**) did not form any complex with tetrathiatetracene (TTT), Br_2-DCNAPQDI (**2**) formed a 1 : 1 CT complex[12] with TTT, namely, TTT·Br_2-DCNAPQDI (black powder) on mixing the each component in 1,2,4-trichlorobenzene. The electrical properties as well as characteristic IR bands of the complex are shown in Table 2. TTT·Br_2-DCNAPQDI exhibited a very broad intra-stack CT absorption band centered at around 3500 cm^{-1}, indicating that this salt exists in a segregated stacking mode in a mixed valence state.[13] However, TTT·Br_2-DCNAPQDI showed a relatively low room temperature conductivity and a fairly high activation energy (E_a) as we see in Table 2. Although single crystal strucutural analysis is needed before evaluating the conductivity of this complex, the degree of CT may be fairly large, because the ν_{CN} band of the complex appeared at lower wave-number region by 22 cm^{-1} than that of neutral Br_2-DCNAPQDI.

Preparation of Cu salts was performed by the direct reactions of DCNAPQDI (**1**) and Br_2-DCNAPQDI (**2**) with $CuBr_2$ in the presence of Cu wire in acetonitrile, affording $(DCNAPQDI)_4Cu_5$ (black powder) and $(Br_2\text{-}DCNAPQDI)_7Cu_6$ (deep purple fine needles).[12] Both of the Cu salts showed semiconducting temperature dependence from room temperature down to 80 K with activation energies listed in Table 2. $(DCNAPQDI)_4Cu_5$ showed a low room temperature conductivity and a high activation energy when compared with those of $(Br_2\text{-}DCNAPQDI)_7Cu_6$. Indeed, $(Br_2\text{-}DCNAPQDI)_7Cu_6$ showed a fairly high room temperature conductivity of 2.3×10^{-1} S·cm^{-1} which is 10^2 times higher than that of $(DCNAPQDI)_4Cu_5$. The activation energy of $(Br_2\text{-}DCNAPQDI)_7Cu_6$ is fairly low. The degree of electron transfer from the Cu to the acceptor is ambiguous at this stage, since valence of Cu is not clear. However, the formal charge on DCNAPQDI in $(DCNAPQDI)_4Cu_5$ is estimated to be around -1. This estimation may be supported from the ν_{CN} band of $(DCNAPQDI)_4Cu_5$ (2157 cm^{-1}) shifted by 19 cm^{-1} further lower wave-number region than that of neutral DCNAPQDI. On the contrary, $(Br_2\text{-}DCNAPQDI)_7Cu_6$ may exist in a partial CT state, because the ν_{CN} band of $(Br_2\text{-}DCNAPQDI)_7Cu_6$ (2161 cm^{-1}) appeared at much higher wave-number region than that of $(DCNAPQDI)_4Cu_5$.

Table 2. Conductivities,[a] activation energies, and IR data[b] of the complexes of DCNAPQDI and Br_2-DCNAPQDI

Complex	$\sigma_{r.t.}$/S·cm^{-1}	E_a/eV	ν_{CN}/cm^{-1}
TTT·Br_2-DCNAPQDI	3.4×10^{-3}	0.168	2150
$(DCNAPQDI)_4Cu_5$	2.2×10^{-3}	0.118	2157
$(Br_2\text{-}DCNAPQDI)_7Cu_6$	2.3×10^{-1}	0.062	2161

[a]Measured by four-probe method on a compressed pellet. [b]Measured with FTIR using KBr disk; the ν_{CN} values of neutral acceptor molecules are listed in Table 1.

In summary, we have first prepared DCNAPQDI and Br_2-DCNAPQDI, a new family of acepleiadylene (a [14]annulene)-based DCNQI type electron acceptors and found that these new acceptors would be useful as a component molecule for the electrical conducting CT complexes or Cu salts. Preparation of single crystalline CT and Cu complexes is in progress.

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10 The typical procedure for the synthesis of **1** is as follows: A solution of **3** (100 mg, 0.43 mmol) in 6.0 ml of dry CH_2Cl_2 was added dropwise to a solution of titanium tetrachloride (409 mg, 2.2 mmol) in 2.2 ml of CH_2Cl_2 during a 30 min period under N_2 and the solution was stirred for 15 min. To this solution, BTC (0.50 ml, 2.2 mmol) was added during 5 min period. The reaction mixture was stirred for 4 h and then poured into cold water. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by the repeated recrystallization in hexane to yield 55 mg of **1** (45%).

11 Selected physical data of DCNAPQDI (**1**): dark brown needles; mp 245 °C (dec.); ^{1}H NMR (300 MHz, δ, $CDCl_3$) 7.10 (2H, s), 7.50 (2H, s), 7.73 (2H, d, $J = 7.4$ Hz), 8.64 (2H, d, $J = 7.4$ Hz); UV-vis (CH_2Cl_2, λ_{max}, nm, log ε) 431 (3.8), 302 (4.0), 231 (4.0); MS (EI, 70 eV, *m/z*, %) 256 ($M^{+\bullet}$, 45); Anal. Calcd. for $C_{18}H_8N_4$: C, 77.13; H, 2.88; N, 19.99%, Found: C, 77.04; H, 2.78; N, 19.81%. Br_2-DCNAPQDI (**2**): dark brown needles; mp 259 °C (dec.); ^{1}H NMR (300 MHz, δ, $CDCl_3$) 7.52 (2H, s), 7.75 (2H, d, $J = 7.4$ Hz), 8.68 (2H, d, $J = 7.4$ Hz); UV-vis (CH_2Cl_2, λ_{max}, nm, log ε) 434 (3.8), 294 (4.0), 231 (4.2); MS (EI, 70 eV, *m/z*, %) 440 ($M^{+\bullet} + 4$, 42), 438 ($M^{+\bullet} + 2$, 70), 436 ($M^{+\bullet}$, 35); Anal. Calcd. for $C_{18}H_6N_4Br_2$: C, 49.35; H, 1.38; N, 12.79%, Found: C, 49.63; H, 1.33; N, 12.51%.

12 The stoichiometries of these complexes were determined by elemental analysis.

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