Synthesis, Properties and Molecular-Orbital Calculations of New $\pi$-Acceptors as ortho-Analogues of DCNQI

Shuji Aonuma$^{1,3}$, Emiko Fujiwara$^{1,4}$, Tsuneki Kanzawa$^2$ and Yuko Hosokoshi$^2$

$^1$Department of Applied Chemistry and Academic Frontier Promotion Center, Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan
$^2$Department of Physical Science, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

E-mail: aonuma@isc.osakac.ac.jp

Abstract. New $\pi$-acceptor molecules, DCNA, DF-DCNA and DBr-DCNA have been synthesized as ortho-analogues of DCNQI, in which two cyanoimino groups are located positions next to each other. Molecular orbital calculations by several methods have been made and compared with the actual molecular geometry and reduction potentials.

1. Introduction

A series of $N,N'$-dicyano-$p$-quinonediimine (DCNQI) with various substituents at positions of 2 and 5 exhibits unique feature, especially strong $\pi$-d interactions of their copper salts.$^5$ The DCNQI molecule plays as both acceptor and ligand. The unique $\pi$-d interactions are constructed by the bidantate DCNQI through the tetrahedral coordination of the terminal cyanoimino (=N–C≡N) groups to the copper ions. In para-quinoid structure, two cyanoimino groups occupy the opposite ends, and $p$-DCNQI molecules show highly symmetrical structure with an inversion center.

New molecular arrangements and electronic structures can be expected by using a ortho-quinoid structure. In ortho-structure, the two coordination groups occupy positions next to each other, and o-DCNQI molecules no longer have an inversion center.

\[ \text{DCNA (R=H)} \]
\[ \text{DF-DCNA (R=F)} \]
\[ \text{DBr-DCNA (R=Br)} \]

To whom any correspondence should be addressed.

Present address: Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan.
Because ortho-quinooid structure is much less stable than the para one, attempted syntheses of o-DCNQI molecules have been failed. In some cases, formation of o-DCNQI has been detected by a spectral analysis, however it was too unstable to isolate.

Meanwhile, DCNA can be readily prepared by the cyanoimination reaction of the corresponding acenaphthoquinone, and is found to be very stable. Similar to o-DCNQI, the two cyanoimino groups of DCNA occupy positions next to each other. A series of these ortho-type quinoid compounds may be a good candidate for complex formation with metal ions such as Cu and chemical control of electron-accepting properties by substitution of the aromatic ring.

In the present paper, we describe synthesis, properties and molecular orbital (MO) calculations of DCNA, DF-DCNA and DBr-DCNA. Molecular modeling based on MO calculations is a powerful tool for designing a new organic molecule. In order to examine reliability of the calculation, experimentally obtained molecular geometry and redox potentials are compared with the calculated values.

2. Experimental

DCNA was synthesized in a 62% yield after recrystallization from acetonitrile by the cyanoimination reaction[6] of acenaphthoquinone (purchased form Aldrich, recrystallized from benzene prior to use):

IR (KBr) ν/cm⁻¹ 3090, 2179, 1576; \(^1\)H-NMR δ/ppm 8.92 (d, 2H), 8.35 (d, 2H), 7.95 (dd, 2H); EI-MS m/z 230, 203, 178, 152. Single crystals of DCNA suitable for X-ray analysis have been obtained as elongated thick plates by recrystallization again from acetonitrile: crystal data for C\(_{14}\)H\(_6\)N\(_4\), triclinic P\(_{\bar{1}}\), a = 8.886(1) Å, b = 3.8277(2) Å, c = 17.984(2) Å, \(\alpha = 77.338(3)^\circ\), \(\beta = 89.834(1)^\circ\), \(\gamma = 64.835(3)^\circ\), \(V = 537.4(1)\) Å\(^3\), Z = 2, R = 0.056, Rw = 0.064.

DF- and DBr-DCNA compounds were similarly prepared from the corresponding dihaloacenaphthoquinones [7] in 28% and 50% yields, respectively. DF-DCNA: IR (KBr) ν/cm⁻¹ 3053,2187,1635,1088; \(^1\)H-NMR δ/ppm 8.97 (d, 2H), 7.59 (dd, 2H); EI-MS m/z 266, 239, 214, 188. DBr-DCNA: IR (KBr) ν/cm⁻¹ 3092, 2179, 1605, 1043; \(^1\)H-NMR δ/ppm 8.73 (d, 2H), 8.31 (d, 2H); EI-MS m/z 388, 362, 336, 308, 228.

Cyclic voltammetry was performed in 0.1M TBAP/PhCN with a Pt working electrode, Ag/AgCl reference electrode, and scan rate of 50mV/s at room temperature using ALS Electrochemical Analyzer Model 660B.

All MO calculations are run with restricted Hartree–Fock wave functions. Full geometry optimization by an eigenvector following (EF) method without restriction of any symmetry was conducted using the MOPAC 2002 program [8] in WinMOPAC 3.9 (Fujitsu Ltd.) with the AM1, PM3 and PM5 parametrizations implemented therein. Gaussian 03W [9] was used for other molecular orbital calculations.

3. Results and discussion

3.1. Synthesis

DCNA, DF-DCNA and DBr-DCNA have been synthesized from the corresponding acenaphthoquinones. As shown in Scheme 1, dibromoacenaphthoquinone (3) has been prepared by bromination of acenaphthene (1) to the dibromide 2 and its oxidation. Halogen-exchange reaction of acenaphthoquinonone 3 with CsF afforded difluoroacenaphthoquinone (4). DF-DCNA and DBr-DCNA are low solubility in conventional organic solvents.

3.2. Molecular structure

Actual molecular structure by X-ray diffraction was compared with the structures by geometry optimized by MO calculations. Semi-empirical (AM1, PM3, PM5), \textit{ab initio} (HF, MP2), and density functional theory (DFT) methods were chosen to see which results best match the experimental geometry. The PM5 method is the newly developed semi-empirical level calculations. Møller-Plesset (MP) method is an economical way to partially correct for the lack of electron
correlation in the Hartree-Fock (HF) method. In the MP2 method, Møller-Plesset correlation energy correction is truncated at second-order. DFT calculations were performed at level with hybrid functionals, B3LYP. These \textit{ab initio} calculations were computed by employing 6-311G(d,p) basis set. There are three possible isomers as shown in figure 1. Heat of formation ($H_f$) calculated by the PM5 method suggest that the \textit{syn} form is the most unstable. There is no marked difference in $H_f$ between

\begin{align*}
\text{anti} & : H_f = 677 \\
\text{meso} & : H_f = 669 \\
\text{syn} & : H_f = 723
\end{align*}

**Figure 1.** Possible isomers of DCNA and Heat of formation ($H_f$) calculated by PM5.

**Figure 2.** Molecular structure of DCNA

**Figure 3.** Molecular arrangement of DCNA molecules.
Table 1. Bond lengths (Å) for DCNA by X-ray and MO calculations.a

| Bond | X-ray | AM1 | PM3 | PM5 | HF | MP2 | B3LYP |
|------|-------|-----|-----|-----|----|-----|-------|
| N(1)-C(11) | 1.288(5) | 1.292 | 1.294 | 1.289 | 1.258 | 1.296 | 1.286 |
| N(3)-C(12) | 1.291(5) | 1.292 | 1.294 | 1.289 | 1.258 | 1.296 | 1.286 |
| N(1)-C(13) | 1.352(5) | 1.367 | 1.378 | 1.366 | 1.336 | 1.343 | 1.325 |
| N(3)-C(14) | 1.343(5) | 1.367 | 1.378 | 1.366 | 1.336 | 1.343 | 1.325 |
| N(2)-C(13) | 1.149(6) | 1.170 | 1.164 | 1.160 | 1.133 | 1.182 | 1.162 |
| N(4)-C(14) | 1.141(6) | 1.170 | 1.164 | 1.160 | 1.133 | 1.182 | 1.162 |
| C(10)-C(11) | 1.459(5) | 1.481 | 1.476 | 1.474 | 1.475 | 1.471 | 1.468 |
| C(4)-C(12) | 1.457(6) | 1.481 | 1.476 | 1.474 | 1.475 | 1.471 | 1.468 |
| C(11)-C(12) | 1.533(5) | 1.544 | 1.518 | 1.534 | 1.526 | 1.509 | 1.518 |
| C(1)-C(2) | 1.377(6) | 1.378 | 1.374 | 1.366 | 1.366 | 1.391 | 1.383 |
| C(7)-C(8) | 1.367(7) | 1.378 | 1.374 | 1.366 | 1.366 | 1.391 | 1.383 |
| C(2)-C(3) | 1.415(6) | 1.424 | 1.422 | 1.423 | 1.423 | 1.420 | 1.417 |
| C(8)-C(9) | 1.396(6) | 1.424 | 1.422 | 1.423 | 1.423 | 1.420 | 1.417 |
| C(3)-C(4) | 1.388(5) | 1.372 | 1.369 | 1.360 | 1.364 | 1.388 | 1.382 |
| C(9)-C(10) | 1.383(5) | 1.372 | 1.369 | 1.360 | 1.364 | 1.388 | 1.382 |
| C(4)-C(5) | 1.425(5) | 1.429 | 1.424 | 1.427 | 1.411 | 1.419 | 1.417 |
| C(10)-C(5) | 1.427(5) | 1.429 | 1.424 | 1.427 | 1.411 | 1.419 | 1.417 |
| C(5)-C(6) | 1.386(5) | 1.398 | 1.391 | 1.386 | 1.388 | 1.412 | 1.407 |
| C(1)-C(6) | 1.413(6) | 1.424 | 1.423 | 1.423 | 1.419 | 1.422 | 1.421 |
| C(6)-C(7) | 1.411(5) | 1.424 | 1.423 | 1.423 | 1.419 | 1.422 | 1.421 |

average errors 0.013 0.013 0.011 0.014 0.015 0.012

a 6-311G(d,p) basis set for *ab initio* calculations.

The actual molecular structure is found to be the anti form by X-ray single crystal analysis (figure 2). The planar DCNA molecules form columnar structure (figure 3).

In the tables 1-3, molecular geometries optimized by the MO calculations are compared to the X-ray data. Average errors in bond lengths (table 1) and angles (table 2) show that semi-empirical PM5 produces results which are comparable to *ab initio* methodology with a very minimum computational cost. Several long-standing faults in AM1 and PM3 have been known, the prediction of geometries often fails. However, obsolete AM1 and PM3 methods still gave fairly good results for the optimized molecular structure of DCNA.

The best matching result was obtained by DFT-B3LYP. In spite of longer computational time of MP2, the matching was not improved. But, it is noteworthy that slight deviation from a molecular plane is reproduced by MP2 (table 3).

3.3. Electron-accepting properties

The electron-accepting properties of DCNA, DF-DCNA and DBr-DCNA were investigated by cyclic voltammetry. All of the voltammograms exhibited two-stage one-electron reduction waves (table 4). The first reduction potential of DCNA is 0.22 V less than that of DMe-DCNQI, indicating the weak electron-accepting property. The annelation of an electron-donating naphthalene ring might lower the electron-accepting property of DCNA. The reduction potentials of DBr-DCNA and DF-DCNA are observed at potentials higher than those of DCNA. The electron-accepting property was enhanced by introducing halogen atoms (F and Br) to DCNA.

Koopmans' theorem is an approximation in MO theory, in which the electron affinity is the negative of the energy of the lowest unoccupied (i.e. virtual) molecular orbital (LUMO) [10]. Despite the neglected orbital relaxation that immediately follows the reduction, such correlations are an efficient tool for prediction of reduction potentials, namely to estimate electron-accepting properties.
Table 2. Bond angles (°) for DCNA observed by X-ray crystal analysis and MO calculations.

| Bond Angle                | X-ray | AM1  | PM3  | PM5  | HF   | MP2  | B3LYP |
|---------------------------|-------|------|------|------|------|------|-------|
| C(11)-N(1)-C(13)         | 119.7(3) | 122.3 | 124.9 | 122.3 | 120.4 | 117.9 | 121.7 |
| C(12)-N(3)-C(14)         | 119.0(4) | 122.3 | 124.9 | 122.3 | 120.4 | 117.9 | 121.7 |
| N(1)-C(13)-N(2)          | 171.7(5) | 172.9 | 173.1 | 171.5 | 176.7 | 174.7 | 175.0 |
| N(3)-C(14)-N(4)          | 172.7(5) | 172.9 | 173.1 | 171.5 | 176.7 | 174.7 | 175.0 |
| N(1)-C(11)-C(10)         | 134.1(3) | 132.3 | 131.3 | 133.1 | 133.5 | 132.7 | 132.5 |
| N(3)-C(12)-C(4)          | 134.4(3) | 132.3 | 131.3 | 133.1 | 133.5 | 132.7 | 132.5 |
| C(12)-C(11)-N(1)         | 119.0(3) | 121.4 | 121.9 | 120.3 | 120.0 | 120.3 | 120.7 |
| N(3)-C(12)-C(11)         | 119.1(4) | 121.4 | 121.9 | 120.3 | 120.0 | 120.3 | 120.7 |
| C(12)-C(11)-C(10)        | 106.9(3) | 106.3 | 106.8 | 106.6 | 106.5 | 107.0 | 106.8 |
| N(3)-C(12)-C(4)          | 119.1(4) | 121.4 | 121.9 | 120.3 | 120.0 | 120.3 | 120.7 |
| C(12)-C(11)-C(10)        | 106.5(3) | 106.3 | 106.8 | 106.6 | 106.5 | 107.0 | 106.8 |
| C(11)-C(10)-C(9)         | 133.9(4) | 133.9 | 134.4 | 134.0 | 133.9 | 134.2 | 134.2 |
| C(12)-C(4)-C(3)          | 133.8(3) | 133.9 | 134.4 | 134.0 | 133.9 | 134.2 | 134.2 |
| C(11)-C(10)-C(5)         | 107.6(3) | 107.5 | 106.9 | 107.1 | 106.6 | 106.3 | 106.5 |
| C(5)-C(4)-C(12)          | 107.2(3) | 107.5 | 106.9 | 107.1 | 106.6 | 106.3 | 106.5 |
| C(10)-C(5)-C(4)          | 112.6(3) | 112.4 | 112.6 | 112.7 | 113.8 | 113.2 | 113.3 |
| C(7)-C(6)-C(1)           | 128.2(4) | 127.6 | 127.2 | 127.6 | 127.2 | 127.4 | 127.7 |
| C(3)-C(2)-C(1)           | 124.1(4) | 122.6 | 122.6 | 122.8 | 122.1 | 122.8 | 122.4 |
| C(9)-C(8)-C(7)           | 123.4(4) | 122.6 | 122.6 | 122.8 | 122.1 | 122.8 | 122.4 |
| C(4)-C(3)-C(2)           | 116.8(3) | 118.5 | 118.4 | 118.2 | 118.3 | 117.8 | 118.2 |
| C(10)-C(9)-C(8)          | 117.0(4) | 118.5 | 118.4 | 118.2 | 118.3 | 117.8 | 118.2 |
| C(5)-C(4)-C(3)           | 119.0(4) | 118.6 | 118.8 | 118.9 | 119.5 | 119.5 | 119.3 |
| C(5)-C(10)-C(9)          | 119.4(4) | 118.6 | 118.8 | 118.9 | 119.5 | 119.5 | 119.3 |
| C(2)-C(1)-C(6)           | 119.7(4) | 120.3 | 120.1 | 120.2 | 120.6 | 120.2 | 120.6 |
| C(8)-C(7)-C(6)           | 121.5(4) | 120.3 | 120.1 | 120.2 | 120.6 | 120.2 | 120.6 |
| C(6)-C(5)-C(4)           | 123.8(3) | 123.8 | 123.7 | 123.6 | 123.1 | 123.2 | 123.4 |
| C(6)-C(5)-C(10)          | 123.6(3) | 123.8 | 123.7 | 123.6 | 123.1 | 123.2 | 123.4 |
| C(1)-C(6)-C(5)           | 116.6(3) | 116.2 | 116.4 | 116.2 | 116.4 | 116.2 | 116.1 |
| C(7)-C(6)-C(5)           | 115.2(4) | 116.2 | 116.4 | 116.2 | 116.4 | 116.2 | 116.1 |

average errors 1.0 1.3 0.8 1.0 0.9 1.1

Table 3. Selected torsion angles (°) for DCNA observed by X-ray crystal analysis and MO calculations.

| Torsion Angle                  | X-ray | AM1  | PM3  | PM5  | HF   | MP2  | B3LYP |
|--------------------------------|-------|------|------|------|------|------|-------|
| C(13)-N(1)-C(11)-C(10)        | −0.1(6) | 0.0  | 0.0  | 0.0  | 0.0  | −0.1 | 0.0   |
| C(14)-N(3)-C(12)-C(4)         | 2.7(6)  | 0.0  | 0.0  | 0.0  | 0.0  | 0.1  | 0.0   |
| N(1)-C(11)-C(12)-N(3)         | −0.9(5) | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0   |
| C(10)-C(11)-C(12)-C(4)        | −1.0(3) | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0   |
| C(4)-C(5)-C(6)-C(1)           | 0.2(5)  | 0.0  | 0.0  | 0.0  | 0.0  | 5.7  | 0.0   |
| C(10)-C(5)-C(6)-C(7)          | −0.7(5) | 0.0  | 0.0  | 0.0  | 0.0  | −5.7 | 0.0   |
| C(10)-C(5)-C(6)-C(1)          | −179(508) | −180.0 | −180.0 | −180.0 | −180.0 | −178.7 | −180.0 |
| C(4)-C(5)-C(6)-C(7)           | 179.3(3) | 180.0 | 180.0 | 180.0 | 180.0 | 178.7 | 180.0 |

a 6-311G(d,p) basis set for ab initio calculations
One-electron reduction potential is formulated as equation (1).

\[ E_{\text{redox}} = \frac{-\Delta H + T\Delta S}{F} \]  

(1)

For the first reduction potential, \( \Delta H \) is energy difference between the anion radical and neutral states. Total energy of the each state is calculated from the sum of energy level of each occupied molecular level (\( \varepsilon_{i} \)) multiplied by number of electrons (\( n_{i} \)). The total energy of the neutral state (\( H_{0}^{0} \)) is:

\[ H_{0}^{0} = \sum_{i=1}^{\text{HOMO}} n_{i} \cdot \varepsilon_{i} \]

Accurate computational prediction of reduction potentials requires comparison of energies for both the neutral and anion radical states. The open-shell nature of the reduced species and solvation effects make the prediction time consuming calculations. However, if electronic feature of the anion radical state is assumed to be similar as that of the neutral state, \( H^{-} \) and \( \Delta H \) can be written as:

\[ H^{-} = H_{0}^{0} + \varepsilon_{\text{LUMO}} \]

\[ \Delta H = H^{-} - H_{0}^{0} = \varepsilon_{\text{LUMO}} \]

Similar entropy change (\( \Delta S \)) and solvation effects are expected among the structurally similar compounds. If these assumptions hold true, correlation between \( E_{\text{redox}} \) and \( \varepsilon_{\text{LUMO}} \) follows Koopmans’ approximation. Equation (1) can be written as follows, where In equation (2), \( A \) is a negative constant, and \( C \) represents solvation and entropy terms.

\[ E_{\text{redox}} = A\varepsilon_{\text{LUMO}} + C \]  

(2)

The calculated \( \varepsilon_{\text{LUMO}} \) are shown in table 4. A good linear correlation that follows equation (2) is obtained between the \( E_{1} \) values and \( \varepsilon_{\text{LUMO}} \) by the \textit{ab initio} calculations. Among them, MP2 and DFT afforded better results than HF. Unexpectedly, the results were slightly better with 6-31G(d,p) than those with 6-311G(d,p).

The results by the semi-empirical calculations are inferior to those by the \textit{ab initio} calculations. In sharp contrast to best match of PM5 to molecular geometry, PM5 overestimates the electron-accepting property of DF-DCNA. By PM3 and PM5, LUMO of DF-DCNA became more negative than that of DBr-DCNA, which is reverse order to be expected from the redox potentials.

The reason for the poor performance of the semi-empirical methods may be relevant to less delocalized LUMO and narrower gap between the LUMO and next LUMO (figure 4). The gap is calculated as less than 0.3 eV by the semi-empirical methods, whereas ca. 0.7 eV by the \textit{ab initio} methods.

**Table 4.** Redox potentials measured by cyclic voltammetry and calculated energy level of LUMO.

| Compounds | Redox potentials / V\textsuperscript{a} | \( \varepsilon_{\text{LUMO}} / \text{eV} \) |
|-----------|---------------------------------|------------------------------------------|
|           | \( E_{1} \) | \( E_{2} \) | AM1 | PM3 | PM5 | HF\textsuperscript{b} | MP2\textsuperscript{b} | B3LYP\textsuperscript{c} | B3LYP\textsuperscript{b} | correlation coefficient |
| DCNA      | −0.13 | −0.91 | −1.67 | −1.80 | −2.01 | −0.190 | −0.564 | −3.78 | −3.99 | 0.927 |
| DF-DCNA   | −0.10 | −0.84 | −2.01 | −2.08 | −2.36 | −0.373 | −0.783 | −3.91 | −4.14 | 0.921 |
| DBr-DCNA  | −0.06 | −0.82\textsuperscript{d} | −2.07 | −2.02 | −2.20 | −0.520 | −0.875 | −4.01 | −4.22 | 0.877 |
| DMe-DCNQI | 0.09  | −0.57\textsuperscript{d} | −2.40 | −2.36 | −2.63 | −0.762 | −1.34 | −4.36 | −4.54 | 0.955 |

\textsuperscript{a} V vs Ag/AgCl in PhCN.
\textsuperscript{b} 6-311G(d,p).
\textsuperscript{c} 6-31G(d,p).
\textsuperscript{d} Irreversible.
More detailed investigations are now in progress, including various DCNQI and TCNQ molecules, newer methods such as PM6 and RM1 (improved parameterization of PM5 and AM1, respectively), and ab initio calculations employing various basis sets.

### 3.4. Anion Radical Salts

In order to confirm conductivity, several attempts have been made to prepare the anion radical salts by electrochemical reduction of DCNA and DBr-DCNA with the metal salts (*e.g.* LiClO$_4$, CuI, (Et$_4$N)$_2$CuBr$_4$, (Et$_4$N)$_2$CoBr$_4$) in acetonitrile solutions. Black tiny needles or powders were obtained from DCNA-Li, DCNA-Cu and DBr-DCNA-Cu and green powders from DBr-DCNA-Hg. No powder or crystals formation was observed with Ni, Co, Ag ions so far.

Among the lithium salts of DCNA, a bundle of needles has been a semiconductor of room-temperature conductivity around $10^5$ Scm$^{-1}$. IR spectra of the lithium salts shows low wavenumber shifts of C≡N and C=N stretching vibrations. In a similar manner as in the case of DCNQI, these bonds are anti-bonding in the LUMO. The downward shifts are indicative of the reduced state of DCNA.

### 4. Conclusion

We have synthesized a new $\pi$-acceptor molecule DCNA, an ortho-analogue of DCNQI. Electron-accepting property of DCNA has been enhanced by halogenations (Br, F) of DCNA. Electro-reductions of DCNA afforded the metal complexes, but those with good conductivity did not obtained so far. Very fast PM5 is most applicable to prediction of molecular structure, but ab initio methodology is required for evaluating electron-accepting property.

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