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Synthesis and characterization of novel strong electron acceptors: bithiazole analogues of tetracyanodiphenoquinodimethane (TCNDQ)

Kazuharu Suzuki,[a] Masaaki Tomura,[b] Shoji Tanaka[a,b] and Yoshiro Yamashita[a,b,*,†]

[a]*Department of Structural Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan*
[b]*Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

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Abstract

Novel electron acceptors, bithiazole analogues of tetracyanodiphenoquinodimethane (TCNDQ), were synthesized by using a Pd-catalyzed coupling reaction of a dibromated precursor with sodium dicyanomethanide. The new acceptors show strong electron-accepting ability and small on-site Coulomb repulsion. The X-ray crystallographic analysis has revealed a planar structure containing a double bond with *E*-configuration. Several charge transfer complexes were obtained with electron donors such as tetrathiafulvalene (TTF). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: organic conductor; electron acceptor; thiazole; crystal structure; charge transfer complex.

A large number of electron donor molecules have been synthesized since the discovery of the first synthetic metal, a charge transfer complex of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ). Organic superconductors have been developed by using TTF derivatives as components.[1] On the other hand, although various kinds of TCNQ derivatives[2] have also been prepared over the past four decades, only a few of the acceptor-based conductors show metallic behavior.[3]

We have recently developed TCNDQ analogue **1**[4] with the two quinonoid ring system and peripheral heteroatoms. In the crystal of **1**, two-dimensional intermolecular heteroatom contacts were observed by X-ray crystallographic analysis. Compound **1** has afforded some highly conducting CT complexes and radical anion salts. As an extension of this work we have now designed a new acceptor molecule **5**, which is an isoelectronic π-system of TCNDQ. Acceptor **2**,[5]

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* Corresponding author. Fax: +81-45-924-5489; e-mail: yoshiro@echem.titech.ac.jp

† Present address: Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan.

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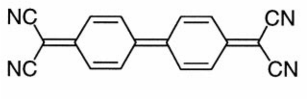
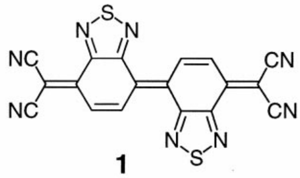
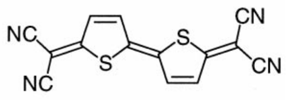
a bithiophene analogue of TCNDQ, and its derivatives have already been synthesized; however, they were all found to be weak acceptors. Nitrogen atoms of the thiazole rings in **5** are expected to enhance its acceptor ability and also work as a functional part for heteroatom contacts.[6,7] According to the MNDO-PM3 calculations,[8] large coefficients of LUMO are observed on the nitrogen atoms of the thiazole rings.



TCNDQ



1



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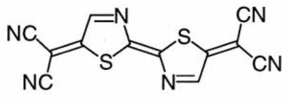
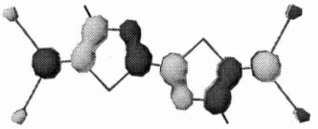


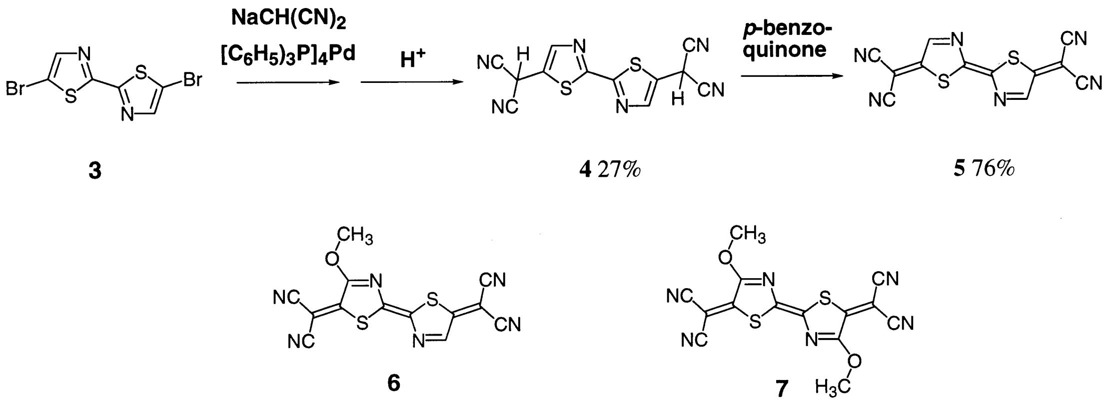
5



LUMO of 5

Attempts to synthesize quinoid acceptors including nitrogen atoms have already been made by several groups.[9–16] However, isolation of those acceptors has not been successful due to their instability. Acceptor **5** is the first quinoid acceptor of this type that has been isolated in the neutral state. We would like to report here its synthesis, redox properties, structures and charge transfer complexes.

Bithiazole[17] reacted with 4 equiv. of *N*-bromosuccinimide in DMF at 60°C for 5 h to afford dibromo bithiazole **3**[20] in 97% yield. Sodium dicyanomethanide[18,19] was allowed to react with **3** in refluxing THF containing 0.1 equiv. of tetrakis(triphenylphosphine)-palladium(0), followed by acidification with HCl to isolate bis(dicyanomethane)bithiazole **4**. Subsequent extraction with dichloromethane and sublimation under reduced pressure gave **4** in 27% yield. Oxidation of **4**[21] was performed with *p*-benzoquinone in dry dichloromethane. Impurities in the crude products were removed by sublimation under reduced pressure at 150°C, and then the desired compound **5**[22] was obtained at 200–250°C in 76% yield (Scheme 1). Recrystallization from dichloromethane



Scheme 1.

gave blue luster black crystals. Acceptor **5** could be kept for more than a year at ambient temperature without decomposition, but it reacts quickly with nucleophilic regents such as water and methanol. Actually, methoxy-substituted derivatives, **6**[23] and **7**,[24] were obtained by addition of methanol to **5** in dichloromethane at room temperature. Compounds **6** and **7** were separated by silica gel column chromatography and recrystallized from dichloromethane.

The redox properties of **5** and **6** were examined by CV measurements. The results are summarized in Table 1 together with those of **1**, **2** and TCNQ. Acceptors **5** and **6** show two reversible one-electron reduction waves. The reduction potentials ($E^1_{1/2}$, $E^2_{1/2}$) of **5** (+0.34, +0.01 V) are higher than those of TCNQ (+0.22, −0.35 V), indicating that **5** is a very strong acceptor owing to the electron-withdrawing effect of the C=N bond. This result indicates that introduction of nitrogen atoms is a useful method for increasing acceptor abilities without using extra substituents. The differences between the first and second reduction potentials (ΔE) decrease in **5** compared to that of TCNQ, suggesting the decrease in on-site Coulomb repulsion in **5** due to the extended π-conjugation. The strong electron acceptability and small on-site Coulombic repulsion indicate the superiority of **5** as an acceptor for organic conductors. Reduction potentials of **6** (+0.10, −0.19 V) are about 0.2 V lower than **5** due to the electron-donating property of the methoxy group.

Table 1
The first and second half-wave reduction potentials[a]

Compound	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	ΔE (V)[b]
1	+0.24	+0.03	0.21
2	−0.03	−0.26	0.23
5	+0.34	+0.01	0.33
6	+0.10	−0.19	0.29
TCNQ	+0.22	−0.35	0.57

[a] Versus SCE, in CH_2Cl_2, $^n Bu_4NClO_4$, scan rate 100 mV sec^{-1}.
[b] $\Delta E = E^1_{1/2} - E^2_{1/2}$.

Absorption maxima of the acceptors are summarized in Table 2. New acceptors show a sharp strong absorption which is characteristic of bis-quinonoid type acceptors. The absorption maxima are red-shifted compared to those of **2** and TCNQ.

Table 2
Absorption maxima of UV–vis spectrum

Compound	λ_{max}[a] (log ε) (nm) (dm^{-3} mol^{-1} cm^{-1})
1	522 (5.10), 486 (4.75)
2	536 (4.80), 512 (4.74)
5	553 (4.85), 513 (4.47)
6	562 (4.44), 527 (4.57)
TCNQ	401 (4.84)

[a] In CH_2Cl_2.

The single crystals of **5** and **6** were obtained by slow dilution of a dichloromethane solution with hexane vapor at −30°C. The molecular structures of the two acceptors have been determined by X-ray crystallographic analyses.[25–27] Figs. 1 and 2 show that both of the acceptors have the *E*-configuration of the central double bond. Acceptor **5** has a planar geometry. The dihedral angles between the dicyanomethylene moiety and the thiazole ring, and the two thiazole rings are 1.8 and 0.0°, respectively. The CH···N hydrogen bonding (2.47 Å), which is shorter than the sum of the van der Waals radii (H–N, 2.75 Å), are observed between hydrogen of the thiazole ring and nitrogen of the cyano group (Fig. 3). Crystals of **6** contain dichloromethane. The molecule **6** also has a planar geometry. The deviation of the methoxy group from the thiazole ring is within 0.03 Å. The dihedral angles between the dicyanomethylene moiety and the thiazole ring, and the two thiazole rings are 4.6, 2.6 and 2.3°, respectively.

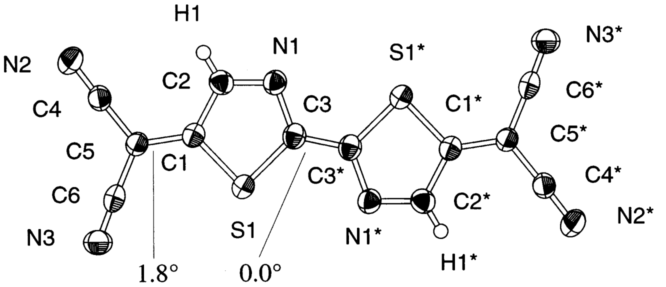


Figure 1. Molecular structure of **5**

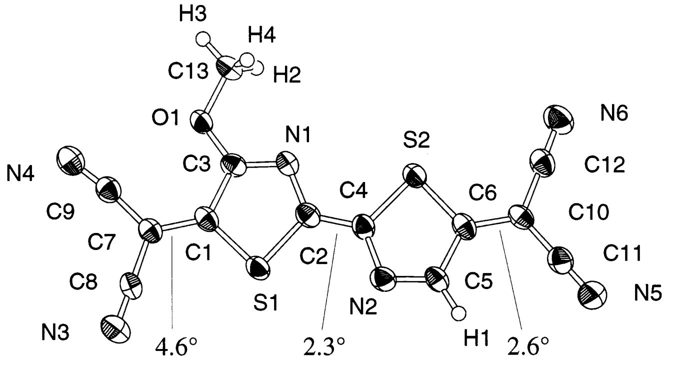


Figure 2. Molecular structure of **6**

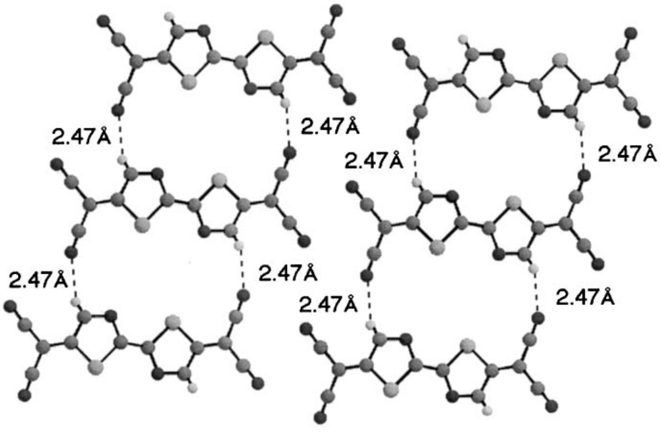


Figure 3. Crystal structure of **5**

Attempts to prepare radical anion salts of **5** and **6** by electrochemical reduction have not been successful. The acceptor **5** afforded charge transfer complexes with TTF, tetramethyltetraselenafulvalene (TMTSF), bis(ethlenedithio)tetrathiafulvalene (BEDT–TTF) and tetrathiatetracene (TTT). The electrical conductivities for the complexes of **5**, measured by using a compressed pellet, are as follows: TTF complex, 2.1×10^{-3} S cm^{-1}; TMTSF complex, 3.1×10^{-5} S cm^{-1}; BEDT–TTF complex, 3.6×10^{-8} S cm^{-1}; TTT complex, 7.7×10^{-3} S cm^{-1}.

Further experiments are now in progress to isolate the single crystals of charge transfer complexes.

Acknowledgements

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20. 5,5′-Dibromo-2,2′-bithiazole **3**: mp 155°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75 ppm (s, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 161.9, 145.1, 112.0 ppm; MS (EI) m/z (relative intensity) 326 (M$^+$, 52), 247 (34), 83 (15), 57 (100); UV–vis (CH_2Cl_2) $\lambda_{\max}$ 341 nm (log ε 4.43); IR (KBr) ν 1695, 1468, 1377, 1142, 1132, 998, 918, 899, 850, 745, 631, 604, 474 cm^{-1}; anal. calcd for $C_6H_2Br_2N_2S_2$: C, 22.10; H, 0.62; N, 8.59. Found C, 22.05; H, 0.48; N, 8.39.
21. [5,5′-Bis(dicyanomethane)]-2,2′-bithiazole **4**: mp 281°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.07 ppm (s, 2H), 5.41(s, 2H); MS (EI) m/z (relative intensity) 296 (M$^+$, 100), 269 (16), 193 (29), 122 (78); UV–vis (CH_2Cl_2) $\lambda_{\max}$ 555 nm (log ε 2.65), 322 (4.22); IR (KBr) ν 3093, 2890, 2182, 1504, 1408, 1308, 1272, 1157, 1136, 1019, 922, 878, 765, 609, 504, 464 cm^{-1}; anal. calcd for $C_{12}H_4N_6S_2$: C, 48.64; H, 1.36; N, 28.36. Found C, 48.77; H, 0.81; N, 28.16. HRMS calcd for $C_{12}H_4N_6S_2$: 295.99389. Found 295.99274 (dev. −3.88 ppm).

22. [2*H*,2′*H*,5*H*,5′*H*-(*E*)-$\Delta^{2,2'}$-Bithiazole]-$\Delta^{5,1''}$,$\Delta^{5',1'''}$-bis(dicyanomethane) **5**: mp>500°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.72 ppm (s, 2H); MS (EI) *m*/*z* (relative intensity) 294 (M^+, 100), 121 (91), 94 (38), 70 (35); UV–vis (CH_2Cl_2) λ_{max} 660 nm (log ε 3.48), 553 (4.85), 513 (4.47), 381 (3.21), 309 (3.81), 260 (3.90); IR (KBr) ν 3075, 2221, 2196, 1505, 1328, 1152, 1118, 900, 733, 654, 627, 592 cm^{-1}; anal. calcd for $C_{12}H_2N_6S_2$: C, 48.97; H, 0.68; N, 28.55. Found C, 49.06; H, 0.00; N, 28.40. HRMS calcd for $C_{12}H_2N_6S_2$: 293.97824. Found 293.97807 (dev. −0.58 ppm).
23. [(2*H*,5*H*-4-Methoxythiazole)-(*E*)-$\Delta^{2,2'}$-(2′*H*,5′*H*-thiazole)]-$\Delta^{5,1''}$,$\Delta^{5',1'''}$-bis(dicyanomethane) **6**: mp 213–215°C (decomp.); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 4.41 ppm (s, 3H), 8.53 (s, 1H); MS (EI) *m*/*z* (relative intensity) 324 (M^+, 99), 188 (100), 173 (30), 123 (23), 108 (32), 94 (18), 82 (11); UV–vis (CH_2Cl_2) λ_{max} 615 nm (log ε 4.10, sh), 562 (4.44), 527 (4.57), 366 (3.24), 260 (3.78); IR (KBr) ν 2218, 1643, 1591, 1538, 1519, 1503, 1442, 1415, 1344, 1313, 1159, 1052, 875, 737, 629 cm^{-1}; HRMS calcd for $C_{13}H_4N_6OS_2$: 323.98880. Found 323.98785 (dev. −2.95 ppm).
24. [2*H*,2′*H*,5*H*,5′*H*-(*E*)-$\Delta^{2,2'}$-Bis(4-methoxythiazole)]-$\Delta^{5,1''}$,$\Delta^{5',1'''}$-bis(dicyanomethane) **7**: MS (EI) *m*/*z* (relative intensity) 354 (M^+, 100), 339 (32), 324 (35), 222 (20), 203 (45), 188 (25), 123 (31), 108 (37), 96 (21), 82 (18), 67 (70); HRMS calcd for $C_{14}H_6N_6O_2S_2$: 353.99937. Found 353.99890 (dev. −1.32 ppm).
25. X-ray reflection data were collected on Rigaku R-AXIS IV imaging plate area detector with graphite monochromated Mo–K_α radiation (50 kV, 100 mA, $\lambda = 0.71069$ Å). All structures were solved by direct method and refined by full-matrix least-squares on F^2 with SHELX-97.[28]
26. Crystal data for **5**: $C_{12}H_2N_6S_2$, $M = 294.31$, triclinic, space group $P\bar{1}$ (No. 2), $a = 6.499(1)$, $b = 9.458(2)$, $c = 5.589(1)$ Å, $\alpha = 91.13(2)$, $\beta = 104.26(1)$, $\gamma = 75.42(1)°$, $V = 322.14(1)$ Å^3, $Z = 1$, $D_{calc} = 1.517$ g cm^{-1}, $T = 207$ K, $R_1 = 0.058$, $wR_2 = 0.154$, G.O.F. = 1.13. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in a difference Fourier-map and refined isotropically. The final full-matrix least-square refinement was based on 1087 observed reflections [$I > 2\sigma(I)$] and 96 variable parameters.
27. Crystal data for **6**: $C_{13}H_4N_6OS_2(CH_2Cl_2)_{0.5}$, $M = 366.80$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.941(5)$, $b = 10.304(3)$, $c = 9.101(3)$ Å, $\alpha = 105.50(1)$, $\beta = 93.71(3)$, $\gamma = 115.75(3)°$, $V = 791.4(6)$ Å^3, $Z = 2$, $D_{calc} = 1.539$ g cm^{-1}, $T = 180$ K, $R_1 = 0.073$, $wR_2 = 0.098$, G.O.F. = 1.56. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by using a riding model. The final full-matrix least-squares refinement was based on 1498 observed reflections [$I > 2\sigma(I)$] and 218 variable parameters.
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