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Furan-Fused TCNQ and DCNQI: Synthesis and Properties

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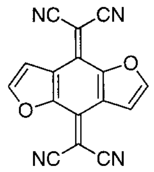
Structural modification of 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been extensively explored to obtain new materials with enhanced conducting properties, principally by means of incorporation of the substituents and of π-system extension. The extension of the π-system has been considered to reduce intramolecular electron repulsion and thereby lead to increased conductivities of their radical anions. The molecular design according to such guideline includes the annulation of benzene,[1] thiophene,[2] thiadiazole,[3] pyrazine,[4] other heterocycles,[5] and polyaromatic rings or multiheterocycles.[6] Despite these ample examples of π-expanded TCNQ derivatives, furan-fused TCNQ, 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*:4,5-*b*′]difuran **1**, has not been reported up to now. In this paper we describe the synthesis of furan-fused TCNQ **1** as well as furan-fused *N,N*′-dicyano-*p*-quinodiimine (DCNQI) **2** and their physicochemical properties in comparison with those of thiophene analogues **3**, on which we have previously reported.[2]



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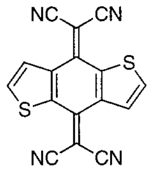

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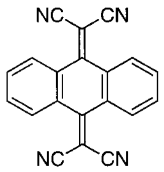

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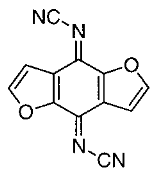

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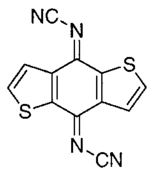

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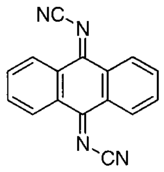

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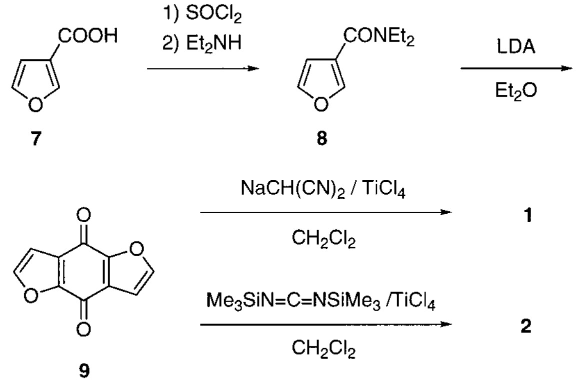
Results and Discussion

Furan-Fused TCNQ. The synthesis of **1** was carried out according to Scheme 1. In a procedure similar to that used for the synthesis of thiophene-fused quinone,[7] furan 3-carboxyamide **8** was treated with 1.05 equiv of LDA in diethyl ether under reflux to afford furan-fused quinone **9** in 19% yield. Quinone **9** was converted to compound **1** in 79% yield by reaction with malononitrile in the presence of $TiCl_4$ by following the procedure described by Hunig.[1b]

Scheme 1



The electrochemical properties of **1** were investigated by cyclic voltammetry. The redox potentials of **1** are listed in Table 1 together with those of several related compounds measured under the same conditions. Compound **1** displays two reversible single-electron redox waves. The first redox potential (${}^1E_{1/2}$) is more anodic than those of thiophene-fused analogue **3** and benzene-fused analogue **5**. The electron affinities of furan and thiophene have been reported to be −1.76, and −1.17 eV, respectively,[8] implying that thiophene possesses stronger acceptor character than furan. However, the reduction potentials of **1** and **3** are not correlated with the electron affinity of the fused heterocycles. A possible interpretation for this observation would be provided on the basis of the free energy loss which can be formulated as the π-resonance energy difference between the neutral and radical anion species. Upon single-electron reduction the central quinonoid ring gains the aromatic stability of benzene, whereas the fused heterocyclic part loses the aromaticity of furan or thiophene, as illustrated below. The aromatic character of furan and thiophene increases in this order.[9] Thus,

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[1] (a) Yamaguchi, S.; Tatemitsu, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1983**, 1229−1230. (b) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618−621. (c) Ong, B. S.; Keoshkerian, B. *J. Org. Chem.* **1984**, *49*, 5002−5003. (d) Nishizawa, Y.; Suzuki, T.; Yamashita, Y.; Miyashi, T.; Mukai, T. *Nippon Kagaku Kaishi* **1985**, 904−909. (e) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556−562.

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[6] (a) Diekmann, J.; Hertler, W. R.; Benson, R. E. *J. Org. Chem.* **1963**, *28*, 2719−2724. (b) Sandman, D. J.; Garito, A. F. *J. Org. Chem.* **1974**, *39*, 1165−1166. (c) Yanagimoto, T.; Takimiya, K.; Otsubo, T.; Ogura, F. *J. Chem. Soc., Chem. Commun.* **1993**, 519−520. (d) Takimiya, K.; Yanagimoto, T.; Yamashiro, T.; Ogura, F.; Otsubo, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1431−1435. (e) Maxfield, M.; Willi, S. M.; Cowan, D. O.; Bloch, A. N.; Poehler, T. O. *J. Chem. Soc., Chem. Commun.* **1980**, 947−948. (f) Acton, N.; Hou, D.; Schwarz, J.; Katz, T. J. *J. Org. Chem.* **1982**, *47*, 1011−1018. (g) Maxfield, M.; Bloch, A. N.; Cowan, D. O. *J. Org. Chem.* **1985**, *50*, 1789−1796.

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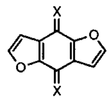
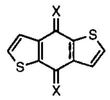
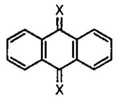
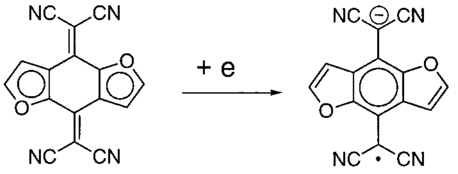
Table 1. Redox Potentials of Various Acceptors

		$^1E_{1/2}{}^a$	$^2E_{1/2}{}^a$	ΔE^b
TCNQ		−0.21	−0.80	0.59
	**1**: X=C(CN)$_2$	−0.35	−0.89	0.54
	2: X=NCN	−0.37	−1.00	0.63
	**3**: X=C(CN)$_2$	−0.38	−0.71	0.33
	4: X=NCN	−0.43	−0.99	0.56
	**5**: X=C(CN)$_2$	−0.77^c		
	6: X=NCN	−0.68	−1.04	0.36

^{a} V vs Fc/Fc$^+$; 0.1 M n-Bu$_4$NBF$_4$ solution in benzonitrile. ^{b} $\Delta E = {}^1E_{1/2} - {}^2E_{1/2}$. ^{c} Single two electron wave was observed.

furan compound **1** is more easily reduced with less resonance energy loss than compound **3**.



The $^1E_{1/2} - {}^2E_{1/2}$ value (0.54 V) of **1** is larger by 0.21 V than that of thiophene analogue **3**, implying that on-site Coulombic repulsion in the dianion of **1** is enhanced as compared with that of thiophene derivative **3**. Generation of two negative charges over the whole molecule would be unfavorable for the oxygen compound, because the polarizability of oxygen is lower than that of sulfur. For highly distorted π-conjugated acceptors such as **5**, a two-electron single wave is observed,[1e] since the π-conjugated system is buckled and separated into two independent electron pools due to steric repulsion between the fused aromatic rings and the dicyanomethylene moieties. Thus, the occurrence of two waves in compound **1** indicates that **1** is not as significantly distorted as the benzene-fused derivative **5**.

The UV/vis spectra of **1** were measured during the constant potential reduction at −0.4 V in DMF (Figure 1). The absorption bands of neutral species at 414 and 440 nm gradually disappear, with concomitant occurrence of new peaks at 497, 701, and 783 nm due to the radical ion species. Well-defined isosbestic points are observed at 455 nm, indicating that no side reactions are involved. With respect to the neutral species, the spectral feature of **1** is essentially the same as that of thiophene analogues **3**.[2b] On the other hand, for radical anions, there is a distinct difference in the 400−600 nm region: the radical anion of **1** exhibits the absorption at 497 nm, whereas the radical anion of **3** exhibits the absorption at 554 nm.[2b]

Molecular Structure in Crystalline Charge-Transfer Complex. Despite our intensive efforts, a single crystal of **1** suited for an X-ray crystallographic analysis could not be obtained. Therefore we determined the crystal structure of a 1:1 charge-transfer complex of **1** with bis(ethylenedithio)tetrathiafulvalene (BEDTTTF). The complex exhibited no electrical conductivity. The crystal structure is shown in Figure 2. The acceptor and donor molecules stack alternately with each other along the c axis.[10] The exocyclic C=C bond length of the quinodimethane moiety (1.369 Å) is similar to that of the neutral TCNQ molecule (1.374 Å),[11] indicating that the acceptor molecule is almost neutral. It is also the case for the donor side: the C=C bond length connecting the two 1,3-dithiole rings is 1.347 Å, corresponding to that of the neutral TTF molecule (1.349 Å).[12] Six atoms of the quinonoid ring of **1** are in one plane. The dihedral angle between the quinonoid plane and the furan ring is 2.1°. That between the quinonoid and the dicyanomethylene moiety is 5.6°. Thus, molecule **1** is much less distorted than thiophene analogue **3**.[2c]

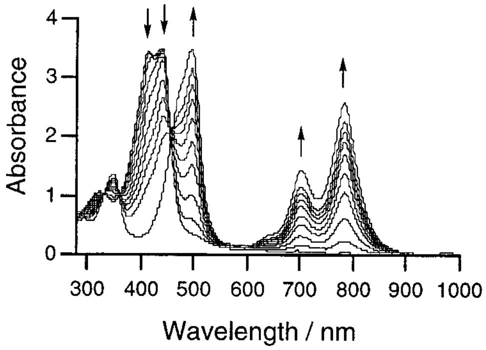


Figure 1. UV/vis spectral change upon electrochemical oxidation of **1** in DMF. The arrows indicate the growth of new absorption maxima which are characteristic of the radical anion produced.

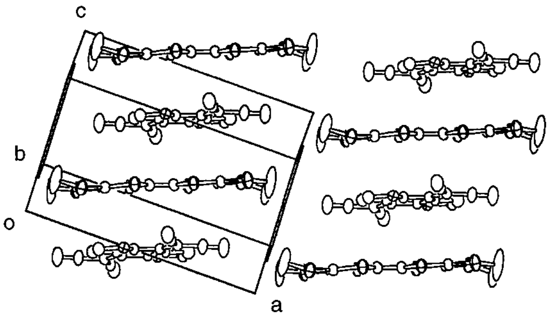
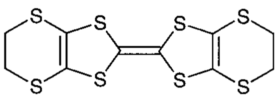


Figure 2. Projection of the columnar arrangement of **1** and BEDTTTF molecules in the crystal structure of **1** (BEDTTTF).



BEDTTTF

The molecular geometry of **1** was also predicted to be planar on the basis of the PM3 semiempirical calculation as implemented in the MOPAC-6.0 system of programs.[13] The optimized geometries of compounds **1** and **3** are

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(9) Fringuelli, F.; Marino, G.; Taticchi, A.; Grandolini, G. *J. Chem. Soc., Perkin Trans. 2* **1974**, 332.

(10) The molecule of **1** shows an orientational disorder with respect to an approximate molecular symmetry of *mm* due to the similarity of the dimensions related with C−O−C and C=C−C moieties of the furan ring. The structure is described for the major fraction.

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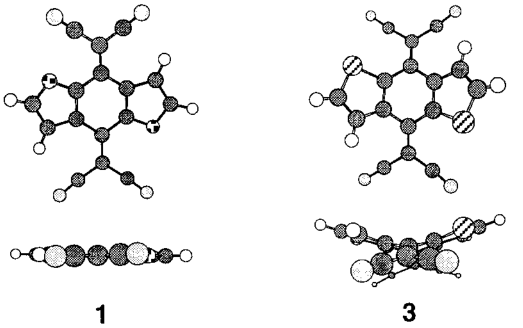

Figure 3. Molecular geometries of **1** and **3** optimized by PM3 calculation.

illustrated in Figure 3. Compound **1** shows a planar structure, while **3** is not planar as revealed by an X-ray analysis.[2c]

Furan-Fused DCNQI. *N*,*N*′-Dicyano-*p*-quinodiimine (DCNQI) derivative **2** was prepared by $TiCl_4$-mediated cyanoimination of precursor quinone **9** in 45% yield.[14] Pure **2** was isolated by recrystallization of the crude products from acetonitrile. The ^1H NMR spectrum of **2** at room temperature occurs between 7.0 and 7.9 ppm as broad signals and exhibited temperature dependence, indicating that the configurational isomers due to the =N−CN inversion are involved in fast equilibrium.[14b]

The redox potentials of **2** as measured by cyclic voltammetry are listed in Table 1. In the DCNQI series **2**, **4**, and **6**, the furan derivative exhibits again the highest electron acceptability. We were interested in determining if **2** forms a coordination polymer with CuI, as realized in thiophene analogue **4**.[15] However, this type of polymer was not obtained for **2**.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were obtained at 500 and 126 MHz, respectively, with samples dissolved in $CDCl_3$. Mass spectra were measured under electron impact at 70 eV. All solvents (benzene, diethyl ether, DMF, and CH_2Cl_2) were purified by using normal methods. Reactions were carried out under a dry, N_2 atmosphere.

3-Diethylcarbamoylfuran (8). A mixture of 3-furoic acid **7** (25.1 g, 0.224 mol) and thionyl chloride (65.3 mL, 0.90 mol) was refluxed for 4 h. To the reaction mixture was added dry benzene (60 mL), and the solution was distilled to remove an excess of thionyl chloride: the treatment with benzene was repeated twice. The resulting mixture was added dropwise to a solution of diethylamine (92.6 mL) in dry CH_2Cl_2 (100 mL) at 0 °C, and the solution was stirred at room temperature and poured into ice water. The furan was extracted three times with CH_2Cl_2. The combined organic extracts were washed with dilute HCl and water, successively, dried over $MgSO_4$, and evaporated. Purification was achieved by chromatography on silica gel (elution with 2:1 ethyl acetate−hexane). **8** was isolated (32.9 g, 88%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.70 (dd, $J = 0.9, 1.5$ Hz, 1H), 7.41 (dd, $J = 1.5, 1.8$ Hz, 1H), 6.59 (dd, $J = 0.9, 1.8$ Hz, 1H), 3.48 (q, $J = 7.0$ Hz, 4H), 1.22 (t, $J = 7.0$ Hz, 6H).

Benzo[1,2-*b*:4,5-*b*′]difuran-4,8-dione (9). To a stirred solution of diisopropylamine (1.76 mL, 12.6 mmol) in diethyl ether (30 mL) at 0 °C was added via syringe a solution of butyllithium (1.6 M, 7.7 mL, 12.6 mmol), and the resulting solution was stirred for 10 min. To this generated LDA solution was added a solution of **8** (2.00 g, 12.0 mmol) in dry diethyl ether (20 mL). The resulting mixture was refluxed for 4 h. Then the solution was cooled before addition of ice water. The dione was extracted three times with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated. The crystalline residue was recrystallized from acetic acid to give **9** (217 mg, 19%) as yellow leaflets: mp > 185 °C (sublimed); ^1H NMR ($CDCl_3$) δ 7.70 (d, $J = 1.8$ Hz, 2H), 6.92 (d, $J = 1.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 170.6, 152.3, 148.4, 128.5, 108.6; IR (KBr) 1666 (C=O) cm^{-1}; MS *m*/*z* 188 (M^+); UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 314 (3.8), 255 (4.0), 246 (4.0), 230 (4.3) nm. Anal. Calcd for $C_{10}H_4O_4$: C, 63.84; H, 2.14. Found: C, 63.78; H, 2.38.

Tetracyanobenzo[1,2-*b*:4,5-*b*]difuran-4,8-dionedimethane (1). To a solution of quinone **9** (499 mg, 2.7 mmol) and malononitrile (1.76 g, 27 mmol) in dry CH_2Cl_2 (160 mL) at 0 °C were added successively $TiCl_4$ (2.9 mL, 27 mmol) and pyridine (4.3 mL, 53 mmol). The mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and poured onto ice. The organic layer was extracted six times with CH_2Cl_2, washed with water, and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from acetonitrile (300 mL) to give pure **1** as violet needles (525 mg, 69%). Concentration of the filtrate afforded additional **1** (76 mg, 10%): mp > 260 °C (dec); ^1H NMR ($CDCl_3$) δ 7.95 (d, $J = 2.2$ Hz, 2H), 7.77 (d, $J = 2.2$ Hz, 2H); IR (KBr) 2224 (C≡N) cm^{-1}; MS *m*/*z* 248 (M^+); UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 436 (4.7), 416 (4.6), 326 (4.0), 248 (4.3) nm. Anal. Calcd for $C_{16}H_4N_4O_2$: C, 67.61; H, 1.42; N, 19.71. Found: C, 67.46; H, 1.71; N, 19.81.

***N*,*N*′-Dicyanobenzo[1,2-*b*:4,5-*b*]difuran-4,8-dionediimine (2).** To a solution of quinone **9** (200 mg, 1.1 mmol) in dry CH_2Cl_2 (50 mL) at 0 °C were added successively $TiCl_4$ (1.1 mL, 11 mmol) and bis(trimethylsilyl)carbodiimide (3.0 mL, 11 mmol). The mixture was refluxed for 15 h. The reaction mixture was cooled to room temperature and poured onto ice. The organic layer was extracted three times with CH_2Cl_2, washed with water, and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from CH_3CN to give pure **2** as a violet powder (114 mg, 45%): mp > 215 °C (dec); ^1H NMR ($CDCl_3$) δ 7.0−7.9 (m); IR (KBr) 2173 (C≡N) cm^{-1}; MS *m*/*z* 236 (M^+); UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 388 (4.4), 372 (4.4), 310 (4.1), 239 (4.3) nm. Anal. Calcd for $C_{12}H_4N_4O_2$: C, 61.02; H, 1.71; N, 23.72. Found: C, 60.81; H, 1.96; N, 23.46.

X-ray Crystallographic Study of (1) (BEDTTTF). Intensity data were collected on a Rigaku RAXIS-IV imaging plate system using graphite-monochromated Mo Kα irradiation ($\lambda = 0.71069$ Å). The structure was solved by a direct method using the program SIR 88.[16] The acceptor molecules show an orientational disorder with respect to the pseudo symmetry of *mm*. The carbon and oxygen atoms at the *peri*-positions of the benzoquinonoid framework were treated to be disordered. The atomic positions and isotropic temperature factors of the disordered atoms were fixed. The hydrogen atoms were located from calculations. All the atoms except for the disordered atoms and hydrogen atoms were refined anisotropically. The occupancy factors for disordered structures were refined to be 0.58:0.42.

Crystal data for $(C_{10}H_8S_8)(C_{16}H_4N_4O_2)$: MW = 668.89, $P2_1/n$ (No. 14), $a = 13.215(3)$ Å, $b = 13.079(3)$ Å, $c = 7.828(1)$ Å, $\beta = 92.77(3)°$, $V = 1351.4(4)$ Å^3, $Z = 2$, $D_c = 1.644$ g cm^{-3}, crystal dimensions = 0.50 × 0.20 × 0.20 mm, $2\theta_{max} = 55.3°$, $N_{obs} = 4193$, $N_{ref}[/I_o/ > 3\sigma(/I_o/)] = 2956$, no. of variables = 172, $R = 0.080$, $R_w = 0.091$, GOF = 8.68.

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Supporting Information Available: Crystallographic details, bond lengths, bond angles, positional parameters, isotropic thermal parameters, and calculated positional parameters for the hydrogen atoms of (**1**) (BEDTTTF). This material is available free of charge via the Internet at http://pubs.acs.org.

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