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Novel Electron Acceptors Bearing a Heteroquinonoid System III: 2,5-Bis(dicyanomethylene)-2,5-dihydrofuran and Its Conjugated Homologues as Novel Oxygen-Containing Electron Acceptors

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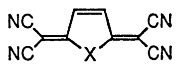
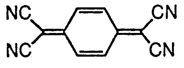
2,5-Bis(dicyanomethylene)-2,5-dihydrofuran with a 2,5-furanoquinonoid skeleton and its extensive conjugated homologues, 5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bifuran (**8a**), and 5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terfuran (**12a**), have been prepared as a new type of oxygen-containing electron acceptors. In the synthetic course of the tetrabromo derivative of **12a**, 3′,4-dibromo-5-(3,5-dibromo-2-furyl)-3,5′-bis(dicyanomethylene)-3,5′-dihydro-$\Delta^{2,2'}$-bifuran was also obtained as an unsymmetrical isomer possessing an unusual 2,3-furanoquinonoid conjugation, whose structure was confirmed on the basis of X-ray crystallographic analysis. In addition, X-ray analysis of the TTF complex of **8a** revealed that the bifuranoquinonoid conjugation has a trans form. These furanoquinonoid compounds behaved as weak electron acceptors, and accordingly failed to form conductive complexes. However, the 3,3′-dibromo derivative of **8a** gave the TTT complex of a very high electrical conductivity.

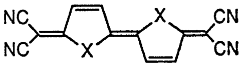
2,5-Bis(dicyanomethylene)-2,5-dihydrothiophene (**1a**) and 2,5-bis(dicyanomethylene)-2,5-dihydroselenophene (**1b**), heteroquinonoid isologues of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[1] are not so good electron acceptors as TCNQ.[2] We recently found that their conjugated homologues (**2**) and (**3**) are qualified as potential components for organic electrical conductors.[3] These acceptors have the double advantage of diminution of on-site Coulomb repulsion due to the extensively conjugated system and of enhancement of intermolecular interaction due to the increasing heteroatoms, thus being able to form various conductive molecular complexes. An extensive study on organic metals based on 2,2′,5,5′-tetrathiafulvalene (TTF) and its derivatives has revealed that the interaction of chalcogen atoms is very important for the high electrical conductivities.[4] One question is whether oxygen atom belonging to the same Group 16 (6B) of the periodic table can exert a similar effect or not. If organic superconductors were BCS superconductors, one would expect a rise of T_c with a change from sulfur to lighter oxygen. In of 4,5:4′,5′-bis(ethylenedioxy)-2,2′,5,5′-tetrathiafulvalene (BEDO-TTF) as a novel oxygen-containing electron donor,[5] and found that the oxygen atoms not only electronically but also sterically contributed to enhancement of intermolecular interaction in (BEDO-TTF)$_{2.4}$I$_3$ salt.[6] On the other hand, we have been much interested in another hetero TCNQ isologue consisting of furanoquinonoid skeleton, which might give some information on the behavior of an oxygen-containing electron acceptor. We here report the syntheses and properties of 2,5-bis(dicyanomethylene)-2,5-dihydrofuran (**5**) and its conjugated homologues.



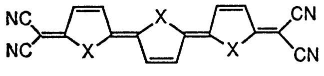
1a, X=S
1b, X=Se



TCNQ



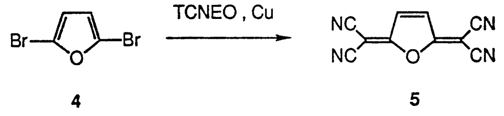
2, X=S, Se



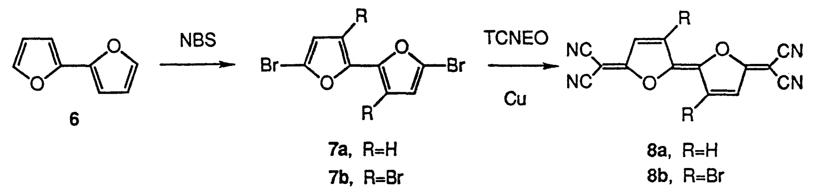
3, X=S, Se

Results and Discussion

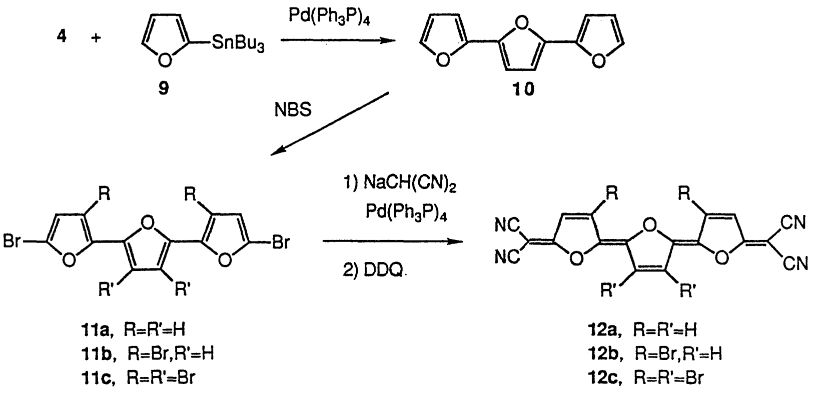
Synthesis. The syntheses of the present furanoquinonoid compounds were carried out in a manner similar to those for thiophene and selenophene series.[1,3] Thus, 2 ,5-dibromofuran (**4**), readily available from bromination of furan with *N*-bromosuccinimide (NBS),[7] was allowed to react with tetracyanoethylene oxide (TCNEO) and copper powder in refluxing 1,3-dibromopropane for 2.5 h to give **5** in 29% yield (Scheme 1). Reisch and Mester reported that 5,5′-dibromo-2,2′-bifuran (**7a**), a precursor of the bifuranoquinonoid homologue (**8a**), was obtained in one step by treatment of furan with NBS in the presence of HgCl$_2$ and Et$_3$N in chloroform.[8] However, we found that the reaction is not reproducible, and instead **7a** was obtained in 82% yield by bromination of 2,2′-bifuran (**6**)[9] with 2 equiv of NBS in benzene at RT (Scheme 2). The subsequent treatment of **7a** with TCNEO gave **8a** in 12% yield. A similar treatment of 3,3′,5,5′-tetrabromo-2,2′-bifuran (**7b**), prepared in 30%



Scheme 1.



Scheme 2.



Scheme 3.

yield from bromination of 2,2′-bifuran (**6**) with 4 equiv of NBS, gave the dibromo derivative **8b** in 34% yield. Treatment of 2,5-dibromofuran (**4**) with 2 equiv of tributyl(2-furyl)stannane (**9**) in the presence of tetrakis(triphenylphosphine)palladium(0) in refluxing toluene gave 2,2′:5′,2″-terfuran (**10**) in 48% yield (Scheme 3). The subsequent brominations with 2 equiv NBS, with 4 equiv NBS, and with 6 equiv NBS led to 5,5″-dibromo derivative (**11a**) in 84% yield, to 3,3″,5,5″-tetrabromo derivative (**11b**) in 48% yield, and to 3,3′3″,4′,5,5″-hexabromo derivative (**11c**) in 16% yield, respectively. However, neither of these compounds on treatment with TCNEO gave the desired terfuranoquinonoid homologues. Alternatively, **12a**, **12b**, and **12c** were obtained in 12%, 25%, and 1.5% yields, respectively, by the substitution reactions of **11** with sodium dicyanomethanide in the presence of tetrakis(triphenylphosphine)palladium(0) as a catalyst, followed by oxidation with DDQ.

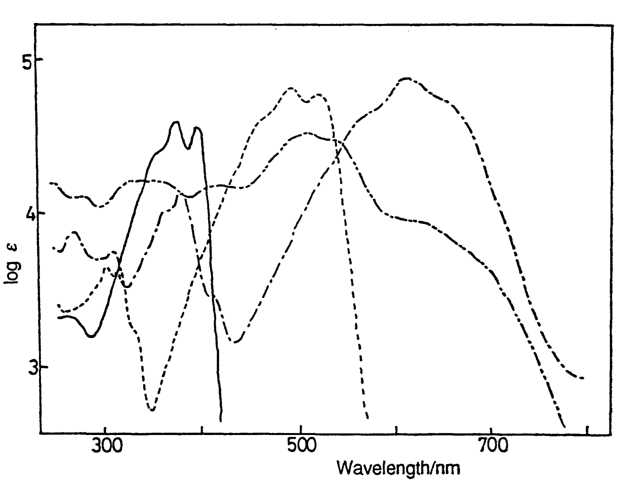
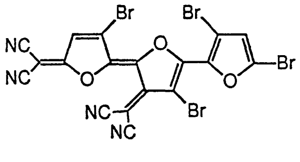


Fig. 1. Electronic spectra of **5** (——), **8a** (----), **12a** (— - —), and **13** (— - - —) in dichloromethane.

Structure. The new acceptors are deeply colored owing to the extensively conjugated electronic structure. As shown in Fig. 1, the electronic absorption spectra of the bifuranoquinonoid and terfuranoquinonoid systems show considerable bathochromic shifts. Two configurations of *syn* and *anti* are apparently possible for the geometry of such polyheteroquinonoid conjugation. We tentatively assigned the configurations of **2** and **3** as *anti*-form, because judging from the molecular model the *syn*-form suffers from steric repulsion between the two hydrogen atoms at 3- and 3′-positions, but the *anti*-form can avoid it.[3] A close similarity of the electronic spectra between **2** and **8** or **3** and **12** suggests the same geometrical situation. We have now obtained unambiguous evidence for the trans configuration on the basis of the X-ray analysis of **8a**·TTF complex described later.

As already mentioned, the reaction of **11c** with TCNEO gave no desired **12c**, but a relatively soluble colored material was instead obtained in 17% yield. The elemental analysis and mass spectrum satisfied the theoretical values based on **12c**, but the electronic



13

spectrum was quite different from the spectral pattern of **12c** (see also Fig. 1). The NMR spectrum showed two singlet peaks at δ=6.97 and 7.59, rather indicating an unsymmetrical isomer. The structure was finally assigned to **13** on the basis of X-ray analysis. Figure 2 shows that it possesses a unique 2,3-furanoquinonoid conjugation in the central heterocycle. In addition, there are observed two marked molecular features due to steric hindrance; the central dicyanomethylene group is deviated from the molecular plane, and both terminal heterocycles, regardless of single or double bond, are attached in a trans fashion to the central one.

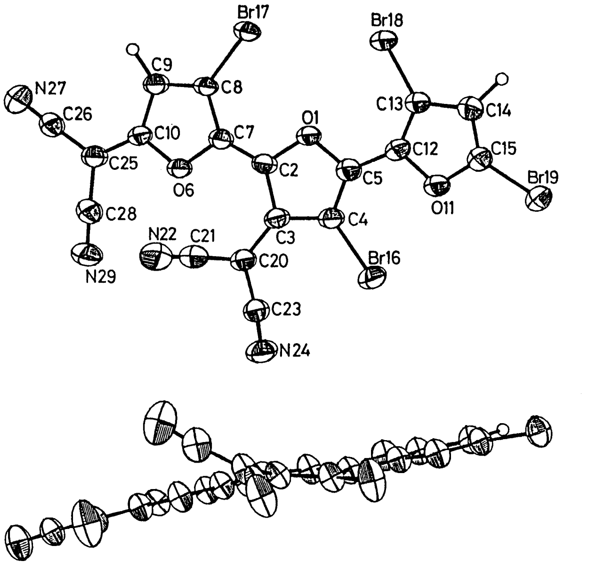


Fig. 2. ORTEP drawing of molecule **13** viewed from above the plane of the central furanoquinonoid ring (above) and from the side (bottom).

Redox Potential. The cyclic voltammograms of the new furanoquinonoid compounds show two pairs of reversible redox waves whose half-wave reduction potentials are summarized in Table 1. All hetero TCNQs do not have so strong electron-accepting abilities as TCNQ. Among three kinds of hetero TCNQs, furanoquinonoid compound (**5**) is a slightly weaker acceptor than the sulfur **1a** or selenium counterpart **1b**. Although its reduction is presumably facilitated by larger electronegativity of the incorporated oxygen atom, the less aromaticity of the resulting furan ring than thiophene or selenophene must have compensated the effect. As already seen in sulfur and selenium series,[3] the extensive conjugation of bifuranoquinonoid homologue (**8a**) relative to **5** lowers the first reduction potential, but fairly enhances the second one, accordingly reducing a difference

Table 1. Half-Wave Reduction Potentials of Furanoquinonoid Acceptors[a)]

Acceptor	$E_{1/2}(1)/\mathrm{V}$	$E_{1/2}(2)/\mathrm{V}$	$\Delta E/\mathrm{V}$
TCNQ	+0.25	−0.47	0.72
1a	+0.07	−0.50	0.57
1b	+0.03	−0.51	0.54
5	+0.03	−0.55	0.58
8a	−0.09	−0.31	0.22
8b	+0.08	−0.12	0.20
12a	−0.09		0
12b	−0.01		0
12c	+0.14		0
13	+0.21	−0.01	0.22

a) Cyclic voltammetry was measured at 100 mV s^{-1} scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte.

Table 2. Charge-Transfer Complexes with Furanoquinonoid Acceptors

Complex	Appearance[a)]	Found (Calcd)[b)]%			ν_{CN}	Dp[c)]	Conductivity[d)]
		C	H	N	cm^{-1}	°C	S cm^{-1}
TTF·**5**	Black prisms[e)]	47.38;	1.31;	13.64	2242	180	1.0×10^{-10}
		(48.23;	1.52;	14.06)			
TTF·**8a**	Black plates[e)]	51.67;	1.70;	11.91	2228	200	3.1×10^{-10}
		(51.71;	1.74;	12.06)			
TTF·**8b**	Black fine prisms[e)]	38.60;	0.92;	8.88	2224	190	1.6×10^{-8}
		(38.60;	0.97;	9.00)			
TTT·**8b**	Black fine needles	49.82;	1.27;	7.13	2203	270	2.4[f)]
		(49.88;	1.31;	7.27)			
TPBP·**8b**	Green fine crystals	66.21;	2.97;	5.23	2200	210	1.3×10^{-7}
		(65.32;	2.97;	6.35)			
TTT·**12b**	Black needles	56.60;	2.03;	3.06	2215	250	1.9×10^{-6}
		(56.10;	1.83;	3.63)[g)]			
TTF·**13**	Reddish purple fine needles	34.72;	1.16;	6.52	2236, 2213	180	4.3×10^{-9}
		(34.07;	0.71;	6.62)			
TTT·**13**	Deep purple powder	50.10;	1.63;	3.17	2214, 2206	230	6.0×10^{-4}
		(50.89;	1.54;	3.30)[g)]			

a) Obtained from chlorobenzene, unless otherwise stated. b) Calculated as 1 : 1 stoichiometry, unless otherwise stated. c) Decomposition temperature. d) Measured on compressed pellets with a two-probe method at RT. e) Obtained from acetonitrile. f) Measured with a four-probe method. g) 3 : 1 Composition of donor and acceptor.

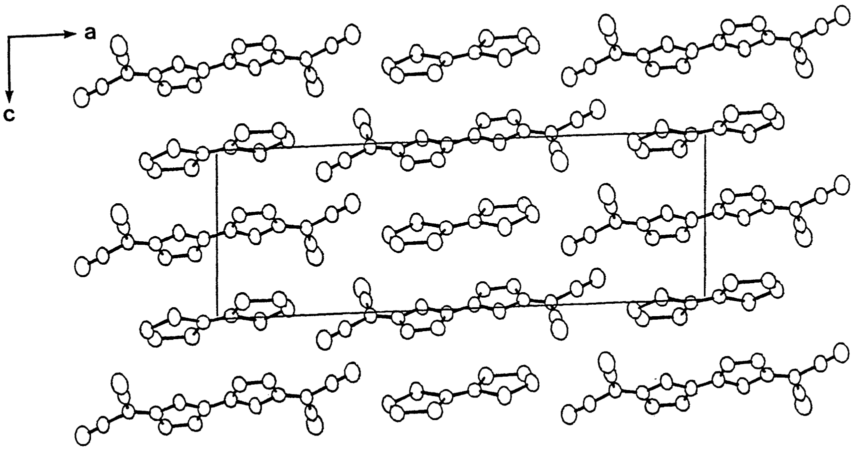


Fig. 3. Crystal structure of **8a**·TTF complex projected along the *b* axis.

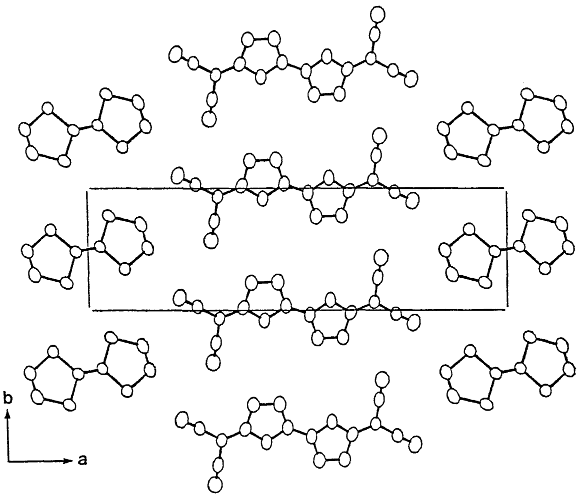


Fig. 4. Crystal structure of **8a**·TTF complex projected along the *c* axis. The shortest intermolecular S-S distance is 3.68 Å.

between the two. Further terfuranoquinonoid conjugation of **12a** leads to coalescence of the first and second potentials. On the other hand, bromo substitution in **8** and **12** appreciably heightens both first and second reduction potentials, serving to improve their accepting abilities. Finally, it is worthwhile to note that 2,3-furanoquinonoid compound (**13**) shows the highest first reduction potential in the linearly conjugated 2,5-furanoquinonoid series and the value is very close to that of TCNQ.

Molecular Complexes. Complexation of the present furanoquinonoid acceptors with donors was difficult on account of the weak electron affinities as well as the weak nonbonded interaction of oxygen relative to sulfur and selenium. Somehow compounds **5** and **8a** formed 1 : 1 crystalline complexes only with tetrathiafulvalene, which were nearly insulating (Table 2). For both complexes, no charge transfer occurred as judged from the unchanged nitrile vibrational frequencies.[10] The TTF complex of **8a** provided good crystals for X-ray analysis. Figure 3 demonstrates that it takes a mixed stacked structure of donors and acceptors. Although mutual S-S contacts of the TTF molecules are observed in a transverse direction, there are no nonbonded interactions due to the oxygen atoms of **8a** (Fig. 4). The molecular structure of the TTF component is very similar to neutral TTF,[11] also supporting no charge transfer. On the other hand, the molecular structure of the furanoquinonoid component has a trans-form and keeps planarity as expected (Fig. 5).

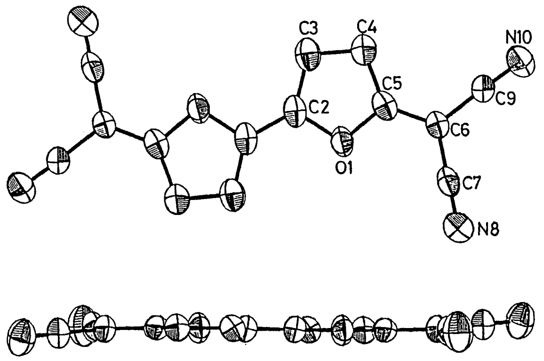
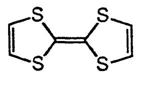
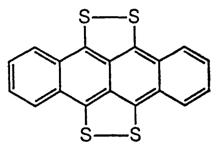


Fig. 5. ORTEP drawing of molecule **8a** viewed from above the plane of the molecule (above) and from the side (bottom).

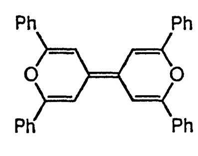
The modified acceptor **8b** behaved as a better electron acceptor than **5** and **8a**, giving 1 : 1 complexes not only with TTF but also with 5,6 : 11,12-bis(dithio)naphthacene (TTT) and 2,2′,6,6′-tetraphenyl-$\Delta^{4,4'}$-bi-4*H*-pyran (TPBP). In the TTT and TPBP complexes, there were observed marked low-



TTF



TTT



TPBP

wavenumber shifts of the nitrile stretching vibrations (2203 and 2200 cm^{-1}) relative to that (2236 cm^{-1}) of neutral **8b**, indicating considerable charge transfer in complexation. Although the TPBP complex was little conductive, the TTT complex showed a very high electrical conductivity (2.4 S cm^{-1}) when measured on a compressed pellet at room temperature. This contrast probably arises from the different stacking modes, that is, mixed stacking or segregated stacking, though their crystal structures have not been clarified yet.

Terfuranoquinonoid acceptors **12a**, **12b**, and **12c** have the advantage of effective diminution of on-site Coulomb repulsion which is one of requirements for producing an organic metal.[12] Unfortunately, their acceptors are too insoluble in ordinary solvents to perform complexation experiment. Only the TTT complex of **12b** was formed, but it was a semiconductor.

Unlike the above 2,5-furanoquinonoid series, compound **13** bearing an unusual 2,3-furanoquinonoid conjugation has a disadvantage of nonplanarity against complexation in spite of strong electron affinity. It thus gave nearly insulating and semiconductive complexes with TTF and with TTT, respectively.

Conclusion

The present furanoquinonoid compounds behaved as weak electron acceptors, though they showed effective diminution of on-site Coulomb repulsion. In addition, the oxygens embedded in their quinonoid conjugation exercised no appreciable nonbonded interaction. Accordingly, they could not form so various molecular complexes as the sulfur and selenium counterparts. However, compound **8b** gave a very high electrical conductor with TTT, suggesting a possibility of modified furanoquinonoid acceptors for developing organic metals.

Experimental

General. Melting points are uncorrected. All chemicals and solvents are of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. NMR spectra were recorded on a JEOL PMX-60 spectrometer (60 MHz) or a JEOL FX-90 spectrometer (90 MHz) using deuteriochloroform as solvent and tetramethylsilane as internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer with a KBr disk method. MS spectra were measured on a Shimadzu GC-MS QP-1000A spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV-160 spectrophotometer using dichloromethane as solvent. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

2,5-Bis(dicyanomethylene)-2,5-dihydrofuran (5). A mixture of 2,5-dibromofuran (**4**)[7] (1.82 g, 8.06 mmol), TCNEO (4.64 g, 32 mmol), and copper powder (2.05 g, 32 mmol) in 1,3-dibromopropane (18 cm^3) was refluxed for 2.5 h. After cooling, it was taken up with dichloromethane (500 cm^3) and filtered through a small amount of silica gel. The filtrate was evaporated and the residue was recrystallized from benzene to give pale yellow needles of **5** (0.45 g, 29% yield): mp 184 °C; IR 2245 cm^{-1} (CN); MS *m/z* 194 (M$^+$); UV $\lambda_{\max}$ 395 nm (ε 36900), 372 (39400), 355 sh (25600), and 260 (2100). Calcd for $C_{10}H_2N_4O$: C, 61.86; H, 1.04; N, 28.86%. Found: C, 61.62; H, 1.21; N, 28.81%.

5,5′-Dibromo-2,2′-bifuran (7a). Into a solution of 2,2′-bifuran (**6**)[9] (1.00 g, 7.5 mmol) in benzene (30 cm^3) was added NBS (2.6 g, 15 mmol), and the mixture was stirred for 1.5 h in the dark. After evaporation of the solvent, the residue was extracted with chloroform. The extract was successively washed with 5% aq sodium hydrogencarbonate and brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography on silica gel with hexane to give a white solid of **7a** (1.78 g, 82%): mp 74—75 °C (lit,[8] mp 76 °C); MS (20 eV) *m/z* 290, 292, and 294 (M$^+$); NMR (60 MHz) δ=6.31 (d, *J*=3.5 Hz, 2H) and 6.45 (d, *J*=3.5 Hz, 2H).

3,3′,5,5′-Tetrabromo-2,2′-bifuran (7b). A mixture of **6** (0.99 g, 7.4 mmol) and NBS (2.63 g, 14.8 mmol) in benzene (30 cm^3) was stirred for 1 h at room temperature in the dark. After the same amount of NBS was further added, the mixture was refluxed for 2 h. The reaction was worked up as described in the part of 5,5′-dibromo-2,2′-bifuran (**7a**). Recrystallization from hexane gave colorless needles of **7b** (0.98 g, 30%): mp 151—152 °C; MS (70 eV) *m/z* 446, 448, 450, 452, and 454 (M$^+$); NMR (60 MHz) δ=6.43 (s). Calcd for $C_8H_2O_2Br_4$: C, 21.37; H, 0.45%. Found: C, 21.44; H, 0.45%.

5,5′-Bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bifuran (8a). TCNEO (1.03 g) and copper powder (457 mg) was added in 1,3-dibromopropane (9 cm^3) and refluxed for 45 min. Into the solution was added a solution of **7a** (525 mg, 1.8 mmol) in 1,3-dibromopropane (6 cm^3), and reflux was continued further 1.5 h. After cooling, the mixture was taken up with dichloromethane and purified by column chromatography on silica gel followed by recrystallization from chlorobenzene to give reddish purple leaflets of **8a** (54 mg, 12% yield): decomp 265 °C; IR 2234 cm^{-1} (CN); MS (70 eV) *m/z* 260 (M$^+$); UV $\lambda_{\max}$ 520 nm (ε 58100), 491 (64900), 314 (4400), and 301 (4500). Calcd for $C_{14}H_4N_4O_2$: C, 64.62; H, 1.55; N, 21.53%. Found: C, 64.62; H, 1.52; N, 21.37%.

3,3′-Dibromo-5,5′-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2'}$-bifuran (8b). A mixture of **7b** (450 mg, 1 mmol), TCNEO (712 mg), and copper powder (254 mg) in 1,2-dibromoethane (8 cm^3) was refluxed for 2 h. After cooling, it was taken up with dichloromethane and chromatographed on silica gel to give the desired product (141 mg, 34% yield): deep purple fine needles from acetonitrile; decomp 220 °C; IR 2236 cm^{-1} (CN); MS (70 eV) *m/z* 416, 418, and 420 (M$^+$); UV $\lambda_{\max}$ 532 nm (ε 35700), 502 (63700), and 310 (5420). Calcd for $C_{14}H_2N_4O_2Br_2$: C, 40.23; H, 0.48; N, 13.40%. Found: C, 40.19; H, 0.45; N, 13.35%.

2,2′:5,2″-Terfuran (10). A mixture of 2,5-dibromofuran (**4**) (2.26 g, 10 mmol), tributyl(2-furyl)stannane (**9**)[13] (7.5 g, 21 mmol), and tetrakis(triphenylphosphine)palladium(0) (578 mg, 0.5 mmol) in toluene (30 cm^3) was refluxed for 1 d in a nitrogen atmosphere. After the solvent was evaporated, aq saturated potassium fluoride (50 cm^3) and hexane (100 cm^3) were added, and the mixture was stirred for 15 min. It was filtered through celite, and the filtrate was extracted with hexane. The extract was washed with brine and dried ($MgSO_4$). After evaporation of the solvent, the residue was chromatographed on silica gel with hexane, and then recrystallization of the eluted colored band from ethanol gave pale yellow needles of **10** (966 mg, 48% yield): mp 62—63 °C (lit,[9] 65 °C); MS m/z 200 (M^+); NMR (60 MHz) δ=6.41 (dd, J=1.8 Hz, J'=3.4 Hz, 2H), 6.50 (m, 4H), and 7.33 (dd, J=0.8 Hz, J'=1.8 Hz, 2H).

5,5″-Dibromo-2,2′ : 5′,2″-terfuran (11a). A mixture of **10** (2.82 g, 14.1 mmol) and NBS (5 g, 28.1 mmol) in benzene (100 cm^3) was stirred for 1.5 h at 40 °C in the dark. After the reaction mixture was filtered, the filtrate was diluted with hexane (100 cm^3) and chromatographed on silica gel with 1 : 1 benzene-hexane. Recrystallization of the eluted solid from hexane gave yellow plates of **11a** (4.22 g, 84% yield): decomp 115 °C; MS (70 eV) m/z 356, 358, and 360 (M^+); NMR (60 MHz) δ=6.28 (d J=1.48 Hz, 2H), 6.45 (d, J=1.48 Hz, 2H), and 6.52 (s, 2H). Calcd for $C_{12}H_6O_3Br_2$: C, 40.26; H, 1.69%. Found: C, 40.26; H, 1.76%.

3,3″,5,5″-Tetrabromo-2,2′ : 5′,2″-terfuran (11b). A mixture of **11a** (2.0 g, 5.6 mmol) and NBS (1.99 g, 11.2 mmol) in benzene (100 cm^3) was refluxed for 5 h. After filtration, the filtrate was diluted with hexane (100 cm^3) and chromatographed on silica gel with 1 : 1 benzene-hexane. Recrystallization of the eluted solid from hexane gave yellow needles of **11b** (1.64 g, 57% yield): mp 144—146 °C; NMR ($CDCl_3$) δ=6.37 (s, 2H) and 6.80 (s, 2H). Calcd for $C_{12}H_4O_3Br_4$: C, 27.94; H, 0.78%. Found: C, 27.84; H, 0.78%.

3,3′,3″,4′,5,5″-Hexabromo-2,2′ : 5′,2″-terfuran (11c). A mixture of **10** (1.15 g, 5.76 mmol) and NBS (2.05 g, 11.5 mmol) in chlorobenzene (50 cm^3) was stirred for 30 min at room temperature, and, after NBS (4.10 g, 23 mmol) was added, the stirring was continued further 30 min. p-Toluenesulfonic acid (10 mg) was added, and the mixture was heated at 110 °C for 18 h. The insoluble succinimide was removed by filtration, and the filtrate was evaporated. The residue was chromatographed on silica gel with 1 : 20 chloroform-hexane, and the eluted yellow solid was collected and recrystallized from benzene-hexane to give yellow needles of **11c** (615 mg, 16% yield): mp 188—189 °C; MS (70 eV) m/z 668, 670, 672, 674, 676, 678, and 680 (M^+); NMR (60 MHz) δ=6.46 (s). Calcd for $C_{12}H_2O_3Br_6$: C, 21.40; H, 0.30%. Found: C, 21.63; H, 0.32%.

5,5″-Bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terfuran (12a). Sodium hydride (60% oil, 760 mg, 19 mmol) was added into a solution of malononitrile (602 mg, 9.1 mmol) in THF (35 cm^3) at 0 °C in a nitrogen atmosphere, and the mixture was stirred for 20 min. Tetrakis(triphenylphosphine)palladium(0) (924 mg, 0.8 mmol) and **11a** (1.5 g, 4.2 mmol) were added into it, which was then refluxed for 2.5 h. DDQ (5.2 g, 23 mmol) was added at room temperature, and reflux was continued for 20 min. After water (50 cm^3) was added, the resulting solid was collected on a celite by filtration and washed with ethanol and then acetone. It was extracted with acetonitrile by use of a Soxhlet apparatus to give the desired product **12a** as deep blue fine precipitates in the extract (161 mg, 12% yield). An analytical sample was recrystallized from acetonitrile-DMF: decomp 210 °C; IR 2224 cm^{-1} (CN); MS (70 eV) m/z 326 (M^+); UV λ_{max} 617 nm (ε 76500), 382 (14000), 310 (5600), and 272 (7700). Calcd for $C_{18}H_6N_4O_3$: C, 66.26; H, 1.85; N, 17.17%. Found: C, 66.31; H, 1.97; N, 17.13%.

3,3″-Dibromo-5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terfuran (12b). This compound was prepared in 25% yield from 3,3″,5,5″-tetrabromo-2,2′ : 5′,2″-terfuran (**11b**) in a similar way as described in the part of 5,5″-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2':5',2''}$-terfuran (**12a**).

Table 3. Final Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations in Parentheses

8a Atom	x	y	z	$B_{eq}/Å^2$ a)
O1	0.5788(2)	0.0847(7)	0.0211(6)	3.78(13)
C2	0.5281(3)	−0.0380(11)	−0.0228(9)	3.64(17)
C3	0.5462(3)	−0.2309(12)	−0.1097(9)	3.98(19)
C4	0.6082(3)	−0.2245(11)	−0.1218(9)	3.78(18)
C5	0.6277(3)	−0.0225(10)	−0.0387(8)	3.40(17)
C6	0.6844(3)	0.0680(10)	−0.0185(8)	3.25(17)
C7	0.6937(3)	0.2676(12)	0.0742(10)	3.84(19)
N8	0.7018(3)	0.4288(11)	0.1460(10)	5.68(21)
C9	0.7367(3)	−0.0311(10)	−0.0919(9)	3.52(17)
N10	0.7787(3)	−0.1030(11)	−0.1515(9)	5.18(19)
TTF Atom	x	y	z	$B_{eq}/Å^2$ a)
S1	0.0894(1)	0.3378(3)	0.0238(3)	3.77(7)
C2	0.0292(3)	0.5218(9)	−0.0159(8)	2.93(15)
S3	0.0523(1)	0.7748(3)	−0.0962(2)	3.80(7)
C4	0.1298(3)	0.7078(12)	−0.1005(10)	4.05(19)
C5	0.1459(3)	0.5115(11)	−0.0463(10)	4.04(19)
13 Atom	x	y	z	$B_{eq}/Å^2$ a)
O1	1.0515(3)	0.3096(2)	0.8371(3)	3.58(8)
C2	0.9558(5)	0.3610(2)	0.7936(4)	3.24(11)
C3	1.0181(4)	0.4312(2)	0.8144(4)	3.45(11)
C4	1.1450(5)	0.4164(2)	0.8882(5)	3.71(12)
C5	1.1667(5)	0.3453(2)	0.8932(4)	3.60(11)
O6	0.7252(3)	0.3948(2)	0.7319(3)	3.56(8)
C7	0.8219(5)	0.3414(2)	0.7593(4)	3.40(11)
C8	0.7479(5)	0.2750(2)	0.7464(4)	3.24(11)
C9	0.6114(5)	0.2882(2)	0.7088(4)	3.42(11)
C10	0.5978(5)	0.3640(2)	0.7008(4)	3.35(11)
O11	1.4067(3)	0.3388(2)	0.9702(3)	3.78(8)
C12	1.2857(4)	0.3022(2)	0.9316(4)	3.50(12)
C13	1.3150(5)	0.2309(2)	0.9361(4)	3.44(11)
C14	1.4573(5)	0.2224(3)	0.9783(4)	3.82(12)
C15	1.5067(5)	0.2889(3)	0.9974(4)	3.67(12)
Br16	1.27493(6)	0.48536(2)	0.95019(6)	5.99(2)
Br17	0.82601(5)	0.18604(2)	0.77736(5)	4.07(1)
Br18	1.19185(6)	0.15604(2)	0.89861(5)	4.07(1)
Br19	1.68220(5)	0.32390(2)	1.05258(5)	4.24(2)
C20	0.9687(5)	0.4951(2)	0.7622(5)	3.96(13)
C21	0.8774(6)	0.4989(3)	0.6476(6)	4.80(15)
N22	0.8125(7)	0.5047(3)	0.5541(6)	7.10(18)
C23	1.0125(5)	0.5626(3)	0.8113(6)	4.62(15)
N24	1.0342(5)	0.6187(2)	0.8474(6)	6.35(17)
C25	0.4857(5)	0.4073(2)	0.6707(4)	3.63(12)
C26	0.3498(5)	0.3785(3)	0.6399(5)	3.77(12)
N27	0.2415(5)	0.3550(3)	0.6186(5)	5.32(13)
C28	0.5034(5)	0.4830(3)	0.6721(5)	4.52(15)
N29	0.5210(5)	0.5421(3)	0.6754(6)	6.98(19)
H9	0.534(6)	0.247(3)	0.676(5)	
H14	1.526(6)	0.171(3)	0.994(5)	

a) $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

Table 4. Interatomic Bond Lengths and Bond Angles with Estimated Standard Deviations in Parentheses

8a	Bond lengths/Å		Bond angles/°		**8a**	Bond lengths/Å		Bond angles/°	
	O1-C2	1.371(7)	C2-O1-C5	107.0(5)				O1-C5-C6	119.4(6)
	O1-C5	1.352(7)						C4-C5-C6	130.5(6)
	C2-C2′	1.372(12)	O1-C2-C2′	118.2(8)		C6-C7	1.426(10)	C5-C6-C7	121.3(5)
	C2-C3	1.424(10)	O1-C2-C3	109.6(5)		C6-C9	1.428(9)	C5-C6-C9	121.3(6)
			C3-C2-C2′	132.2(8)				C7-C6-C9	117.4(5)
	C3-C4	1.364(9)	C2-C3-C4	107.7(6)		C7-N8	1.143(10)	C6-C7-N8	178.7(8)
	C4-C5	1.452(9)	C3-C4-C5	105.7(6)		C9-N10	1.131(9)	C6-C9-N10	177.7(7)
	C5-C6	1.362(8)	O1-C5-C4	110.1(5)					
TTF	Bond lengths/Å		Bond angles/°		TTF	Bond lengths/Å		Bond angles/°	
	S1-C2	1.756(6)	C2-S1-C5	94.8(3)				S3-C2-C2′	122.1(6)
	S1-C5	1.736(7)				S3-C4	1.745(7)	C2-S3-C4	95.0(3)
	C2-C2′	1.337(12)	S1-C2-C2′	123.6(6)		C4-C5	1.325(10)	S4-C4-C5	117.3(5)
	C2-S3	1.760(6)	S1-C2-S3	114.3(3)				S1-C5-C4	118.6(5)
13	Bond lengths/Å		Bond angles/°		**13**	Bond lengths/Å		Bond angles/°	
	O1-C2	1.382(5)	C2-O1-C5	106.4(3)				O6-C10-C25	118.1(4)
	O1-C5	1.378(5)						C9-C10-C25	132.4(4)
	C2-C3	1.459(6)	O1-C2-C3	109.5(4)		O11-C12	1.377(5)	C12-O11-C15	106.1(3)
	C2-C7	1.353(6)	O1-C2-C7	118.9(4)		O11-C15	1.354(5)		
			C3-C2-C7	130.7(4)		C12-C13	1.372(6)	C5-C12-O11	115.4(4)
	C3-C4	1.411(6)	C2-C3-C4	103.0(4)				C5-C12-C13	136.2(4)
	C3-C20	1.390(6)	C2-C3-C20	127.3(4)				O11-C12-C13	108.3(4)
			C4-C3-C20	129.5(4)		C13-C14	1.405(6)	C12-C13-C14	108.2(4)
	C4-C5	1.355(6)	C3-C4-C5	109.7(4)		C13-Br18	1.858(5)	C12-C13-Br18	127.6(3)
	C4-Br16	1.874(4)	C3-C4-Br16	124.6(3)				C14-C13-Br18	124.1(4)
			C5-C4-Br16	125.2(4)		C14-H14	1.17(6)	C13-C14-H14	131(3)
	C5-C12	1.428(6)	O1-C5-C4	110.6(4)		C14-C15	1.347(7)	C13-C14-C15	105.0(4)
			O1-C5-C12	115.6(4)				C15-C14-H14	124(3)
			C4-C5-C12	133.5(4)		C15-Br19	1.850(4)	O11-C15-C14	112.4(4)
	O6-C7	1.380(5)	C7-O6-C10	108.1(3)				O11-C15-Br19	115.2(3)
	O6-C10	1.365(5)						C14-C15-Br19	132.4(4)
	C7-C8	1.438(6)	C2-C7-O6	117.5(4)		C20-C21	1.433(8)	C3-C20-C21	122.7(4)
			C2-C7-C8	135.2(4)		C20-C23	1.422(7)	C3-C20-C23	123.4(5)
			O6-C7-C8	107.2(4)				C21-C20-C23	113.8(4)
	C8-C9	1.356(6)	C7-C8-C9	108.9(4)		C21-N22	1.128(8)	C20-C21-N22	175.2(6)
	C8-Br17	1.852(4)	C7-C8-Br17	125.6(3)		C23-N24	1.136(7)	C20-C23-N24	173.2(5)
			C9-C8-Br17	125.5(3)		C25-C26	1.421(6)	C10-C25-C26	120.8(4)
	C9-H9	1.11(5)	C8-C9-H9	124(3)		C25-C28	1.436(7)	C10-C25-C28	120.1(4)
	C9-C10	1.434(6)	C8-C9-C10	106.2(4)				C26-C25-C28	119.1(4)
			C10-C9-H9	129(3)		C26-N27	1.133(7)	C25-C26-N27	178.1(5)
	C10-C25	1.364(6)	O6-C10-C9	109.6(4)		C28-N29	1.124(7)	C25-C28-N29	177.9(5)

Recrystallization from chlorobenzene gave deep blue fine crystals: mp>300 °C; IR 2223 cm^{-1} (CN); MS (70 eV) *m/z* 482, 484, and 486 (M$^+$); UV $\lambda_{\max}$ 631 nm (ε 76200), 387 (24200), 368 (18300), and 282 (14600). Calcd for $C_{18}H_4N_4O_3Br_2$: C, 44.66; H, 0.83; N, 11.57%. Found: C, 44.43; H, 0.82; N, 11.46%.

3,3′,3″,4′-Tetrabromo-5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,2':5',2''}$-terfuran (12c). The compound **12c** was obtained as bluish green fine prisms in 1.5% yield from 3,3′,3″,4′,5,5″-hexabromo-2,2′:5′,2″-terfuran (**11c**) and sodium dicyanomethanide in a similar manner as described in the part of 5,5″-bis(dicyanomethylene)-5,5′-dihydro-$\Delta^{2,2':5',2''}$-terfuran (**12a**): mp>300 °C; IR 2225 cm^{-1} (CN); MS (70 eV) *m/z* 638, 640, 642, 644, and 646 (M$^+$). Calcd for $C_{18}H_2N_4O_3Br_4$: C, 33.68; H, 0.31; N, 8.73%. Found: C, 33.88; H, 0.33; N, 8.53%.

3′,4-Dibromo-5-(3,5-dibromo-2-furyl)-3,5′-bis(dicyanomethylene)-3,5′-dihydro-$\Delta^{2,2'}$-bifuran (13). A mixture of **11c** (680 mg, 1.0 mmol), TCNEO (1.42 g, 8 mmol), and copper powder (508 mg, 8 mmol) in 1,2-dibromoethane (25 cm^3) was refluxed for 3 h. After cooling, the mixture was chromatographed on silica gel with dichloromethane, and the eluted colored band was collected and recrystallized from acetonitrile to give deep green fine prisms of **13** (108 mg, 17% yield); decomp 295 °C; IR 2235 and 2216 cm^{-1} (CN); MS (70 eV) *m/z* 638, 640, 642, 644, and 646 (M$^+$); FT-NMR (90 MHz, CD_3CN) δ=6.97 (s, 1H) and 7.59 (s, 1H); UV $\lambda_{\max}$ 510 nm (ε 32200), 431 (14400), 410 (14500), 350 (16100), 333 (16000), and 280 (12900). Calcd for $C_{18}H_2N_4O_3Br_4$: C, 33.68; H, 0.31; N, 8.73%. Found: C, 33.87; H, 0.33; N, 8.70%.

Crystal Structure Analyses of 8a · TTF and 13. The X-ray diffraction data were collected with a Rigaku automated diffractometer using Cu*Kα* radiation monochromatized with a graphite plate. Independent reflections 1282 for **8a**·TTF and 2593 for **13** within $2\theta=126°$ ($|F_o|\geqq 3.0\sigma\ (F_o)$) were used for analyses. The crystal data of **8a**·TTF are as follows; monoclinic, space group $P2_1/n$, a=21.853(2), b=6.200(1), c=7.444(2) Å, β=92.67(2)°, Z=2, V=1007.6

(3) Å^3, crystal size 0.33×0.28×0.07 mm^3. The crystal data of **13** are as follows; monoclinic, space group, $P2_1/n$, a=9.627 (1), b=18.827(2), c=10.717(1) Å, β=96.15(1)°, Z=4, V=1931.3 (4) Å^3, and crystal size 0.23×0.10×0.08 mm^3. These structures were solved by the direct method combined with the Monte-Carlo method for the selection of the initial set of phase,[14] and refined by the full-matrix least squares method after applying the absorption correction.[15] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[16] Anisotropic temperature factors were used for the refinement, and hydrogen atoms were not included in the refinement of **8a**·TTF, but in the refinement of **13**. The final R values were 0.073 for **8a**·TTF and 0.032 for **13**. The final atomic parameters are listed in Tables 3 and 4. Computations were carried out at the Information Processing Center of Hiroshima University. Tables of structure factors and anisotropic thermal parameters are deposited as Document No. 8941 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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