

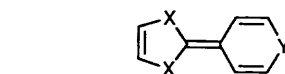
Syntheses and Properties of Derivatives of 2-(Thiopyran-4-ylidene)-1,3-dithiole and Selenium Analogues as Novel Unsymmetrical Electron Donors

Tetsuo Otsubo,* Yutaka Shiomi, Masayuki Imamura, Raita Kittaka, Akiko Ohnishi, Hiromi Tagawa, Yoshio Aso and Fumio Ogura*

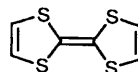
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima 724, Japan

The systematic replacement of the sulfur atoms of 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT) by selenium has been studied in order to develop novel unsymmetrical electron donors. In addition, various substitution derivatives of TPDT and selenium analogues bearing methyl, methylthio, and ethylenedithio groups in the five-membered ring and phenyl groups in the five- and/or six-membered rings were prepared. Cyclic voltammetry indicated that TPDT and its derivatives are qualified as strong electron donors, though their donor abilities are more or less perturbed by the molecular modifications, especially in the five-membered ring rather than in the six-membered ring. They thus formed charge-transfer complexes with typical electron acceptors, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane (DMTCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄), and 3,3'-dichloro-5,5'-dihydro-5,5'-bis(dicyanomethylene)- $\Delta^{2,5}$ -bithiophene (DCBT). Although the resulting complexes showed similar incomplete charge-transfer based on the nitrile vibrational frequencies, their electrical conductivities widely ranged from 10^{-10} to 10 S cm⁻¹. The high conductivities depended on the appropriate combinations of the donors and the acceptors, and did not seem to be directly correlated with the modifications of the donors by the selenium replacement as well as the methyl, methylthio, and ethylenedithio substitutions. However, most of the complexes with the donors bearing phenyl substituents in the six-membered ring were highly conductive, indicating that the phenyl substitution can contribute to the development of the superior donor character of TPDT owing to considerable extension of the π -conjugation system. In contrast, it was not the case with phenyl substitution in the five-membered ring, which could not sterically make such extension. Almost all of the highly conductive complexes showed a charge-transfer electronic transition in the infrared region, being indicative of a segregated stacking type of crystal structures in a mixed-valence state.

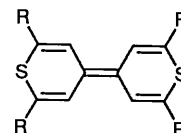
In 1977, Sandman *et al.* reported the occurrence of 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT) which is a hybrid of two typical electron donors, tetrathiafulvalene (TTF) and 4,4'-bithiopyran-ylidene (BTP).¹ However, TPDT has received little attention as an electron donor because it formed a less conductive complex with TCNQ than either symmetrical TTF or BTP.^{1a} Although a high degree of symmetry was previously proposed to be one of the criteria for the design of molecular components for organic metals,² the development of organic metals based on unsymmetrical electron donors is a subject of current interest. In this respect, recent reports have revealed that some unsymmetrically substituted tetrathiafulvalenes and tetraselenafulvalenes can form metallic radical cation salts.³ Furthermore, an unsymmetrical compound based on diselenadithiafulvalene has led to a superconductor.⁴ These findings have prompted us to investigate the potential of TPDT family. The selenium analogues of TPDT have been first designed, in which some or all of the sulfur atoms are systematically replaced by selenium. Introduction of the polar selenium atom might contribute to enhancement of intermolecular interactions. Further modifications have been made by methyl, methylthio, and ethylenedithio substitutions in the five-membered ring of TPDT and selenium analogues, since such derivatives of TTF are of considerable interest as good electron donors.⁵ In addition, phenyl derivatives have been studied, focusing on substitution in the six-membered ring, since the 2,2',6,6'-tetraphenyl-4,4'-bithiopyran-ylidene (TPBTP) acts as a better donor than BTP itself.⁶ Extension of the π -system by phenylation might also contribute to enhancement of intermolecular interactions. In



TPDT X = Y = S
 SPDT X = S, Y = Se
 TPDS X = Se, Y = S
 SPDS X = Y = Se



TTF

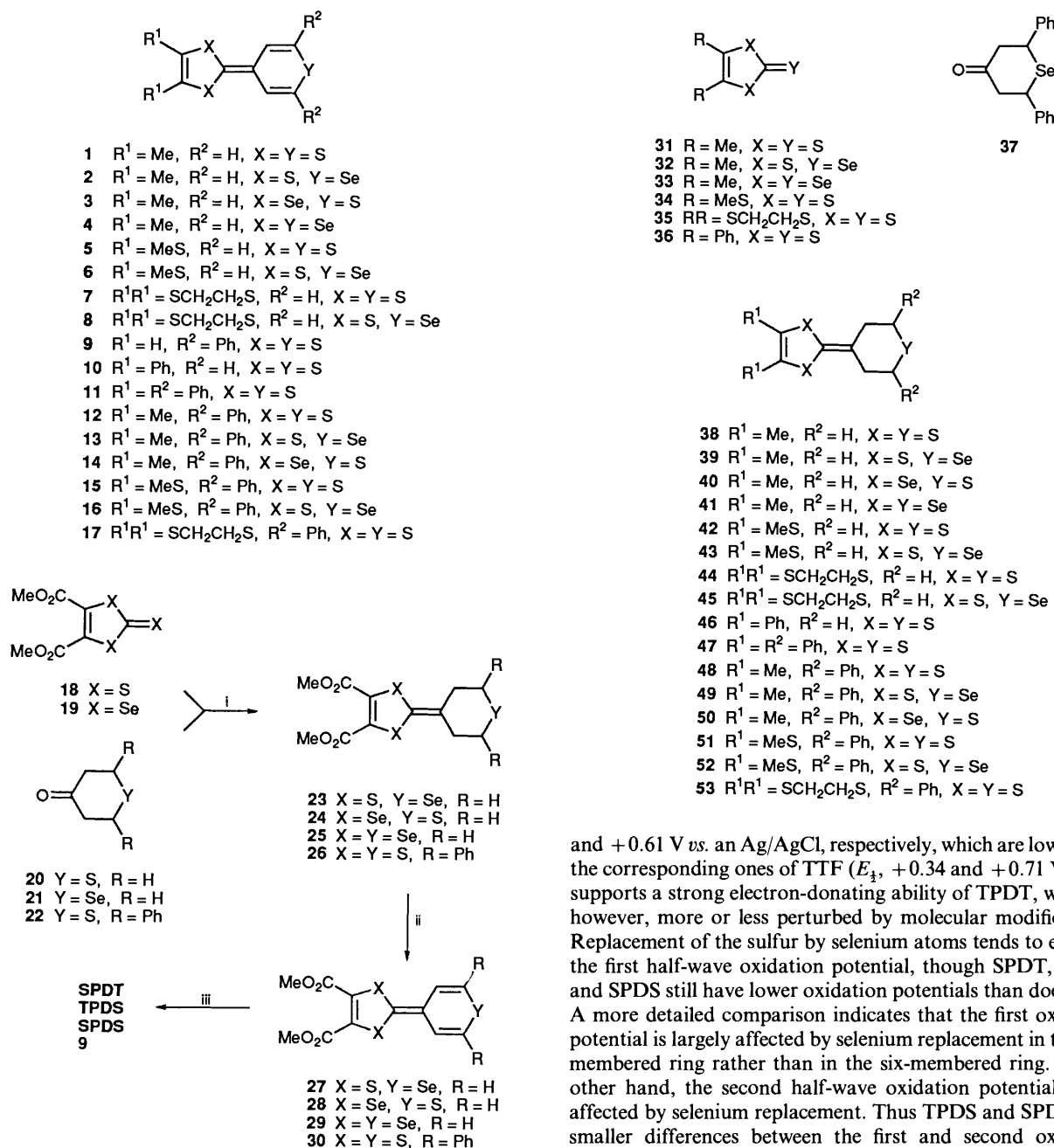


BTP R = H
 TPBTP R = Ph

this paper, we report the syntheses, properties, and charge-transfer complexes of three selenium analogues of TPDT, 2-(selenopyran-4-ylidene)-1,3-dithiole (SPDT), 2-(thiopyran-4-ylidene)-1,3-diselenole (TPDS) and 2-(selenopyran-4-ylidene)-1,3-diselenole (SPDS), and their substitution derivatives 1–17.⁷

Results and Discussion

SPDT, TPDS, SPDS, and 2,6'-diphenyl-TPDT **9** were prepared starting with appropriate combinations of materials **18**–**22** according to the same three-step synthetic procedure as used for TPDT (Scheme 1).¹ For example, treatment of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate **18** with the 4-



Scheme 1 Reagents and conditions: i, $(\text{EtO})_3\text{P}$, benzene, reflux, 12–22 h; ii, chloranil, toluene or xylene, reflux, 12 h; iii, $\text{LiBr}\cdot\text{H}_2\text{O}$, HMPA, 150–160 °C, 0.5–1 h.

oxo selenane **21** in refluxing benzene containing triethyl phosphite gave the cross-coupling product **23** in 23% yield, which was then dehydrogenated with chloranil in refluxing toluene to give 4,5-bis(methoxycarbonyl)-2-thiopyran-4-ylidene-1,3-dithiole **27** in 84% yield. The methoxycarbonyl groups of **27** were hydrolysed and decarboxylated by treating with lithium bromide monohydrate in hexamethylphosphoric triamide (HMPA) at 160 °C to give SPDT in 70% yield. The other derivatives **1–17** with additional functional groups in the five-membered ring were similarly obtained in the two-step sequence of the coupling reactions using materials **20–22** and **31–37** followed by dehydrogenation of the resulting intermediates **38–53**.

TPDT and its derivatives show two reversible one-electron redox waves in the cyclic voltammograms (Table 1). The first and second half-wave oxidation potentials of TPDT are +0.23

and +0.61 V vs. an Ag/AgCl , respectively, which are lower than the corresponding ones of TTF (E_1 , +0.34 and +0.71 V). This supports a strong electron-donating ability of TPDT, which is, however, more or less perturbed by molecular modifications. Replacement of the sulfur by selenium atoms tends to enhance the first half-wave oxidation potential, though SPDT, TPDS, and SPDS still have lower oxidation potentials than does TTF. A more detailed comparison indicates that the first oxidation potential is largely affected by selenium replacement in the five-membered ring rather than in the six-membered ring. On the other hand, the second half-wave oxidation potential is less affected by selenium replacement. Thus TPDS and SPDS have smaller differences between the first and second oxidation potentials, indicating that the selenium replacement in the five-membered ring serves to reduce on-site coulombic repulsion. The additional methyl substituents of **1–4** cause expected lowering of the first oxidation potentials but unexpected elevation of the second ones. In contrast, the methylthio and ethylenedithio substituents of **5–8** cause considerable elevation of both oxidation potentials. In addition, a comparison of the voltammetric data of the three phenyl derivatives **9–11** indicates that phenyl substitution in the five-membered ring considerably enhances the first oxidation potential, but that in the six-membered ring only slightly affects it.

Table 1 also summarizes the electronic absorption data of TPDT derivatives. The spectral shape of TPDT together with those of **9–11** is shown in Fig. 1, being characterized by a strong $\pi\text{-}\pi^*$ absorption band around 350 nm accompanied by a weak absorption at 251 nm and a shoulder at 398 nm. The selenium analogues SPDT, TPDS and SPDS, as a whole, demonstrate similar spectral shapes but with small bathochromic shifts. The methyl, methylthio, and ethylenedithio substituted analogues also cause small bathochromic shifts. On the other hand, a marked spectral change is induced by phenyl substitution;

Table 1 Half-wave oxidation potentials^a and electronic absorption maxima^b of TPDT donors

Compound	$E_{\frac{1}{2}}(1)/V$	$E_{\frac{1}{2}}(2)/V$	$\Delta E/V$	λ_{\max}/nm (log ϵ)
TPDT	+0.23	+0.61	0.38	251 (3.52), 348 (4.36), 359 (4.38), 405sh (3.18)
SPDT	+0.25	+0.60	0.35	259sh (3.44), 365 (4.42), 400sh (3.57)
TPDS	+0.30	+0.61	0.31	256 (3.74), 346 (4.38), 358 (4.45), 375sh (3.88)
SPDS	+0.33	+0.64	0.31	265 (3.63), 350 (4.35), 364 (4.42), 380sh (4.03)
1	+0.19	+0.61	0.42	261 (3.65), 350 (4.38), 364 (4.45)
2	+0.21	+0.63	0.42	269 (3.56), 369 (4.44)
3	+0.27	+0.67	0.40	228 (3.93), 258 (3.79), 346 (4.39), 360 (4.47), 390sh (3.75)
4	+0.30	+0.67	0.37	231 (3.90), 272 (3.75), 367 (4.47), 396sh (3.85)
5	+0.31	+0.65	0.34	267 (3.96), 347sh (4.41), 358 (4.45)
6	+0.33	+0.66	0.33	241sh (3.98), 274 (3.87), 364 (4.43)
7	+0.30	+0.67	0.37	218 (4.11), 278 (3.96), 366 (4.37), 390sh (3.97)
8	+0.30	+0.67	0.37	225 (4.15), 290 (3.95), 372 (4.36), 395sh (4.10)
9	+0.24	+0.61	0.37	248 (4.36), 410 (4.43), 460sh (3.41)
10	+0.27	+0.63	0.36	250sh (4.07), 355sh (4.45), 364 (4.50), 395sh (3.81)
11	+0.28	+0.62	0.34	222 (4.51), 251 (4.57), 415 (4.50), 460sh (3.88)
12	+0.21	+0.58	0.37	249 (4.29), 419.5 (4.27), 460sh (3.59)
13	+0.25	+0.64	0.39	254 (4.25), 424 (4.30), 470sh (3.61)
14	+0.28	+0.61	0.33	250 (4.33), 4.03 (4.24), 460sh (3.68)
15	+0.32	+0.61	0.29	254 (4.49), 413.5 (4.45), 465sh (3.57)
16	+0.37	+0.68	0.31	256 (4.49), 418 (4.45), 470sh (3.57)
17	+0.32	+0.64	0.32	253 (4.43), 424.5 (4.35), 460sh (3.75)

^a Cyclic voltammetry was measured at 100 mV s⁻¹ scan rate with Pt working and counter electrodes and Ag/AgCl reference electrode in 10⁻³ mol dm⁻³ benzonitrile solution containing 0.1 mol dm⁻³ tetrabutylammonium perchlorate as supporting electrolyte. ^b Electronic spectra were measured in acetonitrile solution.

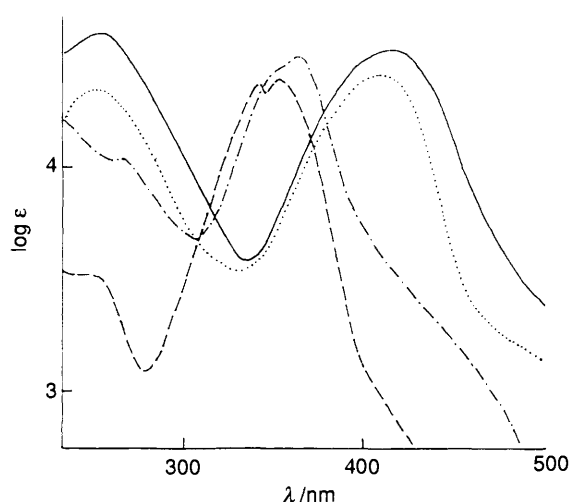


Fig. 1 Electronic absorption spectra of TPDT and its phenyl derivatives **9–11** in acetonitrile: —, TPDT; ---, **10**; ···, **9**; —·—, **11**.

compounds **9** and **11–17**, having phenyl groups in the six-membered ring, show a considerable bathochromic shift of the strong absorption bands beyond 400 nm. However, this is not the case for **10** with phenyl groups only in the five-membered ring. These results indicate clearly that phenylation of the six-membered moiety results in extensive conjugation of the π -system, but that of the five-membered moiety cannot cause such conjugation.

TPDT has the following structural features as already reported by Sandman *et al.*^{1b} The individual rings are nearly planar, but the two rings are not coplanar and tilted by about 12° around the long molecular axis. The crystal structure, as often seen for simple arenes, is packed as paired molecules, which do not strongly interact with each other. In the present work, the structures of two phenyl derivatives **11** and **15** were elucidated by an X-ray crystallographic analysis. As shown in Figs. 2 and 3, the phenyl groups attached to the six-membered ring of both molecules are nearly coplanar with the TPDT skeleton, but the phenyl or methylthio substituents of the five-

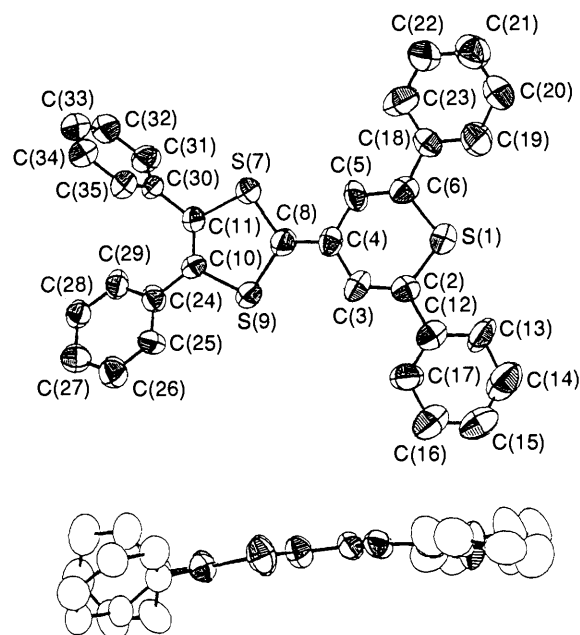


Fig. 2 ORTEP drawing of molecule **11** viewed from above the plane of the TPDT skeleton (above) and from the side (bottom)

membered ring deviate markedly from this plane. This is consistent with the above description based on the electronic spectra. The nonconjugation of the five-membered moiety with the introduced phenyl or methylthio group is due to steric hindrance. Table 2 shows selected bond distances and angles of TPDT skeletons of **11** and **15**, which are approximately similar to molecular dimensions of TPDT itself, but somewhat affected by the substituents, being rather comparable to those of the corresponding bonds in TPBTP⁸ or tetrakis(methylthio)-tetrathiafulvalene (TMTTF).⁹ The lengths of the central double bonds tend to depend on the skeletal tilts. As shown in Fig. 2, the five- and six-membered rings of **11**, as in TPDT, are not coplanar and tilted by about 9°. The central-bond length is 1.347 Å which is almost identical to those of other distorted donors TPDT (1.348 Å), TTF (1.349 Å),¹⁰ and TMTTF

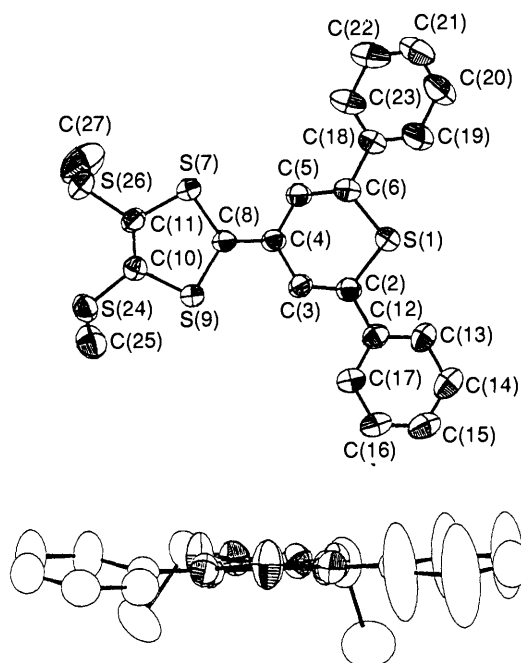


Fig. 3 ORTEP drawing of molecule **15** viewed from above the plane of the TPDT skeleton (above) and from the long molecular axis (bottom)

Table 2 Selected bond lengths and angles for compounds **11** and **15**

	11	15
Bond lengths/Å		
S(1)–C(2)	1.762(10)	1.749(6)
S(1)–C(6)	1.759(9)	1.752(6)
C(2)–C(3)	1.336(13)	1.338(8)
C(3)–C(4)	1.452(12)	1.456(8)
C(4)–C(5)	1.455(14)	1.448(8)
C(4)–C(8)	1.347(13)	1.360(8)
C(5)–C(6)	1.351(14)	1.348(8)
S(7)–C(8)	1.768(9)	1.762(6)
S(7)–C(11)	1.761(9)	1.752(6)
C(8)–S(9)	1.754(10)	1.751(6)
S(9)–C(10)	1.767(9)	1.749(6)
C(10)–C(11)	1.333(12)	1.339(8)
Bond angles/°		
C(2)–S(1)–C(6)	103.6(5)	103.4(3)
S(1)–C(2)–C(3)	123.6(7)	123.0(5)
C(2)–C(3)–C(4)	124.4(9)	125.6(5)
C(3)–C(4)–C(5)	120.8(8)	119.6(5)
C(3)–C(4)–C(8)	119.5(8)	120.1(5)
C(5)–C(4)–C(8)	119.6(8)	120.3(5)
C(4)–C(5)–C(6)	125.0(9)	124.9(5)
S(1)–C(6)–C(5)	122.4(8)	123.3(4)
C(8)–S(7)–C(11)	96.4(4)	96.4(3)
C(4)–C(8)–S(7)	122.8(7)	123.9(4)
C(4)–C(8)–S(9)	124.8(7)	123.3(4)
S(7)–C(8)–S(9)	112.4(5)	112.7(3)
C(8)–S(9)–C(10)	97.2(4)	96.7(3)
S(9)–C(10)–C(11)	116.1(7)	117.0(5)
S(7)–C(11)–C(10)	117.6(7)	116.8(5)

(1.348 Å). On the other hand, the two skeletal rings of **15** take a more planar conformation and are twisted only by 5° as shown in Fig. 3. The central-bond length (1.360 Å) is intermediate between those of the distorted molecules mentioned above and planar BTP derivatives such as TPBTP (1.389 Å) and tetrakis(ethoxycarbonyl)bithiopyranylidene (1.405 Å).¹¹ In contrast to TPDT, both molecules **11** and **15**, in spite of large deviations of the substituents in the five-membered ring from the molecular plane, make uniform stacking columns in the crystal structures

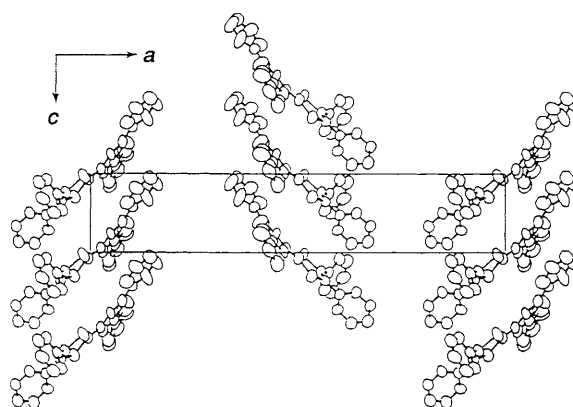


Fig. 4 Crystal structure of molecule **11** projected along the *b* axis

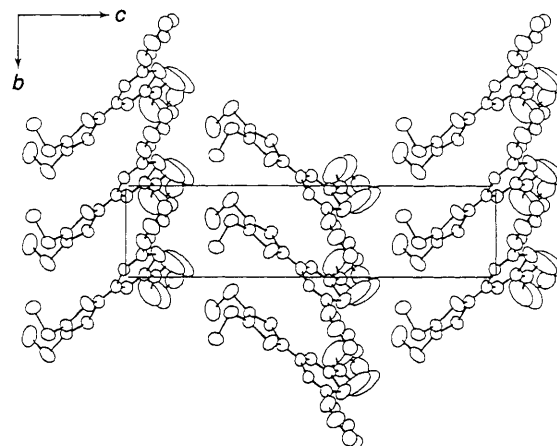
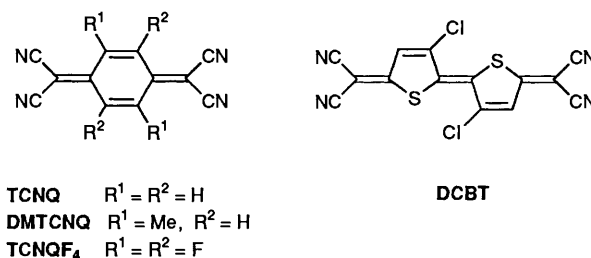


Fig. 5 Crystal structure of molecule **15** projected along the *a* axis

as shown in Figs. 4 and 5. The columnar structure presumably arises from an increase of the strong face-to-face π -interaction of these molecules, which is enhanced by extension of the π -system by the introduction of phenyl groups. This feature enhances the ability of components to constitute highly electrically conductive complexes.²

The charge-transfer complexes of TPDT and selenium analogues were examined with four electron acceptors such as TCNQ, DMTCNQ, TCNQF₄ and DCBT,¹² and their properties are summarized in Table 3. TPDT with these acceptors



formed deeply coloured materials with a 1:1 composition ratio, and showed nitrile vibrational frequencies around 2000 cm^{-1} in the infrared absorption spectra. The absorption maximum (2195 cm^{-1}) of the TCNQ complex is intermediate between those of neutral TCNQ (2232 cm^{-1}) and Na^+TCNQ^- (2174 cm^{-1}), calculated according to the equation of Chappell *et al.*,¹³ corresponding to a fractional degree of 0.64 of charge-transfer. Such incomplete charge-transfer is also expected for the other TPDT complexes with similar shifts. For example, similar calculations of charge-transfer for the TPDT-DMTCNQ complex (2192 cm^{-1}) using DMTCNQ (2230 cm^{-1}) and $\text{Na}^+\text{DMTCNQ}^-$ (2176 cm^{-1}) as the standards, and for the

Table 3 Charge-transfer complexes of TPDT derivatives

Complex	D:A	Appearance ^a	D.p./ °C	Found (Calcd.) ^c /%			$\nu_{\text{CN}}/\text{cm}^{-1}$	CT band ^d 10^{-3} cm^{-1}	$\sigma^e/\text{S cm}^{-1}$
				C	H	N			
TPDT-TCNQ	1:1	Black powder ^b	216	60.0 (59.7)	2.5 (2.5)	13.6 (13.9)	2195	non	7.4×10^{-3}
TPDT-DMTCNQ	1:1	Black powder	> 300	62.3 (61.4)	3.55 (3.3)	13.7 (13.0)	2192	3.5	5.6×10^{-1}
TPDT-TCNQF ₄	1:1	Black needles	> 300	52.05 (50.6)	1.2 (1.3)	11.8 (11.8)	2207	non	6.2×10^{-4}
TPDT-DCBT	1:1	Dark green powder	> 300	47.8 (47.2)	1.4 (1.4)	11.1 (10.0)	2195	4.4	3.2
SPDT-TCNQ	1:1	Purple needles	169	53.3 (53.5)	2.3 (2.2)	12.2 (12.5)	2201	4.0	1.8
SPDT-DMTCNQ	1:1	Black powder	185	55.4 (55.3)	3.0 (3.0)	11.7 (11.7)	2192	6.9	5.6×10^{-4}
SPDT-TCNQF ₄	1:1	Deep green powder	158	46.0 (46.1)	1.1 (1.2)	10.6 (10.75)	2200	8.7	3.4×10^{-4}
SPDT-DCBT	1:1	Black crystals	255	43.5 (43.6)	1.4 (1.3)	9.2 (9.2)	2206	3.5, 8.5	7.4
TPDS-TCNQ	1:1	Black powder	202	49.1 (48.4)	2.0 (2.0)	10.9 (11.3)	2192	5.8	1.2×10^{-2}
TPDS-DMTCNQ	1:1	Purple needles	286	50.3 (50.4)	2.7 (2.7)	10.6 (10.7)	2202	5.7	10.2
TPDS-TCNQF ₄	1:1	Dark green powder	225	42.7 (42.3)	1.4 (1.1)	9.8 (9.9)	2196	non	2.5×10^{-4}
TPDS-DCBT		no complex							
SPDS-TCNQ	1:1	Black needles	203	44.2 (44.2)	1.8 (1.9)	10.3 (10.3)	2193	6.4	4.7×10^{-2}
SPDS-DMTCNQ	1:1	Purple needles	187	48.7 (46.3)	2.6 (2.5)	8.5 (9.8)	2202	6.5	2.7×10^{-8}
SPDS-TCNQF ₄	1:1	Dark green powder	180	38.8 (39.05)	1.4 (1.0)	8.55 (9.1)	2204	11.1	4.2×10^{-8}
SPDS-DCBT		no complex							
1-TCNQ	1:1	Black power ^b	183	61.1 (61.4)	3.5 (3.3)	13.1 (13.0)	2194	4.7	5.0×10^{-1}
1-DMTCNQ	3:4	Black solid ^b	201	64.2 (64.5)	3.4 (3.5)	14.3 (14.0)	2194	3.4	7.3×10^{-1}
2-TCNQ	1:1	Black needles	185	55.4 (55.3)	2.9 (3.0)	11.4 (11.7)	2194	7.6	2.4×10^{-6}
2-DMTCNQ	3:4	Black solid	178	59.2 (59.3)	3.7 (3.9)	12.3 (12.2)	vague	2.8	1.2×10^{-1}
3-TCNQ	1:1	Brown needles	229	50.4 (50.4)	2.7 (2.7)	10.55 (10.7)	2194	5.6	1.7×10^{-3}
3-DMTCNQ	1:1	Brown powder	162	52.1 (52.2)	3.3 (3.3)	10.05 (10.1)	2194	3.4	6.7×10^{-1}
4-TCNQ	1:1	Brown needles	205	46.3 (46.3)	2.4 (2.5)	9.7 (9.8)	2200	6.0	1.6×10^{-6}
4-DMTCNQ	2:3	Brown powder	188	51.8 (52.0)	3.15 (3.1)	11.6 (11.7)	2196	5.9	8.5×10^{-8}
5-TCNQ	1:1	Black plates ^b	190	53.35 (53.4)	2.8 (2.85)	11.5 (11.3)	2197	5.6	6.4×10^{-4}
5-DMTCNQ		no complex							
6-TCNQ	1:1	Black plates	160	48.7 (48.8)	2.6 (2.6)	9.6 (10.3)	2195	6.4	9.6×10^{-5}
6-DMTCNQ		no complex							
7-TCNQ	1:1	Black powder ^b	208	54.9 (53.6)	2.45 (2.45)	11.3 (11.4)	2197	3.4	2.2
7-DMTCNQ	1:1	Black needles ^b	> 300	55.2 (55.35)	3.5 (3.1)	10.45 (10.8)	2200	6.8	5.6×10^{-4}
8-TCNQ	1:1	Black needles	197	48.7 (49.0)	2.1 (2.2)	10.0 (10.4)	2198	3.7	1.1
8-DMTCNQ	1:1	Black powder	170	49.6 (50.4)	3.1 (2.8)	9.4 (10.5)	2207	6.6	1.3×10^{-4}
9-TCNQ	2:3	Black powder	218	68.7 (69.5)	3.3 (3.1)	12.6 (12.8)	2185, 2198	3.5	1.5
9-DMTCNQ	3:2	Dark purple needles	196	69.3 (69.7)	3.8 (3.9)	7.9 (7.4)	2191	3.4	4.8
10-TCNQ		no complex							
10-DMTCNQ	1:1	Black needles ^b	215	70.0 (70.1)	3.7 (3.8)	9.6 (9.6)	2200	non	6.4×10^{-11}

Table 3 Continued

Complex	D:A	Appearance ^a	D.p./ °C	Found (Calcd.) ^c /%			$\nu_{\text{CN}}/$ cm^{-1}	CT band ^d 10^{-3} cm^{-1}	$\sigma^e/$ S cm^{-1}
				C	H	N			
11·TCNQ	1:1	Dark purple powder ^b	211	74.6 (74.8)	3.65 (3.7)	7.9 (7.9)	2184, 2197	non	9.3×10^{-2}
11·DMTCNQ		no complex							
12·TCNQ	3:2	Black powder ^b	208	69.8 (70.0)	3.8 (4.1)	7.0 (7.3)	2185	3.4	1.5×10^{-1}
12·DMTCNQ	1:1	Black powder ^b	203	70.7 (70.8)	4.25 (4.3)	9.15 (9.2)	2191	3.5	4.9×10^{-1}
13·TCNQ	2:3	Black crystals ^b	260	65.4 (65.7)	3.3 (3.3)	11.9 (11.5)	vague	2.6	8.4×10^{-1}
13·DMTCNQ	2:3	Black crystals	212	66.5 (66.7)	4.1 (3.9)	11.1 (10.85)	2198	3.2	1.7×10^{-1}
14·TCNQ	3:2	Black powder ^b	229	61.5 (61.7)	3.3 (3.1)	10.5 (10.8)	vague	3.5	4.1
14·DMTCNQ	3:4	Dark purple solid	213	62.0 (62.45)	3.9 (3.7)	9.6 (9.55)	vague	3.5	3.0
15·TCNQ	1:1	Dark purple needles ^b	195	62.8 (63.1)	3.2 (3.4)	9.0 (8.7)	2201	3.5	2.4
15·DMTCNQ	1:1	Dark purple powder ^b	156	64.1 (63.8)	3.9 (4.1)	8.3 (8.1)	2195	3.5	1.1
16·TCNQ	2:3	Black crystals ^b	196	59.8 (60.3)	3.1 (3.0)	10.3 (10.55)	2196	3.1	1.8
16·DMTCNQ		no complex							
17·TCNQ	1:1	Black needles ^b	198	63.5 (63.3)	2.9 (3.1)	8.7 (8.7)	2201	non	2.4×10^{-7}
17·DMTCNQ	1:1	Black powder ^b	204	64.2 (64.25)	3.7 (3.6)	8.6 (8.3)	2196	non	1.4×10^{-8}

^a Obtained from chlorobenzene unless otherwise stated. ^b Obtained from acetonitrile. ^c Calculated as stoichiometry indicated for the complex.

^d Measured with a KBr disk method. ^e Measured on compressed pellets at room temp. with a four-probe or two-probe method.

TPDT·TCNQF₄ complex (2208 cm⁻¹) using TCNQF₄ (2234 cm⁻¹) and Na⁺TCNQF₄⁻ (2201 cm⁻¹) are 0.70 and 0.79, respectively. Incomplete charge-transfer is one of the important requisites for conductive complexes with 1:1 composition ratio.² The electrical conductivities of the four TPDT complexes differ by four orders of magnitude; the TCNQ and TCNQF₄ complexes showed lower conductivities of 7.4×10^{-4} and $6.2 \times 10^{-4} \text{ S cm}^{-1}$, respectively, while the DMTCNQ and DCBT complexes showed higher electrical conductivities of 5.6×10^{-1} and 3.2 S cm^{-1} , respectively. This difference can be explained by the stacking types of the crystal structures, which can be conveniently distinguished by an electronic transition due to charge-transfer in the infrared region.¹⁴ The more conductive DMTCNQ and DCBT complexes thus showed a broad electronic absorption at 3500 and 4400 cm⁻¹ respectively, indicative of a segregated stacking structure in a mixed-valence state, which is suitable for ready charge migration without coulombic repulsion, that is, high conduction. On the other hand, the less conductive TCNQ and TCNQF₄ complexes did not show such a low energy electron transition, suggesting a mixed stacking structure of alternate donors and acceptors, which is usually characterized by semiconductive behaviour.

The selenium analogues also formed conductive complexes with these acceptors, but the high conductivities above $10^{-1} \text{ S cm}^{-1}$ do not seem to be directly correlated with the selenium introduction. For example, SPDT gave highly conductive complexes with TCNQ (1.8 S cm^{-1}) and with DCBT (7.4 S cm^{-1}), but, contrary to the case of TPDT, a less conductive complex with DMTCNQ. In addition, TPDS gave a conductive complex only with DMTCNQ (10.2 S cm^{-1}) and SPDS no conductive one. These conductive complexes except the TPDS·DMTCNQ complex also showed a CT electronic transition below 5000 cm⁻¹.

Since all of the TCNQF₄ complexes were poorly conductive and TPDS and SPDS formed no crystalline complexes with

DCBT, a comparative study of the other functionalized TPDT derivatives was conducted, limited to complexation with TCNQ and DMTCNQ. 4,5-Dimethyl-TPDT **1** successfully formed highly conductive complexes with both acceptors, though the increase in donor abilities due to methylation did not necessarily affect the degree of charge-transfer, based on the nitrile vibrational frequencies of the complexes. 4,5-Dimethyl SPDT **2** and TPDS **3**, however, gave conductive complexes with only DMTCNQ, and 4,5-dimethyl SPDS **4** with neither acceptors. These results again indicate that replacement of the selenium has no effect on the formation of the conductive complexes.

4,5-Bismethylthio derivatives **5** and **6** gave poorly conductive complexes with TCNQ and no complexes with DMTCNQ. On the other hand, 4,5-ethylenedithio derivatives **7** and **8** formed conductive TCNQ complexes and less conductive DMTCNQ ones. These results suggest steric hindrance by the functional groups, especially the methylthio groups in the complexation. A similar steric problem arises from the phenylation in the dithiole ring; 4,5-diphenyl derivative **10** formed no complex with TCNQ and a nearly insulating complex with DMTCNQ. In addition, tetraphenyl derivative **11** formed no complex with DMTCNQ, though it formed a TCNQ complex with a relatively high conductivity of $9.3 \times 10^{-2} \text{ S cm}^{-1}$. These results are reminiscent of a poor donor ability of 4,4',5,5'-tetraphenyltetrathiafulvalene (TPTF).¹⁵ In contrast, the 2',6'-diphenyl derivative **9** and the other 2',6'-diphenyl derivatives **12**–**16**, bearing additional methyl, methylthio, and ethylenedithio groups, formed highly conductive complexes with both TCNQ and DMTCNQ. All of these highly conductive complexes showed a CT transition in the infrared region as expected. Thus the phenylation of the thiopyran ring favours the formation of a segregated stacking structure in the complexation, and is necessary to improve the electron donation of TPDT. As an exception, no complexation of **16** with DMTCNQ and the formation of poorly conductive

complexes of **17** with the two acceptors again suggest the steric hindrance of the additional methylthio and ethylenedithio groups.

Experimental

General.—Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-30 spectrophotometer. ^1H NMR spectra (60 MHz) were recorded on a JEOL PMX-60 spectrometer or on a Hitachi R-1200 spectrometer using tetramethylsilane as internal standard. Mass spectra were measured at 70 eV on a Shimadzu QP-1000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer or on a Hitachi 330 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. All reactions were carried out under a nitrogen atmosphere. All chemicals and solvent are of reagent grade.

Syntheses of TPDT Derivatives.—A typical experimental procedure is described in the following synthesis of SPDT.

4,5-(Bismethoxycarbonyl)-2-(tetrahydroselenopyran-4-ylidene)-1,3-dithiole **23.**—A mixture of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate **18**¹⁶ (1.3 g, 5.4 mmol), 4-oxoselenane **21**¹⁷ (3.5 g, 21.5 mmol), triethyl phosphite (5 cm³) and dry benzene (40 cm³) was refluxed for 12 h. After evaporation under reduced pressure, the residue was purified by column chromatography on silica gel with benzene and then by recrystallization from benzene–hexane to give **23** as orange needles (0.444 g, 23%), m.p. 95–96.5 °C (Found: C, 39.3; H, 3.8. C₁₂H₁₄O₄S₂Se requires C, 39.45; H, 3.9%; ν_{max} (KBr disc)/cm⁻¹ 1715 (C=O), 1275 and 1250 (CO); δ_{H} (CDCl₃) 2.62 (8 H, A₂B₂ m, CH₂) and 3.80 (6 H, s, CH₃); m/z 366 (M⁺, ⁸⁰Se).

4,5-Bis(methoxycarbonyl)-2-(selenopyran-4-ylidene)-1,3-dithiole **27.** A mixture of **23** (290 mg, 0.79 mmol), chloranil (430 mg, 1.75 mmol), and dry xylene (25 cm³) was refluxed for 12 h. After evaporation under reduced pressure, the residue was purified by column chromatography on silica gel with benzene and then by recrystallization from benzene–hexane to give **27** as black needles (241 mg, 84%); m.p. 123.5–124 °C (Found: C, 39.75; H, 2.7. C₁₂H₁₀O₄S₂Se requires C, 39.9; H, 2.8%; ν_{max} (KBr disc)/cm⁻¹ 1735 and 1718 (C=O); δ_{H} (CCl₄) 3.77 (6 H, s, CH₃), 6.13 (2 H, d, *J* 11, CH) and 6.31 (2 H, d, *J* 11, CH); m/z 362 (M⁺, ⁸⁰Se).

2-(Selenopyran-4-ylidene)-1,3-dithiole (SPDT). A solution of **27** (193 mg, 0.53 mmol) and lithium bromide monohydrate (223 mg, 2.1 mmol) in hexamethylphosphoric triamide (10 cm³) was heated with stirring at 150 °C for 1 h. After cooling, the mixture was diluted with water (100 cm³) and extracted with benzene. The extract was washed with brine and then with water, and dried (MgSO₄). After evaporation, the residue was purified by column chromatography on silica gel with benzene followed by recrystallization from benzene–hexane to give SPDT as yellow plates (91 mg, 70%); m.p. 116–117 °C (Found: C, 39.0; H, 2.6. C₈H₆S₂Se requires C, 39.2; H, 2.5%; δ_{H} (CCl₄) 6.16 (4 H, m, CH) and 6.24 (2 H, s, CH); m/z 246 (M⁺, ⁸⁰Se).

TPDS, SPDS, and **9** with no functional groups in the five-membered ring were prepared in the same three-step sequence using appropriate materials, besides **18** and **21**, dimethyl 2-selenoxo-1,3-diselenole-4,5-dicarboxylate **19**,¹⁸ 4-oxothiane **20**,¹⁹ 2,6-diphenyl-4-oxothiane **22**.^{20*} In addition, the other

TPDT derivatives with additional functional groups in the five-membered ring were prepared in the initial two-step sequence using 4,5-dimethyl-2-thioxo-1,3-dithiole **31**,²¹ 4,5-dimethyl-2-selenoxo-1,3-dithiole **32**,²² 4,5-dimethyl-2-selenoxo-1,3-diselenole **33**,²³ 4,5-bis(methylthio)-2-thioxo-1,3-dithiole **34**,²⁴ and 4,5-(ethylenedithio)-2-thioxo-1,3-dithiole **35**,²⁴ 4,5-diphenyl-2-thioxo-1,3-dithiole **36**,²⁵ and 2,6-diphenyl-4-oxoselenane **37**.²⁶

4,5-Bis(methoxycarbonyl)-2-(tetrahydrothiopyran-4-ylidene)-1,3-diselenole **24.** Obtained in 9% yield from **19** and **20**; orange needles from benzene–hexane; m.p. 135–135.5 °C (Found: C, 34.9; H, 3.4. C₁₂H₁₄O₄SSe₂ requires C, 35.0; H, 3.4%; ν_{max} (KBr disc)/cm⁻¹ 1735 and 1715 (C=O); δ_{H} (CDCl₃) 2.60 (8 H, A₂B₂ m, CH₂) and 3.75 (6 H, s, CH₃); m/z 414 (M⁺, ⁸⁰Se).

4,5-Bis(methoxycarbonyl)-2-(thiopyran-4-ylidene)-1,3-diselenole **28.** Obtained in 86% yield from **24**; black needles from benzene–hexane; m.p. 121–121.5 °C (Found: C, 35.3; H, 2.4. C₁₂H₁₀O₄SSe₂ requires C, 35.3; H, 2.5%; ν_{max} (KBr disc)/cm⁻¹ 1720 and 1705 (C=O); δ_{H} (CDCl₃) 3.70 (6 H, s, CH₃), 5.85 (2 H, d, *J* 11, CH) and 6.00 (2 H, d, *J* 11, CH); m/z 410 (M⁺, ⁸⁰Se).

2-(Thiopyran-4-ylidene)-1,3-diselenole (TPDS). Obtained in 32% yield from **28**; yellow plates from benzene–hexane; m.p. 150–151 °C (Found: C, 32.7; H, 2.1. C₈H₆SSe₂ requires C, 32.9; H, 2.1%; δ_{H} (CCl₄) 5.90 (4 H, s, CH) and 7.06 (2 H, s, CH); m/z 294 (M⁺, ⁸⁰Se).

4,5-Bis(methoxycarbonyl)-2-(tetrahydroselenopyran-4-ylidene)-1,3-diselenole **25.** Obtained in 10% yield from **19** and **21**; orange needles from benzene–hexane; m.p. 105–106 °C (Found: C, 31.4; H, 3.0. C₁₂H₁₄O₄Se₃ requires C, 31.4; H, 3.1%; ν_{max} (KBr disc)/cm⁻¹ 1730 and 1695 (C=O); δ_{H} (CDCl₃) 2.60 (8 H, A₂B₂ m, CH₂) and 3.77 (6 H, s, CH₃); m/z 460 (M⁺, ⁸⁰Se).

4,5-Bis(methoxycarbonyl)-2-(selenopyran-4-ylidene)-1,3-diselenole **29.** Obtained in 70% yield from **25**; red plates from benzene–hexane; m.p. 117–118 °C (Found: C, 31.7; H, 2.2. C₁₂H₁₀O₄Se₃ requires C, 31.7; H, 2.2%; ν_{max} (KBr disc)/cm⁻¹ 1735 (C=O); δ_{H} (CCl₄) 3.75 (6 H, s, CH₃), 5.98 (2 H, d, *J* 12, CH) and 6.38 (2 H, d, *J* 12, CH); m/z 456 (M⁺, ⁸⁰Se).

2-(Selenopyran-4-ylidene)-1,3-diselenole (SPDS). Obtained in 50% yield from **29**; yellow plates from benzene–hexane; m.p. 145 °C (decomp.) (Found: C, 28.2; H, 1.7. C₈H₆Se₃ requires C, 28.3; H, 1.8%; δ_{H} (CCl₄) 6.04 (2 H, d, *J* 11, CH), 6.26 (2 H, d, *J* 11, CH) and 7.05 (2 H, s, CH); m/z 340 (M⁺, ⁸⁰Se).

4,5-Bis(methoxycarbonyl)-2-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3-dithiole **26.** Obtained in 28% yield from **18** and **22**; red needles from benzene–hexane; m.p. 176.5–178 °C (Found: C, 61.2; H, 4.6. C₂₄H₂₂O₄S₃ requires C, 61.25; H, 4.7%; ν_{max} (KBr disc)/cm⁻¹ 1720 (C=O) and 1260 (C–O); δ_{H} (CDCl₃) 2.5–3.0 (4 H, m, CH₂), 3.78 (6 H, s, CH₃), 3.9–4.1 (2 H, m, CH) and 7.27 (10 H, s, PhH); m/z 470 (M⁺).

4,5-Bis(methoxycarbonyl)-2-(2,6-diphenylthiopyran-4-ylidene)-1,3-dithiole **30.** Obtained in 58% yield from **26**; dark brown microcrystals from benzene–hexane; m.p. 173.5–175 °C (Found: C, 61.75; H, 3.8. C₂₄H₁₈O₄S₃ requires C, 61.8; H, 3.9%; ν_{max} (KBr disc)/cm⁻¹ 1740 and 1720 (C=O); δ_{H} (CCl₄) 3.77 (6 H, s, CH₃), 6.18 (2 H, s, CH) and 7.1–7.5 (10 H, br s, PhH); m/z 466 (M⁺).

2-(2,6-Diphenylthiopyran-4-ylidene)-1,3-dithiole **9.** Obtained in 49% yield from **30**; blackish-purple crystals from benzene–hexane; m.p. 195–196.5 °C (Found: C, 68.5; H, 4.0. C₂₀H₁₄S₃ requires C, 68.5; H, 4.0%; δ_{H} (60 MHz; CCl₄) 6.20 (2 H, s, CH), 6.40 (2 H, s, CH) and 7.17 (10 H, s, PhH); m/z 350 (M⁺).

4,5-Dimethyl-2-(tetrahydrothiopyran-4-ylidene)-1,3-dithiole **38.** Obtained in 24% yield from **20** and **31** or in 63% yield from **20** and **32**; faint orange plates from hexane; m.p. 91–91.5 °C (Found: C, 52.1; H, 6.0. C₁₀H₁₄S₃ requires C, 52.1; H, 6.1%; δ_{H} (CDCl₃) 1.87 (6 H, s, CH₃) and 2.50 (8 H, A₂B₂ m, CH₂); m/z 230 (M⁺).

* There are *cis* and *trans* configurations concerning the phenyl stereochemistry of **22**, and the *cis* form was used in the present experiment.

4,5-Dimethyl-2-(thiopyran-4-ylidene)-1,3-dithiole **1**. Obtained in 23% yield from **38**; orange fine needles from hexane; m.p. 120–120.5 °C (Found: C, 53.0; H, 4.4. C₁₀H₁₀S₃ requires C, 53.1; H, 4.45%); $\delta_{\text{H}}(\text{CCl}_4)$ 1.91 (6 H, s, CH₃) and 5.83 (4 H, br s, CH); m/z 226 (M⁺).

4,5-Dimethyl-2-(tetrahydroselenopyran-4-ylidene)-1,3-dithiole **39**. Obtained in 80% yield from **21** and **31**; colourless leaflets from hexane; m.p. 78.5–79 °C (Found: C, 43.3; H, 5.0. C₁₀H₁₄S₂Se requires C, 43.3; H, 5.1%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.87 (6 H, s, CH₃) and 2.60 (8 H, A₂B₂ m, CH₂); m/z 278 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(selenopyran-4-ylidene)-1,3-dithiole **2**. Obtained in 20% yield from **39**; yellow needles from benzene–hexane; m.p. 117–118 °C (Found: C, 43.95; H, 3.6. C₁₀H₁₀S₂Se requires C, 43.95; H, 3.7%); $\delta_{\text{H}}(\text{CCl}_4)$ 1.93 (6 H, s, CH₃) and 6.08 (4 H, s, CH); m/z 274 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(tetrahydrothiopyran-4-ylidene)-1,3-diselenole **40**. Obtained in 39% yield from **20** and **33**; pale yellow plates from hexane; m.p. 99.5–100 °C (Found: C, 37.0; H, 4.3. C₁₀H₁₄SSe₂ requires C, 37.05; H, 4.35%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.93 (6 H, s, CH₃) and 2.50 (8 H, A₂B₂ m, CH₂); m/z 326 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(thiopyran-4-ylidene)-1,3-diselenole **3**. Obtained in 53% yield from **40**; orange needles from benzene–hexane; m.p. 144–145 °C (Found: C, 37.4; H, 3.1. C₁₀H₁₀SSe₂ requires C, 37.5; H, 3.15%); $\delta_{\text{H}}(\text{CCl}_4)$ 1.99 (6 H, s, CH₃) and 5.83 (4 H, br s, CH); m/z 322 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(tetrahydroselenopyran-4-ylidene)-1,3-diselenole **41**. Obtained in 46% yield from **21** and **33**; pale yellow plates from hexane; m.p. 87–87.5 °C (Found: C, 32.4; H, 3.8. C₁₀H₁₄Se₃ requires C, 32.4; H, 3.8%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.90 (6 H, s, CH₃) and 2.60 (8 H, A₂B₂ m, CH₂); m/z 372 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(selenopyran-4-ylidene)-1,3-diselenole **4**. Obtained in 64% yield from **41**; yellow needles from hexane; m.p. 148–149 °C (Found: C, 32.7; H, 2.75. C₁₀H₁₀Se₃ requires C, 32.7; H, 2.75%); $\delta_{\text{H}}(60 \text{ MHz}; \text{CCl}_4)$ 1.98 (6 H, s, CH₃), 5.97 (2 H, d, *J* 11, CH), 6.21 (2 H, d, *J* 11, CH); m/z 368 (M⁺, ⁸⁰Se).

4,5-Bis(methylthio)-2-(tetrahydrothiopyran-4-ylidene)-1,3-dithiole **42**. Obtained in 45% yield from **20** and **34**; pale orange columns from hexane; m.p. 77–78 °C (Found: C, 40.7; H, 4.8. C₁₀H₁₄S₅ requires C, 40.8; H, 4.8%); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.37 (6 H, s, CH₃) and 2.53 (8 H, A₂B₂ m, CH₂); m/z 294 (M⁺).

4,5-Bis(methylthio)-2-(thiopyran-4-ylidene)-1,3-dithiole **5**. Obtained in 72% yield from **42**; yellow needles from hexane; m.p. 106–107 °C (Found: C, 41.2; H, 3.5. C₁₀H₁₀S₅ requires C, 41.3; H, 3.5%); $\delta_{\text{H}}(\text{CCl}_4)$ 2.37 (6 H, s, CH₃) and 5.93 (4 H, s, CH); m/z 290 (M⁺).

4,5-Bis(methylthio)-2-(tetrahydroselenopyran-4-ylidene)-1,3-dithiole **43**. Obtained in 11% yield from **21** and **34**; pale orange needles from hexane; m.p. 83–84 °C (Found: C, 35.15; H, 4.05. C₁₀H₁₄S₄Se requires C, 35.2; H, 4.1%); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.36 (6 H, s, CH₃) and 2.58 (8 H, s, CH₂); m/z 342 (M⁺, ⁸⁰Se).

4,5-Bis(methylthio)-2-(selenopyran-4-ylidene)-1,3-dithiole **6**. Obtained in 64% yield from **43**; pale yellow needles from hexane; m.p. 101–101.5 °C (Found: C, 35.55; H, 2.9. C₁₀H₁₀S₄Se requires C, 35.6; H, 3.0%); $\delta_{\text{H}}(\text{CCl}_4)$ 2.37 (6 H, s, CH₃) and 5.93 (4 H, s, CH); m/z 338 (M⁺, ⁸⁰Se).

4,5-(Ethylenedithio)-2-(tetrahydrothiopyran-4-ylidene)-1,3-dithiole **44**. Obtained in 32% yield from **20** and **35**; pale blue plates from benzene–hexane; m.p. 165.6–166 °C (Found: C, 41.0; H, 4.0. C₁₀H₁₂S₅ requires C, 41.1; H, 4.1%); $\delta_{\text{H}}(60 \text{ MHz}; \text{CDCl}_3)$ 2.55 (8 H, A₂B₂ m, CH₂) and 3.26 (4 H, s, SCH₂); m/z 292 (M⁺).

4,5-(Ethylenedithio)-2-(thiopyran-4-ylidene)-1,3-dithiole **7**. Obtained in 43% yield from **44**; orange needles from benzene–hexane; m.p. 170–171 °C (Found: C, 41.6; H, 2.7. C₁₀H₈S₅ requires C, 41.6; H, 2.8%); $\delta_{\text{H}}(\text{CCl}_4)$ 3.28 (4 H, s, CH₂) and 5.77 (4 H, br s, CH); m/z 288 (M⁺).

4,5-(Ethylenedithio)-2-(tetrahydroselenopyran-4-ylidene)-1,3-

dithiole **45**. Obtained in 13% yield from **21** and **35**; pale yellow needles from benzene–hexane; m.p. 139–140 °C (Found: C, 35.3; H, 3.4. C₁₀H₁₂S₂Se requires C, 35.4; H, 3.6%); $\delta_{\text{H}}(60 \text{ MHz}; \text{CDCl}_3)$ 2.73 (8 H, A₂B₂ m, CH₂) and 3.25 (4 H, s, SCH₂); m/z 340 (M⁺, ⁸⁰Se).

4,5-(Ethylenedithio)-2-(selenopyran-4-ylidene)-1,3-dithiole **8**. Obtained in 28% yield from **45**; yellowish orange prisms from benzene–hexane; m.p. 167–169 °C (Found: C, 35.6; H, 2.35. C₁₀H₈S₄Se requires C, 35.8; H, 2.4%); $\delta_{\text{H}}(\text{CCl}_4)$ 3.27 (4 H, s, CH₂) and 6.18 (4 H, br s, CH); m/z 336 (M⁺, ⁸⁰Se).

4,5-Diphenyl-2-(tetrahydrothiopyran-4-ylidene)-1,3-dithiole **46**. Obtained in 15% yield from **20** and **36**; yellow needles from benzene–hexane; m.p. 158.5–159 °C (Found: C, 67.7; H, 5.1. C₂₀H₁₈S₃ requires C, 67.75; H, 5.1%); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.58 (8 H, A₂B₂ m, CH₂) and 7.21 (10 H, s, PhH); m/z 354 (M⁺).

4,5-Diphenyl-2-(thiopyran-4-ylidene)-1,3-dithiole **10**. Obtained in 10% yield from **46**; orange needles from benzene–hexane; m.p. 183–184 °C (Found: C, 68.75; H, 4.0. C₂₀H₁₄S₃ requires C, 68.5; H, 4.0%); $\delta_{\text{H}}(\text{CCl}_4)$ 5.99 (4 H, s, CH) and 7.18 (10 H, s, PhH); m/z 350 (M⁺).

4,5-Diphenyl-2-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3-dithiole **47**. Obtained in 11% yield from **22** and **36**; orange needles from benzene–hexane; m.p. 231.5–233 °C (Found: C, 76.2; H, 5.15. C₃₂H₂₆S₃ requires C, 75.8; H, 5.2%); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.5–3.0 (4 H, m, CH₂), 4.11 (2 H, dd, *J* 11 and 3.5, CH), 7.19 (10 H, s, PhH) and 7.36 (10 H, s, PhH); m/z 506 (M⁺).

4,5-Diphenyl-2-(2,6-diphenylthiopyran-4-ylidene)-1,3-dithiole **11**. Obtained in 54% yield from **47**; red fine needles from benzene–hexane; m.p. 215–216 °C (Found: C, 76.45; H, 4.4. C₃₂H₂₂S₃ requires C, 76.45; H, 4.4%); $\delta_{\text{H}}(\text{CCl}_4)$ 6.35 (2 H, br s, CH) and 7.19 (20 H, s, PhH); m/z 502 (M⁺).

4,5-Dimethyl-2-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3-dithiole **48**. Obtained in 30% yield from **22** and **31** or in 47% yield from **22** and **32**; orange fine needles from benzene–hexane; m.p. 246.5–247 °C (Found: C, 69.1; H, 5.7. C₂₂H₂₂S₃ requires C, 69.1; H, 5.8%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.87 (6 H, s, CH₃), 2.5–3.0 (4 H, m, CH₂), 4.00 (2 H, dd, *J* 10 and 4, CH) and 7.27 (10 H, s, PhH); m/z 382 (M⁺).

4,5-Dimethyl-2-(2,6-diphenylthiopyran-4-ylidene)-1,3-dithiole **12**. Obtained in 13% yield from **48**; reddish purple leaflets from benzene–hexane; m.p. 223–224 °C (Found: C, 69.9; H, 4.6. C₂₂H₁₈S₃ requires C, 69.8; H, 4.8%); $\delta_{\text{H}}(\text{CCl}_4)$ 1.93 (6 H, s, CH₃), 6.30 (2 H, s, CH) and 7.1–7.4 (10 H, br s, PhH); m/z 378 (M⁺).

4,5-Dimethyl-2-(2,6-diphenyltetrahydroselenopyran-4-ylidene)-1,3-dithiole **49**. Obtained in 34% yield from **31** and **37**; colourless needles from benzene–hexane; m.p. 246.5–247.5 °C (Found: C, 61.5; H, 5.1. C₂₂H₂₂S₂Se requires C, 61.5; H, 5.2%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.89 (6 H, s, CH₃), 2.82 (4 H, m, CH₂), 4.34 (2 H, dd, *J* 4 and 11, CH) and 7.35 (10 H, br s, PhH); m/z 430 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(2,6-diphenylselenopyran-4-ylidene)-1,3-dithiole **13**. Obtained in 13% yield from **49**; dark red needles from chlorobenzene–acetonitrile; m.p. 246–248 °C (Found: C, 62.05; H, 4.6. C₂₂H₁₈S₃ requires C, 62.1; H, 4.3%); $\delta_{\text{H}}(\text{CCl}_4)$ 1.99 (6 H, s, CH₃), 6.50 (2 H, s, CH) and 7.45 (10 H, m, PhH); m/z 426 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3-diselenole **50**. Obtained in 25% yield from **22** and **33**; yellow fine needles from benzene–hexane; m.p. 248 °C (Found: C, 55.45; H, 4.6. C₂₂H₂₂SSe₂ requires C, 55.5; H, 4.7%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.93 (6 H, s, CH₃), 2.62 (4 H, m, CH₂), 4.05 (2 H, dd, *J* 7 and 8, CH) and 7.30 (10 H, br s, PhH); m/z 476 (M⁺, ⁸⁰Se).

4,5-Dimethyl-2-(2,6-diphenylthiopyran-4-ylidene)-1,3-diselenole **14**. Obtained in 12% yield from **50**; deep red fine needles from benzene–hexane; m.p. 219–221 °C (Found: C, 55.9; H, 3.7. C₂₂H₁₈SSe₂ requires C, 55.9; H, 3.8%); $\delta_{\text{H}}(\text{CCl}_4)$ 2.04 (6 H, br

s, CH₃), 6.11 (2 H, s, CH) and 7.3–7.5 (10 H, br s, PhH); *m/z* 472 (M⁺, ⁸⁰Se).

4,5-Bis(methylthio)-2-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3-dithiole 51. Obtained in 45% yield from **22** and **34**; golden fine needles from benzene–hexane; m.p. 153–153.5 °C (Found: C, 59.1; H, 4.9. C₂₂H₂₂S₅ requires C, 59.15; H, 5.0%); δ_H(CDCl₃) 2.37 (6 H, s, CH₃), 2.75 (4 H, m, CH₂), 3.9–4.2 (2 H, m, CH) and 7.27 (10 H, s, PhH); *m/z* 446 (M⁺).

4,5-Bis(methylthio)-2-(2,6-diphenylthiopyran-4-ylidene)-1,3-dithiole 15. Obtained in 85% yield from **51**; deep red needles from benzene–hexane; m.p. 145 °C (Found: C, 59.6; H, 4.0. C₂₂H₁₈S₅ requires C, 59.7; H, 4.1%); δ_H(CCl₄) 2.42 (6 H, s, CH₃), 6.22 (2 H, s, CH), and 7.1–7.4 (10 H, br s, PhH); *m/z* 442 (M⁺).

4,5-Bis(methylthio)-2-(2,6-diphenyltetrahydroseleopyran-4-ylidene)-1,3-dithiole 52. Obtained in 38% yield from **34** and **37**; faint yellow fine needles from benzene–hexane; m.p. 230–230.5 °C (Found: C, 53.5; H, 4.4. C₂₂H₂₂S₄Se requires C, 53.5; H, 4.5%); δ_H(CDCl₃) 2.37 (6 H, s, CH₃), 2.79 (4 H, m, CH₂), 4.33 (2 H, dd, *J* 5 and 10, CH) and 7.36 (10 H, s, PhH); *m/z* 494 (M⁺, ⁸⁰Se).

4,5-Bis(methylthio)-2-(2,6-diphenylseleopyran-4-ylidene)-1,3-dithiole 16. Obtained in 60% yield from **52**; deep red needles from benzene–hexane; m.p. 155.5–156 °C (Found: C, 54.0; H, 3.7. C₂₂H₁₈S₄Se requires C, 54.0; H, 3.7%); δ_H(CDCl₃) 2.41 (6 H, s, CH₃), 6.47 (2 H, s, CH), and 7.44 (10 H, m, PhH); *m/z* 490 (M⁺, ⁸⁰Se).

4,5-Ethylenedithio-2-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3-dithiole 53. Obtained in 38% yield from **22** and **35**; pale yellowish green needles from benzene–hexane; m.p. 243–244 °C (Found: C, 59.4; H, 4.5. C₂₂H₂₀S₅ requires C, 59.4; H, 4.5%); δ_H(CDCl₃) 2.5–3.0 (4 H, m, CH₂), 3.25 (4 H, s, CH₂), 4.00 (2 H, dd, *J* 10 and 4, CH) and 7.28 (10 H, s, PhH); *m/z* 444 (M⁺).

4,5-Ethylenedithio-2-(2,6-diphenylthiopyran-4-ylidene)-1,3-dithiole 17. Obtained in 43% yield from **53**; deep red needles from benzene–hexane; m.p. 211–211.5 °C (Found: C, 59.8; H, 3.65. C₂₂H₁₆S₅ requires C, 59.95; H, 3.7%); δ_H(CCl₄) 3.27 (4 H, s, CH₂), 6.27 (2 H, s, CH), and 7.1–7.4 (10 H, br s, PhH); *m/z* 440 (M⁺).

Charge-Transfer Complexes.—All complexes described in this report were prepared by mixing the two hot saturated solutions of donor and acceptor in acetonitrile or chlorobenzene under an argon atmosphere. The complexes precipitated out on cooling, which were collected by filtration and dried *in vacuo*.

Crystal Structure Determination.—**Structure analysis and refinement.** The X-ray diffraction data were collected with a Rigaku AFC-6C automated four-circle diffractometer using Cu-Kα radiation (λ = 1.5418 Å) monochromatized with a graphite plate. Using 2θ–ω scan mode with ω scan width = 1.3 + 0.14 tan θ for **11** and 1.5 + 0.14 tan θ for **15** at a scan rate of 4 deg min⁻¹, *N* independent reflections were measured up to 2θ = 126°, and *N*_o of these having |*F*_o| ≥ 3.0σ(*F*_o) were used in the structure analyses. The structures were solved by the Monte-Carlo direct method²⁷ using MULTAN78 program system²⁸ for the selection of the initial set of phase, and refined by the full-matrix least squares program on *F*² without absorption correction. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.²⁹ Anisotropic temperature factors were used for the refinement, and hydrogen atoms were not included in the refinement. ORTEP³⁰ was used for drawing of the molecular and crystal structures. Computations were carried out at the Information Processing Center of Hiroshima University. Tables of anisotropic thermal parameters, final

atomic co-ordinates and the full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.*

Crystal data for 11. Crystallized from acetonitrile. Crystal dimensions 0.63 × 0.06 × 0.05 mm³. *M* = 502.73, tetragonal, space group *P4/n*, *a* = *b* = 30.175(4), *c* = 5.6681(7) Å, *V* = 5160.8(9) Å³, *Z* = 8, *D*_x = 1.295 g cm⁻³, μ(Cu-Kα) = 26.34 cm⁻¹. *N* = 3723, *N*_o = 1879; *R* = 0.082.

Crystal data for 15. Crystallized from benzene–hexane. Crystal dimensions 0.59 × 0.21 × 0.07 mm³. *M* = 442.71, monoclinic, space group *C2/c*, *a* = 38.044(2), *b* = 5.2080(9), *c* = 21.394(2) Å, β = 91.654(6)°, *V* = 4237.1(8) Å³, *Z* = 8, *D*_x = 1.388 g cm⁻³, μ(Cu-Kα) = 48.86 cm⁻¹. *N* = 3289, *N*_o = 2805; *R* = 0.087.

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* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

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