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

Yutaka Shiomi, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura*

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

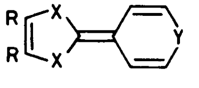
The selenium analogues of 2-(thiopyran-4-ylidene)-1,3-dithiole and its 4,5-bis(methylthio) and 4,5-(ethylenedithio) derivatives have been prepared as a new series of unsymmetrical electron donors; some of their complexes with 7,7,8,8-tetracyanoquinodimethane are electrically highly conductive.

2-(Thiopyran-4-ylidene)-1,3-dithiole (TPDT) (**1**) is a hybrid of two typical electron donors, tetrathiafulvalene (TTF) (**9**) and bithiopyranylidene (BTP) (**10**), but has received little attention in this respect. Sandman *et al.* reported that it formed a less conductive complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ) than either symmetrical TTF or BTP.[1] Although a high degree of symmetry has been recently proposed as one of the criteria for the molecular design of organic metals,[2] 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] This has stimulated us to investigate TPDT analogues as a new series of unsymmetrical donors. We here report the syntheses and properties of three selenium analogues (**2**)—(**4**) in which some or all of the sulphur atoms of TPDT are replaced by selenium. In addition, the 4,5-bis(methylthio) and 4,5-(ethylenedithio) derivatives (**5**)—(**8**) are described.

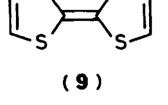
Compounds (**2**)—(**4**) were prepared according to the same three-step synthetic procedure as the parent TPDT (**1**) (Scheme 1).[1] Thus, treatment of dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (**11**)[5] with tetrahydroselenopyran-4-one (**14**)[6] in refluxing benzene containing triethyl phosphite gave a cross-coupling product (**15**; X = S, Y = Se) in 23% yield, which was dehydrogenated with chloranil (tetrachloro-1,4-benzoquinone) in refluxing xylene. The product (**16**; X = S, Y = Se) (84% yield) was decarboxylated with lithium bromide in hexamethylphosphoric triamide (HMPA) at 150 °C to give 2-(selenopyran-4-ylidene)-1,3-dithiole (**2**) in 70% yield. A combination of (**12**)[7] and (**13**) as starting materials similarly led to 2-(thiopyran-4-ylidene)-1,3-diselenole (**3**) in 2.5% overall yield, and (**12**) and (**14**) led to 2-(selenopyran-4-ylidene)-1,3-diselenole (**4**) in 3% overall yield. The 5,6-bis(methylthio) and 5,6-(ethylenedithio) derivatives (**5**)—(**8**) were obtained in the same two-step sequence from 4,5-bis(methylthio)-1,3-dithiole-2-thione (**17**)[8] or 4,5-(ethylenedithio)-1,3-dithiole-2-thione (**18**);[8] overall yields (**5**) 32%, (**6**) 7%, (**7**) 14%, and (**8**) 4%.

TPDT and its analogues show two reversible one-electron redox waves in cyclic voltammograms. The introduction of a selenium atom or an alkylthio group tends to enhance the first half-wave oxidation potential (Table 1). A more detailed comparison indicates that replacement of the pyran oxygen by selenium only slightly affects the first oxidation potential. On the other hand, the second half-wave oxidation potentials are largely unaltered (or slightly lowered) by these molecular modifications. Thus compounds (**2**), (**7**), and (**8**) have the ability to reduce on-site coulombic repulsion.[2]

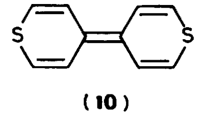
All compounds formed 1 : 1 black charge-transfer complexes with TCNQ. The complexes, except those of the methylthio derivatives (**5**) and (**6**), are electrically more conductive than the TPDT complex (see also Table 1). The poor conductivities of the complexes of (**5**) and (**6**) are reminiscent of that of tetrakis(methylthio)-TTF–TCNQ complex.[9] The bulk of the substituent seems to prevent the constituent molecules from forming conductive stacking



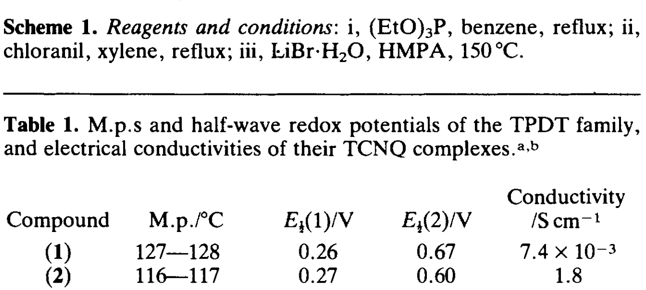
(**1**) R = H, X = Y = S
(**2**) R = H, X = S, Y = Se
(**3**) R = H, X = Se, Y = S
(**4**) R = H, X = Y = Se
(**5**) R = MeS, X = Y = S
(**6**) R = MeS, X = S, Y = Se
(**7**) RR = $-SCH_2CH_2S-$, X = Y = S
(**8**) RR = $-SCH_2CH_2S-$, X = S, Y = Se



(**9**)



(**10**)

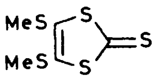


Scheme 1. *Reagents and conditions*: i, $(EtO)_3P$, benzene, reflux; ii, chloranil, xylene, reflux; iii, $LiBr \cdot H_2O$, HMPA, 150 °C.

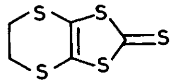
Table 1. M.p.s and half-wave redox potentials of the TPDT family, and electrical conductivities of their TCNQ complexes.[a,b]

Compound	M.p./°C	$E_{\frac{1}{2}}(1)$/V	$E_{\frac{1}{2}}(2)$/V	Conductivity /S cm^{-1}
(1)	127—128	0.26	0.67	7.4×10^{-3}
(2)	116—117	0.27	0.60	1.8
(3)	150—151	0.35	0.69	1.2×10^{-2}
(4)	145 (dec.)	0.36	0.68	4.7×10^{-2}
(5)	106—106.5	0.36	0.69	6.4×10^{-3}
(6)	101—101.5	0.38	0.68	9.6×10^{-5}
(7)	170—171	0.29	0.57	7.8×10^{-2}
(8)	167 (dec.)	0.31	0.63	3.8

[a] Cyclic voltammetry was carried out in dichloromethane containing 0.1 M-Bu_4NClO_4 with a glassy carbon electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1}. [b] Conductivities were measured for compressed pellets by a four-probe method at room temperature.



(17)



(18)

columns in the crystal structures. The complexes of (**2**) and (**8**) are extremely highly conductive, perhaps as a consequence of increasing intermolecular interaction and reduced on-site coulombic repulsion of the donors without substantial loss of donor character. In conclusion, the present study demonstrates the potential of some members of the TPDT family as novel unsymmetrical electron donors.

This work was supported by a grant-in-aid of scientific research from the Ministry of Education, Science, and Culture, Japan.

Received, 23rd February 1988; Com. 8/00702K

References

1 D. J. Sandman, A. P. Fisher, III, T. J. Holmes, and A. J. Epstein, *J. Chem. Soc., Chem. Commun.*, 1977, 687.
2 G. Saito and J. P. Ferraris, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2141.
3 K. Kikuchi, T. Namiki, I. Ikemoto, and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1986, 1472, and references cited therein.
4 K. Kikuchi, M. Kikuchi, T. Namiki, K. Saito, I. Ikemoto, K. Murata, T. Ishiguro, and K. Kobayashi, *Chem. Lett.*, 1987, 931.
5 L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456.
6 M. D. Thompson, E. M. Holt, and K. D. Berlin, *J. Org. Chem.*, 1985, **50**, 2580.
7 M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, 1976, **41**, 882.
8 G. Steimecke, H. J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.
9 M. Mizuno, A. F. Garito, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18.