NEW EXTENDED DONORS, 2,2'-(2,5-DIHYDROTHIOPHENE-2,5-DIYLIDENE)BIS(1,3-BENZODITHIOLE)S AND THEIR ELECTROCONDUCTIVE COMPLEXES WITH ELECTRON ACCEPTORS[1]

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Summary: New extended donors, 2,2'-(2,5-dihydrothiophene-2,5-diylidene)bis(1,3-benzodithiole) and its di- and tetra-methyl derivatives having a chalcogen atom and four additional sp^2 carbons at the central part of dibenzotetrathiafulvalene (DBTTF) molecule have been synthesized. The electrochemical properties and conductivities of their complexes have been demonstrated characterising a good coplanar conformation in the oxidised states.

An increasing current interest in solid-state electrical conductivity of organic charge-transfer complexes or radical salts has stimulated many efforts aimed at developing new and valuable π-donors to provide highly conductive complexes and to clarify the mechanisms of the conductivity. Recently, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) having chalcogen atoms at the external part of TTF has been reported to form superconductive complexes[2,3] where the two-dimensionality is achieved by not only the internal but also external chalcogens.[4,5]

On the other hand the incorporation of chalcogen atom(s) into the central part of TTF molecule could be one of the other strategies for establishing highly electroconductive complexes. So far bis(1,3-dithiolylidene)tetrathiapentalene derivatives[6] have been synthesized, which, however, show rather high oxidation potentials and their complex formation has never been reported. As the other examples of this sort of donors, we have here designed 2,5-dihydrothiophenediylidenebis-1,3-dithiole 1 (DTBDT) and its dibenzo derivative 2 (DTBBDT) which are expected to meet the numerous criteria[7] for bringing about high conductivity by the following reasons: i) the electron donating ability would be enhanced by the extension of the π-system, ii) the corresponding radical cation and dication states would be stabilized by the conjugative effect of the central sulfur atom and by the aromaticity of the thiophene ring created upon the oxidation, iii) the on-site Coulomb repulsion in the dication state would be diminished, and iv) the intermolecular, interstack bonding might be strengthened by the S⋯S contact associated with the central chalcogen atom. Moreover, the lower symmetry of 1 and 2 might stabilize the metallic state by preventing the metal-insulator transition.
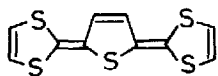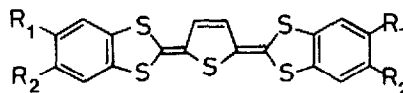

1   **2** : R₁=R₂=H, **3** : R₁=Me, R₂=H, **4** : R₁=R₂=Me

We synthesized previously different kinds of extended cyclic cross-conjugated compounds with a thienoquinonoid ring and clarified their electronic structures.[8] In the course of our studies, we report here the synthesis and electrochemical properties of new Weitz-type donors DTBBDT's (2, 3, and 4), as well as the electroconductivities of their complexes with acceptors, characterizing the changes effected by the thienoquinonoidal extension.

The present route to donors $\underline{2}$, $\underline{3}$, and $\underline{4}$ is shown in Scheme 1. 2,5-Thiophenedi-carbaldehyde was treated with 2 molar equivalents of benzene-1,2-dithiol in refluxing benzene for 1.5 hr in the presence of a catalytic amount of p-toluenesulfonic acid to give 2,5-bis(benzodithiol-2-yl)thiophene $\underline{5a}$ in 48% yield.[9] The removal of a hydride ion from $\underline{5a}$ with triphenylmethyl tetrafluoroborate by refluxing in dichloromethane for 2 hr afforded mono-cation $\underline{6a}$ in 77% yield as brown-red crystals. The dithiolyl proton of $\underline{6a}$ was abstracted easily by the subsequent treatment with an excess of triethylamine in dichloromethane giving the desired extended donor $\underline{2}$ as orange needles in 70% yield. Dimethyl $\underline{3}$[10] and tetramethyl derivatives $\underline{4}$ were also synthesized in better yields starting from 4-methyl- and 4,5-dimethyl-benzene-1,2-dithiol, respectively via the route similar to that for $\underline{2}$.

$a : R_1 = R_2 = H$

$b : R_1 = Me, R_2 = H$

$c : R_1 = R_2 = Me$

Scheme 1
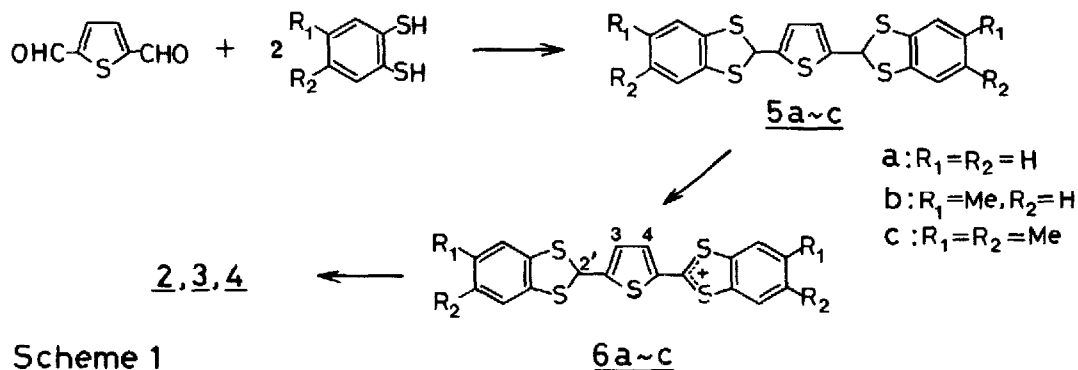
Compounds $\underline{2}$, $\underline{3}$, and $\underline{4}$ are quite stable in solid state and in solution, whereas iso-π-electronic donor $\underline{7}$ has been reported to be air-sensitive and unstable in solution. All new compounds were substantiated by the spectral data described in Table 2 and elemental analyses.

Cyclic voltammograms of $\underline{2}$, $\underline{3}$, and $\underline{4}$ showed two well-defined reversible one-electron oxidation waves corresponding to the formation of the radical cations and dications of these compounds. This is a noticeable contrast to the electrochemical properties of other extended donors $\underline{7}$,[11] $\underline{8}$,[12] and $\underline{9}$,[13a] all of which undergo one step two-electron oxidation in cyclic voltammetry. The oxidation potentials, ΔE, and log K_{sem} values are summarized in Table 1 along with those of some related compounds, which are measured under the same conditions except $\underline{9}$.[13b] The E_1^{ox} of $\underline{2}$ is nearly comparable to that of TTF (0.38 V). The E_1^{ox} and E_2^{ox} of $\underline{2}$ are lower by 0.31 V and 0.42 V than those of DBTTF, respectively, and this enhancement of donor ability in $\underline{2}$ appears to be more significant than that in $\underline{9}$ whose oxidation potential is lower by about 0.18 V than that of DBTTF. Thus the difference between $\underline{2}$ and $\underline{9}$ would be mainly ascribed to the central hetero atom and heteroaromatic stabilization of the thiophene ring created by the one- and two-electron oxidations. The E_1^{ox} and E_2^{ox} values become lower with an increase in the number of methyl groups in the order of $\underline{2} < \underline{3} < \underline{4}$, in consistent with the electron donating properties of this group.

$\underline{7}$ $\qquad$ $\underline{8}$ $\qquad$ $\underline{9}$
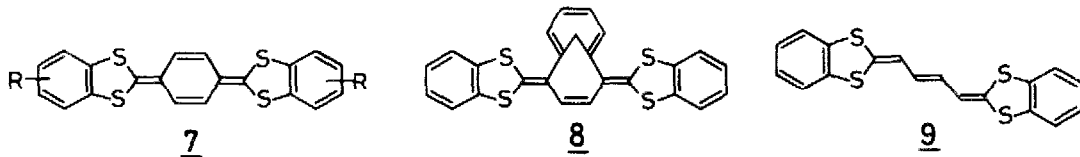
As expected, ΔE values of $\underline{2}$, $\underline{3}$, and $\underline{4}$ are smaller than those of TTF (0.33 V) and DBTTF indicating the diminished on-site Coulomb repulsion in the dication states of the formers. The same is true of other extended donors, $\underline{7}$, $\underline{8}$, and $\underline{9}$. However, a different feature in DTBBDT's is the higher thermodynamic stability of the cation radicals, which is clearly demonstrated by the larger semiquinone formation constants K_{sem} values of DTBBDT's than those of $\underline{7}$, $\underline{8}$, and $\underline{9}$. The preferable thermodynamic stabilization would result primarily from the enhanced conjugative interaction between the terminal dithiolyl radical cation and the central chalcogen atom incorporated in the thiophene ring in DTBBDT's. Because of the effective delocalization of the odd electron or the positive charge on the thiophene ring, each ring of DTBBDT can maintain a good coplanar conformation in the radical cation or dication state.

Table 1. Electrochemical properties of donors (DTBBDT's and some reference compounds) and electrical conductivities of their complexes with TCNQ, DDQ, and iodine.

Donor	Electrochemical property[a]				Electric conductivity ρ/Ω cm		
	E_1^{ox}/V	E_2^{ox}/V	$\Delta E(E_2^{ox}-E_1^{ox})$	$\log K_{sem}$	TCNQ (D:A=1:1)	DDQ (D:A=1:1)	I_x (D:A=1:3)
$\underline{2}$ DTBBDT	+0.34	+0.58	+0.24	4.14	1.2×10^2	6.4×10^3	2.7×10^6
$\underline{3}$ Me$_2$DTBBDT	+0.30	+0.54	+0.24	4.14	4.9×10	5.5×10^2	3.0×10^4
$\underline{4}$ Me$_4$DTBBDT	+0.28	+0.52	+0.24	4.14	——	6.3×10^2	4.8×10^2
DBTTF	+0.65	+1.0	+0.35	6.03	5.4×10^6	5.8×10	1.4×10^8
$\underline{7}$	+0.27		$\simeq 0$	$\simeq 0$	——	2.8×10^5	unstable
$\underline{8}$	+0.27		$\simeq 0$	$\simeq 0$	——	6.2×10^6	——
$\underline{9}$[b]	+0.47		$\simeq 0$	$\simeq 0$	——	——	——

a: 0.1 mol dm^{-3} Et$_4$NClO$_4$ in EtCN; Pt electrode; scan rate 50 mV s^{-1}; V vs SCE.　b: Ag/AgCl.

DTBBDT's reacted immediately with tetracyanoquinodimethane (TCNQ) and with DDQ producing stable charge-transfer (CT) complexes (black or dark green, and dark purple, respectively) and with iodine generating radical salts (dark brown), whose electroconductivities at room temperature on their compressed pellets[14] are listed in Table 1. The conductivities of the DTBBDT's-DDQ complexes are 10^3-10^4 times higher than those of $\underline{7}$ (R=Me)[11b] and $\underline{8}$.[12] This may be ascribed to the thermodynamic stability of the radical cation as well as the better coplanar conformations in the oxidized states which increases quite favorably the interstack bonding in the complex states. The $\underline{2}$- and $\underline{3}$-TCNQ complexes would be in partial CT conditions with the degree of CT, Z = 0.70 − 0.75,[15] and indeed show 10^4-10^5 times higher conductivities than that of DBTTF.[16] The DTBBDT's-DDQ complexes are supposed to be completely ionic based on the $E_1(D)$ − $E_1(A)$ values[7] and the disappearance of the IR spectral carbonyl bands, nevertheless the conductivities of $\underline{3}$- and $\underline{4}$-DDQ complexes are rather high among the fully ionized complexes. This is also true for the iodine complex of $\underline{4}$. As shown by the complexes of $\underline{2}$, $\underline{3}$, and $\underline{4}$ in Table 1, methyl substitution causes an increase in the conductivity of the complex. More reliable discussion on the intermolecular, interstack bonding will be made after the X-ray analysis.

In conclusion, DTBBDT and its alkyl derivatives are proved to be stable Weitz-type donors exhibiting higher electron donating abilities and smaller on-site Coulomb repulsion in the dication state than their mother compound DBTTF. The relatively high electroconductivities of their complexes with acceptors would be attributed to the enhanced thermodynamic stabilities of the radical cations brought about by the conjugative effect of the central chalcogen atom of the heteroaromatic ring. From these findings DTBDT $\underline{1}$ and its derivatives are predicted to be promising donors to form organic metals, whose preparation is currently in progress.

Table 2. Physical and spectral data of DTBBDT's (2, 3, 4) and mono-cations (6a, 6b, 6c).

Compd.	mp (°C)	MS m/z (%)	IR (KBr) cm^{-1} / ^1H NMR (CDCl$_3$) δ, ppm	UV-VIS λ max nm (log ε)
2	>300	386(100)	IR { 3050, 1565, 1544, 1447, 1435, 1160, 1121	a 453(4.91), 476(4.98)
3	266–268	414(100)	3050, 2900, 1550, 1534, 1510, 1455, 1155	a 454(4.63), 480(4.69)
4	295–298	442(100)	3030, 2900, 1550, 1533, 1440, 1150	a 456(4.29), 483(4.35)
6a	>300	——	^1H NMR { 6.11 (H-2'), 7.39 (H-3), 8.13 (H-4)	b 452(4.39)
6b	108–110	——	6.11 (H-2'), 7.43 (H-3), 8.17 (H-4) 2.31 (Me), 2.61 (Me)	b 458(4.34)
6c	125–126	——	6.06 (H-2'), 7.38 (H-3), 8.16 (H-4) 2.20 (2Me), 2.48 (2Me)	b 466(4.46)

a: in THF,   b: in dichloromethane

References and Notes

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14. Conductivities were measured by using a two-probe method.

15. If the complexes consist of segregate stacks: J. C. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, J. Am. Chem. Soc., 103, 2442 (1981).

16. Complexation and conductivity measurement were performed under the same conditions.