SYNTHESIS AND PROPERTIES OF TETRATHIAFULVALENE DERIVATIVES CONTAINING QUINOID STRUCTURES: NOVEL ELECTRON DONORS OF ORGANIC CONDUCTORS

Katsuhiro Saito,* Chikayuki Sugiura, Emi Tanimoto, Katsushi Saito, and Yoshiro Yamashita+

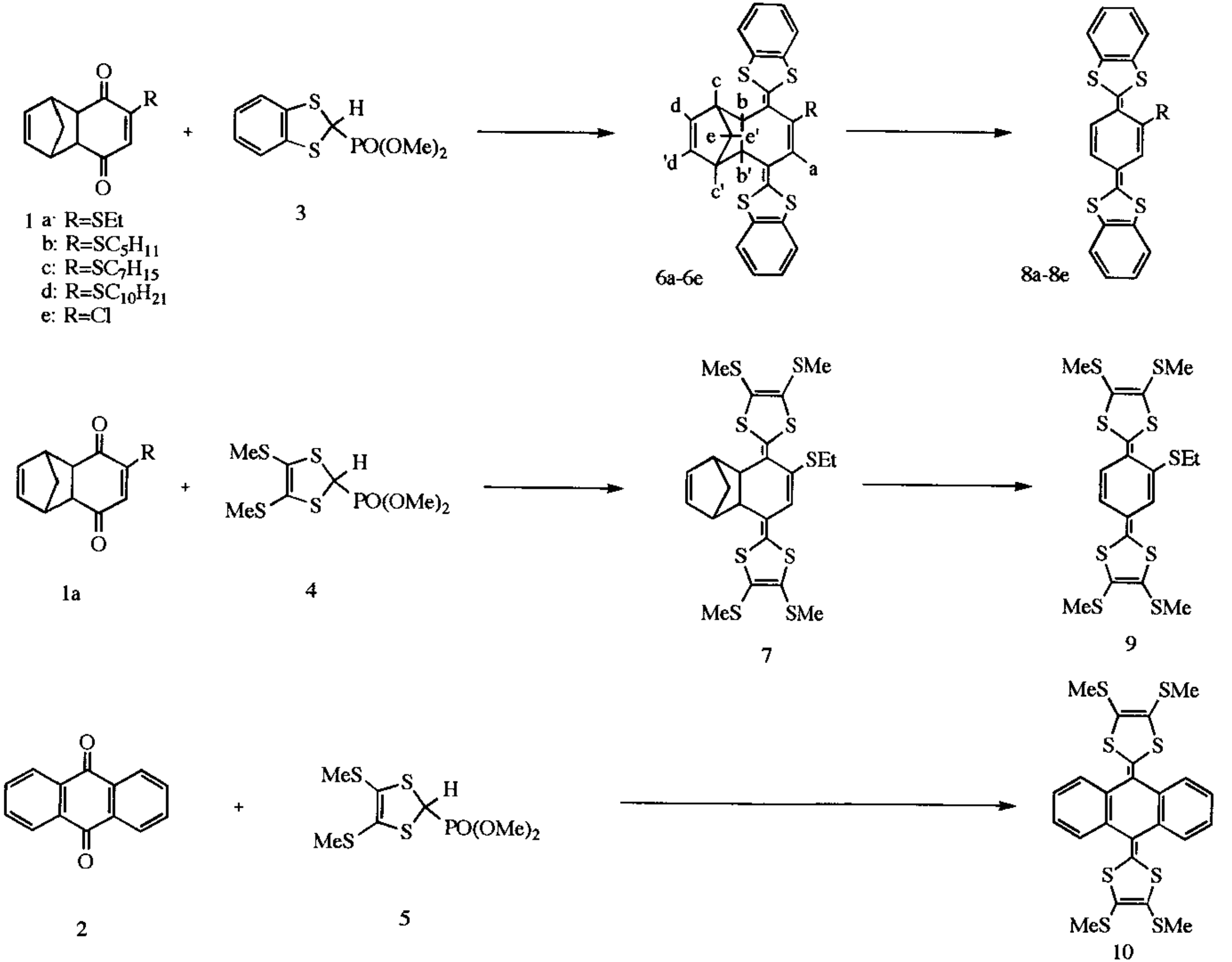
Department of Applied Chemistry, Nagoya Institute of technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan
+Institute for Molecular Science, Myodaiji-cho, Okazaki, 444, Japan

Abstract —— Wittig-Horner reactions of 2-dimethoxyphosphinyl-1,3-dithiole derivatives with a benzoquinone-cyclopentadiene adduct and anthraquinone afforded new types of electron donors with alkylthio groups for organic conductors which showed reversible oxidation waves on cyclic voltammetries and formed conductive charge-transfer complexes with TCNQ or DDQ.

Much attention has been focused on the organic conductors, some of which show superconductivity at liq. He temperature.[1] At the present stage, the critical temperatures of organic conductors for superconductivity are low as compared with those of ceramic conductors. However, distinct molecular and crystal structures of the organic cunductors have offered many valuable informations concerning the relations between their conductivities and structural factors.[1]

Organic conductors involving superconductors are generally composed of charge-transfer complexes between electron donors and electron acceptors. Tetrathiafulvalene is one of the most important electron donor and various kinds of derivatives have been synthesized.[2] Extention of π-conjugation and introduction of substituents usually improve the properties of the electron donors.[3] Introduction of quinoid structure and alkylthio groups is considered to enhance the electron donating abilities and the solubilities, respectively.[4]

The authors have now synthesized several tetrathiafulvalene derivatives containing quinoid structures with alkylthio substituents and investigated their redox potentials on cyclic voltammetries and conductivities of their complexes with tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). Here these results are discussed.



1 a: R=SEt
b: R=SC$_5$H$_{11}$
c: R=SC$_7$H$_{15}$
d: R=SC$_{10}$H$_{21}$
e: R=Cl
3
6a-6e
8a-8e
1a
4
7
9
2
5
10
R
H
PO(OMe)$_2$
MeS
SMe
SEt
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a
b
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Reaction of 1a[5] with four equimolar amounts of 3 in the presence of 4.4 molar equivalents of n-butyllithium in dry THF at −78°C for 10 min afforded orange yellow crystals of 6a in 61% yield.[6] Pyrolysis of 6a under a reduced pressure (20 mmHg) at 180°C for 2 min gave a quantitative amount of 8a. The analogous reactions of 1b–1e with 3 followed by thermolysis of the adducts gave 8b–8e. Reaction of 1a with 4 under the same reaction conditions as above gave a 56% yield of 7, which was pyrolyzed to give a quantitative amount of 9. Reaction of 2 with 5 under the analogous reaction conditions as above formed 10 in quantitative yield.[7] Compounds (8) and (9) were unstable and readily turned to tarry materials. Therefore, they were used immediately to measure cyclic voltammetries and to form charge-transfer complexes.

Table. Oxidation Potentials of Donors and Conductivities of Complexes

Donors	Potentials[a]			Acceptors	ξ (cm^{-1})[c]	Ratio[d]	Conduct.[e]
	E^1	E^2	ΔE[b]			(D:A)	(S cm^{-1})
8a	+0.26	+0.47	0.21	TCNQ	2178	1:2	1.0×10^{-2}
8b	+0.25	+0.48	0.23	TCNQ	2199	1:1.8	1.5×10^{-3}
8c	+0.27	+0.49	0.22	TCNQ	2180	2:3	1.0×10^{-3}
8d	+0.26	+0.50	0.24	f)			
8e	+0.73	+1.15	0.42	TCNQ	2199	1:1.3	5.5×10^{-3}
9	+0.20	+0.34	0.14	DDQ	1638	1:2.7	1.6×10^{-7}
10	+0.52[g]			DDQ	1551	1:1.8	8.0×10^{-10}

a) V vs. SCE, 0.1 mol dm^{-3} Et_4NBF_4 in CH_2Cl_2, Pt electrode.

b) $\Delta E = E^2 - E^1$.

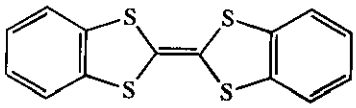
c) Wave numbers of nitrile (TCNQ) or carbonyl goups (DDQ) in ir spectra of complexes.

d) Molar ratios between donors and acceptors, which were determined on the basis of elemental analyses.

e) Measuredon compressed pellets by a two-probe technique at room temperature.

f) No complex was available with both TCNQ and DDQ.

g) Two-electron oxidation potential at one stage.



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Oxidation potentials measured by cyclic voltammetries are summarized in the Table. Two well defined reversible one-electron oxidation waves are observed for donors (8) and (9). The dihydroanthracene derivative (10) shows a two-electron oxidation wave, indicating the decreased on-site Coulomb repulsion due to the extended π-conjugation. New dibenzotetrathiafulvalene (DBTTF) derivatives (8a-8d) have lower oxidation potentials than those of DBTTF (11) itself (E^1=0.73V and E^2=1.15V), suggesting that the electron donating ability of 8a-8d are improved.

The chloro derivatives (8e) has the same oxidation potentials as those of DBTTF. Chlorine atom is expected to increase the potentials by an inductive effect. In the present case the positive effect caused by an introduction of the quinoid structure is compensated by the negative one caused by the chlorine atom. Both first (E^1) and second (E^2) oxidation potentials of 8a-8d show almost the same values, suggesting that the difference in length of the thioalkyl groups have almost no effects on the oxidation potentials. Comparing 8b and 9, both of which have ethylthio groups, the potentials of 9 are lower than those of 8b, indicating that the benzo-annelation is unfavorable for the donating ability.

Donors 8a, 8b, 8c, and 8e formed complexes with TCNQ but failed to form complexes with DDQ. Contrary to this, 9 and 10 afforded complexes with DDQ but not with TCNQ. Both TCNQ and DDQ afforded no complexes with 8d. Molar ratios between donors and acceptors, wave numbers of the typical functional groups of the complexes in ir spectra, and conductivities of complexes are summarized in the Table. All of the complexes with TCNQ exhibit good conductivities as semiconductors. The difference in the length of the carbon chains in the thioalkyl groups again seems to have no significant effect on the conductivities.

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5. A preparatory experiment taught that in order to proceed the condensation reactions with 3 or 4 it was needed to protect one of the double bond of benzoquinone derivatives with appropreate protecting groups.
6. Reactions of 3 or 4 with naphthoquinone derivatives afforded no expected condensation products such as 8 or 9 but resulted in quantitative recoveries of the starting materials.
7. Melting points, elemental analyses determined by high resolution mass spectra and ^{1}H nmr spectral properties of the products are as follows.

6a : mp 150–154°C. Hrms (FAB): m/z 506.03278. Calcd for $C_{27}H_{22}S_5$: m/z 506.03251. ^{1}H Nmr (C_6D_6) δ: 1.17 (t, 3H, Me), 1.23 (d, H_e), 1.46 (m, $H_{e'}$), 2.53 (q, 2H, CH_2), 2.93 (dd, H_b), 3.27 (dd, $H_{b'}$), 3.60 (m, H_c and $H_{c'}$), 5.90 (m, H_d and $H_{d'}$), 6.57 (s, H_a), 6.3–7.2 (m, 8H, aromatic protons). Coupling constants in Hz: $J_{ee'}$=8.0, $J_{bb'}$=9.0, J_{bc}=$J_{b'c'}$=3.6.

6b: mp 131–132°C. Hrms (FAB): m/z 548.07701. Calcd for $C_{30}H_{28}S_5$: m/z 548.07946. ^{1}H Nmr (C_6D_6) δ: 0.84–2.64 (m, 13H, SC_5H_{11}, H_e, and $H_{e'}$), 2.97 (dd, H_b or $H_{b'}$), 3.29 (dd, H_b or $H_{b'}$), 3.63 (m, H_c and $H_{c'}$), 5.95 (m, H_d and $H_{d'}$), 6.6–7.1 (m, 9H, H_a and aromatic protons). Coupling constants in Hz: $J_{ee'}$=8.0, $J_{bb'}$=9.4, J_{bc}=$J_{b'c'}$=3.5, $J_{ee'}$=8.5.

6c: mp 131–132°C. Hrms (FAB): m/z 576.11353. Calcd for $C_{32}H_{32}S_5$: m/z 576.11076. ^{1}H Nmr (C_6D_6) δ: 0.85–2.66 (m, 17H, SC_7H_{15}, H_e, and $H_{e'}$), 2.97 (dd, H_b or $H_{b'}$), 3.28 (dd, H_b or $H_{b'}$), 3.62 (m, H_c and $H_{c'}$), 5.99 (m, H_d and $H_{d'}$), 6.6–7.1 (m, 9H, H_a and aromatic protons). Coupling constants in Hz: $J_{bb'}$=9.4, J_{bc}=$J_{b'c'}$=3.3, $J_{ee'}$=8.8.

6d: yellow oil. Hrms (FAB): m/z 618.15613. Calcd for $C_{35}H_{38}S_5$: m/z 618.15869. ^{1}H Nmr (C_6D_6) δ: 0.85–2.66 (m, 23H, $SC_{10}H_{21}$, H_e, and $H_{e'}$), 3.0 (dd, H_b or $H_{b'}$), 3.3 (dd, H_b or $H_{b'}$), 3.6 (m, H_c and $H_{c'}$), 6.0 (m, H_d and $H_{d'}$), 6.5–7.1 (m, 9H, H_a and aromatic protons). Coupling constants in Hz: $J_{bb'}$=10.0, J_{bc}=$J_{b'c'}$=4.7.

6e : mp 158°C (decomp). Hrms (FAB): m/z 479.98725. Calcd for $C_{25}H_{17}ClS_4$: m/z 479.99017. ^{1}H Nmr (C D) δ: 1.13 (ddd, H). 1.39 (ddd, H), 2.86 (dd, H), 3.14

(dd, $H_{b'}$), 3.54–3.56 (m, H_c and $H_{c'}$), 5.89 (dd, $H_{d'}$), 5.97 (dd, H_d), 6.32 (s, H_a), 6.6–7.0 (m, 8H, arom). Coupling constants in Hz: $J_{bb'}$=9.2, J_{bc}=$J_{b'c'}$=3.5, J_{cd}=$J_{c'd'}$=3.0, $J_{dd'}$=6.3, $J_{ee'}$=8.3.

7: mp 117°C (decomp). Hrms (FAB): m/z 589.95329. Calcd for $C_{23}H_{26}ClS_9$: m/z 589.95084. ^{1}H Nmr (C_6D_6) δ: 1.06 (d, H_e), 1.08 (t, 3H, CH_3, CH_3), 1.39 (d, $H_{e'}$), 1.86 (s, 3H, SCH_3), 1.95 (s, 3H, SCH_3), 2.02 (s, 6H, SCH_3), 2.43 (q, 2H, CH_2), 2.79 (dd, H_b or $H_{b'}$), 3.10 (dd, H_b or $H_{b'}$), 3.45–3.54 (m, H_c and $H_{c'}$), 5.83 (dd, H_d or $H_{d'}$), 5.93 (dd, H_d or $H_{d'}$), 6.41 (s, H_a). Coupling constants in Hz: $J_{bb'}$=9.6, J_{cd}=$J_{c'd'}$=3.6, $J_{dd'}$=5.8, $J_{ee'}$=8.0.

8a: mp 190–200°C. Ms m/z (rel intensity): 440 (M^+, 55), 154 (100). Ir (KBr): 2924, 1516, 1447, 739 cm^{-1}.

8b: mp 144–147°C. Ms m/z (rel intensity): 482 (M^+, 100), 154 (64). Ir (KBr): 2922, 1518, 1447, 729 cm^{-1}.

8c: mp 123–130°C. Ms m/z (rel intensity): 510 (M^+, 100), 154 (18). Ir (KBr): 2924, 1508, 1422, 739 cm^{-1}.

8d: mp 90–92°C. Ms m/z (rel intensity): 552 (M^+), 154 (100). Ir (KBr): 2924, 1508, 1448, 739 cm^{-1}.

8e: mp 290°C (decomp). Ms m/z (rel intensity): 414 (M^+, 4), 154 (100), Ir (KBr): 3052, 1514, 739 cm^{-1}.

9: mp 211°C (decomp). Ms m/z (rel intensity): 524 (M^+, 8), 154 (100). Ir (KBr); 2920, 1655, 1422, 1260, 870 cm^{-1}.

10: mp 310–311°C. Hrms (Fab): m/z 563.9324. Calcd for $C_{29}H_{20}S_8$: m/z 563.9329. ^{1}H Nmr ($CDCl_3$) δ: 2.40 (s, 12H, SCH_3), 7.32–7.62 (m, 8H, aromatic protons).

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