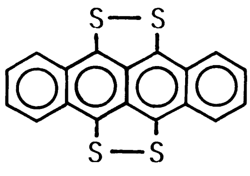
CHEMISTRY LETTERS, pp. 567-570, 1990.

2,3-Dimethyl and 2,3,6,7-Tetramethyl Derivatives of Anthra[1,9-cd:4,10-c'd']bis[1,2]dichalcogenoles as New Electron Donors

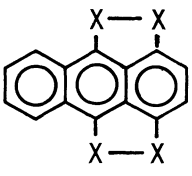
Kazuo TAKIMIYA, Hisakazu MIYAMOTO, Yoshio ASO,
Tetsuo OTSUBO, and Fumio OGURA*
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Saijo, Higashi-Hiroshima 724

The title compounds involving all chalcogen heterocycles of sulfur, selenium, and tellurium were synthesized as new electron donors, in which the introduced methyl groups served to improve not only the donor character but also the solubility. They with TCNQ, DMTCNQ, or TCNQF$_4$ formed various charge-transfer complexes, some of which were electrically high-conductive.

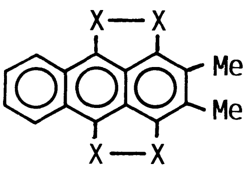
Since naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole (**1**, abbreviated to tetrathiotetracene or TTT) was found to form electrically high-conductive molecular complexes like TTF,1) polyacenes bearing similar peri-dichalcogen bridged structures have been searched as another prototype of superior electron donors. One of such polyacenes is anthra[1,9-cd:4,10-c'd']bis[1,2]dithiole (**2a**, abbreviated to TTA),2) and its selenium isologue (**2b**, TSA) is also known.3) However, they did not have so strong donor characters as TTT. In addition, their low solubilities hindered a comprehensive study on complexation. Although current interest has been directed towards the development of conducting organotelluriums, its tellurium isologue is still unknown. We have designed the introduction of alkyl groups into tetrachalcogenoanthracene (**2**). This might make considerable improvements in donor character and solubility as already seen



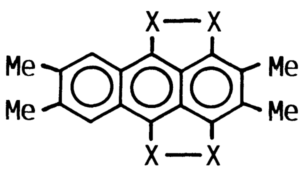
1, TTT



2a, X=S, TTA
2b, X=Se, TSA



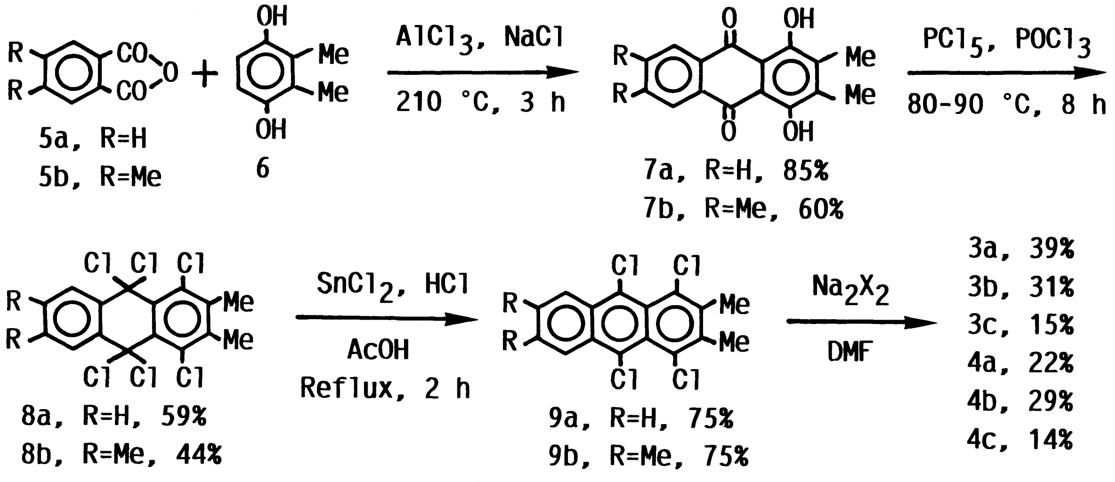
3a, X=S, DMTTA
3b, X=Se, DMTSA
3c, X=Te, DMTTeA



4a, X=S, TMTTA
4b, X=Se, TMTSA
4c, X=Te, TMTTeA

in tetrachalcogenonaphthalene series.[4] We now wish to report the syntheses and properties of 2,3-dimethyl derivatives (**3**) and 2,3,6,7-tetramethyl derivatives (**4**) and their charge-transfer complexes.

The syntheses of **3** and **4** were carried out by a general method which involved the reaction of the corresponding tetrachloro aromatic compounds with an alkali metal dichalcogenide in a dipolar aprotic solvent as shown in Scheme 1. Treatments of 1,4,9,10-tetrachloro-2,3-dimethyl-anthracene (**9a**), prepared in a few steps from phthalic anhydride (**5a**) and 2,3-dimethylhydroquinone (**6**), with sodium disulfide and with sodium diselenide in refluxed *N*,*N*-dimethylformamide (DMF) for 9 h gave the sulfur heterocycle **3a** (DMTTA) in 37% yield and the selenium heterocycle **3b** (DMTSA) in 31% yield, respectively.[5] On the other hand, the tellurium heterocycle **3c** (DMTTeSA) was formed in 15% yield only by treatment with sodium ditelluride at just 100 °C. A set of tetramethyl analogues **4a** (TMTTA), **5b** (TMTSA), and **4c** (TMTTeA) was also completed by the same reaction sequence starting with 4,5-dimethylphthalic anhydride (**5b**) and **6**.



Scheme 1.

All the tetrachalcogenoanthracenes show two reversible redox waves in the cyclic voltammetry. The half-wave oxidation potentials of TTA (**2a**), 0.36 and 0.75 V, and TSA (**2b**), 0.35 and 0.71 V, are almost comparable to those of a typical electron donor TTF, 0.34 and 0.72 V vs. Ag/AgCl. Introduction of methyl groups actually lowers these values in the expected order of dimethylation and tetramethylation. This effect is more eminent in the first half-wave oxidation potential than in the second one. On the other hand, substitution of selenium for sulfur in any series of parent, dimethyl, and tetramethyl derivatives gives little influence on the oxidation potentials. However, substitution of tellurium results in considerable lowering of both potentials. As a result, the tellurium

Table 1. Some Properties and Half-Wave Oxidation Potentials (V) of **3** and **4**[a)]

Compound	Appearance	Mp/°C	$E_{1/2}(1)$	$E_{1/2}(2)$	ΔE
DMTTA (**3a**)	blackish purple needles	261	0.32	0.73	0.41
DMTSA (**3b**)	black crystals	289	0.31	0.72	0.41
DMTTeA (**3c**)	black needles	>300	0.20	0.63	0.43
TMTTA (**4a**)	blackish purple needles	>300	0.26	0.69	0.43
TMTSA (**4b**)	black crystals	>300	0.26	0.68	0.42
TMTTeA (**4c**)	black powder	>300	0.16	0.55	0.39

a) Cyclic voltammetry was carried out at 100 mV/s scan rate in 10^{-3} M benzonitrile containing 0.1 M tetrabutylammonium perchlorate using platinum electrodes and an Ag/AgCl reference electrode.

compounds **3c** and **4c** have very strong donating abilities which are comparable to that of TTT (**1**) with $E_{1/2}$ 0.19 and 0.56 V.

The stronger donating abilities as well as better solubilities of the present compounds **3** and **4** than parent TTA and TSA facilitated a study of their complexation. They all formed various charge-transfer complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ), its 2,3,4,5-tetrafluoro derivative ($TCNQF_4$), and 2,5-dimethyl derivative (DMTCNQ), but the stoichiometry and electrical conductivities of these complexes were systematically different depending on combinations of the used components as summarized in Table 2. The TCNQ complexes of the TTA and TSA derivatives favor 1:2 composition of donor to acceptor even when both components are mixed in equimolar amounts in chlorobenzene, and the electrical conductivities measured on the compressed pellets are in the range of 0.05-1.2 Scm^{-1}. These high conductivities are normally ascribable to mixed valence of the TCNQ component. In contrast, stronger TTeA donors form the TCNQ complexes of 1:1 composition, which are less conductive. In addition, all the complexes with a stronger acceptor $TCNQF_4$ are 1:1 stoichiometric and low-conductive. These complexes correspond to Mott insulators, because the increasing donor or acceptor characters cause almost complete charge transfer as indicated by low frequencies of the infrared nitrile vibration.[6)] On the other hand, all the complexes with DMTCNQ possess 2:1 stoichiometry of donor and acceptor, but only the complexes of the dimethyl-substituted donors as well as TMTTeA are relatively conductive. The low conductivities of the TMTTA and TMTSA complexes in spite of mixed valence of the donor components are ascribable to their less charge transfer which is supported by the high frequencies of the infrared nitrile vibration (2214 and 2210 cm^{-1}). This result is apparently in conflict with the above electrochemical tendency and possibly related to sterical crowding of methyl groups of both components on complexation. The TMTTeA complex showing a relatively high conductivity, however, has considerable charge transfer (ν_{CN} 2183 cm^{-1}), suggesting a

Table 2. Complexation of 3 and 4 with TCNQ, $TCNQF_4$, and DMTCNQ

Complex	D:A[a]	Appearance	Mp/°C	ν_{CN}	Conductivity[b]
DMTTA•TCNQ	1:2	black needles	214(dec)	2206	9.6×10^{-1}
DMTSA•TCNQ	1:2	black needles	238(dec)	2203	1.2
DMTTeA•TCNQ	1:1	black powder	>300	2186	8.3×10^{-6}
TMTTA•TCNQ	1:2	black needles	225(dec)	2204	5.0×10^{-2}
TMTSA•TCNQ	1:2	black needles	237(dec)	2207	2.7×10^{-1}
TMTTeA•TCNQ	1:1	black needles	>300	2187	1.8×10^{-6}
DMTTA•$TCNQF_4$	1:1	black powder	>300	2200	2.2×10^{-6}
DMTSA•$TCNQF_4$	1:1	purple powder	>300	2199	5.4×10^{-6}
DMTTeA•$TCNQF_4$	1:1	black powder	>300	2198	1.8×10^{-7}
TMTTA•$TCNQF_4$	1:1	purple needles	240(dec)	2202	5.0×10^{-7}
TMTSA•$TCNQF_4$	1:1	purple needles	272(dec)	2201	5.2×10^{-7}
TMTTeA•$TCNQF_4$	1:1	blue powder	>300	2201	4.4×10^{-6}
DMTTA•DMTCNQ	2:1	brown needles	219(dec)	2198	9.5×10^{-1}
DMTSA•DMTCNQ	2:1	black needles	236(dec)	2172	5.3×10^{-1}
DMTTeA•DMTCNQ	2:1	black powder	>300	2186	1.2×10^{-3}
TMTTA•DMTCNQ	2:1	black needles	241(dec)	2214	7.7×10^{-7}
TMTSA•DMTCNQ	2:1	black needles	>300	2210	1.2×10^{-5}
TMTTeA•DMTCNQ	2:1	black powder	>300	2183	4.6×10^{-2}

a) Composition was determined on the basis of elemental analyses.
b) Electrical conductivities were measured on compressed pellets at room temperature by a four-probe method or a two-probe method.

strong intermolecular interaction due to tellurium contacts.

Further study on other charge-transfer complexes is now under way.

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

References

1) L. C. Isett and E. A. Perez-Albuerne, Ann. N. Y. Acad. Sci., 313, 395 (1978); J. Riga, J. J. Verbist, F. Wudl, and A. Kruger, J. Chem. Phys., 69, 3221 (1978) and references cited therein.

2) S. Ohnishi, T. Nogami, and H. Mikawa, Tetrahedron Lett., 1983, 2401; T. Nogami, H. Tanaka, S. Ohnishi, Y. Takase, and H. Mikawa, Bull. Chem. Soc. Jpn., 57, 22 (1983).

3) S. Ohnishi, T. Nogami, and H. Mikawa, Chem. Lett., 1982, 1841.

4) T. Otsubo, N. Sukenobe, Y. Aso, and F. Ogura, Chem. Lett., 1987, 315; Synthetic Metals, 27, B509 (1988).

5) All new compounds were characterized by spectroscopic and elemental analyses.

6) J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, J. Am. Chem. Soc., 103, 2442 (1981).

(Received January 12, 1990)