CHEMISTRY LETTERS, pp. 1861-1864, 1986.

Tetrakis(n-alkyltelluro)tetrathiafulvalene (TTeC$_n$-TTF)

Naoko OKADA, Hideki YAMOCHI, Fumihiko SHINOZAKI,[†]
Kokichi OSHIMA,[††] and Gunzi SAITO*
The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106
[††] Cryogenic Center, The University of Tokyo, Bunkyo-ku, Tokyo 113

A series of tetrakis(n-alkyltelluro)tetrathiafulvalene (TTeC$_n$-TTF) was synthesized where n ranges from 1 to 18. Some chemical and physical properties of TTeC$_n$-TTF were studied and compared with those of the sulfur analogues; tetrakis(n-alkylthio)tetrathiafulvalene (TTC$_n$-TTF).

A variety of tetrachalcogeno derivatives of tetrathiafulvalene; TYR-TXF (Fig. 1) are very promising molecules which serve as electron donors in the field of synthetic metals. For example, many BEDT-TTF (X,Y = sulfur, R,R = $-(CH_2)_2-$) complexes have characteristic features on their structural and physical properties including superconductivity.[1)] By modifying the chalcogen atoms or the size of the outer ring of BEDT-TTF, various kinds of molecules can be obtained such as BMDT-, BPDT-, and BVDT-TTF, and selenium analogues of them.[2)] All of them are classified into the capped $C_6X_4Y_4$ compounds.[3,4)] As for the capped $C_6X_4Y_4$ compounds, we have reported on the peculiar structural and physical features of tetrakis(n-alkylthio)tetrathiafulvalene (TTC$_n$-TTF) (X,Y = sulufur, R = $-C_nH_{2n+1}$, n = 1-18) and their complexes.[3-6)]

TTC$_n$-TTF molecules are composed of two kinds of segments; one is the C_6S_8 moiety and the other is the four alkyl chains. In crystal state, the C_6S_8 moiety bends when the alkyl chains are short but it becomes flat with the long alkyl chains ($n \geqq 4$). The C_6S_8 moiety piles up one after the other tightly by the aid of the van der Waals (vdw) interactions of the alkyl chains when the alkyl chains are long enough (Fastener effect).[6)] The central flat C_6S_8 groups form one dimensional face-to-face regular stacks having short S··S contacts (3.57 Å for TTC$_9$-TTF) along the stacks. Consequently a conduction path to give rise to high conductivity is provided. The Fastener effect is a combination of the vdw interations of the side alkyl chains and the resonance interactions of the C_6S_8 segments. Considering the C··C contacts (3.99-4.35 Å for TTC$_9$-TTF) of the side alkyl chains between the neighboring two molecules along the stacks, it is reasonable to expect that the Fastener effect might be enhanced if the sulfur atoms (vdw radius: 1.80 Å) of TTC$_n$-TTF are

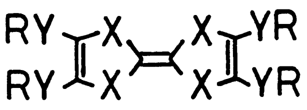


Fig. 1. TYR-TXF. X,Y = sulfur, selenium, or tellurium.

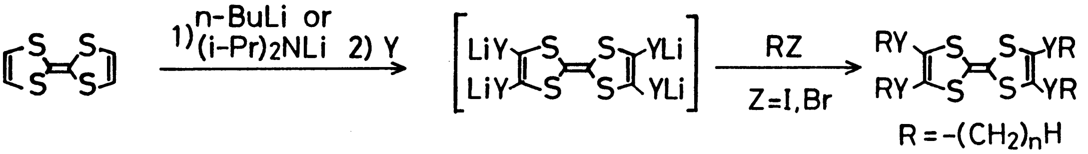
[†] On leave of absence from Nippon Chemi-Con Corp., Ome, Tokyo 198.

replaced by selenium (1.90 Å) or tellurium (2.06 Å) atoms.

The bent C_6S_8 group of TTC_1-TTF becomes also flat on the formation of charge transfer (CT) complexes with several acceptors. This conformational change of TTC_1-TTF is one of the main reasons why a metallic complex of TTC_1-$TTF(I_3)_{0.82}$ has been obtained from this bent donor.$^{5)}$ Intermolecular S··S contacts are observed along the molecular long axis of TTC_1-TTF in its compounds using only outer sulfur atoms. Contrary to that, in the BEDT-TTF compounds both outer and inner sulfur atoms participate in the formation of the S··S contacts along the molecular short axis. As a result the extent of the S··S contacts in TTC_1-TTF compounds is not as favorable as that in the BEDT-TTF compounds. Therefore the electrical dimensionality of TTC_1-TTF complexes is less than that of BEDT-TTF complexes. It is known that the spread of the donor HOMO is related to the dimensionality of the complex. The ratio of the atomic populations between the outer sulfuf (P_{out}) and the inner (P_{in}) is 0.148 for BEDT-TTF, but in the case of uncapped TTC_1-TTF the ratio (Pout/ P_{in} = 0.452) is three times bigger than that of BEDT-TTF. This may indicate the possibility of getting enough two dimensionality to suppress the Peierls instability of the CT complexes without using the inner chalcogens of uncapped TYR-TXF when the outer chalcogen Y is big enough and has sufficient atomic populations.

Accordingly we have synthesized tetrakis(n-alkyltelluro)tetrathiafulvalene ($TTeC_n$-TTF) by substituting outer sulfur atoms of TTC_n-TTF with tellurium atoms and studied their physical properties. $TTeC_n$-TTF (n = 1-18) was synthesized by the method developed by Aharon-Shalom et al.$^{7)}$ (Method A) or using n-butyl lithium (Method B) (Scheme 1) but the Method B gave poor yields (Table 1).

To the 75 ml THF solution of lithium diisopropylamide (LDA) (9.79 mmol) was added TTF (0.500 g, 2.45 mmol) at -78 °C and stirred for 2.5 h at the same temperature. To the resulting yellow suspension, 9.79 mmol of amorphous tellurium powder was added at -78 °C. The solution was stirred for 30 min then the temperature was gradually raised to 0 °C. It took about 2 h until no tellurium remained when the reaction solution was dark red with brownish yellow precipitates. Alkyl halide (iodide for n = 1,2; bromide for n = 3-18) (19.6 mmol) was added to the cold solution (-78 °C). The solution was stirred for 1 h then gradually warmed to room temperature. After stirring for additional 1.5 h, water was added to the reaction mixture. Then two methods were employed depending on n . (1) n = 2-11: The crude product was extracted with ether. The organic layer was washed with water several times and then brine. The organic layer was dried with anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was recrystallized from $CHCl_3$-MeOH, $CHCl_3$-petroleum ether, or petroleum ether-MeOH. (2) n = 1, 12-18: The crude product was washed with water and then MeOH. The residue was recrystallized from $CHCl_3$ or petroleum ether. By using both (1) and (2) methods the yield was about 40-80 % (not optimized) after purification based on TTF. All the elemental analyses were within the experimental error (C, H, N, and S). The color of $TTeC_n$-



Scheme 1. Synthetic scheme of TYC_n-TTF (Y = selenium or tellurium).

TTF changes gradually from orange to orange yellow with the increase of n . The yields, melting points, and redox potentials of TTeC$_n$-TTF are summarized in Table 1.

Table 1. Yields, melting points, and redox potentials of TTeC$_n$-TTF

n	Yield/%		Mp θm/°C	$E^1_{1/2}$	$E^2_{1/2}$	T/°C$^{b)}$
1	66	A$^{a)}$	175.2-176.2	0.52	0.91	18
	--	A	-----7)			
2	67	A	90.2-91.2	0.51	0.91	18
	35	A	88-90 7)			
3	60	A	62.2-62.7	0.51	0.91	18
4	38	A	85.7-86.5	0.51	0.92	18
5	62	A	56.9-57.4	0.51	0.93	18
	29	B				
6	68	A	46.0	0.52	0.92	18
7	67	A	49.9-50.2	0.51	0.92	19
8	48	A	57.7	0.51	0.92	24
9	63	A	65.2-65.7	0.51	0.92	24
10	52	A	72.7	0.52	0.93	18
11	58	A	77.5-78.5	0.52	0.93	24
	23	B				
12	58	A	82.2-82.7	0.52	0.92	19
13	33	A	87.2-87.4	0.50	0.91	26
14	45	A	89.2-90.3	0.50	0.90	26
15	52	A	92.2-93.0	0.50	0.90	26
16	77	A	94.2-94.6	0.51	0.91	24
17	69	A	96.2-97.2	0.51	0.91	30
18	76	A	97.5-98.2	0.51	0.91	30

a) Method A: LDA, Method B; n-BuLi. b) Redox potentials (V) measured at T °C vs. SCE, in 0.1 M Bu_4NBF_4/ CH_2ClCH_2Cl, Pt electrodes.

By the same synthetic procedures, selenium analogues (TSC$_n$-TTF) were prepared (n = 1: mp = 93.5-93.7 °C, $E^1_{1/2}$ = 0.58 V; n = 8: mp = 48.7-49.2 °C, $E^1_{1/2}$ = 0.59 V vs. SCE). The details will be reported soon.

The redox potentials of TTeC$_n$-TTF were measured by cyclic voltammetry (vs. SCE, 0.1 M Bu_4NBF_4/CH_2ClCH_2Cl, Pt electrodes) (Table 1). The first redox potentials ($E^1_{1/2}$ = (E^1_{pa} + E^1_{pc})/2) of TTeC$_n$-TTF are compared with those of the representative TTF derivatives in Fig. 2.

$E^1_{1/2}$ of a series of TTeC$_n$-TTF is almost constant within experimental error (0.51 ± 0.01 V) indicating that the molecular ionization potentials of TTeC$_n$-TTF are independent of the length of the alkyl chains. The same feature has been already noticed in the series of TTC$_n$-TTF where $E^1_{1/2}$ is 0.64 ± 0.01 V and almost equal to those of the capped analogues; BMDT-, BEDT-, and BPDT-TTF. The replacement of the outer sulfur atoms of TTC$_n$-TTF by tellurium atoms decreases $E^1_{1/2}$ by 0.13 V. This is in contrast with the fact that the replacement of the inner sulfur atoms of TTF moiety by selenium or tellurium atoms usually increases $E^1_{1/2}$ of the donors; HMTTF (0.42 V vs. SCE) vs. HMTTeF (0.58 V vs. SCE). Therefore two kinds of substitutions of chalcogen atoms effect oppositely on $E^1_{1/2}$. The larger $E^1_{1/2}$ of TTC$_n$-TTF than that of TTeC$_n$-TTF is ascribed mainly to the fact that the electron-withdrawing effect of alkylthio group is stronger than that of alkyltelluro group.

The second redox potentials ($E^2_{1/2}$ = 0.91 ± 0.02 V) and the difference between $E^1_{1/2}$ and $E^2_{1/2}$ (ΔE = 0.40 ± 0.02 V) of TTeC$_n$-TTF are also independent of the length of the alkyl chains. This ΔE value of 0.40V is, therefore, larger than that of TTC$_n$-TTF (0.30 ± 0.01 V) and is attributed mainly to the small resonance effect between tellurium and carbon atoms, which leads to the lower degree of electron delocalization of TTeC$_n$-TTF than that of TTC$_n$-TTF. But it is considered that there is still π electron density on the outer alkyltelluro groups, since ΔE of TTeC$_n$-

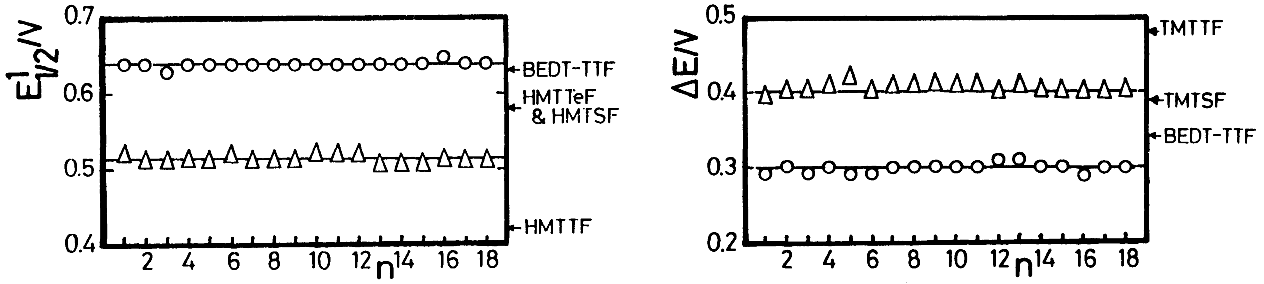


Fig. 2. Redox properties of TYR-TTF and TTF derivatives.
Δ: TTeC$_n$-TTF, ○: TTC$_n$-TTF.

TTF is smaller than that of TTF. Furthermore tellurium atoms have large polarizability which is suitable for making ΔE small. Consequently ΔE of TTeC$_n$-TTF is as the same as that of TMTSF (0.39 V) which is considered to have small on-site Coulomb repulsive energy.

The melting points of TTeC$_n$-TTF are compared with those of TTC$_n$-TTF in Fig. 3. These two kinds of compounds show similar dependence of the melting points on the length of the alkyl chains. Tellurium compounds have the higher melting points than the corresponding sulfur analogues by about 10-20 °C except for the case of n = 1 and 4. The extremely high melting point of TTeC$_1$-TTF compared with that of TTC$_1$-TTF may be ascribed to the strong Te··Te contacts. Between n = 2 and 5, the melting points depend on whether n is even or odd.

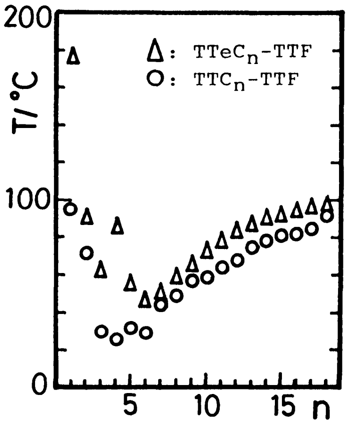


Fig. 3. Melting points of TYC$_n$-TTF.

As a preliminary result, TTeC$_1$-TTF gave CT complexes with F$_4$TCNQ and TCNQ. F$_4$TCNQ complex is greenish black powder with $\sigma_{r.t.} = 6.7 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. TCNQ gave black rhombic single crystals with $\sigma_{r.t.} = 1.0 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. More precise properties of the TTeC$_1$-TTF complexes will be reported soon.

This work was supported by the Grant-in-Aid for Scientific Research (No. 60470004) and by that for Special Research on "Properties of Molecular Assembly" (No. 60104001) and "New Superconducting Materials" (No. 60113003) from the Ministry of Education, Science and Culture.

References

1) Proc. of ICSM'84, Mol. Cryst. Liq. Cryst., 119, 120, 125, 126 (1985); Proc. of ICSM'86, Synth. Metals in press; Proc. of Yamada Conf. XV, Phy. and Chem. of One-Dimens. Conductors, Physica B in press.
2) M. Mizuno, A. F. Garito, and M. P. Cava, J. Chem. Soc., Chem. Commun., 1978, 18; R. R. Schumaker, V. Y. Lee, and E. M. Engler, J. Phys. (Paris), Colloq., 44, C3-1139 (1983); V. Y. Lee, Proc. of Yamada Conf. XV, Abstr. No. 27P-24; V. Y. Lee, Proc. of ICSM'86, Abstr. No. 2B-03.
3) P. Wu, G. Saito, K. Imaeda, Z. Shi, T. Mori, T. Enoki, and H. Inokuchi, Chem. Lett., 1986, 441.
4) G. Saito, Proc. of Yamada Conf. XV, Physica B in press.
5) P. Wu, T. Mori, T. Enoki, K. Imaeda, G. Saito, and H. Inokuchi, Bull. Chem. Soc. Jpn., 59, 127 (1986).
6) H. Inokuchi, G. Saito, P. Wu, K. Seki, T. B. Tang, T. Mori, K. Imaeda, T. Enoki, Y. Higuchi, K. Inaka, and N. Yasuoka, Chem. Lett., 1986, 1263.
7) E. Aharon-Shalom, J. Y. Becker, J. Bernstein, S. Bittner, and S. Shaik, Tetrahedron Lett., 26, 2783 (1985).

(Received August 2, 1986)