CHEMISTRY LETTERS, pp. 441-444, 1986.

UNCAPPED ALKYLTHIO SUBSTITUTED TETRATHIAFULVALENES (TTC_n-TTF) AND THEIR CHARGE TRANSFER COMPLEXES

Peiji WU, Gunzi SAITO,*† Kenichi IMAEDA, Zurong SHI,
Takehiko MORI, Toshiaki ENOKI, and Hiroo INOKUCHI
Institute for Molecular Science, Okazaki 444
† The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106

A series of tetraalkylthio substituted tetrathiafulvalenes (TTC_n-TTF) was prepared. The syntheses, molecular and crystal structures, and physical properties of TTC_n-TTF reveal marked differences from those of BEDT-TTF. The conformational change of TTC_1-TTF molecule on the formation of charge transfer complexes and the mode of the S··S contacts are described in connection with those of BEDT-TTF compounds.

Recently BEDT-TTF (bisethylenedithiolo-tetrathiafulvalene) compounds have attracted much interests since the discovery of the two-dimensional electrical property and superconductivity in several BEDT-TTF cation radical salts.[1)] These characteristic electrical and electronic properties are largely ascribed to the increased intermolecular interactions mainly due to the additional four sulfur atoms to TTF moiety. BEDT-TTF molecules form two-dimensional S··S network, which tends to prevent the nesting of the Fermi surface against CDW.[2)] It may be said that the C_6S_8 segment is responsible not only for the increased dimensionality but also for the increased polarizability and the decreased on-site Coulomb repulsion whether the outer sulfur atoms are capped or uncapped (Fig. 1).

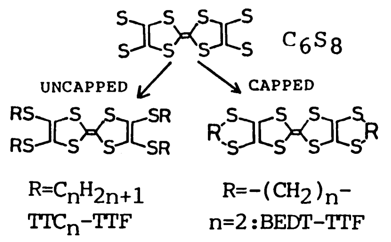

Fig. 1.

BEDT-TTF and its analogues are formed by capping the outer sulfur atoms of the C_6S_8 group. This capping restricts the motional freedom of the outer sulfur atoms and consequently may increase the transfer integrals in solid complexes compared with those in the following complexes of the uncapped derivatives. The uncapped ones, on the other hand, are expected to have more motional freedom of the outer substituents than that of the capped ones. This might be an unfavorable factor to obtain highly conductive CT complexes. However, the uncapped analogues may acquire some new additional function depending on the size, shape, and nature of the substituent besides that exerted by the C_6S_8 segment. Until now no chemical, physical, and structural investigations have been done systematically on the uncapped C_6S_8 compounds and their CT complexes, so real features about the above assumptions are open questions. We present here the syntheses, properties, and structures of these materials and compare with those of the capped donors in the limited case where the substituents are normal alkyl groups on purpose to explore organic metals, superconductors, and new functional CT complexes.

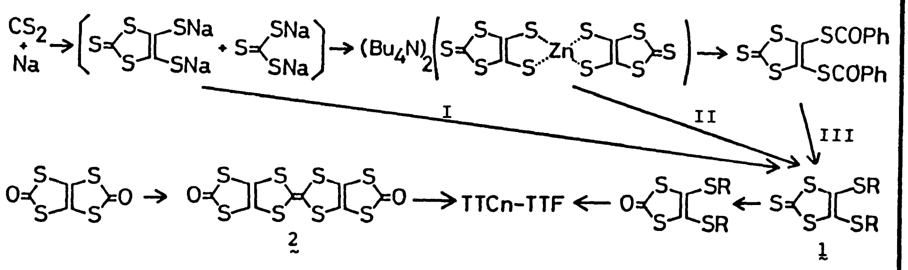

Fig. 2. Synthetic scheme of TTC_n-TTF.

The synthetic scheme (Fig. 2) is composed of known and simple procedures.$^{3)}$ To obtain thione 1, there are three routes I–III and they give almost the same yield (I, C_1 70, C_8 98%; II, C_1 80, C_5 88%; III, C_1 72, C_2 95%). The thione was converted to ketone in the yield of 80-96% and the purified ketone was coupled to give TTC_n-TTF by $(MeO)_3P$ or $(EtO)_3P$ where the yield decreases with increasing the length of the alkyl chain (C_1 90, C_8 52%). An alternative route includes the coupling of thiapendione to 2 (≈95%) which was then ionized to $C_6S_8^{-4}$, and this tetrakis anion was treated with the corresponding alkylhalide to give TTC_n-TTF in the yield which also decreases with increasing n (C_3 96, C_4 87, C_5 73, C_6 70, C_{10} 72, C_{11} 70, C_{12} 81, C_{13} 75, C_{14} 70, C_{15} 64, C_{17} 63%). For the synthesis of the symmetrical uncapped alkylthio substituted TTFs, the route from thiapendione is superior to the other three routes with respect to the easiness of the working up and the yield, though this route gives very low yield in the case of the capped ones ($-(CH_2)_n-$, 0, 35, 37% from 2 for n=1, 2, and 3, respectively).$^{4)}$ The crude TTC_n-TTF was purified by column chromatography with silica gel and then recrystallization.

Fig. 3 represents the melting points of TTC_n-TTF in which n changes from 1 to 18. Maybe reflecting the increased motional freedom of the n-alkylthio groups in solid, the melting points of these uncapped donors are considerably lower than those of the capped ones (Mp (dec.)=191.0, 242.5, and 265 °C for $-(CH_2)_n-$, n=1, 2, and 3, respectively). The melting points decrease rapidly with increasing n at initial stage (96.5 and 24.6 °C for n=1 and 4, respectively) then increase gradually to n=18 (87.7 °C). The thermodynamics of these systems are under investigation to elucidate the melting point behavior.

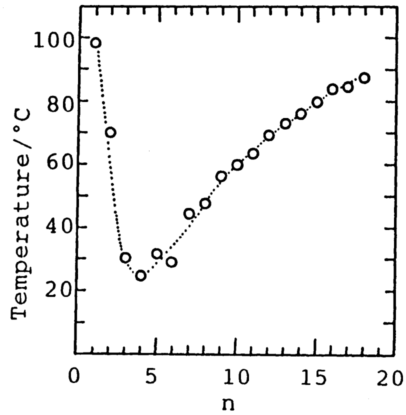

Fig. 3. Melting point of TTC_n-TTF system.

We have studied the donor ability of these uncapped donors on the basis of the gas and solid phase ionization potentials, redox potentials in solution, and CT complex formation. The oxidation potentials of a series of TTC_n-TTF determined by cyclic voltammogram are almost constant (0.55 V vs. Ag/Ag^+, CH_2ClCH_2Cl) indicating that the alkyl groups give minor effect on the ionization potentials of TTC_n-TTF. In accordance with that, it is known that the adiabatic ionization potential of TTC_1-TTF in gas phase (6.29 eV) is comparable to that of BEDT-TTF (6.21 eV).$^{5)}$ On the other hand, the ionization potentials of TTC_n-TTF in solid state depend on the length of the alkyl chain. The threshold ionization potential in solid state of TTC_9-TTF (4.6_5 eV) is much smaller than that of TTC_1-TTF (5.0_5 eV) and is even smaller than that of BEDT-TTF (4.7_8 eV).$^{6)}$ This drastic decrease of the ionization potential of TTC_9-TTF is ascribed to the unique conformation and stacking manner (vide infra) which cannot be realized with the capped derivatives. As for the polarizability and the on-site Coulomb repulsive energy, the uncapped TTC_n-TTF and BEDT-TTF are approximately equivalent in these terms judging from the redox properties and the photoelectron measurements. Therefore, all these properties concerning with the electronic structure are strongly in favor of the donor ability of TTC_n-TTF.

On the contrary, the molecular structure is strongly unfavorable for the formation of CT complex. Not only the terminal methyl groups but also two outer tetrathioethylene groups of TTC_1-TTF are bent in solid state where the dihedral angles between the outer and the central tetrathioethylene planes are 19 and 23°, which are about 1.5 times bigger than those observed in BEDT-TTF (12-15°), and the terminal methyl groups form dihedral angles 101-104° with the outer tetrathioethylene planes.[7)] This boat-like structure relaxes with increasing n and TTC_9-TTF has a chair-like structure with the central C_6S_8 group flat.[8)] The four long alkyl groups assemble TTC_9-TTF molecules in a fashion that the C_6S_8 groups can pile up one after the other tightly so that the π-electrons of C_6S_8 groups interact strongly leading to the small ionization potential in solid state. At any rate, from a structural point of view, it may be reasonably speculated that no metallic nor even conductive CT complexes can be accessible from those deformed donor component molecules.

However, the results are not so. We obtained a variety of CT complexes of TTC_1-TTF and a few complexes of TTC_2-TTF. These complexes range from insulator to even metallic compound, from neutral to ionic one, and from alternating to segregated type. For example, TCNQ gives 1:1 and 2:1 insulating complexes with neutral ground state in alternating stack as DDAA and DDADDA, respectively, and triiodide gives 1:0.82 metallic complex with partial CT state in segregated stack. Table 1 summarizes some representative complexes in hand with their molecular ratio (D:A), melting point (°C), resistivity at room temperature (ρ_{RT} Ωcm), activation energy (ε_a eV), ionicity, and stacking manner. Preparation of complexes of other TTC_n-TTF are now in progress.

From the study of these complexes, two characteristic features are abstracted. The first one is related to the molecular conformation of the donor that the bent neutral TTC_1-TTF molecule becomes almost flat on the formation of CT complex. In the alternating type, the terminal methyl groups are still out of the C_6S_8 plane which is now almost planar. This situation has some resemblance to that observed in the BEDT-TTF system where the central C_6S_8 segment becomes almost flat though the terminal ethylene groups are still out of the plane. On the other hand, in the segregated type,

Table 1. TTC_1-TTF charge transfer complex

Acceptor	D:A	Mp θm/°C	ρ_{RT}/Ω cm	ε_a/eV	Ionicity	Stack
DDQ	1:1	142	2.1x10$^{a)}$	0.087	partial	
p-Bromanil	1:1	124	5.4x10^{6}	0.46	neutral	A
TCNQ	1:1	111	3.8x10^{5}	0.30	neutral	A
	2:1	105	5.5x10^{4}	0.17	neutral	A
HCBD	1:1	170	3.8x10^{3}	0.21	partial	S
AsF_6	1:1	220	1.6x10^{3}	0.17	ionic	S
I_3	1:0.82	138	7x10^{-3}	metallic	partial	S

DDQ:2,3-dichloro-5,6-dicyano-p-benzoquinone, HCBD:hexacyanobutadiene, a) Compaction sample, Stack: A=alternating, S=segregated.

the whole molecule becomes flat. It is expected that the C_6S_8 segment can become planar by the loss of some amount of electron as has been observed in the BEDT-TTF compounds. But at this stage, the reason why the bent neutral molecule becomes flat cannot be explained precisely because both of the electronic and structural aspects should be taken into account simultaneously since the neutral TTC_9-TTF also exhibits planar C_6S_8 segment. Anyway the drastic structural change of TTC_1-TTF is one of the important reasons why a metallic complex TTC_1-TTF$(I_3)_{0.82}$ has been obtained from this bent neutral molecule.

The second feature is concerning about the mode of the S··S atomic contacts which have been ascribed to one of the origins of the two-dimensional nature for many BEDT-TTF compounds, where the contacts are observed along the molecular short axis of BEDT-TTF. In comparison with that, the specific contacts are observed along the molecular long axis in the neutral TTC_1-TTF. In the CT complexes of TTC_1-TTF the S··S contacts still exist along the molecular long axis but the efficiency of the contacts seems weakened considerably since the terminal methyl groups prevent the proximate approach of the neighboring two TTC_1-TTF molecules. However, we predict that strong contacts can be constructed utilizing uncapped donors in the case where the substituents are small and the complex has an appropriate molecular arrangement in the crystal or the substituents have a function to induce a tight contact.

This work was supported by the Grant-in-Aid for Scientific Research (No. 60470004) and 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) G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, Solid State Commun., 42, 557 (1982), E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnic, A. V. Zvarykina, and L. I. Buravov, JETP Lett., 39, 12(1984), M. Tokumoto, H. Bando, K. Murata, H. Anzai, N. Kinoshita, K. Kajimura, T. Ishiguro, and G. Saito, Synthetic Metals, 13, 9(1986), G. Saito, T. Sugano, H. Yamochi, M. Kinoshita, K. Oshima, M. Suzuki, C. Katayama, and J. Tanaka, Chem. Lett., 1985, 1037, and references cited therein.
2) G. Saito, T. Enoki, H. Inokuchi, and H. Kobayashi, J. Physique Colloq., 44, C3-1215(1983), and H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, J. Am. Chem. Soc., 105, 297(1983).
3) R. R. Schumaker and E. M. Engler, J. Am. Chem. Soc., 99, 5521(1977), M. H. Harley and J. Q. Chambers, J. Org. Chem., 46, 775(1981), G. Steimeck, H-J. Sieler, R. Kirmse, and E. Hoyer, Phorous and Sulfur, 7, 49(1979), K. Hartke, T. Kissel, J. Quante, and R. Matusch, Chem. Ber., 113, 1898(1980), and R. Schulz, A. Schweig, K. Hartke, and J. Koster, J. Am. Chem. Soc., 105, 4519(1983).
4) G. Saito, H. Hayashi, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 120, 341(1985).
5) N. Sato, G. Saito, and H. Inokuchi, Chem. Phys., 76, 79(1983).
6) K. Seki, T. B. Tang, T. Mori, P. J. Wu, G. Saito, and H. Inokuchi, J. Chem. Soc., Faraday Trans 2, accepted.
7) C. Katayama, M. Honda, H. Kumagai, J. Tanaka, G. Saito, and H. Inokuchi, Bull. Chem. Soc. Jpn., 58, 2272(1985).
8) Y. Higuchi et al. to be published.

(Received December 6, 1985)