A Novel TTF-based Electron-donor with Imidazole-annelation Having Hydrogen-bonding and Proton-transfer Abilities

Yasushi Morita,*[1] Yosuke Yamamoto,[1] Yumi Yakiyama,[1] Tsuyoshi Murata,[1] and Kazuhiro Nakasuji*[2]
[1]*Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043*
[2]*Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505*

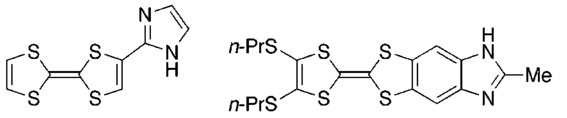
(Received October 9, 2007; CL-071109; E-mail: morita@chem.sci.osaka-u.ac.jp)

A TTF derivative with an imidazole-annelation having hydrogen-bond and proton-donor/acceptor abilities was newly synthesized. The donor formed a two-dimensional structure by hydrogen-bonds and π stacks in the crystal. The imidazole-annelation increased the electron-donating ability of the donor.

Tetrathiafulvalene (TTF) system, a strong electron donor giving a stable radical cation species, has been intensively studied in the research fields of organic conductors[1] and molecule-based electronic materials.[2] In the recent study of TTF chemistry, introduction of hydrogen-bond (H-bond) interaction has provided important strategies for molecular design to control molecular arrangement in charge-transfer (CT) complexes and salts.[3] Furthermore, the cooperation between CT and proton-transfer (PT) at H-bond site has served as an attractive phenomena in the development of exotic molecule-based materials.[4]

Our recent study for CT complexes of an imidazole-substituted TTF derivative (TTF-Im) has disclosed the electronic and structural modulation effects of H bonds to achieve highly conducting CT complexes.[5] Furthermore, the PT ability of imidazole moiety demonstrated simultaneous CT and PT complexes.[5b] To enhance the cooperation between CT on TTF and PT on imidazole moieties, an integration of the π-electronic systems of both TTF and imidazole moieties is preferable. In this respect, we have designed and synthesized a novel π-extended TTF derivative in which an imidazole ring is annelated through benzene ring (**1**, Chart 1). Since TTF derivatives directly connected with H-bond moieties such as hydroxy and amino groups are not known probably owing to their air-instability, a benzene ring is inserted between TTF and imidazole moieties. A variety of TTF-based electron donors annelated with aromatic rings such as benzene, pyrazine, pyrrole, and thiophene[2b,6] have been prepared. Notably any imidazole-annelated TTF derivatives, however, are not known. Here, we report the synthesis, crystal structure, redox, and PT properties, and CT complexes of **1**.

Synthetic procedure of **1** is illustrated in Scheme 1. The reaction of **2**[7] with AcOH and protection of N–H group by tosyl group gave imidazole-annelated benzo-1,3-dithiole-2-thione **3**. The cross-coupling reaction between **3** and 4,5-bis(*n*-propylthio)-1,3-dithiole-2-one (**4**)[7] using $P(OEt)_3$ followed by the treatment with KOH yielded **1**. The alternative preparation of **1** was performed by the imidazole-ring formation of **5** which was prepared from **2** and **4**.[7] The former procedure is preferable for the chemical modification on TTF skeleton, while the latter is more convenient for the introduction of substituent groups into imidazole ring by using various carboxylic acids. As expected, insertion of benzene ring resulted in good air-stability of **1**. The flexible *n*-propylthio group increased the solubility in conventional organic solvents (CH_2Cl_2, acetone, THF, MeCN, etc.) The vapor diffusion method using hexane/$CHCl_3$ gave single crystals of **1** suitable for X-ray crystal structure analysis as yellow platelets containing $CHCl_3$ molecules.[8]



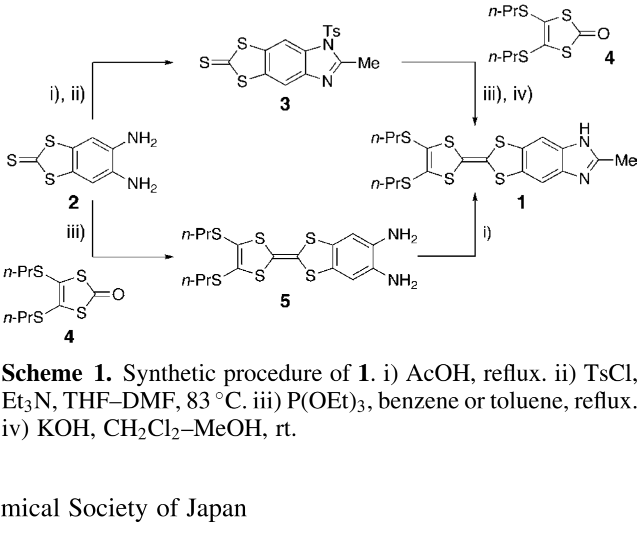
TTF-Im 1

Chart 1.

The crystal of **1**·$CHCl_3$ had an orthorhombic system, where two **1** (A and B) and two $CHCl_3$ solvent molecules were crystallographically independent. The N–H protons of both **1**-A and **1**-B were disordered into two sites with a site occupancy factor of 0.5. A part of the benzimidazole and 1,3-dithiole moieties in the skeleton were nearly coplanar because of the π delocalization, while the whole molecular skeleton is bent at sulfur atoms of the terminal 1,3-dithiole moiety (bent angles = 23.2° for **1**-A and 22.8° for **1**-B, see Supporting Information).[9]

In the crystal structure, **1**-A and **1**-B molecules were alternately connected by N–H···N H bonds on imidazole rings (2.84 and 2.96 Å) to each other forming a one-dimensional structure along the *a* axis (Figure 1). In addition, both **1**-A and **1**-B molecules stacked individually to form uniform π-stacking columns along the *b* axis with a face-to-face distance of 3.56 Å (Figure 1). To reduce the steric repulsion of bulky *n*-propylthio groups, the stacks had a slip-stack manner with slip distances of ca. 0.4 and 7.2 Å along the molecular short and long axes, respectively (see Supporting Information).[9] These intermolecular interactions constructed a two-dimensional structure. Solvent molecules existed in the space between π-stacking columns.

Density functional theory (DFT) calculation of **1** at B3LYP/6-31G* level indicates that imidazole-annelation of di(*n*-propylthio)benzo-TTF (**6**) increases the HOMO level by 0.163 eV



Scheme 1. Synthetic procedure of **1**. i) AcOH, reflux. ii) TsCl, Et_3N, THF–DMF, 83 °C. iii) $P(OEt)_3$, benzene or toluene, reflux. iv) KOH, CH_2Cl_2–MeOH, rt.

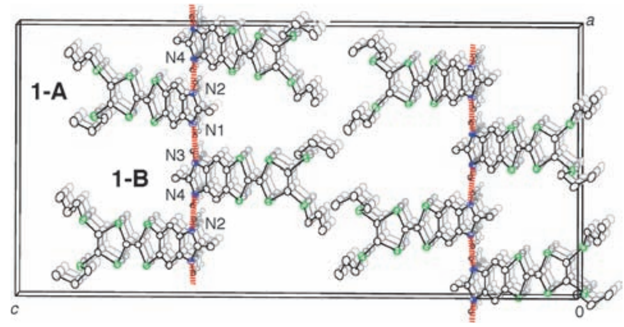


Figure 1. Crystal structure of **1** viewed nearly along the *b* axis showing H-bonded and π-stacking structures. H bonds are illustrated by red dotted lines. Hydrogen atoms and solvent molecules are omitted. The gray and light gray molecules locate in the $b = -1$ and -2 layers, respectively.

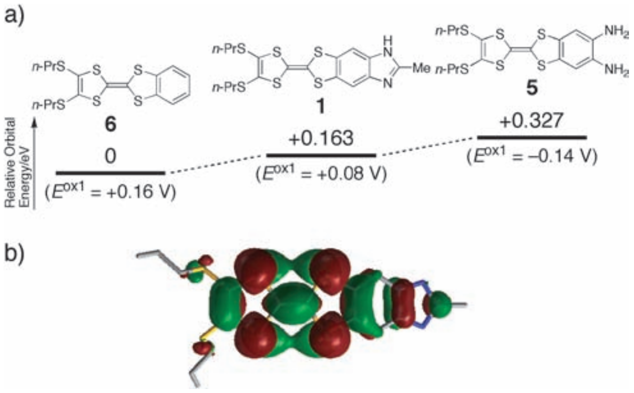


Figure 2. a) Comparison of calculated HOMO energies of **6**, **1**, and **5**. Parentheses are the first oxidation potentials (E^{ox1}) obtained by CV measurements (V vs. Fc/Fc$^+$). b) HOMO orbital of **1**.

and thus strengthens the electron-donating ability (Figure 2a). The calculation also indicates that a part of HOMO coefficient of **1** locates on the imidazole ring, showing an integration of the π-electronic systems (Figure 2b). Actually, in the cyclic voltammetry (CV) measurement, the first oxidation potential (E^{ox1}) of **1** was evaluated as +0.08 V vs. Fc/Fc$^+$, which is lower by 0.08 V than that of **6**. Compared with diamino derivative **5**, the electron-donating ability of **1** was weaker because of the electron-withdrawing nature of C=N group in imidazole moiety (Figure 2a).

The pK_{a1} and pK_{a2} values of **1** were estimated as 4.2 and ca. 13.5, respectively, by pH-dependent electronic spectra (see Supporting Information).[9] These results demonstrate that the proton-accepting ability of **1** is weaker than imidazole and benzimidazole (pK_{a1} = 6.9 and 5.4, respectively) while the proton-donating ability is close to those of imidazole and benzimidazole (pK_{a2} = 14.5 and 12.6, respectively).[10]

Donor–acceptor CT complexes of **1** with TCNQ, F$_4$TCNQ, and DDQ were prepared by the direct mixing method. All complexes possessed a 1:1 composition ratio. IR and electronic spectra characterized the TCNQ complex as a neutral CT complex and the others as fully ionic CT complexes (see Supporting Information).[9] These complexes were insulators (room-temperature conductivity $<10^{-7}\,\mathrm{S\,cm^{-1}}$).

In conclusion, we have designed and synthesized a new imidazole-annelated TTF derivative **1**, which exhibits a structural regulation ability by robust H bonds and π stacks. Furthermore, **1** demonstrated the multiple functions, namely, electron-donating and PT abilities, which are the most important factors to realize cooperative CT and PT systems[4] and to develop multifunctional organic conductors. Complex formation with various electron acceptors and chemical modifications on **1** to prepare conductive and/or PT coupled CT complexes are in progress. The extended π-electronic structure of **1** is also intriguing from the viewpoint of development of electronic molecular materials such as organic field-effect transistor (OFET).[2]

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8 Crystal data of **1**$\cdot$CHCl$_3$: $C_{19}H_{21}Cl_3N_2S_6$, $M_r = 576.11$, orthorhombic, space group, $Pna2_1$ (No. 33), $a = 19.6729(3)$, $b = 6.0880(1)$, $c = 41.0682(7)$ Å, $V = 4918.6(1)$ Å^3, $Z = 8$, $D_{calcd} = 1.556\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Cu}\,K\alpha) = 82.28\,\mathrm{cm^{-1}}$, $T = 93$ K, 4542 unique reflections ($R_{int} = 0.118$). The structure was refined to $R_1 = 0.042$, $wR_2 = 0.105$ for 4200 reflections with $I > 2\sigma(I)$ and 548 parameters, goodness-of-fit = 1.022. CCDC-665456.

9 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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