Transformation of Double Hydrogen-bonding Motifs of TTF–Uracil System by Redox Change

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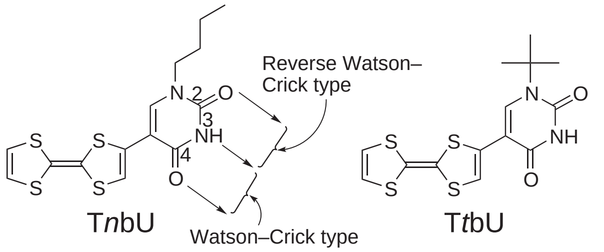
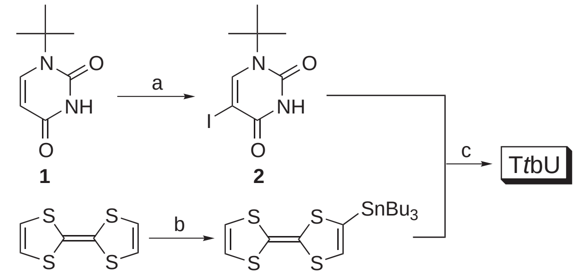
A TTF derivative with an N^1-*tert*-butyluracil moiety, T*t*bU, was prepared as a new electron-donor molecule capable of multiple hydrogen-bondings. Formation of the two different types of double hydrogen-bonding motifs, Watson–Crick and reverse Watson–Crick types, was demonstrated for the first time between T*t*bU and its I_3^- salt in the crystalline states.

In the field of organic conducting materials, hydrogen-bonded (H-bonded) charge transfer (CT) complexes and salts based on tetrathiafulvalene (TTF) derivatives are actively investigated in view of not only crystal engineering[1] but also control of donor/acceptor ratio and electronic properties such as ionicity of component molecules.[2–4] Focusing on nucleobases capable of multiple H-bondings, we recently reported design and synthesis of a TTF derivative with an N^1-*n*-butyluracil moiety, T*n*bU.[5] Considering the H-bonding motifs in the dimer of uracil moiety, three kinds of double H-bondings, Watson–Crick (3,4–3,4), reverse Watson–Crick (2,3–2,3), and their mixed types (2,3–3,4), can be formed.[5,6] In this context, energy differences in dimers of uracil itself are reported to be small by quantumn chemical calculations.[7] In fact, the H-bonded dimers of both types were exemplified in minor modification of molecular structures and of the condition of crystallization.[8,9] In the course of studies on a series of N^1-alkyluracil derivatives of TTF for designing molecule-based organic conductors, we have found transformation of H-bonding motifs in the uracil moiety by redox change from neutral state to radical cation state in a new TTF derivative with a N^1-*tert*-butyluracil moiety, T*t*bU.[10] Here, we report on the first demonstration of the different H-bonding motifs in the crystals of T*t*bU and its I_3^- salt.



T*t*bU was synthesized by the Stille coupling reaction with tributylstannylated-TTF and N^1-*tert*-butyl-5-iodouracil (**2**) prepared from N^1-*tert*-butyluracil (**1**)[11] (Scheme 1).[12] An oxidation potential of T*t*bU was evaluated by cyclic voltammetry (CV) in DMF solution, and T*t*bU exhibited two-stage one-electron oxidation waves.[13]



Scheme 1. Synthetic method of T*t*bU. Reagents and conditions: a) 2 equiv. ICl, MeOH, 50 °C; b) *n*-BuLi, THF, −78 °C; then $ClSnBu_3$, −78 °C; c) 10 mol % $Pd(PPh_3)_4$, toluene, 110 °C.

Single crystals of T*t*bU suitable for X-ray structure analysis were obtained by vapor diffusion method using DMF–water.[14] Dihedral angle between the TTF and uracil moieties is 4°, and the whole skeleton of T*t*bU is almost planar. Complementary double H-bondings of the Watson–Crick type were formed between the uracil moieties (NH···O, 2.86 Å, Figure 1). Furthermore, there is a $\pi\cdots\pi$ interaction between the two T*t*bU molecules (see Supporting Information).

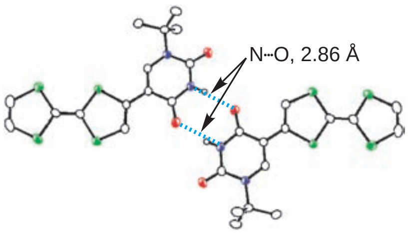


Figure 1. Crystal structure of T*t*bU. Double H-bondings with Watson–Crick type were formed between the uracil moieties. Hydrogen atoms except that for the N–H group of the uracil moiety are omitted for clarity.

The I_3^- salt of T*t*bU, $\mathrm{T}t\mathrm{bU}^{\bullet+}\cdot\mathrm{I_3}^{-}\cdot(\mathrm{ClCH_2CH_2Cl})_{0.5}$, was prepared by diffusion method using $ClCH_2CH_2Cl$ solutions of T*t*bU and I_2, and X-ray structure analysis was conducted.[14] Dihedral angle between the TTF and uracil moieties is 25°, and T*t*bU$^{\bullet+}$ is more twisted compared with T*t*bU, while conformation between the TTF and uracil moieties is the same as that of T*t*bU. An H-bonded dimer with the reverse Watson–Crick type was formed between the uracil moieties of T*t*bU$^{\bullet+}$ (NH···O, 2.84 Å, Figure 2a). Furthermore, there is a π-dimer of T*t*bU$^{\bullet+}$ in head-to-tail fashion with an interplanar distance of 3.2 Å as well as several short S···S and S···I contacts, resulting in a two-dimensional layer structure (Figure 2b). Difference of H-bonding motifs in the two crystal structures is also confirmed by IR spectra in KBr (Figure 3).[5] The carbonyl stretching frequency of the 4-position in the uracil moiety markedly shifted from 1654 to 1676 cm^{-1} upon oxidation, showing clear change of H-bonding motifs in the uracil moiety. This I_3^- salt was insulator with low electric conductivity below 10^{-8} $S\,cm^{-1}$.

To investigate origin of the unique transformation of H-bonding motifs by redox change, we have carried out density functional theory calculations based on the crystal structures of T*t*bU and T*t*bU$^{\bullet+}$, showing the large HOMO and SOMO coefficients on the TTF moieties, respectively (Figure 4 and see

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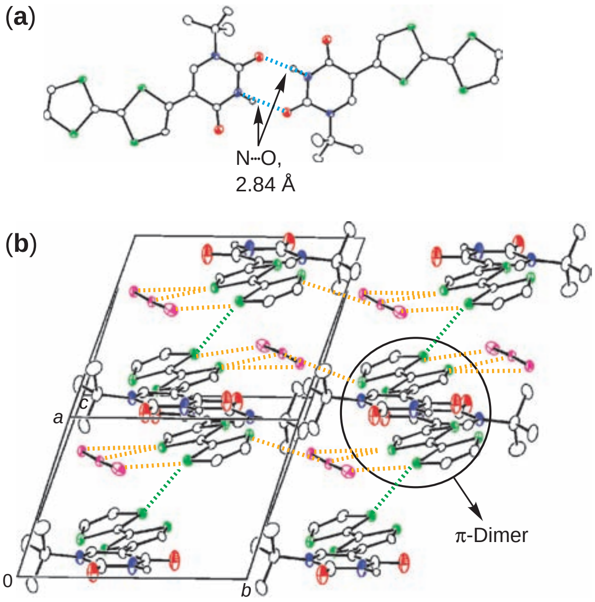

Figure 2. Crystal structure of T*t*bU$^{\bullet+}$•I_3^-•$(ClCH_2CH_2Cl)_{0.5}$. (a) H-bonded dimer of T*t*bU$^{\bullet+}$ formed between the uracil moieties and (b) two-dimensional layer structure through π-dimer with an interplanar distance of 3.2 Å, several S···S (green dotted line) and S···I contacts (orange dotted line). Hydrogen atoms except that for the N–H group of the uracil moiety are omitted for clarity.

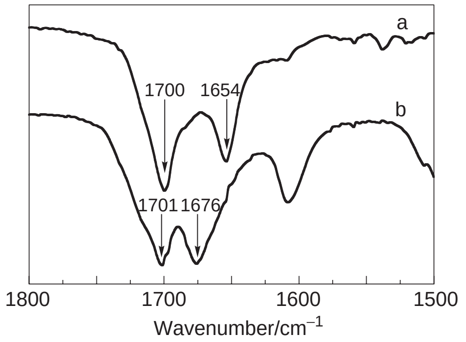

Figure 3. IR spectra of (a) T*t*bU and (b) T*t*bU$^{\bullet+}$•I_3^-•$(ClCH_2CH_2Cl)_{0.5}$ in the frequency region from 1500 to 1800 cm^{-1} in KBr pellets. Their IR spectra in the region from 500 to 4000 cm^{-1} are shown in Supporting Information.

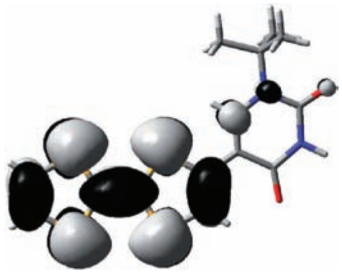

Figure 4. HOMO of T*t*bU. The calculation was carried out at the RB3LYP/6-31G(d) level of theory based on the crystal structure of T*t*bU.

Supporting Information). Experimentally, the difference of bond lengths of the uracil moieties between T*t*bU and T*t*bU$^{\bullet+}$ is 0.001–0.017 Å, being small but significant magnitude (see Supporting Information). In addition to these intramolecular factors, influence of counter ions, crystal packing, and other intermolecular non-covalent interactions cannot be excluded. Thus, the origin of the transformation of the H-bonding motifs is not clear at present.

In summary, we have demonstrated that the different double H-bonding motifs between the uracil moieties were formed between T*t*bU and its I_3^- salt in the crystalline states. From the viewpoints of crystal engineering and electronic modulation, clarification of the relationship between H-bonding interactions and ionic characters of the molecules will bring important information to control and predict crystal structures, and study is now going along this line.

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6 In the crystal of T*n*bU, Watson–Crick type of H-bonded dimer was formed between two T*n*bU molecules. However, no other types of H-bonded dimers were obtained in its CT complexes and salts.

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10 Studies of other TTF derivatives with an N^1-alkyluracil moiety will be reported elsewhere.

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12 Selected physical data. T*t*bU: brownish orange powder, mp 258–259 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 9H), 6.73 (s, 2H), 7.29 (s, 1H), 7.58 (s, 1H), 11.6 (brs, 1H); EI-MS *m*/*z* 370 (M^+, 29%); Anal. Calcd for $C_{14}H_{14}N_2O_2S_4$: C, 45.38; H, 3.81; N, 7.56%. Found: C, 45.35; H, 3.73; N, 7.43%. T*t*bU$^{\bullet+}$•I_3^-•$(ClCH_2CH_2Cl)_{0.5}$: black crystal, mp 166–168 °C (dec); Anal. Calcd for $(C_{14}H_{14}N_2O_2S_4)(I_3)(ClCH_2CH_2Cl)_{0.3}$: C, 22.45; H, 1.96; N, 3.59%. Found: C, 22.07; H, 1.94; N, 3.54%.

13 CV was carried out under the following conditions: 1 mM solution in DMF with 0.1 M $Et_4N^+ClO_4^-$ as a supporting electrolyte at room temperature vs Fc/Fc^+, Au working electrode and Pt counter electrode; 0.1 V/s. Oxidation potentials of T*t*bU and TTF were as follows: −0.12, +0.10 V; −0.08, +0.12 V.

14 Crystal data for T*t*bU: $C_{14}H_{14}O_2N_2S_4$, fw = 370.52, triclinic, space group, $P\bar{1}$ (No. 2), $a = 7.218(3)$, $b = 9.456(3)$, $c = 12.926(5)$ Å, $\alpha = 81.77(3)$, $\beta = 78.03(4)$, $\gamma = 68.13(3)^\circ$, $V = 798.8(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.540$ g/cm^3, μ (Mo Kα) = 6.01 cm^{-1}, $T = 200(1)$ K; 3590 unique reflections ($R_{int} = 0.029$). The structure was refined to $R_1 = 0.033$, $wR_2 = 0.079$ for 2699 reflections with $I > 3\sigma(I)$ and 200 parameters, goodness-of-fit = 1.939. CCDC-279854. Crystal data for T*t*bU$^{\bullet+}$•I_3^-•$(ClCH_2CH_2Cl)_{0.5}$: $C_{15}H_{16}O_2N_2S_4I_3Cl$, fw = 800.71, triclinic, space group, $P\bar{1}$ (No. 2), $a = 7.564(1)$, $b = 9.734(2)$, $c = 17.546(4)$ Å, $\alpha = 79.79(2)$, $\beta = 81.35(2)$, $\gamma = 74.13(2)^\circ$, $V = 1215(1)$ Å^3, $Z = 2$, $D_{calcd} = 2.187$ g/cm^3, μ (Mo Kα) = 43.24 cm^{-1}, $T = 150(1)$ K; 5471 unique reflections ($R_{int} = 0.033$). The structure was refined to $R_1 = 0.030$, $wR_2 = 0.078$ for 3797 reflections with $I > 2\sigma(I)$ and 244 parameters, goodness-of-fit = 0.91. CCDC-279855. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposite@ccdc.cam.ac.uk).

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