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Terthiophene Radical Cations End-Capped by Bicyclo[2.2.2]octene Units: Formation of Bent π-Dimers Mutually Attracted at the Central Position

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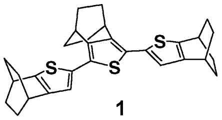
π-Conjugated polymers and oligomers have been attracting much attention because of their potential applicability to electronic devices.[1] Under the p-doped state, π-dimer formation as well as π-stacking of the radical cation (polaron) of oligomers is known to be important for the electric conduction.[2] In this context, Miller, Mann et al. first succeeded in isolation and X-ray crystal analysis of the π-dimer of the radical cation of a terthiophene end-capped by phenyl groups.[3] Because of the intrinsic instability of the radical cations in general, this work has remained as a rare example of the detailed structural study on this important species.[4]

On the other hand, we have developed a technique to stabilize the cationic species of π-conjugated systems by annelation with bicyclo[2.2.2]octene (abbreviated as BCO) units so that even their isolation as stable single crystals has become possible.[5] Thus, we have isolated the salts of a series of cationic oligothiophenes entirely annelated with BCO units,[6] including terthiophene **1**, and revealed their properties as single molecules having no intermolecular interactions owing to the steric effects of the BCO units. We now report the structure and electronic interaction of the radical cation of terthiophene **2**, which lacks for steric protection at the center of the molecule so that some electronic interaction at this position might be possible.



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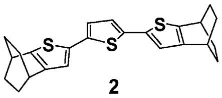

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Terthiophene **2** was synthesized in 96% yield by palladium-catalyzed cross coupling of 2,5-dibromothiophene with 2-stannylthiophene annelated with a BCO unit. The UV−vis spectrum of **2** in CH_2Cl_2 showed an absorption at λ_{max} 379 nm, that is 16 nm longer in wavelength than that of **1**,[7] probably because of better planarity of the terthiophene π-system.[8] The cyclic voltammetry of **2** in CH_2Cl_2 exhibited reversible oxidation at $E_{1/2}$ + 0.31 V versus Fc/Fc^+, which is 0.04 V higher than that of **1** owing to the loss of an electron-donating BCO unit.

Upon one-electron oxidation with $NO^+SbF_6^-$, terthiophene **2** was converted to deeply blue-colored radical-cation salt $\mathbf{2}^{\bullet+}SbF_6^-$ in 88%, which is highly stable under air. The UV−vis−NIR spectrum of $\mathbf{2}^{\bullet+}$ in CH_2Cl_2 at a concentration of 2.4×10^{-4} M showed a similar shape (λ_{max} 618 and 931 nm) to that of radical cation $\mathbf{1}^{\bullet+}$ (λ_{max} 586 and 920 nm). At this concentration, no change in the spectrum of $\mathbf{2}^{\bullet+}$ was observed upon lowering the temperature from 300 K down to 180 K. In our previous work,[6] we have shown that molecules of $\mathbf{1}^{\bullet+}SbF_6^-$ are completely separated from each other both in the crystal and solution phases based on similar observations. Thus, no π-dimer formation is assumed to take place for $\mathbf{2}^{\bullet+}$ as far as the concentration and temperature are limited to these ranges.

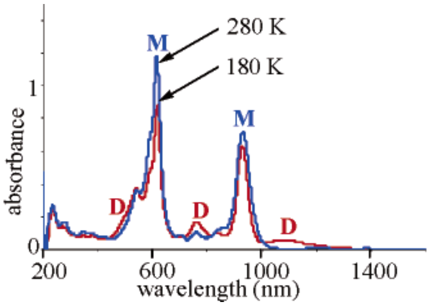

Figure 1. UV−vis−NIR spectra of $\mathbf{2}^{\bullet+}$ at the concentration of 1.2×10^{-3} M in CH_2Cl_2. M and D correspond to the monomer and dimer, respectively.

However, for the 5-times more concentrated solution of $\mathbf{2}^{\bullet+}$ (1.2×10^{-3} M), a spectral change became appreciable upon lowering the temperature. As shown in Figure 1, new absorptions at 490, 762, and 1080 nm appeared at low temperature, accompanied by lowering of the absorptions at 618 and 931 nm of the monomeric radical cation. The new absorptions are assignable to the π-dimer (D) as judged by comparison with reported data.[2a−c,3b] This spectral change was reversible. The analysis of this temperature-dependent process afforded thermodynamic parameters for π-dimer formation as $\Delta H = -6.7$ kcal/mol and $\Delta S = -27$ eu.[9] These values are comparable to the values reported for dimerization of radical cation of 2,5″-dimethylterthiophene ($\Delta H = -10$ kcal/mol and $\Delta S = -25$ eu).[2a] The less negative value of ΔH for $\mathbf{2}^{\bullet+}$ is ascribed to the lower stability of the π-dimer of $\mathbf{2}^{\bullet+}$ because of the steric repulsion of bulky BCO units at both ends.

The ESR measurements of the solution of $\mathbf{2}^{\bullet+}$ in CH_2Cl_2 conducted at exactly the same concentration as that for the above-mentioned UV−vis−NIR measurements (1.2×10^{-3} M) indicated that the signal intensity clearly decreases as the temperature is lowered. Since the π-dimer is in the singlet state and spinless, this observation supports the formation of the π-dimer at low temperature.[10]

Recrystallization of $\mathbf{2}^{\bullet+}SbF_6^-$ from CH_2Cl_2 gave single crystals that are suitable for X-ray crystal structural analysis. The result of the analysis at 100 K revealed a characteristic π-dimer structure. As shown in Figure 2, units of radical cation $\mathbf{2}^{\bullet+}$ are paired, and each cationic unit in a pair strongly interacts with each other as indicated by mutual attraction at the central part where the steric hindrance is minimal. This causes the molecules to apparently bend: for example, the dihedral angles between the mean planes of neighboring thiophene rings are 14.6(3)° and 11.8(4)°.[11] The closest intermolecular distances are 2.976(10) Å between the two C_β atoms of the central rings, 3.091(10) Å between the C_α atoms, and 3.779(3) Å between the S atoms. Both of the C−C distances are much shorter than the sum of van der Waals radii of sp^2-C atoms,that is, 3.40 Å. It is remarkable that such a strong attractive

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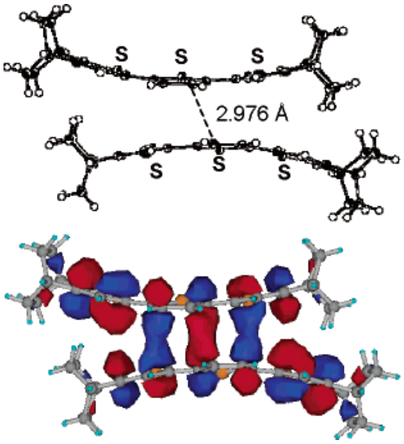

Figure 2. (a) ORTEP drawing of the π-dimer moiety $(\mathbf{2}^{\bullet+})_2$; (b) calculated KS-HOMO using the structure determined by X-ray structural analysis.

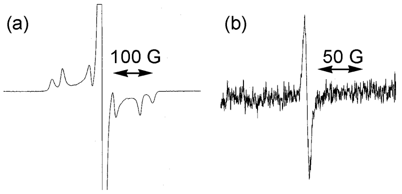

Figure 3. (a) An ESR spectrum of $\mathbf{2}^{\bullet+}$ at 400 K exhibiting a signal for a thermally accessible triplet state of π-dimer $(\mathbf{2}^{\bullet+})_2$ and that for monomeric radical cation $\mathbf{2}^{\bullet+}$ ($g = 2.0016$). (b) A signal at a half-field ($g = 4.0072$).

interaction operates between the two positively charged species. This is taken as the clear evidence that a $\pi-\pi$ interaction can surpass the electrostatic repulsion and destabilization by structural deformation. This strong interaction was confirmed by a single point energy calculation for the KS HOMO of the π-dimer at the B3LYP/6-31+G(d) level. As shown in Figure 2b, substantial overlap of the SOMOs of $\mathbf{2}^{\bullet+}$ is clearly observed at the central part.

In the crystal packing structure, the π-dimers are stacked in a stairlike fashion and no interaction is observed between the different pairs (see Supporting Information).

Theoretical calculations at B3LYP/6-31G(d) level on the monomeric form of radical cation $\mathbf{2}^{\bullet+}$ indicate that the all-anti conformer is more stable than the all-syn conformer by 1.3 kcal/mol. However, each radical cation in the single crystal of the π-dimer of $\mathbf{2}^{\bullet+}\mathrm{SbF}_6^-$ takes the all-syn conformation with the two terthiophene moieties overlapped with sliding by a half of the thiophene molecular unit. This is presumably ascribed to more effective MO interactions between the all-syn conformers (for more detailed discussion, see Supporting Information).

When the X-ray analysis of $\mathbf{2}^{\bullet+}\mathrm{SbF}_6^-$ was conducted at a higher temperature (298 K), distances between the interacting π-systems were found to be slightly elongated: the distance for $\mathrm{C}_\beta-\mathrm{C}_\beta$, $\mathrm{C}_\alpha-\mathrm{C}_\alpha$, and S−S became 3.03(2), 3.14(2), and 3.812(6) Å, respectively. Although the extent is minute, this may be taken as a piece of evidence for the stronger association of the π-dimer at a lower temperature.

The ESR spectrum of $\mathbf{2}^{\bullet+}\mathrm{SbF}_6^-$ in solid state at 300 K showed a single-line signal at $g = 2.0016$. This can be ascribed to the monomeric radical cation, which should be present in the defect of crystal or in an amorphous phase. However, as shown in Figure 3, when the sample was heated to 400 K a new triplet-state signal was observed ($D = 127$ G, $E = 23$ G), which is assigned to a *thermally excited triplet state* of the π-dimer. At a half-field ($g = 4.0072$), a weak signal emerged at 400 K and disappeared at 300 K, in accordance with the above observation. To the best of our knowledge, this is the first observation of the triplet state of the *radical-cation π-dimer* that was thermally generated.[12,13]

In summary, we have shown that the electronic interaction between the central positions of radical cations of terthiophene end-capped by BCO units is so strong that the considerably bent π-dimer is formed. The extraordinarily high stability of the radical-cation π-dimer has enabled us to access its thermally excited triplet state for the first time and demonstrate the utility of the present strategy for detailed studies on this important species.

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Supporting Information Available: Synthesis, spectral, and X-ray crystallographic data (in CIF format) for crystals **2** and $\mathbf{2}^{\bullet+}\mathrm{SbF}_6^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The possible steric repulsion between bridgehead hydrogen atoms of the central BCO unit and sulfur atoms in **1** should be unfavorable for the planarization.

(9) Calculated according to the method reported by Bäuerle et al. (ref 2b).

(10) Thermodynamic parameters for π-dimer formation roughly calculated based on the ESR data are $\Delta H \approx -6$ kcal/mol and $\Delta S \approx -18$ eu.

(11) This bending brings about some pyramidalization for the sp^2 carbon atoms at the connecting positions. However, the averaged bond angles at the most pyramidalized carbon is 119.80°, which does not consume much energy. We thank one of the referees for directing our attention to this point.

(12) Several trials for estimation of the singlet-triplet energy gap using the ESR data at a temperature range of 180−400 K afforded the most possible value to be in the range of 5−7 kcal/mol.

(13) As to the formation of singlet π-dimers of radical cation or anion ($\mathrm{TCNE}^{\bullet-}$ in particular), see, for example, (a) Del Sesto, R. E.; Miller, J. S.; Lafuente, P.; Novoa, J. J. *Chem. Eur. J.* **2002**, *8*, 4894−4908. (b) Lü, J.-M.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 12161−12171.

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