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Novel Cyclooctatetraene Radical Cation Planarized by Full Annelation with Bicyclo[2.1.1]hexene Units

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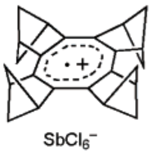
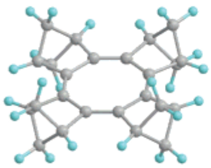
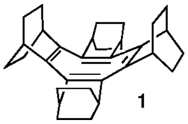
ABSTRACT





A novel cyclooctatetraene (COT) radical cation fully annelated with bicyclo[2.1.1]hexene units was prepared as $SbCl_6^-$ salt, and planarity of the octagonal ring was clarified by ESR and theoretical calculations. Its longest wavelength absorption (630 nm) is blue-shifted from that (745 nm) of COT radical cation annelated with bicyclo[2.2.2]octene units due to the widening of the HOMO–SOMO gap accompanying the flattening of the COT ring.

It is widely accepted that cyclooctatetraenes (COTs) have a tub-shaped structure with alternating double bonds.[1] The radical cation of COT[2] and its dibenzo derivative[3] have also been shown to possess a nonplanar geometry, whereas the other ionic species of COTs (i.e., radical anion,[4] dianion,[4] and dication[5]) adopt a planar conformation. The radical cation of COT is a highly unstable species like most hydrocarbon radical cations. However, in our previous study, annelation of bicyclo[2.2.2]octene units to the COT ring, as in **1**,[6] was shown to remarkably stabilize the radical cation due to steric protection and "Bredt's rule protection"[7] as well as inductive and $\sigma-\pi$ conjugative effects. Thus, radical cation salt $\mathbf{1}^{\bullet+}SbCl_6^-$ was isolated as stable crystals and allowed the first X-ray structural analysis of COT radical cation, showing that the central ring of $\mathbf{1}^{\bullet+}$ has a tub-shaped structure.[8]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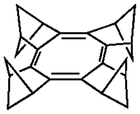
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On the other hand, we recently synthesized a novel COT **2**, in which the COT ring is constrained to adopt a planar conformation by annelation with bicyclo[2.1.1]hexene units[9] due to the widening of the inner angle of the COT ring by pinching with the highly strained bicyclic system. In the radical cation of COT **2**, stabilization effects similar to those mentioned above can be expected, but the intrinsic strain in bicyclo[2.1.1]hexene was anticipated to work unfavorably. Here we report the result of the one-electron oxidation of **2**

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and properties of obtained $\mathbf{2}^{\bullet+}$ $SbCl_6^-$ as the first planar COT radical cation, whose flattened geometry is ascribed to the constraint by highly strained bicyclo[2.1.1]hexene units.

The cyclic voltammetry on planar COT **2** exhibits a well-defined reversible oxidation wave at such a low potential as +0.07 V vs Fc/Fc^+ in CH_2Cl_2 at room temperature,[9] suggesting the ready formation and stability of the corresponding radical cation. In fact, the radical cation salt $\mathbf{2}^{\bullet+}SbCl_6^-$ was prepared by chemical oxidation of **2** using 1.5 equiv of $SbCl_5$ in CS_2[10] under argon at −78 °C. The resulting precipitates were separated, washed with cold CS_2, and dissolved in CH_2Cl_2. Then, hexane was added onto the solution and diffused slowly at −78 °C. After 8 days, dark purple microcrystals were obtained in 55% yield, which contained $\mathbf{2}^{\bullet+}$ (see below) and the counteranion $SbCl_6^-$ in a ratio of nearly 1:1 as judged from elemental analysis.[11] Unfortunately, however, the crystal size was too small to be analyzed by X-ray crystallography. The crystals can be stored under argon at −20 °C for at least 2 months without decomposition.

The ESR spectrum of a CH_2Cl_2 solution of the obtained crystals (0.3 mM as $\mathbf{2}^{\bullet+}SbCl_6^-$) under vacuum at −73 °C exhibited a signal with well-resolved hyperfine structure as shown in Figure 1a (g value = 2.0032). From the simulation analysis (Figure 1b), the spectrum was found to involve the couplings of 1.08 G (8H), 0.49 G (8H), and 0.10 G (8H), suggesting the presence of $\mathbf{2}^{\bullet+}$ having a planar structure with D_{4h} symmetry. We conducted DFT calculations on $\mathbf{2}^{\bullet+}$ at the B3LYP/6-31G(d) level,[12] and the optimized structure was also found to be planar as shown in Figure 1c. Several calculations conducted with various shapes of tub forms as initial structures for $\mathbf{2}^{\bullet+}$ all converged to the planar structure shown in Figure 1a as the optimized form, thus confirming the present result.[13] The coupling constants of H^{anti}, H^{syn}, and $H^{bridgehead}$ were calculated to be −1.14 G, −0.49 G, and −0.07 G, respectively for the planar structure of $\mathbf{2}^{\bullet+}$. These values are in fairly good agreement with the experimental values, again supporting the planar conformation for $\mathbf{2}^{\bullet+}$. On the other hand, the stability of $\mathbf{2}^{\bullet+}$ in solution is reduced in comparison with $\mathbf{1}^{\bullet+}$ and the ESR signal of $\mathbf{2}^{\bullet+}$ attenuated in CH_2Cl_2 at 25 °C even under vacuum, with a half-life of ca. 1.5 h.

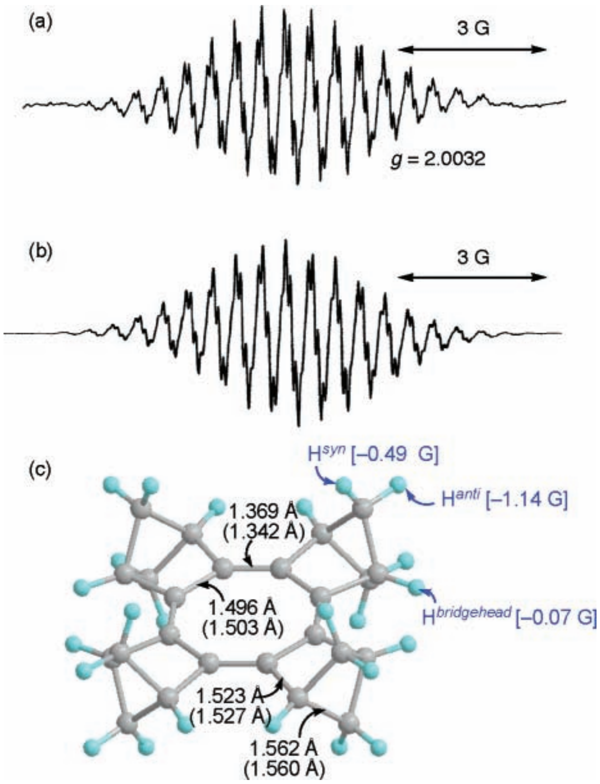

Figure 1. (a) ESR spectrum of $\mathbf{2}^{\bullet+}SbCl_6^-$ in CH_2Cl_2 at −73 °C. (b) Simulated spectrum by the use of the coupling constants of 1.08 G (8H), 0.49 G (8H), and 0.10 G (8H). (c) The optimized structure of $\mathbf{2}^{\bullet+}$ at the B3LYP/6-31G(d) level. Calculated values of coupling constants are shown in square brackets together with those for C−C bond lengths and the corresponding lengths of neutral **2** in parentheses.

In the optimized structure of neutral **2** (B3LYP/6-31G-(d)), the lengths of the $C(sp^2)=C(sp^2)$ double bond and the $C(sp^2)-C(sp^2)$ single bond of the COT ring were calculated to be 1.342 and 1.503 Å, respectively, which are slightly longer but in reasonable agreement with the observed values (the averaged values; 1.331(1) Å and 1.500(1) Å, respectively).[9] It is to be noted that the $C(sp^2)-C(sp^2)$ single bond in **2** is considerably elongated to minimize the strain in the bicyclo[2.1.1]hexene system. In the case of **1**, reduction of the bond-length alternation upon one-electron oxidation was observed by X-ray structural analysis.[8] In a similar manner, elongation of the original $C(sp^2)=C(sp^2)$ double bond and shortening of the original $C(sp^2)-C(sp^2)$ single bond are expected by calculations for $\mathbf{2}^{\bullet+}$ (Figure 1c). At the same time, $C(sp^2)-C(sp^3)$ and $C(sp^3)-C(sp^3)$ single bonds in bicyclo[2.1.1]hexene units are calculated to be slightly shortened and elongated, respectively. This might be taken as the result of the $\sigma-\pi$ conjugation in the cationic state[10] although the extent is minute. The shortening of the endocyclic $C(sp^2)-C(sp^2)$ bond of the bicyclic system should

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(10) Matsuura, A.; Nishinaga, T.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 10007.

(11) Calcd for $C_{24}H_{24}Cl_6Sb$: C, 44.56; H, 3.74. Found: C, 40.52; H, 3.65. Because of the intrinsic instability of this salt under air, the repeated analysis did not give any better result.

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(13) For neutral COT **2**, the planar conformer is calculated to be more stable than a D_{2d} tub-shaped conformer by 30.1 kcal mol^{-1}. This large energy difference is due to unfavorable double bond shift to the endocyclic position of the highly strained bicyclic system in the tub conformers. Similarly, the tub structure in radical cation $\mathbf{2}^{\bullet+}$ is unfavorable because a part having double-bond character has to be placed in the endocyclic position.

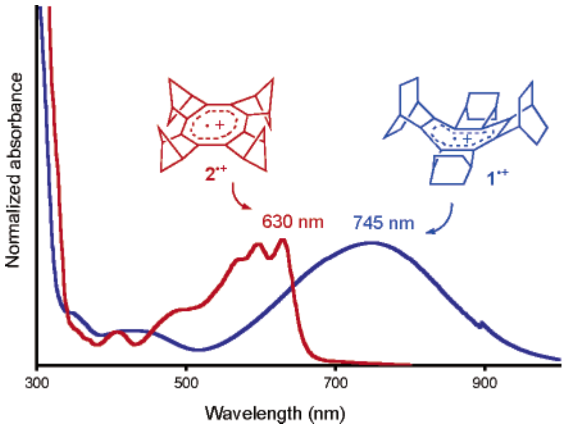

Figure 2. Electronic absorption spectra of $\mathbf{1}^{\bullet+}SbCl_6^-$ and $\mathbf{2}^{\bullet+}SbCl_6^-$ in CH_2Cl_2 at room temperature.

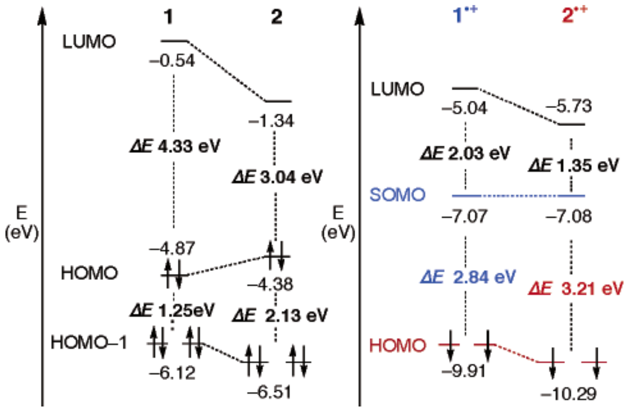

Figure 3. MO diagrams of COTs **1** and **2** and their radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. The energy levels were calculated at the B3LYP/6-31G(d) level. For the radical cations, only β-orbitals, which are relevant to the longest wavelength absorption, of the unrestricted DFT calculations are shown.

increase the strain in this system, which may be the reason for the reduced stability of radical cation $\mathbf{2}^{\bullet+}$ in solution.

Another point to be noted is that the longest wavelength absorption in the electronic spectrum of $\mathbf{2}^{\bullet+}$ shows a considerable hypsochromic shift in comparison with $\mathbf{1}^{\bullet+}$. As shown in Figure 2, the absorption maximum is observed at 630 nm for $\mathbf{2}^{\bullet+}$, while it is 745 nm for $\mathbf{1}^{\bullet+}$. In general, the enhancement of planarity in π-conjugated systems, causing the more effective π-conjugation, is expected to induce a bathochromic shift of the longest wavelength absorption. However, a reversed tendency is observed when the longest wavelength absorption is compared between planar radical cation $\mathbf{2}^{\bullet+}$ and tub-shaped radical cation $\mathbf{1}^{\bullet+}$. This unusual phenomenon can be interpreted as follows. On the basis of time-dependent density functional theory (TD-DFT, B3LYP/6-31+G(d)//B3LYP/6-31G(d)) and semiempirical ZINDO calculations, the longest wavelength absorption of $\mathbf{2}^{\bullet+}$ (630 nm, 1.97 eV) is assigned to the HOMO→SOMO transitions (TD-DFT, 531 nm ($f = 0.0385$); ZINDO, 649 nm ($f = 0.0799$)). For $\mathbf{1}^{\bullet+}$, the longest wavelength absorption (745 nm, 1.66 eV) is also assigned to the HOMO→SOMO transition,[8] which is lower in energy compared with that for $\mathbf{2}^{\bullet+}$. As shown in Figure 3, the difference of the Kohn−Sham energy level (B3LYP/6-31G(d)) between HOMO (SOMO in radical cation) and HOMO-1 (HOMO in radical cation) in neutral **1** is 1.25 eV, while the energy difference becomes 2.13 eV in planar COT **2**. A similar change in energy difference accompanying planarization of the COT ring was shown in β-orbitals of unrestricted calculation of the radical cations, that is, 2.84 eV for $\mathbf{1}^{\bullet+}$ and 3.21 eV for $\mathbf{2}^{\bullet+}$. As a result, the HOMO→SOMO transition energy of $\mathbf{2}^{\bullet+}$ is shown to be greater despite the planarization in the π-system, according to either of these calculations.

In summary, we succeeded in the synthesis of COT radical cation salt $\mathbf{2}^{\bullet+}SbCl_6^-$ annelated with bicyclo[2.1.1]hexene units. The ESR and electronic absorption spectra of $\mathbf{2}^{\bullet+}SbCl_6^-$, as well as the results of theoretical calculations, were all consistent with the planar structure for the radical cation of COT **2**, which is flattened by the annelation with highly strained bicyclo[2.1.1]hexene units.

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Supporting Information Available: Cartesian coordinates of optimized structures of **1**, $\mathbf{1}^{\bullet+}$, **2,** and $\mathbf{2}^{\bullet+}$ (B3LYP/6-31G(d)). This material is available free of charge via the Internet at http://pubs.acs.org.

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