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First X-ray Structure of a Cyclooctatetraene Cation Radical: The Hexachloroantimonate of the Tetrakis(bicyclo[2.2.2]octeno)cyclooctatetraene Cation Radical[†]

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In contrast to the cyclooctatetraene (COT) dianions and anion radicals which have been extensively studied,[1] experimental studies on the cationic species of COT are quite limited because of its instability under oxidative conditions. For example, the 6π-aromatic dication of the di- or tetrasubstituted derivative has been reported to be generated only under stable-ion conditions at low temperature (−80 to −20 °C):[2] the cation radical of the parent COT has been observed by ESR in solution only by the use of a rapid-flow technique[3a] or in a Freon matrix at low temperature (−196 °C) ;[3b,c] the electronic spectrum has also been taken on the matrix-isolated species.[3b,c] However, like the cation radicals of other olefinic hydrocarbons, the COT cation radical is a highly unstable species, whose structure has only been inferred from the ESR coupling constant[3a] and from theoretical calculations.[4]

Previously we reported the synthesis of a COT derivative (**1**) fully annelated with bicyclo[2.2.2]octene.[5] Such structural modification with a bicycloalkene framework has been proved to be remarkably effective in the stabilization of tropylium ion[6] and benzene cation radical.[7] Here we report the first isolation of the hexachloroantimonate salt of the cation radical $\mathbf{1}^{\cdot+}$ as a stable single crystal and the X-ray determination of its structure.

Cyclic voltammetry of the COT **1** in acetonitrile–dichloromethane (3:1) (with 0.1 M $\mathrm{Bu_4N^+ClO_4^-}$ as an electrolyte) at room temperature under argon exhibited a well-defined reversible one-electron oxidation wave at $E_{1/2} = +0.48$ V vs Ag/Ag⁺ together with an irreversible oxidation peak at +0.99 V. This result implies that **1** provides a stable cation radical even at room temperature and a less stable dication upon further oxidation. In fact, electrolytic oxidation in an ESR cell at an electrode potential of +0.5 V vs Ag/Ag⁺ in dichloromethane gave a green solution, which exhibited an ESR spectrum composed of nine lines with relative intensities proportional to the coefficients in the binomial expansion ($a_H = 0.194$ mT, $g = 2.0023$) as shown in Figure 1.[8] This signal was persistent at room temperature for several hours even after the anodic current was cut off.

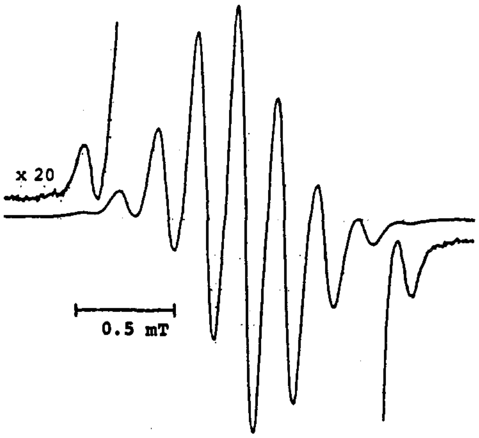
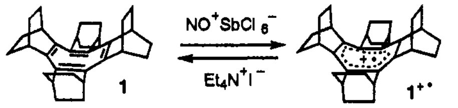


Figure 1. ESR spectrum of $\mathbf{1}^{\cdot+}$ electrolytically generated in dichloromethane containing $\mathrm{Bu_4N^+ClO_4^-}$ (0.1 M).

Scheme I



As shown in Scheme I, chemical one-electron oxidation of **1** by the use of 1 equiv of $\mathrm{NO^+SbCl_6^-}$[9] occurred instantly in dichloromethane at room temperature to give a dark green solution. Reprecipitation with benzene afforded a 76% yield of crude $\mathbf{1}^{\cdot+}\mathrm{SbCl_6^-}$ as a dark green solid. The single crystal of $\mathbf{1}^{\cdot+}\mathrm{SbCl_6^-}$,[10] obtained as described below in 20% yield, was stable at room temperature under air for several hours and can be stored in a refrigerator for more than 6 months without any decomposition. Upon dissolution in dichloromethane, this salt gave the same ESR signal as the one obtained by electrolytic oxidation, and it was reduced back to the starting **1** quantitatively by $\mathrm{Et_4N^+I^-}$ in acetonitrile.

A single crystal of $\mathbf{1}^{\cdot+}\mathrm{SbCl_6^-}$ was grown by slow diffusion of benzene into a saturated solution of $\mathbf{1}^{\cdot+}\mathrm{SbCl_6^-}$ in dichloromethane. X-ray crystallography[11] revealed the structure of $\mathbf{1}^{\cdot+}\mathrm{SbCl_6^-}$ as shown in Figure 2. The averaged values for bond lengths and

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[†] Dedicated to Professor Robert West on the occasion of his 65th birthday.

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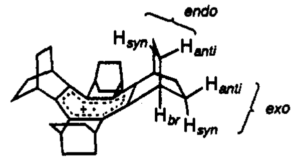
(8) This coupling is tentatively assigned as due to the eight *anti* protons of the *endo*-site ethano bridge, since the highest spin density (0.0022) is found on this proton by INDO calculation: we thank Dr. Shuji Aonuma for the calculation. The smaller spin densities residing on other protons (0.0013 on $\mathrm{H}_{bridgehead}$, −0.0008 on *exo*-H_{anti} , −0.0005 on *endo*-H_{syn} , and −0.0004 on *exo*-H_{syn}) seem to be the cause of broadening of the ESR signal. The results of more precise theoretical calculations and an ENDOR investigation will be reported elsewhere.



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(10) Mp 134–135 °C dec. IR (KBr): ν 2935, 2860, 1653, 1487, 1452, 1147, 1024, and 668 cm⁻¹. Anal. Calcd for $\mathrm{C_{32}H_{40}Cl_6Sb}$: C, 50.63; H, 5.31; Cl, 28.02. Found: C, 50.28; H, 5.31; Cl, 27.93.

(11) Crystal data for $\mathbf{1}^{\cdot+}\mathrm{SbCl_6^-}$ at 20 °C: tetragonal, space group *P*4*cc*, $a = 18.525(3)$ Å, $c = 19.261(4)$ Å, $V = 6610(8)$ Å³, $Z = 8$, $d_{calc} = 1.526$ g cm⁻³, $\mu(\mathrm{Mo}\,K\alpha) = 134$ mm⁻¹. A total of 4348 with 2238 independent reflections were collected on a STOE STADI 4 diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXS86) and refined by full matrix least squares (SHELXL93); $R(F) = 0.029$ based on 1662 reflections with $|F| \geq 4\sigma F$, $wR^2 = 0.069$.

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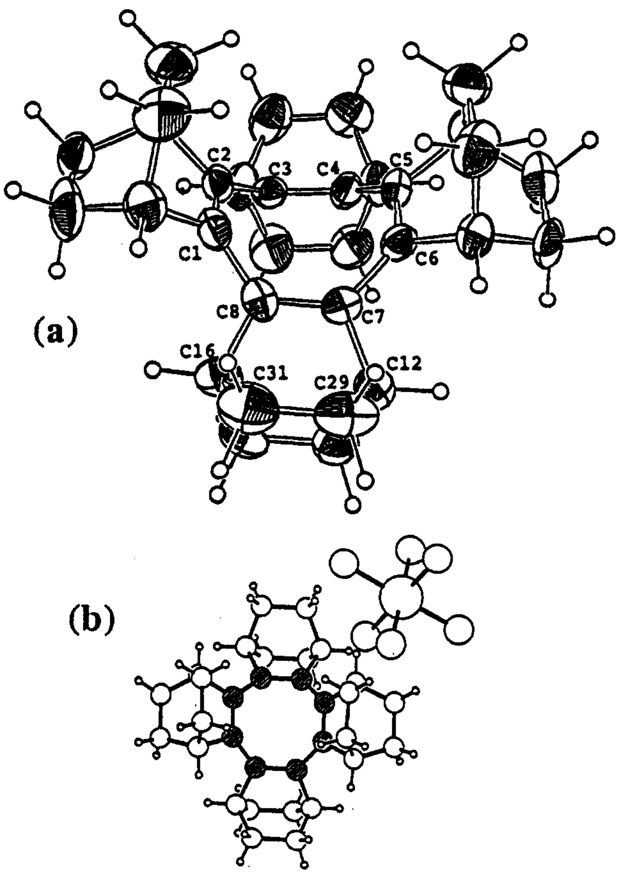

Figure 2. X-ray crystal structure: (a) ORTEP view of $\mathbf{1}^{\cdot+}$; (b) top view of $\mathbf{1}^{\cdot+}\mathrm{SbCl}_6^-$. Selected bond lengths (Å) and angles (deg): C1–C2, 1.389(10); C2–C3, 1.440(10); C3–C4, 1.356(10); C4–C5, 1.444(11); C5–C6, 1.377(10); C6–C7, 1.445(11); C7–C8, 1.338(11); C8–C1, 1.464(10); C8–C16, 1.529(10); C16–C31, 1.540(10); C29–C31, 1.537(13); C6–C7–C8, 126.1(7); C7–C8–C1, 127.9(7); C7–C8–C16, 114.1(6); C8–C7–C12, 113.8(8).

Table I. Comparison of Calculated and Observed Structural Parameters for the Neutral and Cationic COTs

species	method	bond lengths, Å	C–C–C angle, deg
COT[a]	MINDO/2	1.355, 1.473	125.3
$\mathrm{COT}^{\cdot+}$ [a]	MINDO/2	1.379, 1.442	129.9
1[b]	X-ray cryst[c]	1.339(1), 1.465(1)	126.6(1)
$\mathbf{1}^{\cdot+}$ [d]	X-ray cryst[c]	1.365(5), 1.448(5)	125.8(5)
$\mathbf{1}^{\cdot+}$ [d]	AM1	1.382, 1.425	128.0
$\mathbf{1}^{\cdot+}$ [d]	MNDO	1.410, 1.450	126.6

[a] Reference 4. [b] Reference 5. [c] Esd's of mean values in parentheses. [d] This work.

angles of the central COT ring are given in Table I together with some calculated values for COT, $\mathrm{COT}^{\cdot+}$, and $\mathbf{1}^{\cdot+}$. The results of X-ray crystallography indicated that the central eight-membered ring of $\mathbf{1}^{\cdot+}$ is in a tub form, which is different only in bond lengths from that in the neutral **1**.[5]

As to the cation radical of the parent COT, earlier theoretical calculations by MINDO/2 predicted that the extent of bond-length alternation would be reduced as compared with neutral COT and the eight-membered ring somewhat flattened[4] (see Table I) so that the more effective π-conjugation would result. In good agreement, the X-ray structure of $\mathbf{1}^{\cdot+}\mathrm{SbCl}_6^-$ reveals elongation of the original double bond in **1** by 0.026 Å and shortening of the single bond by 0.017 Å. The bond angle of $\mathbf{1}^{\cdot+}$, however, does not change very much, presumably due to the nonbonded interaction between the bridgehead hydrogens of the surrounding bicycloalkene framework, which would prevent the central ring from flattening. These results were qualitatively reproduced also by AM1 and MNDO calculations as shown in Table I.

The dark green salt of $\mathbf{1}^{\cdot+}\mathrm{SbCl}_6^-$ exhibits essentially the same electronic spectrum in the solid state ($\lambda_{\max}$ (KBr pellet) 745 and 475 nm) and in solution ($\lambda_{\max}$ ($\mathrm{CH_2Cl_2}$) 745 (log ϵ 3.66) and 438 nm (3.10)), indicating no structural change in $\mathbf{1}^{\cdot+}$ between these two phases. Previously, the cation radical of the parent COT in freon matrix at −196 °C was reported to have a red color absorbing at 507 nm.[3b,c] In order to elucidate the cause of the considerable bathochromic shift in $\mathbf{1}^{\cdot+}$, the MNDO calculations of Koopmans energies were conducted for the neutral molecule at the cation geometry obtained by X-ray analysis.[12] The energy gap between the a_1 orbital (HOMO, which is SOMO in cation radical) and the degenerate e orbital (the second HOMO) and that between the a_1 and b_2 (the third HOMO) orbitals were found to be 1.62 eV (763 nm) and 2.56 eV (484 nm),[13] respectively, in good agreement with the observed absorptions. This narrowing of energy gaps could be qualitatively interpreted by relative destabilization of lower orbitals (e and b_2) in $\mathbf{1}^{\cdot+}$,[3c] in which flattening of the COT ring is prohibited for steric reasons, as compared with the parent $\mathrm{COT}^{\cdot+}$, which is predicted to be more flattened.

In summary, we have succeeded in the first isolation and X-ray structure determination of the cation radical salt of a COT derivative $\mathbf{1}^{\cdot+}$, and we have experimentally proved the previous prediction for the structure of the COT cation radical. The remarkable stability of $\mathbf{1}^{\cdot+}$ is ascribed to the full annelation of the COT ring with a rigid bicycloalkene framework. Attempts are now in progress for further oxidation of $\mathbf{1}^{\cdot+}$ to generate the 6π-aromatic dication $\mathbf{1}^{+2}$.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen positions and numbering scheme of $\mathbf{1}^{\cdot+}\mathrm{SbCl}_6^-$ (9 pages); listing of observed and calculated structure factors (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) The MNDO calculation of the neutral molecule at the AM1 optimized cation geometry gave 1.77 and 2.66 eV (701 and 465 nm), while that for the MNDO optimized geometry afforded 1.47 and 2.22 eV (845 and 465 nm).