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Formation of a Novel Arenium Ion from the Radical Cation of a Twisted Triphenylene Fully Annelated with Bicyclo[2.2.2]octene Units

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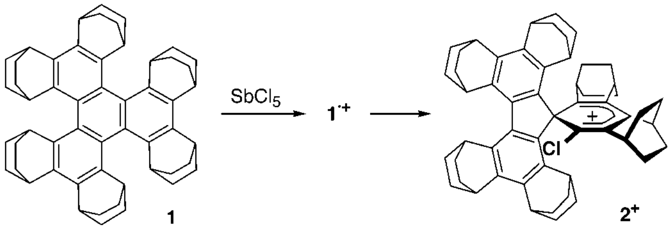
ABSTRACT



Triphenylene 1 was synthesized by palladium-catalyzed cyclotrimerization of a benzyne annelated with two bicyclo[2.2.2]octene (BCO) units. Theoretical calculations indicated that 1 is constrained to a twisted conformation with a C_2 symmetry as a result of steric repulsion between the BCO units. The one-electron oxidation of 1 with $SbCl_5$ gave the corresponding radical cation $1^{•+}$, which abstracted a chlorine atom in the medium with the concomitant rearrangement to form novel arenium ion 2^+.

Since the discovery of fullerenes, increasing attention has been paid to the polycyclic aromatic hydrocarbons (PAHs) with curved π-systems.[1] Because one of the most intensively investigated properties of fullerenes is their ionic states,[2] ions of curved PAHs are also studied in order to compare their properties with those of the fullerenyl ions. Although there has been extensive study of the anionic species of curved PAHs[1] as well as those of fullerenes,[2] less attention has been paid to the cationic species because of their intrinsic instability. Previously, we prepared various cyclic π-conjugated systems annelated with bicyclo[2.2.2]octene (BCO) units, which have been found to be quite effective for the stabilization of cationic species[3] including radical cations.[4] In the course of these studies, reports on the synthesis of highly twisted triphenylene derivatives appeared.[5−7] Such studies motivated us to prepare triphenylene derivative **1**, the π-system of which was also expected to be highly twisted as a result of steric repulsion between the BCO units. In this paper, we report the synthesis and properties of triphenylene **1** and its radical cation $\mathbf{1}^{•+}$, which was found to

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[1] (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (b) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

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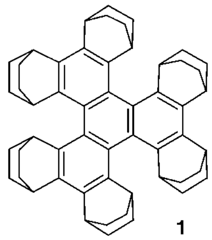
undergo a novel rearrangement to form arenium ion $\mathbf{2}^+$ having a spiro connection with a fluorene moiety.



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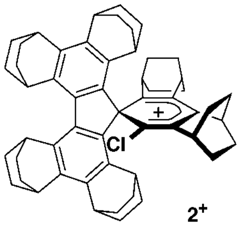
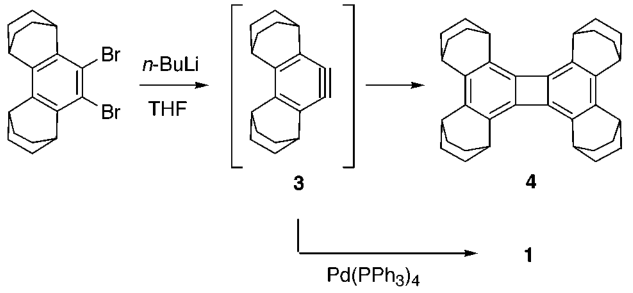


2⁺

In our previous study, BCO-annelated benzyne **3**, generated from the corresponding *o*-dibromobenzene by the treatment with *n*-BuLi in THF at −78 °C, was shown to give biphenylene **4**.[8] However, in the presence of $Pd(PPh_3)_4$ as a catalyst,[5] the cyclotrimerization of **3** took place, instead of cyclodimerization, to give triphenylene **1** in a 9% yield (Scheme 1).

Scheme 1



The severe steric congestion between the BCO units surrounding the triphenylene π-system in **1** is expected to cause twisting of the π-system, and the degree of twisting is quite intriguing. However, despite repeated attempts, no single crystal suitable for X-ray structural analysis has thus far been obtained. Therefore, the geometry optimization of **1** was performed by theoretical calculations using AM1, HF/3-21G, HF/6-31G(d), and B3LYP/6-31G(d) methods.[9] For twisted triphenylenes possessing symmetrical substitution patterns, both of two possible conformers with C_2 and D_3 symmetries have been observed in the X-ray structures.[6,7,10]

Table 1. Calculated Energy Differences between C_2 and D_3 Conformers and End-to-End Twist Angle[a] of C_2 Conformer of **1**

method	$\Delta E(D_3 - C_2)$ (kcal/mol)	end-to-end twist (deg)
AM1	3.6[b]	64.3
HF/3-21G	11.9	61.5
HF/6-31G(d)	8.8	62.6
B3LYP/6-31(d)	*c*	61.0

[a] The angle between C2−C3 and C8a−C9a bonds. See Figure 1 for the numbering. [b] The difference of the calculated heats of formation. [c] The optimization for the D_3 conformer was not completed.

In the reported examples, perfluoro-,[10] perchloro-,[6a,b] and peraryloxy-triphenylenes[7] showed C_2 structures, whereas only the hexabenzo derivative[6c] preferred a D_3 conformation. These results were well reproduced by AM1 and HF/3-21G calculations,[5c,6] demonstrating the reliability of these calculations. The calculated results for triphenylene **1** are shown in Table 1 and Figure 1. From the comparison of the calculated energies shown in Table 1, the C_2 conformer was found to be more stable than the D_3 conformer,[11] and even in the case of the optimized structure with the C_2 conformation, a highly twisted structure is apparent as shown in Figure 1. Thus, the end-to-end twist[12] of **1** (Table 1) is rather comparable to that of the perchloro derivatives (57°).[6a,b]

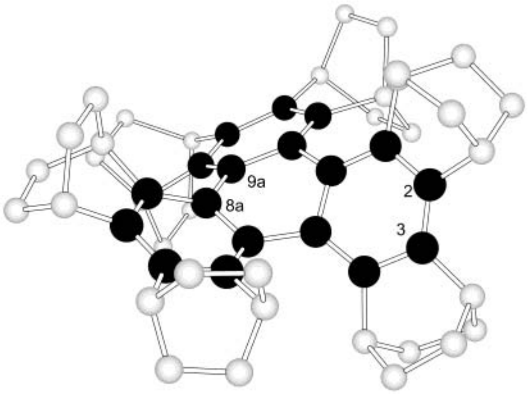


Figure 1. The optimized structure of **1** with C_2 conformation at the HF/6-31G(d) level. Hydrogen atoms are omitted for clarity.

As shown in Figure 2, the cyclic voltammetry (CV) of **1** measured in CH_2Cl_2 exhibited a reversible one-electron oxidation wave at $E_{1/2}$ +0.44 V vs Fc/Fc$^+$, which is remarkably lower than the oxidation potential of the irreversible CV peak for unsubstituted triphenylene measured in benzonitrile (E_{pa} +1.50 V). This is apparently due to the intrinsic electronic effects of annelation with BCO units,

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(11) The HF calculations tend to overestimate the energy difference; see ref 5c.

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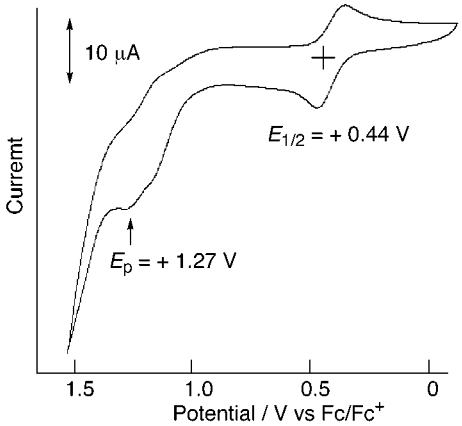

Figure 2. Cyclic voltammogram of **1** in CH_2Cl_2 with $Bu_4N^+ClO_4^-$ as a supporting electrolyte (0.1 M); scan rate 100 mV/sec.

which can raise the HOMO level of the π-system through the inductive electron donation and $\sigma-\pi$ interaction.[3,4] Moreover, the large deviation from planarity would cause additional elevation of the HOMO level in **1**. These assumptions are supported by the HF/6-31G(d) calculations as follows. The calculated HOMO level of **1** (−6.73 eV) was 0.81 eV higher than that of the corresponding twisted π-system in **1** (−7.54 eV) with all of the BCO groups replaced by hydrogens, and it (i.e., the HOMO of the twisted π-system) was still 0.16 eV higher than that of unsubstituted planar triphenylene (−7.70 eV).

On the other hand, the reversibility of this oxidation wave indicates that the generated radical cation of **1** is sufficiently stable in the time-scale of the CV measurement (scan rate 100 mV/sec). Actually, the chemical one-electron oxidation of **1** in CH_2Cl_2 with $SbCl_5$ (1.5 equiv) gave a dark green solution, which displayed an intense and broad single-line signal in the ESR measurement at room temperature (g = 2.003). The yield of this radical species was almost quantitative, judging from the comparison of the integrated peak intensity with that of the previously isolated persistent radical cation salts.[4c] When the oxidation reaction of **1** with $SbCl_5$ was conducted in less polar solvents such as CS_2 and hexane, a dark green solid was formed, which also exhibited an ESR signal. This was considered to be the radical cation salt $\mathbf{1}^{\bullet+}SbCl_6^-$, since it was reduced with $Et_4N^+I^-$ in CS_2 to reproduce **1** almost quantitatively. The theoretical calculations (B3LYP/6-31G(d)) predicted that a C_2 structure of $\mathbf{1}^{\bullet+}$ is also more stable than the D_3 structure by 5.9 kcal/mol and that the end-to-end twist angle is 66.4°.

However, when a solution of $\mathbf{1}^{\bullet+}SbCl_6^-$ in CH_2Cl_2 was allowed to stand at room temperature, the green color of $\mathbf{1}^{\bullet+}$ gradually changed to purple as the intensity of the ESR signal decreased, with a half-life of ca. 2 h, thus suggesting the formation of a new closed-shell species. A slow diffusion of hexane into the resulting purple solution in CH_2Cl_2 afforded purple-colored single crystals. The X-ray crystallographic analysis[13] revealed the newly formed product to be the arenium-ion salt $\mathbf{2}^+SbCl_6^-$ possessing a spiro connection with the bicycloannelated fluorene moiety (Figure 3). The presence of a chlorine atom in $\mathbf{2}^+$ was confirmed by FAB-MS spectroscopy (m/z 743 (M^+)), and the arenium-ion character was apparent in the ^{13}C NMR spectrum, which demonstrated three signals for cationic carbons at δ 212.9, 187.6, and 173.6 ppm. The salt, $\mathbf{2}^+SbCl_6^-$, was obtained almost quantitatively from **1**, and it was stable as a solid at room temperature in an inert atmosphere and could be stored as a CH_2Cl_2 solution for several months without apparent decomposition. This stability[16] can be ascribed to the effects of annelation with the two BCO units[3] and also to the spiroconjugation effect of the fluorenyl unit.[17]

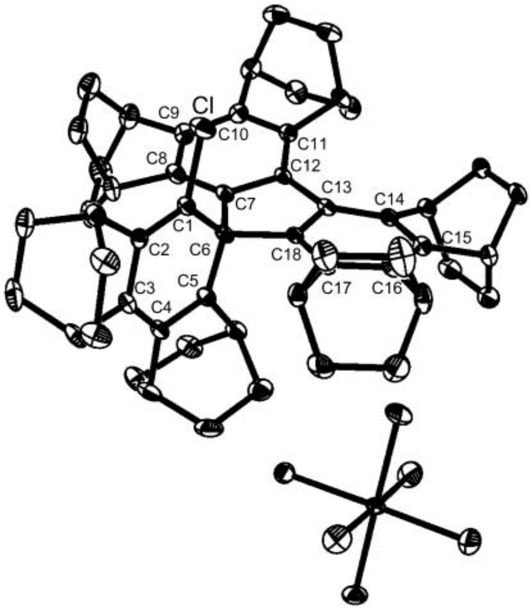

Figure 3. ORTEP drawing of $\mathbf{2}^+SbCl_6^-$. A disordered solvent molecule was eliminated with SQUEEZE[14] processed with the program implemented in PLATON-96.[15] Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are 1.363(4) (C1−C2), 1.432(5) (C2−C3), 1.394(5) (C3−C4), 1.388(4) (C4−C5), 1.475(5) (C5−C6), 1.489(5) (C1−C6), 1.705(4) (C1−Cl), 1.545(5) (C6−C7), 1.555(5) (C6−C18), 100.3(3)° (C7−C6−C18).

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(13) Crystal data for $\mathbf{2}^+SbCl_6^-$: $C_{54}H_{60}Cl_7Sb$, FW = 1078.92, triclinic; space group P-1; a =12.8788(12) Å, b = 14.5910(14) Å, c = 15.2880(15) Å, α = 99.849 (2)°, β = 94.577 (2)°, γ = 112.193 (2)°, V = 2587.8(4) Å^3, Z = 2, D_{calc} = 1.385 Mg/m^3. Intensity data were collected at 123 K on a Bruker SMART APEX diffractometer with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 25655 reflections were measured, and 13115 were independent. The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares on F^2 (SHELXL-93). The presence of a disordered solvent molecule in the lattice was evident, and the SQUEEZE[14] data processed with the program implemented in PLATON-96[15] were used for the further refinement. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located by calculation; the refinement converged to R_1 = 0.0598, wR_2 = 0.1270 ($I > 2\sigma(I)$), and GOF = 1.006.

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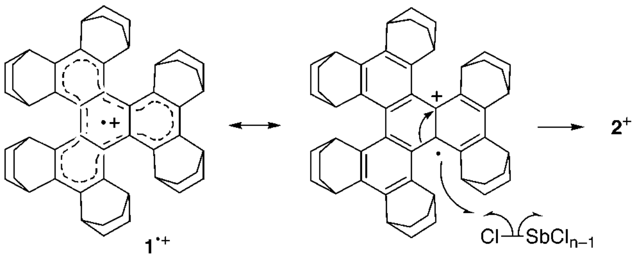
(16) As to the rare example of X-ray crystal structures of arenium-ion salts, see: Rathore, R.; Hecht J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13278−13279.

The transformation of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{+}$ involves an abstraction of a chlorine atom and contraction of the central six-membered ring. The source of the chlorine atom in $\mathbf{2}^{+}$ is considered to be $SbCl_6^-$, or a related species such as $SbCl_3$ or $SbCl_5$, and not to be CH_2Cl_2 because $\mathbf{2}^{+}$ was not detected by FAB-MS spectroscopy when $\mathbf{1}^{\bullet+}$ was generated by one-electron oxidation of **1** with $NO^+SbF_6^-$ in CH_2Cl_2. In general, $SbCl_5-CH_2Cl_2$ is a widely used medium for the one-electron oxidation of PAHs[4a,18] and a chlorine abstraction by a PAH radical cation is rather unusual. On the other hand, the ring contraction of the central six-membered ring of $\mathbf{1}^{\bullet+}$ to form a σ-radical cation is a highly endothermic process according to the B3LYP/6-31G(d) calculations ($\Delta E = +42.9$ kcal/mol). Thus, we assume that the abstraction of a chlorine atom and the ring contraction take place in a concerted manner, as shown in Scheme 2. Apparently, the release of strain in $\mathbf{1}^{\bullet+}$ upon transformation into $\mathbf{2}^{+}$ is the most important driving force of this unusual reaction.

In summary, we described the synthesis and properties of highly strained triphenylene **1** and its radical cation $\mathbf{1}^{\bullet+}$, both of which possess a twisted π-system with a C_2 symmetry according to the theoretical calculations. The radical cation salt $\mathbf{1}^{\bullet+}SbCl_6^-$ was generated almost quantitatively with $SbCl_5$ in CH_2Cl_2, but it readily abstracted a chlorine atom from either one of antimony chloride species with a concomitant rearrangement to quantitatively produce the novel arenium-ion salt $\mathbf{2}^{+}SbCl_6^-$, the precise structure of which was determined by X-ray crystallography. The stability of this arenium ion is ascribed to the $\sigma-\pi$ interaction with the bicyclic frameworks, as well as to the spiro-conjugation with the fluorenyl moiety.

Scheme 2



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Supporting Information Available: Detailed experimental procedures with ^{1}H and ^{13}C NMR spectra of **1** and $\mathbf{2}^{+}$, ESR spectrum of $\mathbf{1}^{\bullet+}$, FAB-MS spectra of $\mathbf{2}^{+}$, and CIF data of $\mathbf{2}^{+}SbCl_6^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The theoretical calculations (B3LYP/6-31G(d)) indicated that the coefficients of HOMO and LUMO were delocalized in both fluorene and arenium-ion moieties in $\mathbf{2}^{+}$.

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