A Novel Carbodication Composed of Two Tris(bicyclo[2.2.2]octeno)tropylium Units Connected by a Triple Bond: Synthesis, Structure, and Properties

Akifumi Kagayama,[1a] Koichi Komatsu,*,[1a] Tohru Nishinaga,[1a] Ken'ichi Takeuchi,[1b] and Chizuko Kabuto[1c]

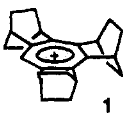
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, and Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980, Japan

Received February 28, 1994[⊗]

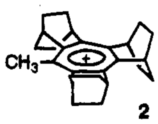
The titled dication, bis[tris(bicyclo[2.2.2]octeno)tropyliumyl]acetylene dication **3**, which is the first example of the acetylene having two tropylium ion units at both ends, has been synthesized by stepwise introduction of the tris(bicyclo[2.2.2]octeno)cycloheptatrienyl unit to acetylene followed by hydride abstraction. The results of X-ray crystallography indicated that the two tropylium rings are twisted with each other by the angle of 44° and the tropylium ring is slightly bent into a boat form. The dication **3** was neutralized in 50% aqueous acetonitrile via two steps at the pH values of 7.0 and 11.5, which correspond to the pK_{R^+} values of the dication and the half-neutralized monocation, respectively. Thus, the dication **3** is 6 pK_{R^+} units destabilized compared with the corresponding monocation (pK_{R^+} 13.0) due to the intramolecular electrostatic repulsion of the positive charge. The cyclic voltammetry indicated that the dication **3** undergoes two reversible one-electron reductions consecutively in dichloromethane. The electrochemical reduction of **3** as well as chemical reduction with zinc powder in dichloromethane–acetonitrile afforded a blue solution of the corresponding cation radical $\mathbf{3}^{\bullet+}$, but not the diradical, as shown by ESR experiments.

Introduction

The tropylium ion triannelated with bicyclo[2.2.2]octene framework, **1**, was found to exhibit remarkably high thermodynamic stability (pK_{R^+} 13.0) due to both inductive and σ-conjugative effects of the rigid σ-frameworks.[2] However, effects of the substituent at the 7-position have not been examined except for the 7-methyl derivative **2**: the 7-methyl substituent in **2** was found to destabilize the cation by 0.6 pK_{R^+} unit[2] in spite of its electron-donating ability. This destabilization was attributed to the possible distortion of the tropylium ring from planarity due to severe steric congestion generated between the methyl group and bridgehead hydrogens.



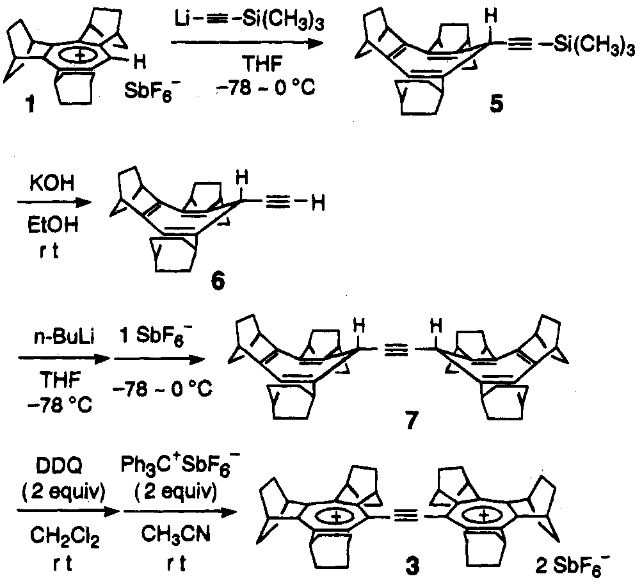
1

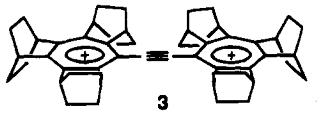


2

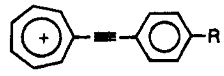
On the basis of these results, we have designed the dication **3** having two units of monocation **1** at both sides of acetylene, for which we could expect the effects of π-conjugative interaction without much steric congestion. As to the parent tropylium ion substituted with an ethynyl group, the arylethynyl derivatives **4** are known,[3] but there has been no report on the dication with two tropylium units at both sides of acetylene. Here we report the synthesis of the dication **3** as the first example of such dications, together with its structural, thermodynamic, and electrochemical properties.

Scheme 1





3



4 (R = H, OCH_3)

Results and Discussion

Synthesis. Synthesis of the dication **3** was carried out as shown in Scheme 1. Reaction of the cation **1** with

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) (a) Institute for Chemical Research, Kyoto University. (b) Kyoto University. (c) Tohoku University.

(2) (a) Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633–634. (b) Komatsu, K.; Akamatsu, H.; Aonuma, S.; Jinbu, Y.; Maekawa, N.; Takeuchi, K. *Tetrahedron* **1991**, *47*, 6951–6996.

(3) Jutz, C.; Voithenleitner, F. *Chem. Ber.* **1964**, *97*, 1337–1348.

Table 1. Spectral Data for the SbF_6^- Salts of 3 and 1

	^1H NMR δ/ppm (CD_3CN, 270 MHz)			^{13}C NMR δ/ppm (CD_3CN, 67.8 MHz)				IR ν/cm^{-1} (KBr)			UV−vis λ_{max}/nm (log ε) (CH_3CN)
compd	$\cdots CH \cdots^+$	CH	CH_2	$\cdots CH \cdots^+$	≡C−	CH	CH_2				
3·$2SbF_6^-$		4.46	2.07	167.8	104.7	40.9	24.7[a]	2947	2871	1617	282 (4.83)
		(4 H)	(24 H)	166.9		36.9		1457	1455	1365	386 (4.39)
		4.09	1.51	164.0		36.7		1327	1276	1172	
		(8H)	(24 H)	135.6				1139	1029	815	
								657			
1·SbF_6^{-b}	8.55	4.13	2.03	168.3		42.7	25.0	2951	2873	1625	256 (4.71)
	(1 H)	(2 H)	(12 H)	166.0		36.6	24.8	1458	1420	1320	308 (4.01)
		4.07	1.43	163.9		36.1	24.7	1270	1245	1173	
		(2 H)	(12 H)	144.2				1040	1025	814	
		3.56						658			
		(2 H)									

[a] Three signals are supposedly overlapping as judged from the signal intensity. [b] Data from ref 2.

[(trimethylsilyl)ethynyl]lithium followed by desilylation afforded the ethynylcycloheptatriene **6** in 50% yield. Lithiation of **6** and repeated reaction with **1** gave the dicycloheptatrienylacetylene **7** in 41% yield. Direct hydride abstraction from **7** using a trityl salt resulted in formation of the dication **3** in <32% yield accompanied by serious contamination with unremovable impurity. However, the hydride abstraction by the use of 2 equiv of dichlorodicyano-*p*-benzoquinone (DDQ) and anion exchange with trityl hexafluoroantimonate yielded the desired dication salt, **3**·$2SbF_6^-$, in 59% yield as yellow needles, which are analytically pure and stable under air.

Spectral Properties. The dication **3** was fully characterized by the spectral data shown in Table 1. Also shown are those of the monocation **1** for comparison.

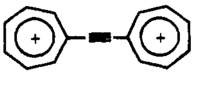
The ^1H NMR chemical shifts of **3** are generally similar to those of **1** except for a signal for one of the bridgehead protons, which extends over in front of the triple bond and is thus deshielded by 0.37 ppm compared with the rest of bridgehead protons. The presence of a triple bond is evidenced by the ^{13}C NMR signal at δ 104.7 ppm. In the electronic spectrum the longest wavelength absorption exhibits a bathochromic shift by about 80 nm as compared with **1**, indicating the π-conjugative effect between the two tropylium units and the acetylenic π-systems.[4]

Structure. It is of particular interest to examine the relative geometry of the two π-systems conjugatively connected to both sides of a triple bond. When we assume that a π-system is conjugated with only one set of p-orbitals of the triple bond, the two π-systems would take the conformation either coplanar or perpendicular to each other. On the other hand, there might not be any specifically favored orientation for the two π-systems if the cylindrically symmetric structure of the π-clouds is considered more significantly for the triple bond.

In the case of diphenylacetylene, MO calculations using CNDO (or INDO) indicated that the energy difference between the coplanar and the perpendicular geometries is negligibly small, i.e., 0.7 kcal/mol (or 0.4 kcal/mol), with the perpendicular geometry being slightly more stable;[5] however, the experimental results from X-ray crystallography and UV spectroscopy on diphenylacetylene and from measurement of dipole moment of bis(3-chlorophenyl)acetylene all indicated that the two benzene rings are in a coplanar geometry both in solid state and in solution.[5]

Thus, we carried out the X-ray crystallography on a single crystal of **3**·$2SbF_6^-$. Unfortunately, the small size of the crystal and disorder in SbF_6^- anion prevented us from obtaining a sufficiently low *R* factor to allow detailed discussion on the precise structure ($R = 0.117$). Also, it was found that two benzene molecules (from recrystallization solvent) were contained in the crystal of **3**·$2SbF_6^-$. However, the discussion on general structural features of the whole molecule could be made safely. The observed structure is shown in Figure 1. It reveals that the two seven-membered rings are rotated with each other with the dihedral angle of the mean planes being 44°.

We also conducted semiempirical MO calculations (AM1) for ditropyliumylacetylene dication (**9**) as a simplified model. The results indicated that as the dihedral angle between the two seven-membered rings changes from 0° (coplanar) to 90° (perpendicular) the heat of formation exhibits a very slight decrease in a monotonous way, the energy difference between the coplanar and the perpendicular models being quite minute (0.15 kcal/mol). Thus, there seems to be almost no energy barrier for ring rotation in **9**. The experimentally observed geometry of the two π-systems in **3** could be considered as the result of a compromise between the conjugative stabilization in a coplanar geometry and the repulsive interaction between the two cationic moieties in which the positive charge is delocalized by the σ-π interaction.[2] Also, the steric repulsion between the bridgehead hydrogens of the two tropylium units opposite to each other (marked as H_{opp} in Figure 2; see below) may be contributing.

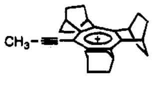


9

Another structural feature to be noticed in the X-ray structure of **3** is that the tropylium ring is not planar but somewhat folded to a boat form as shown in Figure 1c. This unexpected feature is presumably due to steric congestion caused by surrounding bicyclic frameworks, though such effect should be smaller than that in the methyl derivative **2**.[6]

---

[4] In comparison, the propyn-1-yltropylium derivative **8** exihibited the longest-wavelength absorption in acetonitrile at λ_{max} 348 nm (log ε 3.99), which is in between those of **3** and **1**: Kagayama, A.; Komatsu, K. Unpublished results.



8

[5] Liberles, A.; Matlosz, B. *J. Org. Chem.* **1971**, *36*, 2710−2713.

[6] In this connection it is desirable to have the X-ray crystal structures of the monocations **1** and **2**. However, we have not succeeded in obtaining single crystals of the salts of these cations.

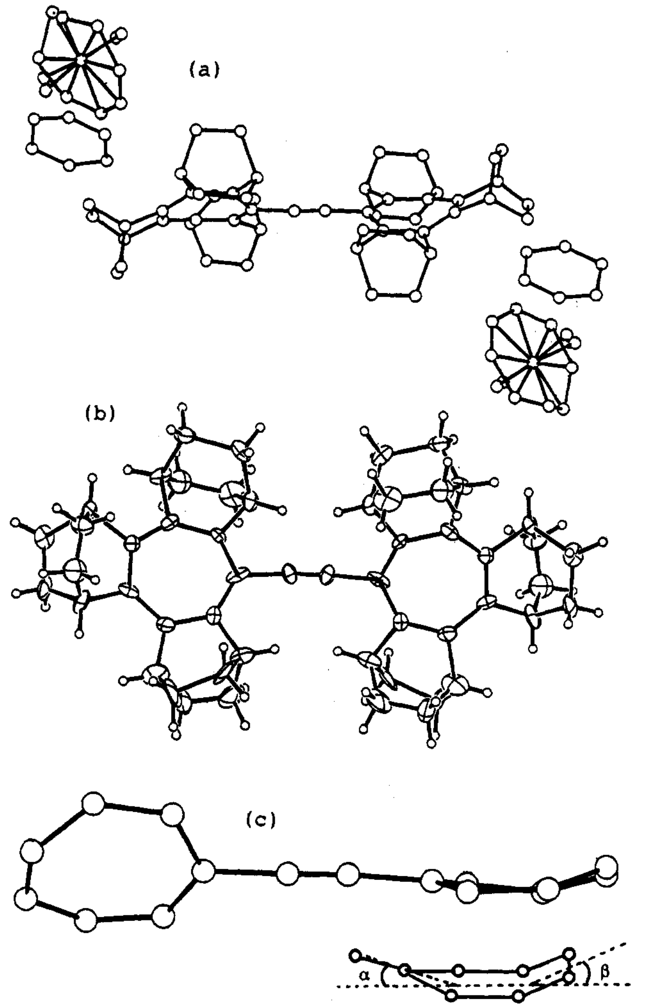


Figure 1. X-ray crystal structures. (a) The structure of $3{\cdot}2SbF_6^-{\cdot}2C_6H_6$: the six F atoms in the SbF_6^- anion could not be precisely located due to the disorder and are represented by 12 atoms; hydrogen atoms are deleted for clarity. (b) Top view of the dication **3**. (c) Side view of the central ditropyliumylacetylene framework: the dihedral angle between the bow and the central portion (α) is 10.9° and the angle between the stern and the central portion (β) is 18.7°.

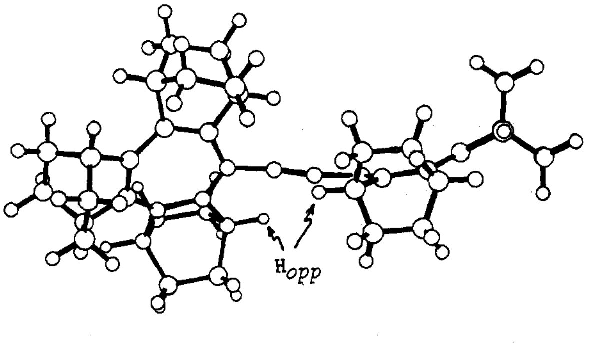


Figure 2. AM1-calculated structure of the dication **3**.

The AM1 calculations conducted for the optimized structure of **3** gave a result quite similar to the X-ray structure as shown in Figure 2 with the twisting angle between the two tropylium units being 53°.

Thermodynamic Stability. In order to examine the thermodynamic stability of the dication having such characteristic π-conjugation, the pK_{R^+} value of **3** was measured by spectrophotometric titration in 50% aqueous acetonitrile. The hydrolysis was found to occur via two steps as shown in Figure 3.

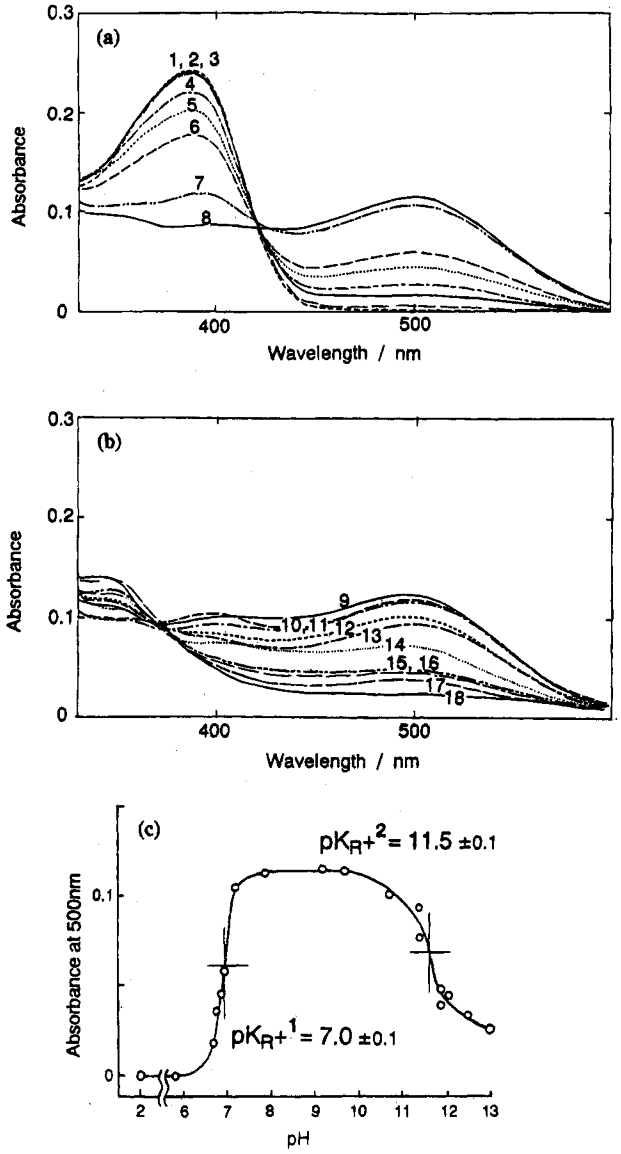
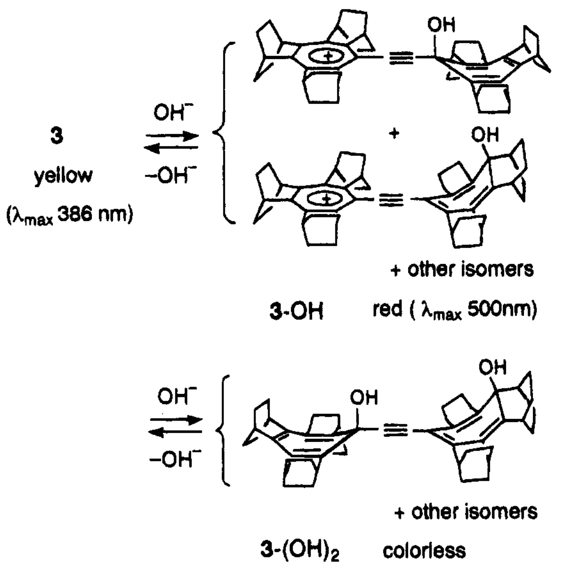


Figure 3. pK_{R^+} measurement of $3{\cdot}2SbF_6^-$ (9×10^{-6} M) in 50% aqueous acetonitrile. (a, b) Dependence of the UV–vis spectra upon pH (a: spectrum 1, pH 2.2; 2, 5.4; 3, 6.6; 4, 6.7; 5, 6.8; 6, 6.9; 7, 7.2; 8, 7.4; b: spectrum 9, pH 7.9; 10, 9.2; 11, 9.7; 12, 10.7; 13, 11.3; 14, 11.4; 15, 11.9; 16, 12.1; 17, 12.4; 18, 13.0). (c) Plot of the absorbance at 500 nm against pH.

As the pH value of the solution was increased from 2 to 8, the color of the solution changed from yellow to red and the UV–vis spectrum exhibited a decrease in absorption at 386 nm with a concomitant appearance of new absorption at 500 nm. As the pH was increased further, the red color faded and was gone at pH values larger than 12. These color changes corresponding to the change in pH were completely reversible.

From the plot of the absorbance at 500 nm against pH (Figure 3c), the pK_{R^+} values of the original dication **3** and the half-neutralized monocation were determined as 7.0 ± 0.1 and 11.5 ± 0.1, respectively. Compared with the cations **1** (pK_{R^+} 13.0)[2] and **2** (pK_{R^+} 12.4),[2] the stability of dication **3** is lowered by 5–6 pK_{R^+} units, while that of the monocation is not so much different from that of **2**. Apparently, the destabilization of **3** is ascribed to the electrostatic repulsion between the two positively charged units. Upon neutralization, there appear to be formed isomeric mixtures of monocationic alcohols **3**-OH and then the diols **3**-$(OH)_2$. From the considerable batho-

Scheme 2



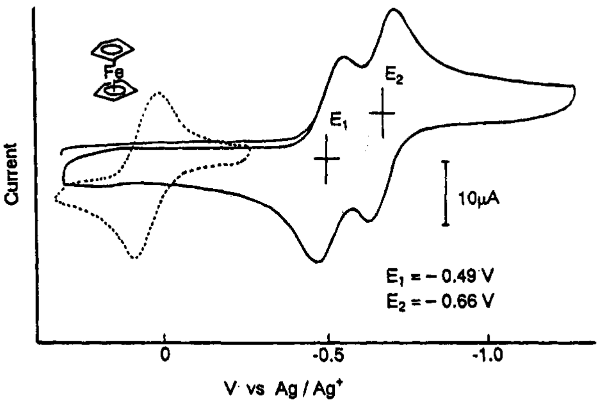


Figure 4. Cyclic voltammogram of $3{\cdot}2SbF_6^-$ in dichloromethane: sample, 0.3 mM; supporting electrolyte, tetrabutylammonium perchlorate (0.1 M); scan rate, 100 mV/s. (Dotted line is the voltammogram of ferrocene added as an internal standard after the measurement.)

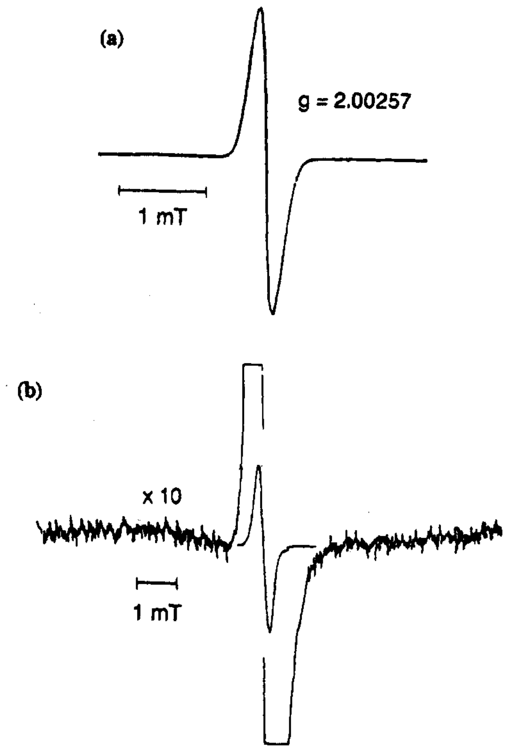


Figure 5. ESR spectra of the cation radical $3^{\cdot+}$ generated by electrolysis in dichloromethane recorded at (a) room temperature and (b) at −120 °C.

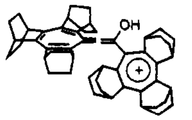
chromic shift of the visible absorption of the half-neutralized monocation (λ_{max} 500 nm), it is supposed that, upon the first neutralization, the hydroxide ion attacks not only the ethynyl-substituted carbon but also the other carbons of the tropylium ring to give the monocation with extended π-conjugation as shown in Scheme 2.[7]

Red–Ox Behavior. In contrast to the cations **1** and **2**, which were reduced irreversibly upon cyclic voltammetry (CV),[2] the dication **3** exhibited two reversible reduction waves at −0.49 and −0.66 V vs Ag/Ag⁺ as shown in Figure 4, with the first reduction potential lower than the monocation **1** by 0.6 V upon comparison of the peak potentials. Thus, the dication **3** is supposed to give consecutively the cation radical and the neutral species both of which can persist in solution.

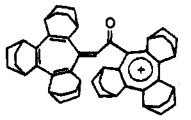
When the ESR spectrum was measured under the electrolytic conditions with the potential changed stepwise by 0.1 V from −0.1 to −1.0 V vs Ag/Ag⁺, a strong single-line signal with a peak-to-peak width of 0.3 mT, shown in Figure 5a, began to appear at the potential of −0.4 V and kept almost the same intensity over the potential ranging to −1.0 V. The feature of this signal[8] remained the same at the whole potential range and the signal persisted at room temperature under argon atmosphere for at least 15 min after the cathodic current was cut off. During the electrolysis, the color of the solution in a region close to the working electrode turned to dark blue. Even after the exhaustive reduction with the potential over −1.0 V, there was observed no sign for generation of a triplet diradical, such as a $\Delta m = 2$ signal at the half-field (~160 mT) or any fine structure for the sample solution frozen to a glass at −120 °C (Figure 5b). From these results, the single-line signal is considered as due to the cation radical $3^{\cdot+}$. The two-electron reduced product appears to form a closed-shell molecule although no spectral study could be made because of its extreme instability.

---

[7] One reviewer suggested that the first neutralization might cause the hydroxide-ion attack at the ethynyl carbon to give a tautomeric mixture of monocations A and B, which might also explain the considerable bathochromic shift. However, the completely neutralized species formed by further neutralization of A and/or B should still maintain a heptafulvene-type partial structure and should be colored on the basis of the yellow color observed for the corresponding heptafulvene derivative: Aonuma, S.; Komatsu, K.; Maekawa, N.; Takeuchi, K. *Chem. Lett.* **1991**, 767. This is against our present experimental observation.



A



B

On the other hand, one might argue that some isomers of the completely neutralized form 3-(OH)₂ in Scheme 2 should also be colored now that the π-conjugated monocation 3-OH is red. We consider that the coloration in 3-OH arises from the intramolecular charge-transfer-type interaction, that is, the transition from HOMO localized at the ethynylcycloheptatriene moiety to considedrably low LUMO localized at the tropylium ring. In contrast, the fully neutralized species 3-(OH)₂ are simply composed of two cycloheptatriene rings connected by an acetylenic bond, and the π–π* transition band is not necessarily in the visible range.

[8] Even by all the efforts such as application of lower modulation width and/or lowering the concentration, no hyperfine structure was observed probably due to too many small couplings with the interacting protons present in the bicyclic frameworks.

The dication **3** was also chemically reduced by zinc powder in dichloromethane−acetonitrile (9:1) to generate a dark blue solution, which exhibited the ESR signal identical to that in Figure 5a and the electronic absorption at λ_{max} 597 nm.[9] This solution also did not show any evidence for a triplet diradical by the same ESR experiment as described above. Although the cation radical $\mathbf{3}^{\cdot+}$ was stable in solution, it seemed to decompose by evaporation of the solvent under high vacuum since no blue color was regenerated by dissolution of the residue in the same solvent transferred by vacuum distillation.

In an attempt to obtain more information about the structure of the fully reduced product, the reaction of **3** with zinc powder was conducted in acetonitrile−THF (1:1).[10] In our previous work, zinc powder in acetonitrile was shown to reduce *tert*-butyltropylium ion,[11a] which has the reduction potential[11b] about 0.1 V higher than that for the second reduction step for the dication **3**. The color of the solution changed to dark blue and then to red with formation of dark red precipitates suggesting the formation of new species, possibly the fully reduced one. This red material did not show any ESR signal, but the definite determination of its structure was hampered by its ready decomposition or polymerization as deduced from its weak and broad ^{13}C NMR spectrum.

Thus, the solvent polarity was found to strongly affect the reduction pathway of the dication **3**. Studies on the one- and two-electron reduction processes for the similar dications having a *p*- or *m*-phenylene spacer instead of a triple bond are now under way and will be reported in a forthcoming paper.

Experimental Section

General Procedures. Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Elemental analysis was performed by the Microanalytical Center, Kyoto University, Kyoto. NMR spectra were recorded on JEOL GSX270 (270 MHz for ^1H and 67.8 MHz for ^{13}C NMR) or on JEOL FX90 (90 MHz for ^1H) spectrometers using Me_4Si as an internal standard. IR spectra were taken on a Perkin-Elmer 1640 spectrometer. UV−vis spectra were taken on a Hitachi 200-10 spectrometer. ESR spectra were recorded on JEOL PE-2X or on JES-SRE2X spectrometer. The mass spectrum was taken on a JEOL JMS-SG spectrometer. Cyclic voltammograms were obtained by the use of a Hokuto-Denko HA104 potentiostat, a HB107A function generator, a Hitachi 057 X-Y recorder, and a three-electrode cell composed of platinum wire working and counter electrodes and a Ag/0.01 M $AgNO_3$ (acetonitrile) reference electrode. The observed potential was corrected with reference to ferrocene ($E_{1/2}$ +0.083 V) added as an internal standard after each measurement. A Sartorius 4503MP6 microbalance was employed for weighing samples less than 1 mg.

THF was freshly distilled from sodium benzophenone ketyl before use. Dichloromethane and acetonitrile were refluxed and distilled over P_2O_5 under nitrogen. All reactions where anhydrous conditions were required were conducted under an atmosphere of argon or nitrogen. Medium-pressure liquid chromatography (MPLC) was carried out using silica gel 60 (E. Merk, particle size 0.040−0.063 mm, 230−400 mesh ASTM) as a stationary phase and hexane as an eluent. Commercial tetrabutylammonium perchlorate was recrystallized from hexane and ethyl acetate. 1,2:3,4:5,6-Tris(bicyclo[2.2.2]octeno)tropylium hexafluoroantimonate ($\mathbf{1}{\cdot}SbF_6^-$)[2b] and trityl hexafluoroantimonate ($Ph_3C^+SbF_6^-$)[12] were prepared following the literature procedure.

7-[(Trimethylsilyl)ethynyl]-1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (5). A solution of 1.6 M *n*-BuLi in hexane (0.19 mL, 0.30 mmol) was added dropwise to a stirred solution of (trimethylsilyl)acetylene (0.037 mL, 0.025 g, 0.26 mmol) in THF (4 mL) at −78 °C, and the resulting mixture was stirred for 1 h at −78 °C and for 0.5 h at 0 °C. Then, the mixture was cooled to −78 °C again, and a suspension of $\mathbf{1}{\cdot}SbF_6^-$ (82 mg, 0.14 mmol) in THF (3 mL) was slowly added. After being stirred for 1 h at −78 °C, the mixture was slowly warmed to room temperature over 0.5 h, evaporated under reduced pressure, and extracted with ether. The ethereal solution was evaporated to give 78 mg of a pale yellow powder, which was shown to contain about 50 mg (0.12 mmol, 81% yield) of **5** by ^1H NMR analysis. Separation of the crude product by the use of MPLC afforded **5** (33 mg, 54%) as an unstable white powder, which decomposed slowly in the solid state under vacuum and more rapidly in $CDCl_3$:[13] mp 151−162 °C dec; ^1H NMR($CDCl_3$, 270 MHz) δ 2.88 (br s, 6 H), 2.48 (s, 1 H), 1.70−1.25 (m, >24 H), 0.19 (s, 9 H); ^{13}C NMR ($CDCl_3$, 67.8 MHz)[14] δ 31.7, 31.3, 27.5, 26.6, 26.4, 26.3, 25.8, 0.3; IR (KBr) 2174 (C≡C, m) cm^{-1}.

7-Ethynyl-1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (6). The crude product from the above reaction containing 36 mg (0.086 mmol) of **5** was dissolved in 10 mL of ethanol. To this solution was added dropwise a 0.1 M solution of KOH in ethanol (12 mL) at room temperature. The solution was stirred for 3 h with occasional heating to reflux under nitrogen. The solution was evaporated under reduced pressure and extracted with ether. The ethereal solution was evaporated to give 35 mg of a pale yellow powder, which was shown to contain about 25 mg (0.071 mmol, 83% yield) of **6** by ^1H NMR analysis. Separation with MPLC afforded **6** (15 mg, 50%) as a white powder, which was as unstable as **5**: mp 92−97 °C dec; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.90, 2.88 (br s × 2, 6 H), 2.55 (d, J = 2.4 Hz, 1 H), 1.70−1.25 (m, >25 H); ^{13}C NMR ($CDCl_3$, 67.8 MHz)[14] δ 31.8, 31.3, 29.7, 26.6, 26.4, 26.2, 25.8; IR (KBr) 3320 (C≡CH, s), 2119 (C≡C, w) cm^{-1}. Anal. Calcd for $C_{27}H_{32}$: C, 90.95; H, 9.05. Found: C, 89.14; H, 9.32.[13]

Bis[2,3:4,5:6,7-tris(bicyclo[2.2.2]octeno)cycloheptatrien-1-yl]acetylene (7). To a solution of the crude product from the above reaction containing 22 mg (0.062 mmol) of **6** in THF (4 mL) was added dropwise a 1.5 M solution of *n*-BuLi in hexane (0.050 mL, 0.075 mmol) at −78 °C, and the resulting mixture was stirred for 1 h at −78 °C and for 10 min at 0 °C. Then, the mixture was cooled again to −78 °C, and a suspension of $\mathbf{1}{\cdot}SbF_6^-$ (47 mg, 0.083 mmol) in THF (3 mL) was added slowly. The mixture was stirred for 0.5 h at −78 °C and was slowly warmed to room temperature over 1 h. The solution was evaporated under reduced pressure and extracted with ether (4 mL × 4) and benzene (8 mL). The organic solution was evaporated and the residue separated by MPLC to yield 20 mg (48%) of **7** and 10 mg (45%) of unchanged **6**. The compound **7** was more stable than its precursors **5** and **6** but slowly decomposed in $CDCl_3$ solution: mp 112−113 °C dec; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.17 (br s, 4 H), 2.91 (br s, 8 H), 2.70 (s, 2 H), 1.70−1.21 (br m, >48 H); ^{13}C NMR ($CDCl_3$, 67.8 MHz)[14] δ 32.0, 31.4, 27.6, 26.7, 26.4, 25.8, 24.3; MS *m/z* 686 (M^+). Anal. Calcd for $C_{52}H_{62}$: C, 90.90; H, 9.10. Found: C, 90.10; H, 9.01.[13]

Bis[tris(bicyclo[2.2.2]octeno)tropyliumyl]acetylene Hexafluoroantimonate ($\mathbf{3}{\cdot}2SbF_6^-$). (a) A Method Using DDQ. A solution of DDQ (21 mg, 0.091 mmol) in dichlo-

---

[9] The molar extinction coefficient (ϵ) was calculated as 3.7×10^4 assuming that the cation radical $\mathbf{3}^{\cdot+}$ was formed quantitatively.

[10] THF was added so as to increase the solubility of the formed species.

[11] (a) Okamoto, K.; Komatsu, K.; Sakaguchi, O. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2431−2436. (b) The reduction peak potential for *tert*-butyltropylium ion was determined as −0.61 V vs Ag/AgNO$_3$ in acetonitrile (Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011−4024), while that for **3** was found to be −0.49 V in acetonitrile (nearly one-step, two-electron reduction).

[12] Thummel, R. P.; Chayangkoon, P. *J. Org. Chem.* **1983**, *48*, 596−601.

[13] No satisfactory elemental analysis was obtained because of the instability.

[14] Only the aliphatic CH, CH_2, and CH_3 carbons were recorded. Weaker signals for fully substituted carbons could not be observed due to the decomposition during the measurement.

romethane (2 mL) was added dropwise to a stirred solution of **7** (29 mg, 0.042 mmol) in dichloromethane (6 mL) to give a dark red solution. After being stirred for 0.5 h at room temperature, the solution was concentrated to ca. 2 mL. To this solution was added ether (15 mL) to cause the formation of black precipitates, which were collected by filtration and dried under vacuum to give 52 mg of a black powder. This product was dissolved in 15 mL of acetonitrile, and to this solution was added dropwise a solution of $Ph_3C^+SbF_6^-$ (44 mg, 0.093 mmol) in 2 mL of acetonitrile with stirring at room temperature. The resulting orange-yellow solution was evaporated and the residue redissolved in 1.5 mL of dichloromethane–acetonitrile (2:1). To this solution was added ether (15 mL) to cause the formation of yellow precipitates, which were collected by filtration and dried under vacuum to give crude **3**·2SbF$_6^-$ as a yellow powder (39 mg). Recrystallization by slow diffusion of ethyl acetate into a saturated solution of the crude product in dichloromethane yielded **3**·2SbF$_6^-$ as pale yellow needles (28 mg, 59%): mp 218–221 °C dec. The spectral data are shown in Table 1. Anal. Calcd for $C_{52}H_{60}F_{12}Sb_2$: C, 54.00; H, 5.23. Found: C, 53.75; H, 5.44. A single crystal of **3**·2SbF$_6^-$·C$_6$H$_6$ for X-ray crystallography was obtained by slow diffusion of benzene into a saturated solution of **3**·SbF$_6^-$ in dichloromethane.[15]

(b) A Direct Method Using Trityl Hexafluoroantimonate. A solution of $Ph_3C^+SbF_6^-$ (17 mg, 0.036 mmol) in dichloromethane (2 mL) was added dropwise to a stirred solution of **7** (12 mg, 0.017 mmol) in dichloromethane (5 mL) to yield a dark green solution. After being stirred for 10 min at room temperature, the solution was concentrated to ca. 1 mL. To this solution was added ether (10 mL) to cause the formation of orange precipitates, which were collected by filtration and dried under vacuum to give an orange powder (7 mg) which contained **3**·2SbF$_6^-$ as a major component and some impurity as shown by ^{1}H NMR. Recrystallization by slow diffusion of ethyl acetate into a saturated solution of the crude product in dichloromethane did not improve the purity.

X-ray Crystallography. A pale yellow crystal with small sizes of 0.07 × 0.2 × 0.5 mm, which were cut from the cracked crystals, was used for the data collection on a Rigaku automated four circle diffractometer (AFC5PR), equipped with a rotating anode (45 kV, 200 mA), using graphite-monochromated MoKα radiation ($\lambda = 0.710\ 69$ Å). Crystal data are as follows: $a = 10.760(4)$ Å, $b = 30.041(10)$ Å, $c = 19.674(6)$ Å, $V = 6360(5)$ Å^3, the space group = *Iba*2 (No. 45), Z = 4 for $C_{52}H_{60}{\cdot}2SbF_6{\cdot}2C_6H_6$, $D_{calcd} = 1.371$ g cm^{-3}, μ(MoKα) = 9.23 cm^{-1}. Low-temperature equipment was used to maintain the stability of crystal (120 K). The ω scan mode with a scan rate of 1° min^{-1} was employed with a scan range of $1.2 + 0.30\tan\theta$. A total of 3464 reflections within $2\theta = 54.7°$ were collected. Lp correction and the empirical absorption correction using the ψ-scan method were applied.

The structure was solved by direct methods combined with the heavy atom method. In an asymmetric unit, one SbF$_6^-$ anion, a half moiety of cation, and one benzene solvent molecule are included. Although F atoms were found to be disorderly, the cation molecule and benzene molecules were found in the definite positions. The full-matrix least-squares refinement gave the reasonable decrease by introducing an anisotropic temperature factor for Sb atom. However, all carbon atoms could not refined anisotropically. Finally carbon atoms of the seven-membered ring were refined anisotropically, and all hydrogens were included in the calculated positions. The final cycle of refinement was carried out using 1711 observed reflections within $I > 2\sigma(I)$ converged to the final $R = \sum||F_o| - |F_c||/\sum|F_o|$ value of 0.117 and $Rw = [(\sum_w(|F_o| - |F_c|)^2/\sum_w F_o^2)]^{1/2}$ of 0.112. The maximum and minimum peaks on the final difference Fourier map correspond to 1.09 and −2.41 e Å^{-3}, respectively. The relatively high *R* value and structural parameters of a low accuracy were caused by the poor quality and small size of the crystal as well as the disorder of the SbF$_6^-$ anion. All computations were performed using the Rigaku Texsan software package system (TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985).

The pK_{R^+} Determination. For the preparation of a sample solution, each 0.5-mL portion of the stock solution, prepared by dissolving 2 mg of **3**·2SbF$_6^-$ in acetonitrile (5 mL), was pipetted out and made up to 20 mL by adding H$_2$O (0.5 mL) and acetonitrile–H$_2$O (1:1). The sample solution with higher basicity or acidity were made by addition of 1 to 3 drops of either 0.01, 0.1, 1, and 2 N NaOH or 0.1, 1, and 3 N HCl. The UV–vis spectrum of the sample solution was recorded using a 1-cm quartz cell. Immediately after the spectrum was recorded, the pH of each sample solution was determined on a Horiba M-8S pH meter. The observed absorbance at 500 nm was plotted against pH to give a two-step titration curve, and each midpoint was taken as the pK_{R^+} value (Figure 3c).

ESR Measurement. (a) Electrolytic Reduction. An originally made electrolytic cell was used. The cell consisted of a 5-mm-o.d. Pyrex glass tube (length, 65 mm) which was connected to a 3-mm-o.d. tube (length, 40 mm) at the bottom and a 20-mm-o.d. tube (length, 40 mm) at the top. A platinum wire (diameter, 0.5 mm) reaching the bottom, which was shielded with a polyethylene tube except at the bottom part, served as a working electrode, while a coiled gold wire (diameter, 0.5 mm) placed in an upper part served as a counter electrode. A reference electrode (Ag/AgNO$_3$) was also inserted into an upper part together with a capillary polyethylene tube for the purpose of introducing an argon gas.

A solution of **3**·2SbF$_6^-$ (3.7 mg, 0.0032 mmol) in 5 mL of a 0.1 M solution of tetrabutylammonium perchlorate in dichloromethane was placed in this cell. The solution was electrolyzed after bubbling with argon for a few minutes, and then the ESR spectrum was recorded.

(b) Chemical Reduction with Zinc Powder. A 9-mm-o.d. Pyrex glass tube having a 5-mm-o.d. ESR sample tube (length, 300 mm) as a side arm was used, which was connectable to a vacuum line. In the 9-mm tube was placed **3**·2SbF$_6^-$ (2.9 mg, 0.0025 mmol) together with a short capillary tube containing zinc powder (3.3 mg, 0.050 mmol), and the tube was evacuated to 10^{-4} mmHg. A solvent (1.0 mL) placed in a flask connected to a vacuum line was degassed and dried by repeating the freeze–pump–thaw cycle for three times over CaH$_2$ and then transferred to the 9-mm tube by vacuum distillation. After the 9-mm tube was sealed off, **3**·2SbF$_6^-$ was dissolved in the solvent and thoroughly mixed with zinc powder, and the ESR spectrum was recorded immediately.

UV–Vis Measurements of the Cation Radical 3$^{\cdot+}$. A vacuum-proof quartz cell (cell path, 1 mm) was used, which was connected to a Pyrex glass tube having side arms.[16] In one side arm was placed **3**·2SbF$_6^-$ (0.584 mg, 5.05 × 10^{-4} mmol) together with a small capillary tube containing zinc powder (1.0 mg, 0.015 mmol), and the tube was evacuated to 10^{-4} mmHg. The solvent (3.0 mL) was degassed and dried as described above and transferred into another side arm by vacuum distillation. After the glass tube was sealed off, **3**·2SbF$_6^-$ was dissolved and mixed well with zinc, and the UV–vis spectrum was recorded immediately.

Acknowledgment. Support of the present work by the Nishida Research Fund for Fundamental Organic Chemistry and by a Grant-in-Aid for Scientific Research on Priority Areas (No. 06226240) from the Ministry of Education, Science and Culture, Japan, is gratefully acknowledged.

Supplementary Material Available: Copies of ^{1}H NMR spectra of **5**, **6**, **7**, and **3**·2SbF$_6^-$ and a ^{13}C NMR spectrum of **3**·2SbF$_6^-$ (5 pages). This material is contained in 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.

---

(15) The author has deposited atomic coordinates for **3**·2SbF$_6^-$ with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(16) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Kinoshita, T.; Aonuma, S.; Nagai, M.; Miyabo, A. *J.Org. Chem.* **1990**, *55*, 996–1002.