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Syntheses, Properties, and Redox Behaviors of 7-Phenyl-1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)tropylium Ion and the Dications Composed of Two 1,2:3,4:5,6-Tris(bicyclo[2.2.2]octeno)tropylium Units Connected by *p*- and *m*-Phenylene Spacers

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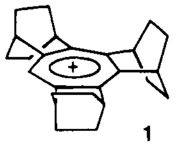
The stable carbodications composed of two tris(bicyclo[2.2.2]octeno)tropylium units connected by a *p*-phenylene (**7**) and a *m*-phenylene spacer (**8**) were synthesized, together with the corresponding monocation having a 7-phenyl substituent (**6**) as a reference compound, and their properties were fully characterized. The pK_{R^+} values of **6**, **7**, and **8** were determined in 50% aqueous acetonitrile to be 12.0, 11.5, and 10.4, respectively. The 7-phenyl substituent, which is supposedly nearly perpendicular to the tropylium ring, destabilizes the cation by 1 p*K* unit. The two cation units at the *p*-phenylene positions in **7** were neutralized simultaneously, but those in **8** were neutralized stepwise; the pK_{R^+} value for the half-neutralized monocation was 12.2. Upon one-electron reduction monocation **6** gave a stable free radical persisting in solution at room temperature. *p*-Phenylene-connected dication **7** did not give any radical species but instead gave a closed-shell hydrocarbon upon one-step, two-electron reduction. In the case of *m*-phenylene-connected dication **8**, two very closely spaced reduction steps were observed upon cyclic voltammetry, and the resulting fully reduced species was identified as a triplet diradical by low-temperature ESR.

Introduction

Tropylium ion **1**, annelated with three bicyclo[2.2.2]-octene units, is highly stabilized by the inductive and $\sigma-\pi$ conjugative effects of the rigid bicyclic σ-frameworks.[1] As the substituent at the 7-position, both simple alkyl and unsaturated groups were shown to destabilize cation **1**.[2] However, it is of interest to construct a carbodication by connecting two molecules of **1** at the 7-position with a π-conjugative spacer and examine how the thermodynamic stability would be changed and how the whole π-system would behave upon consecutive one-electron reduction processes.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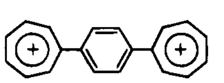
Dications **2**,[3] **3**,[4] and **4**[5] are typical examples of carbodications having Hückel aromatic systems connected by a phenylene spacer. However, except for the pK_{R^+} data measured for **4**, there have been no specific data regarding either the redox or thermodynamic properties of these dications.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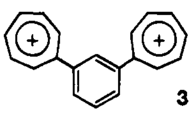
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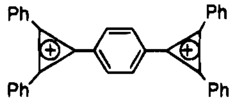

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In a previous study, we synthesized dication **5**, which has a triple bond as a spacer, and examined its behavior upon one-electron reduction.[6] Radical cation $\mathbf{5}^{\bullet+}$ was smoothly produced and appeared stable in solution, but the product of further reduction, which was considered to be a closed-shell species (a cummulene), was highly unstable and could not be identified spectroscopically. In the present paper, we report the synthesis and properties, particularly the redox behavior, of dications having *p*- (**7**) and *m*-phenylene spacers (**8**), as well as the corresponding phenyl-substituted monocation **6** as a reference compound.

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(1) (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.

(2) The corresponding 7-methyl derivative (ref 1) and the 7-(cycloheptatrienylethynyl) derivative (ref 6) showed pK_{R^+} values in 50% aqueous acetonitrile of 12.4 and 11.5, respectively, as compared with the value of 13.0 for cation **1**.

(3) Murray, R. W.; Kaplan, M. L. *Tetrahedron Lett.* **1965**, 2903−2909.

(4) Murray, R. W.; Kaplan, M. L. *Tetrahedron Lett.* **1967**, 1307−1312.

(5) Eicher, T.; Berneth, H. *Tetrahedron Lett.* **1973**, 2039−2042.

(6) Kagayama, A.; Komatsu, K.; Nishinaga, T.; Takeuchi, K.; Kabuto, C. *J. Org. Chem.* **1994**, *59*, 4999−5004.

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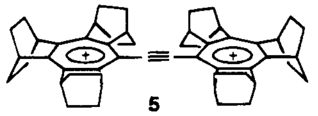

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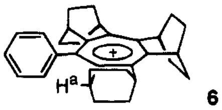

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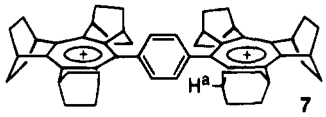

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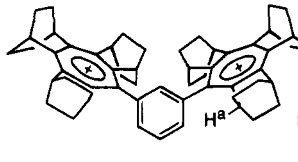

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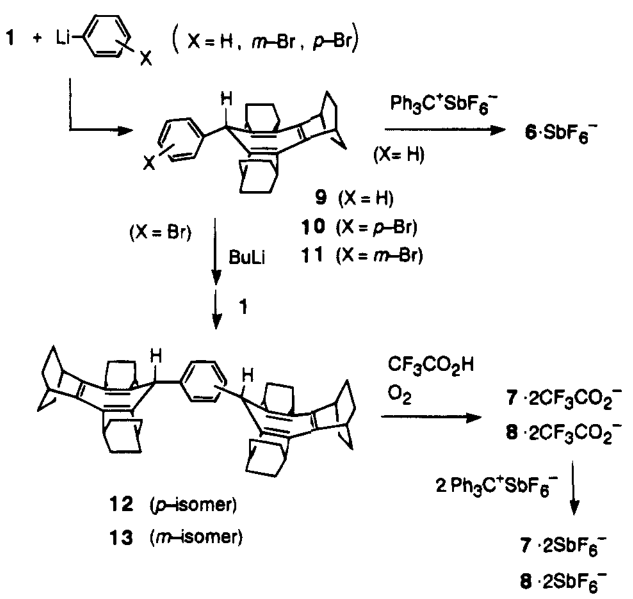
Results and Discussion

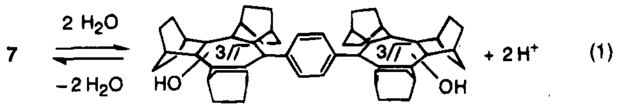
Synthesis. Syntheses of cations **6**–**8** were carried out as shown in Scheme 1.[7] The reaction of cation **1** with phenyllithium gave cycloheptatriene **9**, and subsequent hydride abstraction with trityl cation smoothly afforded phenylated monocation **6**, though the latter reaction was unusually slow. Similarly, addition of cation **1** to the (cycloheptatrienylphenyl)lithiums generated from **10** and **11** afforded di(cycloheptatrienyl)benzenes **12** and **13**. However, in contrast to the corresponding intermediates in the syntheses of **6** and parent *m*- and *p*-phenylenebis(tropylium ion) **2** and **3**,[3,4] **12** did not react with trityl cation even at 80 °C in acetonitrile for 24 h.[8] Transformation of **12** and **13** to dications did take place under aerobic oxidation conditions in the presence of trifluoroacetic acid, as has been observed for oxidation of tris(bicyclo[2.2.2]octeno)cycloheptatriene to cation **1**.[1b] After exchange of the counteranion to SbF_6^-, dication salt $\mathbf{7}{\cdot}2SbF_6^-$, as well as $\mathbf{8}{\cdot}2SbF_6^-$, was isolated as an air-stable white powder, which is again in contrast to the red color reported for parent dication **2**.[3]

Spectral Properties. Monocation **6** and dications **7** and **8** were fully characterized by the spectral data shown in Table 1, which also includes the data for monocation **1** for comparison. A ^1H NMR signal for the highest-field bridgehead proton in **6**–**8** resonates at 0.3 to 0.4 ppm higher than that of **1**; the shift implies that this signal corresponds to the proton (H^a) that sticks out in front of the phenyl ring in the shielding zone. Thus, the benzene ring at the 7-position of these cations is believed to be nearly perpendicular to the plane of the tropylium ring. The results of semiempirical MO calculations with AM1 for cation **6** indicate that the two aromatic rings are twisted by 83.0°, as shown in Figure 1. Apparently, there is no π-conjugation between the phenyl and tropylium rings. The absence of conjugation is reflected in the UV absorptions of **6**–**8**, which exhibit only a slight bathochromic shift compared with **1**. There is no further bathochromic shift for dications **7** and **8** as compared with **6**; the extinction coefficients of the dications are twice as large as those of monocation **6**.

Thermodynamic Stability. As a measure of the thermodynamic stability, the pK_{R^+} values of the cations were determined spectrophotometrically in 50% aqueous acetonitrile. As expected because of the inductive effect of the phenyl substituent, monocation **6** (pK_{R^+} 12.0 ± 0.2)[9] is less stabilized than **1**[1] by 1.0 p*K* unit. In the case of dication **7**, which has a *p*-phenylene spacer, the two cation units behave independently of each other and are neutralized almost simultaneously (eq 1) at pH 11.5 (± 0.2)[9], which is taken as the pK_{R^+} value. That this value is 0.5 p*K* unit lower than the value for **6** reflects destabilization due to the through-bond electrostatic repulsion of the two positively charged units. In comparison, two cationic units in dication **8** located at *m*-phenylene positions were neutralized in two-steps (eq 2) at pH 10.4 (±0.3)[9] and 12.2 (±0.2),[9] values which correspond to the pK_{R^+} of the dication and the half-neutralized monocation, respectively. Thus, dication **8** itself is even more destabilized than *p*-phenylene-connected dication **7** by 1.1 p*K* unit, whereas the half-neutralized monocation of **8** is almost as stable as monocation **6**.

Scheme 1





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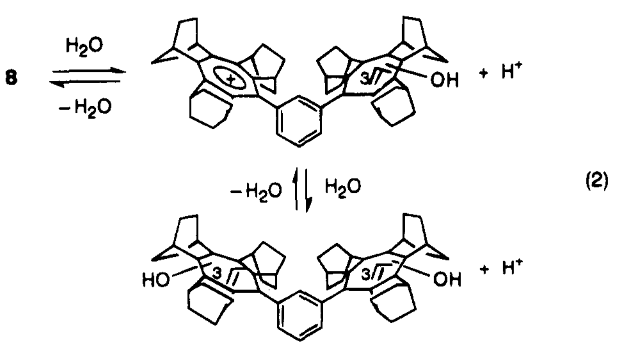

(2)

Red–Ox Behavior. Reflecting its extraordinarily high stability, monocation **1**, as well as its 7-methyl

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[7] In the literature, parent dications **2** and **3** were prepared by the reaction of tropylium ion with dimetalated benzenes and subsequent hydride abstraction (ref 3, 4). In the present work, we preferred stepwise introduction of the cycloheptatrienyl unit because of the rather limited amount of the tropylium ion **1** available.

[8] This inertness might be ascribed to the presence of bulky bicyclic frameworks on the second cycloheptatriene unit that sterically hinder the approach of the trityl cation.

[9] Rather large errors are due to the low solubility of these cations in 50% aqueous acetonitrile, which causes some fluctuation in absorbance of the UV spectra.

Table 1. Spectral Data for the SbF_6^- Salts of Cations 1 and 6–8

compd	^{1}H NMR δ, ppm (CD$_3$CN, 270 MHz)				^{13}C NMR δ, ppm (CD$_3$CN, 67.8 MHz)				IR ν, cm^{-1} (KBr)			UV–vis λ_{max}, nm (log ϵ) (CH$_3$CN)
	$\dot{-}$CH$\dot{-}^{+}$	H(Ph)	CH	CH$_2$	$\dot{-}$CH$\dot{-}^{+}$	C(Ph)	CH	CH$_2$				
1·SbF_6^- [a]	8.55 (1 H)	–	4.13 (2 H) 4.07 (2 H) 3.56 (2 H)	2.03 (12 H) 1.43 (12 H)	168.3 166.0 163.9 144.2	–	42.7 36.6 36.1	25.0 24.8 24.7	2951 1458 1270 1040 658	2873 1420 1245 1025	1625 1320 1173 814	256 (4.71) 308 (4.01)
6·SbF_6^- [b]	–	7.55 (2 H) 7.26 (3 H)	4.09 (2 H) 4.06 (2 H) 3.17 (2 H)	2.09– 1.44 (24 H)	165.98 164.10 163.32 155.43	140.94 129.41 128.63 126.39	38.72 36.15 35.95	24.20 24.07 23.90	3010 1474 1298 819	2946 1456 1137 706	2870 1328 1031 656	260 (4.67) 314 (3.92)
7·2SbF_6^-	–	7.46 (4 H)	4.14 (4 H) 4.11 (4 H) 3.24 (4 H)	2.10 (24 H) 1.49 (24 H)	166.20 165.31 164.67 155.10	142.12 128.63	39.73 36.95 36.64	24.80 24.60 24.60	3010 1475 1326 1031	2946 1460 1298 817	2870 1339 1136 656	261 (4.98) 314 (4.23)
8·2SbF_6^-	–	7.82 (1 H) 7.48 (2 H) 7.18 (1 H)	4.10 (4 H) 4.07 (4 H) 3.25 (4 H)	1.93 (24 H) 1.40 (24 H)	166.02 165.34 164.76 154.62	143.00 131.44 127.82 125.52	39.80 36.96 36.64	24.75 24.59 24.46	3010 1617 1365 1172 815	2947 1457 1327 1139 657	2871 1455 1276 1029	260 (4.96) 316 (4.24)

[a] Data from ref 1. [b] NMR spectra were measured in CDCl$_3$.

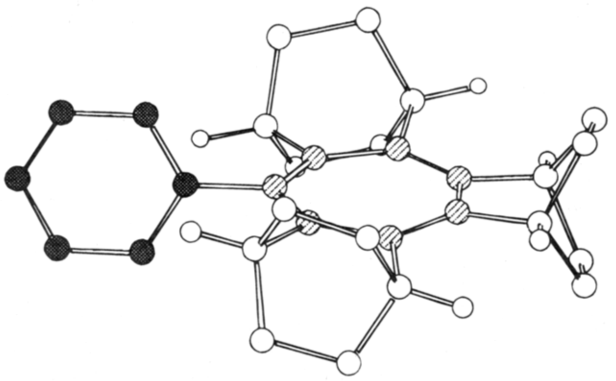

Figure 1. AM1 calculated structure of cation **6**. The methylene and phenyl hydrogens are omitted for clarity. The dihedral angle between the phenyl and tropylium rings is 83.0°.

derivative, hardly undergoes one-electron reduction; its cathodic peak potential (E_{pc}) in acetonitrile is −1.12 V vs Ag/Ag$^+$ (−1.09 V for the 7-methyl derivative)[1a] upon cyclic voltammetry (CV), as compared with −0.51 V for the parent tropylium ion.[1b] The reduction was irreversible for these cations under the conditions of CV measurement at a scan rate of 0.1 V s^{-1}. In contrast, 7-phenyl derivative **6** in acetonitrile exhibited a well-defined reversible redox wave at $E_{1/2}$ −1.12 V (E_{pc} −1.15 V), as shown in Figure 2a. This clearly indicates the generation of a free radical, which is stabilized by severe steric hindrance for dimerization and also by the lack of any hydrogen atom that could be abstracted from the radical; abstraction of a bridgehead hydrogen of the bicyclic framework, that is at the α-position of the alkyl group, is prevented by Bredt's rule. In accordance, a strong single-line ESR signal[10] with a peak-to-peak width of 3.0 G (g = 2.0023) was observed upon electrolytic reduction of cation **6** at −1.5 V in CH$_2$Cl$_2$ and was found to persist at least for 0.5 h at room temperature after the cathodic current was cut off.

It is of particular interest to examine the behavior of dications **7** and **8** upon one- and two-electron reductions and to clarify the fate of fully reduced species. The CV of **7** in acetonitrile exhibited the voltammogram shown in Figure 2b. A single cyclic scan exhibited a characteristic feature with an anodic peak positively shifted by about 0.5 V from the cathodic peak. The cathodic peak (E_{pc} −1.01 V) is in the potential range comparable to those of related cations **1** and **6** and apparently corresponds to a one-step, two-electron reduction. Therefore the anomalous voltammogram must have arisen from the anodic shift due to the extra energy required upon oxidation of the completely reduced species back to dication **7**. One possible cause for this extra energy requirement could be some structural change from the reduced form to the dication. Since no ESR signal was observed even upon extensive electrolytic reduction, the reduced species from **7** cannot have any unpaired spin. It is assumed that the two free radicals generated at the p-positions prefer to form closed-shell covalent molecule **16**, which would readily relax into boat form **17** (Scheme 2). Because of the rigid bicyclic frameworks surrounding the seven-membered ring, the boat form is much more stable than the planar structure, which involves severe steric repulsion between the bridgehead- and *ortho*-hydrogens.[11] Thus, considerable energy is required to transform boat structure **17** back to planar radical cation **14**, and this energy could be the origin of the unusual positive shift of the anodic peak in the voltammogram. A similar potential shift associated with change in molecular geometry has typically been observed upon reduction of azacyclooctatetraene derivatives and cyclooctatetraene.[12]

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(10) In spite of various attempts such as reducing the modulation width and lowering the concentration, no hyperfine structure was observed, probably because of the presence of too many hydrogens coupling with the unpaired electron.

(11) The molecular mechanics calculations by MM2(87) indicated that boat structure **17** in Scheme 2 is 96 kcal mol^{-1} more stable than structure **16**, in which the π-conjugated system is enforced to be planar.

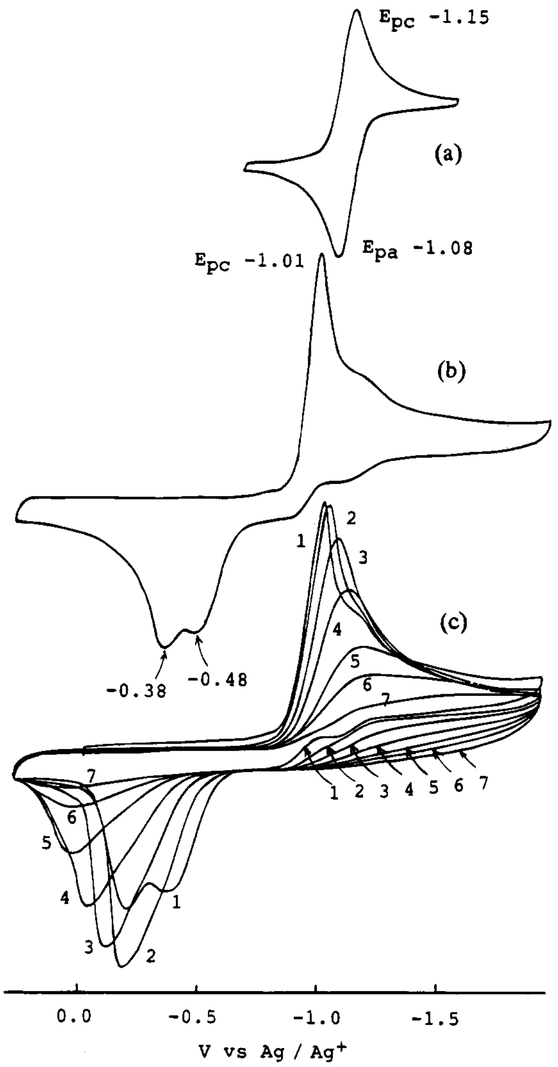
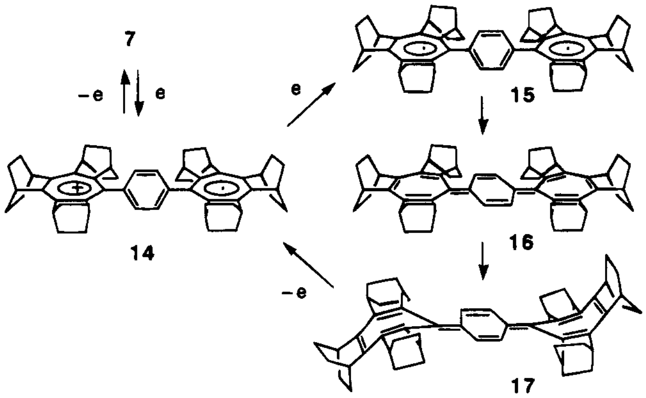


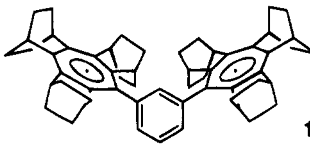
Figure 2. Cyclic voltammograms of (a) monocation **6** (0.5 mM), (b) dication **7** (0.5 mM) (the first cyclic scan), (c) dication **7** (the first to seventh scans; the number of scan is shown in the figure). All voltammograms were obtained in acetonitrile containing Bu_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate, 0.1 V s^{-1}.

Scheme 2



On each repeated cycle, the voltammogram of **7** exhibited a gradual decrease in peak currents, as shown in Figure 2c. After electrolysis at a constant potential of −1.5 V, the working electrode was found to be coated with a film of red-brown solid, which was barely soluble in common organic solvents. This material is believed to have been formed by polymerization or decomposition of presumably unstable hydrocarbon **17**, although the spectroscopic examination of its structure was hampered by its insolubility.

In contrast to dication **7**, *m*-phenylene type dication **8** is expected to give a non-Kékule type electronic structure upon two-electron reduction. Dication **8** in dichloromethane exhibited the voltmmogram shown in Figure 3. The voltammogram is characterized by barely separated two-step reduction waves at $E_{1/2}$ −1.14 and −1.24 V vs Ag/Ag$^+$, which are completely reversible. Thus, electron transfer to **8** is believed to occur without much structural change to yield the corresponding radical cation and diradical consecutively, in contrast to the case of **7**. The ESR spectrum measured upon electrolytic reduction of **8** in acetonitrile−THF (1:4) at a potential of −1.5 V showed a single-line signal (g = 2.0026), which was analogous to that of the 7-phenylated monoradical obtained from **6**. When the solution was solidified at −120 °C, there was observed an ESR signal with a fine structure typical for a triplet diradical with zero-field splitting parameters D = 0.0054 cm^{-1} and E < 0.0001 cm^{-1}, as shown in Figure 4.[13] Thus, two-electron reduction of dication **8** generates diradical **18**, which cannot be transformed into a closed-shell structure. By comparison of reported D values for *m*-xylylene (**19**, D = 0.011 cm^{-1})[14] and Schlenk's hydrocarbon (**20**, 0.008 cm^{-1}),[15] the distance between two radical centers in **18** is estimated as 8 Å, compared to 6 Å for **19** and 7 Å for **20**. This value seems to be in good agreement with structure **18**, in which each of the two spins is completely delocalized in each one of the seven-membered rings.



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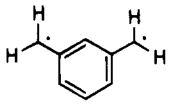

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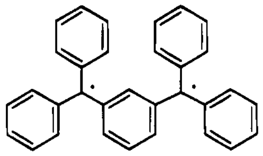

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Experimental Section

For general experimental procedures and instruments used, see the previous paper.[6]

7-Phenyl-1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)tropylium Hexafluoroantimonate (6·SbF$_6^-$). A solution of 2.0 M PhLi in hexane (0.15 mL, 0.30 mmol) was added dropwise to a stirred suspension of salt **1**·SbF$_6^-$ (56.4 mg, 0.0994 mmol) in THF (1 mL) at −78 °C. The mixture was stirred for 10 min at −78 °C and slowly warmed to rt over 15 min. After being treated with water, the mixture was extracted with diethyl ether. The extract was washed with aqueous sodium chloride, dried, and evaporated to dryness. Separation by medium pressure liquid chromatography (MPLC) over silica gel 60 (Merck Co.) with hexane as the eluent yielded 7-phenyl-1,2:

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(12) Anderson, L. B.; Hanson, J. F.; Kakihana, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1971**, *93*, 161−167, and the references cited therein. There is also the "square scheme" proposed for describing redox reactions coupled with structural or chemical changes: Richards, T. C.; Geiger, W. E. *J. Am. Chem. Soc.* **1994**, *116*, 2028−2033.

(13) Unfortunately, a search at lower fields for an absorption for the half-field (Δm = 2) transition was unsuccessful.

(14) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628−630.

(15) Kothe, G.; Denkel, K.-H.; Sümmermann, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906−907.

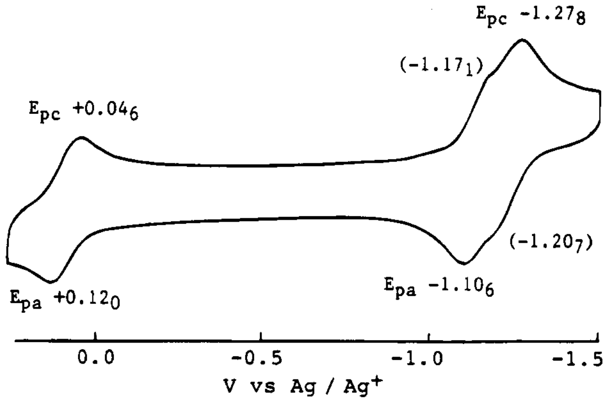

Figure 3. Cyclic voltammogram of dication **8** (0.5 mM) in dichloromethane containing Bu_4NClO_4 (0.1 M) as a supporting electrolyte, with ferrocene (0.5 mM) added as an internal standard ($E_{1/2}$, +0.083 V vs Ag/Ag$^+$); scan rate, 0.1 V s^{-1}.

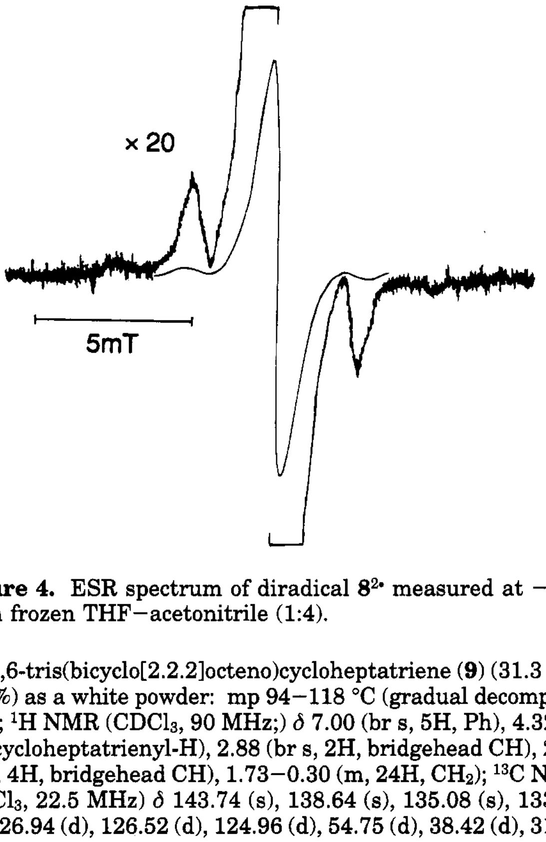

Figure 4. ESR spectrum of diradical **8**$^{2•}$ measured at −120 °C in frozen THF−acetonitrile (1:4).

3,4:5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**9**) (31.3 mg, 77.1%) as a white powder: mp 94−118 °C (gradual decomposition); ^{1}H NMR ($CDCl_3$, 90 MHz;) δ 7.00 (br s, 5H, Ph), 4.32 (s, 1H, cycloheptatrienyl-H), 2.88 (br s, 2H, bridgehead CH), 2.67 (br s, 4H, bridgehead CH), 1.73−0.30 (m, 24H, CH_2); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 143.74 (s), 138.64 (s), 135.08 (s), 133.69 (s), 126.94 (d), 126.52 (d), 124.96 (d), 54.75 (d), 38.42 (d), 31.59 (d), 31.45 (d), 28.21 (t), 26.48 (t), 26.16 (t), 25.91 (t), 25.67 (t; two signals overlapped); UV (cyclohexane) λ_{max} 275 nm (log ε 3.82); MS m/z 408 (M$^+$).

A solution of trityl hexafluoroantimonate (125 mg, 0.261 mmol) in acetonitrile (1.8 mL) was added dropwise to a stirred solution of cycloheptatriene **9** (106 mg, 0.260 mmol) in dichloromethane (1.5 mL). The resulting yellow-orange solution was heated at 50 °C for 20 h. The color became pale yellow. The solution was evaporated to dryness, and the residual solid was reprecipitated from dichloromethane (0.5 mL)/diethyl ether (16 mL) to give salt **6**·SbF_6^- as a white powder (98.3 mg, 58.8%); mp >300 °C. Anal. Calcd for $C_{31}H_{35}F_6Sb$: C, 57.87; H, 5.48. Found: C, 57.93; H, 5.44. For the spectral data, see Table 1.

***p*-Phenylenebis{tris(bicyclo[2.2.2]octeno)tropylium} Hexafluoroantimonate (7·2SbF$_6^-$).** A solution of (*p*-bromophenyl)lithium was prepared by addition of 1.5 M butyllithium in hexane (1.0 mL, 1.5 mmol) to a stirred solution of *p*-dibromobenzene (328 mg, 1.39 mmol) in THF (1 mL) at −78 °C. To a stirred suspension of **1**·SbF_6^- (96.5 mg, 0.231 mmol) in THF (1 mL) at −78 °C was added a solution of 1.0 mL of (*p*-bromophenyl)lithium (0.8 mmol), and the mixture was stirred for 7 min at −78 °C. After being warmed to rt, the mixture was worked up and separated by MPLC in the manner described above for the preparation of cycloheptatriene **9** to give 7-(*p*-bromophenyl)-1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**10**) (101 mg, 89.5%) as a white powder; mp 128−135 °C (gradual decomposition); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.10 (d, 2H, ArH), 6.82 (d, 2H, ArH), 4.23 (s, 1H, cycloheptatrienyl-H), 2.88 (br s, 2H, bridgehead CH), 2.70 (br s, 2H, bridgehead CH), 2.60 (br s, 2H, bridgehead CH), 1.71−0.38 (m, 24H, CH_2); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 142.80, 138.83, 134.65, 133.99, 130.17, 129.50, 128.23, 54.21, 38.33, 31.56, 31.46, 28.13, 26.42, 26.07, 25.97, 25.73, 25.63. Anal. Calcd for $C_{31}H_{35}Br$: C, 76.37; H, 7.24. Found: C, 76.10; H, 7.47.

To a stirred solution of *p*-(bromophenyl)cycloheptatriene **10** (103 mg, 0.211 mmol) in THF (1.5 mL) at −78 °C was added 1.53 M butyllithium in hexane (0.15 mL, 0.23 mmol). To this solution was added a suspension of **1**·SbF_6^- (179 mg, 0.315 mmol) in THF (1.5 mL), and the mixture was stirred at −78 °C for 15 min. After being warmed to rt, the mixture was worked up as described above to give a crude product and unchanged **1**·SbF_6^-. Thorough washing of this mixture with acetonitrile (4 mL) in an ultrasonic bath afforded *p*-bis{2,3:4,5:6,7-tris(bicyclo[2.2.2]octeno)cycloheptatrien-1-yl}benzene (**12**) (100 mg, 64.3%) as a barely soluble white powder; mp 275−280 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.63 (s, 4H, Ar-H), 4.20 (s, 2H, cycloheptatrienyl-H), 2.81 (br s, 4H, bridgehead CH), 2.67 (br s, 4H, bridgehead CH), 2.54 (br s, 4H, bridgehead CH), 1.59−0.56 (m, 48H, CH_2); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 138.99, 138.34, 135.18, 133.78, 125.37, 54.50, 38.80, 31.63, 31.56, 27.87, 26.57, 26.21, 25.93, 25.75, 25.44.

To a solution of *p*-dicycloheptatrienylbenzene **12** (52.0 mg, 0.0703 mmol) in dichloromethane (4 mL) was added TFA (0.30 g, 2.6 mmol), and oxygen gas was bubbled in for a few seconds. The solution was stirred in a stoppered flask at rt for 3 days, after which period a pale brown suspension resulted. The mixture was evaporated to dryness, redissolved in dichloromethane (2 mL), and stirred magnetically. To this solution was added a 0.11 M solution of trityl hexafluoroantimonate in dichloromethane, drop by drop, until the yellow-orange color of trityl cation began to remain in the solution, for which a total of 0.93 mL (0.10 mmol of the trityl cation) was required. After additional stirring for 10 min, the solvent was evaporated, and the residual yellowish solid was thoroughly washed, under sonification, successively with diethyl ether (5 mL) and with diethyl ether−dichloromethane (3 mL + 2 mL) to give salt **7**·2SbF_6^- (61.8 mg, 72.5%) as an off-white powder; mp >300 °C. Anal. Calcd for $C_{56}H_{64}F_{12}Sb_2$: C, 55.65; H, 5.34. Found: C, 55.60; H, 5.33. For the spectral data, see Table 1.

***m*-Phenylenebis{tris(bicyclo[2.2.2]octeno)tropylium} Hexafluoroantimonate (8·2SbF$_6^-$).** In the manner described for the preparation of the *para*-substituted compound, the reaction of **1**·SbF_6^- (262 mg, 0.462 mmol) and (*m*-bromophenyl)lithium (1.82 mmol) afforded 7-(*m*-bromophenyl)-1,2:3,4:5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**11**) (153 mg, 68.0%) as a white powder; mp 137−143 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.11−6.86 (m, 4H, Ar-H), 4.28 (s, 1H, cycloheptatrienyl-H), 2.89 (br s, 2H, bridgehead CH), 2.71 (br s, 2H, bridgehead CH), 2.62 (br s, 2H, bridgehead CH), 1.72−0.38 (m, 24H, CH_2); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 146.54, 138.90, 134.56, 134.13, 130.04, 128.14, 127.93, 125.68, 120.84, 54.34, 38.27, 31.54, 31.42, 28.17, 26.39, 26.12, 25.92, 25.64, 25.57. Anal. Calcd for $C_{31}H_{35}Br$: C, 76.37; H, 7.24. Found: C, 76.14; H, 7.37.

By a method similar to the one described above, *m*-(bromophenyl)cycloheptatriene **11** (113 mg, 0.232 mmol) was transformed into *m*-bis{2,3:4,5:6,7-tris(bicyclo[2.2.2]octeno)cycloheptatrien-1-yl}benzene (**13**) (119 mg, 69.0%) as a barely soluble white powder; mp 247−249 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.79 (s, 1H, ArH), 6.61−6.54 (m, 3H, ArH), 4.15 (s, 2H, cycloheptatrienyl-H), 2.82 (br s, 4H, bridgehead CH), 2.68 (br s, 4H, bridgehead CH), 2.54 (br s, 4H, bridgehead CH), 1.62−0.51 (m, 48H, CH_2); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ

141.31, 138.36, 134.78, 133.49, 126.41, 124.78, 123.83, 55.14, 38.58, 31.71, 31.57, 27.72, 26.57, 26.50, 26.05, 25.73, 25.67. Anal. Calcd for $C_{56}H_{66}$: C, 91.00; H, 9.00. Found: C, 88.81; H, 8.92.[16]

In the manner described above, a solution of *m*-dicycloheptatrienylbenzene **13** (107 mg, 0.145 mmol) and TFA in dichloromethane was stirred under oxygen for 3 days and then treated with trityl hexafluoroantimonate (136 mg, 0.283 mmol) to give salt **8**·2SbF$_6^-$ (114mg, 65.0%) as an off-white powder; mp >300 °C. Anal. Calcd for $C_{56}H_{64}F_{12}Sb_2$: C, 55.65; H, 5.34. Found: C, 55.49; H, 5.45. For the spectral data, see Table 1.

The pK_{R^+} Determination. A pH 10 buffer solution was prepared by mixing 0.2 M glycine in 50% aqueous acetonitrile (25 mL) and 0.2 M NaOH in 50% aqueous acetonitrile (19 mL) and diluting with 50% acetonitrile to 100 mL.[17] For the preparation of a sample solution, each 0.5 mL portion of the stock solution, prepared by dissolving 2−3 mg of cation salt in acetonitrile (5 mL or 10 mL), was pipetted out and diluted to 20 mL with H_2O (0.5 mL) and the buffer solution prepared as described above. Sample solutions with higher acidity or basicity were made by addition of 1−3 drops of 10% HCl, H_2SO_4, or 10% NaOH. The UV-vis spectra of the sample solutions were 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 the cation's characteristic absorption was plotted against pH to give the titration curve, whose midpoint was taken as the pK_{R^+} value.

ESR Measurement. Electrolytic reduction was carried out as described in a previous paper,[6] using an originally made electrolytic cell in a 0.1 M solution of tetrabutylammonium perchlorate in dichloromethane.

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Supplementary Material Available: Copies of ^1H and ^{13}C NMR spectra of cations **6−8** and cycloheptatrienes **9−13**, and UV-vis spectra and pK_{R^+} measurement data of cations **6−8** (21 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.

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(16) No satisfactory elemental analysis was obtained because of the instability.

(17) Gomori, G. In *Methods in Enzymology*; Colowick, S. P., Kaplan, N. O., Eds.; Academic Press: New York, 1955; Vol. 1, p 145.