Structural Studies on the Radical Cations of Benzene, Naphthalene, Biphenylene, and Anthracene Fully Annelated with Bicyclo[2.2.2]octene Frameworks

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Received April 25, 2000

Abstract: The cyclic voltammetry of benzene **1**, naphthalene **2**, biphenylene **3**, and anthracene **4** fully annelated with bicyclo[2.2.2]octene showed that their cationic species have enhanced kinetic and thermodynamic stability as compared with the corresponding polymethyl analogues. Chemical one-electron oxidation of these neutral aromatic hydrocarbons led to facile isolation of their radical cation salts, which are persistent at ambient temperature even in air, and allowed X-ray crystallographic determination of their structures for the first time for the *monomer* radical cations of alkyl-substituted benzene, naphthalene, and biphenylene. The π-systems of these radical cations are planar except for that of the naphthalene radical cation $\mathbf{2}^{\bullet+}$. The structure of the benzene ring of $\mathbf{1}^{\bullet+}$ precludes the observation of a static Jahn−Teller distortion in the crystal at −100 °C. For the radical cations of **2**−**4**, the geometrical changes in π-systems upon one-electron oxidation are consistent with what can be predicted from the orbital coefficients of the HOMO of the neutral molecules. Characteristic changes in the lengths of the σ-bonds of the bicyclic framework involved in $\sigma-\pi$ conjugation (C−C hyperconjugation) were also observed. Theoretical calculations, using ab initio molecular orbital (HF/6-31G*) and density functional (B3LYP/6-31G*) methods, have been used to interpret the experimental data.

Introduction

Organic radical cations have been of fundamental interest in a variety of contexts for both organic and physical chemists.[1] In particular, those of π-conjugated hydrocarbons have been extensively studied by ESR spectroscopy.[2,3] Radical cations of some polyacenes such as naphthalene and anthracene have not only been the subject of the conventional ESR studies but also recently been the focus of revisited attention since they were suggested to exist in interstellar space.[4] Organic radical cations are also quite important as electron-transfer catalysts in organic synthesis.[5] They also serve as building blocks for molecular devices such as organic conductors[6,7] and ferromagnets[8] in material science. For such applications, heteroatom-centered and/or -containing radical cations have been employed for reasons of stability, accessibility, and enhancement of intermolecular interaction.

In contrast, hydrocarbon radical cations are usually highly reactive species, which are prone to further transformations such as nucleophilic attack, deprotonation, rearrangement, fragmentation, polymerization, etc.[3b−d,9] The introduction of n- or π-conjugative substituents such as NR_2, OR, and Ar groups is essential to obtain thermally stable radical cations. Such substitution, however, makes it difficult to quantitatively evaluate the inherent structural changes of the π-system upon removal of one electron, due to considerable charge delocalization over the substituents.[10] Substitutions by simple alkyl groups would not induce such significant changes in the electronic nature of

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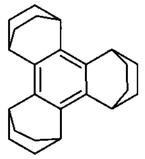
10.1021/ja0014436 CCC: $19.00

π-systems, but the lability of C−H bonds at the carbon atoms directly attached to cationic or radical centers still renders radical cations elusive. Furthermore, in the case of radical cations with insufficient thermodynamic stability, preferential formation of radical cation "π-dimers"[6,10b,11] is problematic and often occurs instead of the formation of less stable monomeric cations. Therefore, it has only been possible to characterize most monomeric hydrocarbon radical cations by spectroscopic methods such as ESR and electronic absorption spectroscopy, and examples of structural characterization by X-ray crystallography are quite rare. This limitation is in sharp contrast to the numerous examples of successful isolation and X-ray structural determination of various aromatic hydrocarbon radical anions,[12] dianions,[13] a radical trianion,[14] and even a tetraanion.[15] Thus, the synthesis and isolation of stable aromatic hydrocarbon radical cations and the elucidation of their structures still remain as an important issue in organic chemistry.

As an approach to the highly stable hydrocarbon (radical) cations without relying on stabilization by extra π-conjugative substituents, we have designed and synthesized several monocyclic conjugated π-systems fully annelated with a rigid σ-framework, bicyclo[2.2.2]octene (abbreviated as BCO).[16] Such structural modification with bicycloalkane frameworks has proven to be quite effective for the stabilization of the positively charged π-systems owing to electronic factors such as inductive and σ−π conjugative (C−C hyperconjugative) effects,[17] as well as steric factors such as Bredt's rule protection[18] and the steric bulkiness of the bicyclic frameworks. This is exemplified by our previous works on the most stable tropylium ion[16a] and cyclooctatetraene radical cation.[19] In the case of the polycyclic aromatics fully annelated with BCO units, similar stabilization has been demonstrated for the radical cations derived from naphthalene **2**,[20] biphenylene **3**,[21] and anthracene **4**.[22] Here, we report the full account of the isolation of the crystalline radical cation salts derived from **1**−**4**, their spectral properties, and the results of X-ray crystallographic determination of their structures.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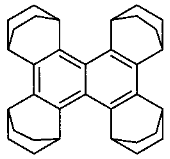
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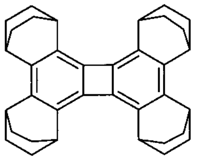
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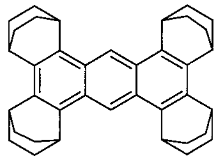
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Results and Discussion

Electrochemistry. To examine the effect of BCO annelation upon the donor ability of the π-electronic systems, cyclic voltammetry was performed in 1,1,2,2-tetrachloroethane using tetra-*n*-butylammonium perchlorate as a supporting electrolyte. The values for the oxidation potentials of **1**−**4**, together with those of the corresponding methyl derivatives for comparison, are listed in Table 1. These results reveal the enhanced π-donor ability of the neutral hydrocarbons **1**−**4** and thus increased thermodynamic stability of the cationic species of the BCO-annelated systems compared with their methyl analogues.

Octamethyl analogues of naphthalene, biphenylene, and anthracene exhibited only one reversible one-electron oxidation wave; no oxidation wave was observed in the case of hexamethylbenzene under the present conditions. Although hexamethylbenzene has been reported to exhibit an oxidation wave in more polar solvents such as dichloromethane or acetonitrile, it

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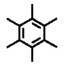
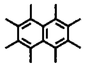
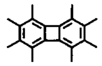
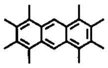
Table 1. The Oxidation Potentials[a] (V vs Fc/Fc$^+$) of **1**−**4** and Their Corresponding Methyl Analogues

compd	$E_{1/2}$ (I)	E_{pa} (II)	compd	$E_{1/2}$ (I)[b]
1	+1.08	—		—
2	+0.33	+1.17		+0.52
3	+0.25	+1.00		+0.36
4	+0.17	+0.86		+0.38

[a] In 1,1,2,2-tetrachloroethane containing 0.1 M *n*-Bu$_4$NClO$_4$ at 25 °C; scan rate 20 mV s^{-1}. [b] No second oxidation wave was observed.

remains irreversible at a scan rate even as high as 10 V s^{-1} in acetonitrile, due to the facile loss of the α-proton.[23] In sharp contrast, such a deprotonation is prohibitive in $\mathbf{1}^{\bullet+}$ because it would lead to the formation of bridgehead olefin and hence to a violation of Bredt's rule, which would account for the complete reversibility of the anodic oxidation of **1**. Compounds **2**−**4** were oxidized at lower potentials than the methyl analogues by 0.11−0.21 V, and showed even the second oxidation waves, although they remained irreversible even at higher scan rates. It is noteworthy that such a low potential as the value of the $E_{1/2} = +0.17$ V vs Fc/Fc$^+$ was observed for **4** despite its being a pure hydrocarbon.

Such facile oxidizability observed for **1**−**4** can be explained by a more substantial elevation of the HOMO energy levels than in the corresponding methyl analogues due not only to the inductive effects of the larger alkyl substituents but also to the operation of the $\sigma-\pi$ interaction (C−C hyperconjugation) of the σ-bonds that are rigidly fixed at the position nearly parallel to the p-orbitals of the π-systems.

The Charge-Transfer Interaction. From the results of cyclic voltammetry, the hydrocarbons **2**−**4** with remarkably low oxidation potentials are expected to act as good π-donors. For example, mixing of **4** with a strong π-acceptor, tetracyanoethylene (TCNE), in dichloromethane at room temperature resulted in the rapid and quantitative formation of [4+2] adduct,[22] while mixing with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in dichloromethane caused a pale orange coloration: the electronic absorption spectrum showed a charge-transfer (CT) absorption at 550 nm. This value is considerably blue-shifted compared with that of the CT band of the parent anthracene−TCNQ complex ($\lambda_{CT} = 790$ nm in chloroform)[24] despite the stronger donor ability of **4** than that of anthracene (E_{pa} +1.04 V vs Fc/Fc$^+$ in dichloromethane). This indicates that the electrostatic energy ω (expressed as $hc/\lambda_{CT} = I_P - E_A - \omega$)[25] gained by the interaction of **4** with TCNQ is much weaker than that of anthracene with TCNQ; this phenomenon is ascribed to the steric congestion arising from the full annelation of BCO units, which strongly diminishes the donor−acceptor interaction. In the cases of **2** and **3**, no CT band was observed with TCNQ, even in the presence of higher concentration of the acceptor. This would in part be due to the steric congestion mentioned above[26] and would also be due to the decreased donor ability of **2** and **3** compared with **4**.

X-ray Crystallography of the Neutral Molecules. The molecular structures of **1**−**4** were determined by X-ray crystallography. The averaged lengths of the aromatic bonds, together with those of the corresponding parent arenes,[27] are listed in Table 3. The π-systems were found to be planar in **1**, **3**, and **4**, but nonplanar in **2**, which has a slightly undulating acene core composed of two shallow boats as a consequence of the steric repulsion between the bridgehead hydrogens at the *peri* positions. As to the bond lengths of the π-systems, it has been demonstrated that the annelation of the bicyclic frameworks to benzene gives rise to a bond alternation with the *exo* bonds shortened and the *endo* bonds elongated with respect to the bicyclic appendages.[28] However, the degree of bond alternation is minute in **1** ($R_{\text{endo}} - R_{\text{exo}} = 0.011$ Å), and the differences in each of the π-bond lengths between **2**−**4** and the corresponding parent arenes are also quite small (within 0.01 Å), except for the substantially elongated bond *d* in **2**. Therefore, it can be concluded that the annelation of BCO units imposes only little strain upon the entire system of aromatic rings, and BCO-annelated derivatives should serve as the appropriate model compounds for the evaluation of the structural changes upon removal of electron(s).

Isolation and Structural Characterization of Radical Cation Salts. By the use of antimony(V) pentachloride as an oxidant (1.5 molar equiv) in carbon disulfide at 0 °C, the hexachloroantimonate salts of the radical cation of **1**−**4** were isolated in essentially quantitative yield as ruby red ($\mathbf{1}^{\bullet+}$), dark green ($\mathbf{2}^{\bullet+}$), blue violet ($\mathbf{3}^{\bullet+}$), and dark green ($\mathbf{4}^{\bullet+}$) crystals, respectively (eq 1).

$$2\ \text{donor} + 3\ \text{SbCl}_5 \rightarrow 2\ \text{donor}^{\bullet+}\text{SbCl}_6^- + \text{SbCl}_3 \qquad (1)$$

It is noteworthy that these radical cation salts are quite robust in the solid state even at ambient temperature in air. Solutions of the radical cations of **2**−**4** in dichloromethane showed absolutely no color decay under vacuum. Although $\mathbf{1}^{\bullet+}\text{SbCl}_6^-$ was found to be somewhat less stable than other salts, it can be handled in air for a short period of time, and can be stored for a prolonged period at 0 °C under an inert atmosphere.

Single crystals suitable for X-ray crystallographic analysis were grown by liquid diffusion technique (see the Experimental Section), and this allowed the first unambiguous structural determination of the *monomeric* radical cations of benzene, naphthalene, and biphenylene with no π-conjugative substituents. As to the anthracene radical cation, Kochi et al. have reported the X-ray crystallography of the 1,2,3,4,5,6,7,8-octamethyl derivative obtained by the chemical oxidation of bis(pentamethylphenyl)methane.[9c] However, their discussion fo-

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(28) (a) Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102. (b) Bürgi, H.-B.; Baldridge, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454. (c) Frank. N. L.; Baldridge, K. K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 4389. (d) Cardullo, F.; Giuffrida, D.; Kohnke, F. H.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 339. (e) Cossu, S.; Lucchi, O. D.; Lucchini, V.; Valle, G.; Balci, M.; Dastan, A.; Demirci, B. *Tetrahedron Lett.* **1997**, *38*, 5319. (f) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012.

Table 2. Crystallographic Data for **1**−**4**, $\mathbf{1}^{\bullet+}SbCl_6^{-}\cdot C_2H_2Cl_4$, $\mathbf{2}^{\bullet+}SbCl_6^{-}$, $\mathbf{3}^{\bullet+}SbCl_6^{-}\cdot 2CH_2Cl_2$, and $\mathbf{4}^{\bullet+}SbCl_6^{-}\cdot 0.5(CH_2Cl_2\cdot C_6H_6)$

	1	2	3	4
formula	$C_{24}H_{30}$	$C_{34}H_{40}$	$C_{36}H_{40}$	$C_{38}H_{42}$
fw	318.50	448.69	472.71	498.75
temp, °C	23	23	23	23
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$	$P2/c$	$P\bar{1}$
a, Å	11.623(1)	9.482(2)	10.701(2)	9.612(2)
b, Å	10.240(2)	10.432(2)	6.646(2)	11.331(2)
c, Å	15.639(1)	6.263(1)	18.382(2)	6.646(1)
α, deg		98.12(1)		95.14(2)
β, deg	101.271(8)	102.15(1)	96.43(1)	106.94(1)
γ, deg		77.79(1)		96.32(2)
V, Å^3	1825.6(5)	588.9(2)	1299.0(4)	682.6(2)
Z	4	1	2	1
d(calcd), g/cm^3	1.159	1.265	1.208	1.213
no. of total reflns	3054	1892	2819	2182
no. of obsd reflns	1993 ($I > 3\sigma(I)$)	1435 ($I > 3\sigma(I)$)	1718 ($I > 3\sigma(I)$)	1544 ($I > 3\sigma(I)$)
R,[a] R_w[b]	0.041, 0.061	0.044, 0.068	0.049, 0.071	0.045, 0.069
GOF	1.20	1.21	1.36	1.48
max, min peaks in final diff map, e Å^{-3}	0.15, −0.14	0.17, −0.18	0.24, −0.20	0.14, −0.24

	$\mathbf{1}^{\bullet+}SbCl_6^{-}\cdot C_2H_2Cl_4$	$\mathbf{2}^{\bullet+}SbCl_6^{-}$	$\mathbf{3}^{\bullet+}SbCl_6^{-}\cdot 2CH_2Cl_2$	$\mathbf{4}^{\bullet+}SbCl_6^{-}\cdot 0.5(CH_2Cl_2\cdot C_6H_6)$
formula	$C_{26}H_{32}SbCl_{10}$	$C_{34}H_{40}SbCl_6$	$C_{38}H_{44}SbCl_{10}$	$C_{41.5}H_{46}SbCl_7$
fw	820.82	783.16	977.05	914.74
temp, °C	−100	−100	−100	−100
crystal system	orthorhombic	tetragonal	triclinic	orthorhombic
space group	$Pnma$	$I4_1cd$	$P\bar{1}$	$Pca2_1$
a, Å	18.3159(3)	17.6265(9)	10.1079(5)	20.6525(3)
b, Å	12.1764(2)		11.6330(5)	13.5310(2)
c, Å	15.0990(2)	21.0194(6)	9.6888(3)	28.0975(6)
α, deg			113.238(2)	
β, deg			93.586(3)	
γ, deg			100.874(3)	
V, Å^3	3367.41(8)	6530.6099	1016.12(8)	7851.8(2)
Z	4	8	1	8
d(calcd), g/cm^3	1.619	1.593	1.597	1.548
no. of total reflcns	3717	1851	4236	8675
no. of obsd reflcns	3311 ($I > 3\sigma(I)$)	1607 ($I > 3\sigma(I)$)	4033 ($I > 3\sigma(I)$)	7652 ($I > 3\sigma(I)$)
R,[a] R_w[b]	0.071, 0.128	0.047, 0.066	0.050, 0.080	0.037, 0.050
GOF	1.38	1.07	1.40	1.12
max, min peaks in final diff map, e Å^{-3}	2.86, −1.82	0.82, −1.11	0.84, −1.84	0.95, −1.54

[a] $R = \Sigma(|F_o - F_c|)/\Sigma(|F_o|)$. [b] $R_w = \{\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2\}^{1/2}$.

cused mainly on stacking properties and no description was given about the geometrical changes of the π-system as compared with the neutral form. The ORTEP views of the hexachloroantimonate salts of the radical cation derived from **1**−**4** are illustrated in Figures 1−4, respectively, and the selected bond lengths, together with those of the corresponding neutral molecules, are listed in Table 3. Detailed discussion of the structural features of each radical cation is described in the following sections.

The Structure of the Benzene Radical Cation, $\mathbf{1}^{\bullet+}$. The crystal was found to contain severely disordered molecules of 1,1,2,2-tetrachloroethane used as a solvent,[29] which precluded the precise determination of the structural parameters. The use of various other solvents or solvent systems did not yield a better single crystal. This disorder could not be obviated even by the low-temperature (−150 °C) data collections, and is held responsible for the disorder around the bicyclic frameworks of $\mathbf{1}^{\bullet+}$. However, the structure of the benzene ring of $\mathbf{1}^{\bullet+}$, which is the most interesting part of the molecule, appears to be little affected by the disorder in the solvent molecule.

The shortest nonbonding distance between the chlorine atom of $SbCl_6^{-}$ and the aromatic carbon atom (4.45 Å) is much longer than the sum of the van der Waals radii of carbon and chlorine (3.5 Å), being indicative of the absence of specific interaction between the counteranion and the cationic center. The benzene ring is planar, as shown by the internal angles at C1, C2, and C3 (119.6(3), 119.5(5), and 120.9(3)°, respectively) and the sum of the angles (720.0°). The C−C bond lengths in the ring (average 1.424 Å) are somewhat larger than those in the neutral molecule **1** (average 1.395 Å). Since the HOMO of **1** is doubly degenerate (e″), removal of one electron in a vertical process leads to an []e^3 configuration, a degenerate ^{2}E″ electronic state, which must undergo the Jahn−Teller distortion to break the orbital degeneracy. Theoretical calculations show that there are two types of Jahn−Teller distorted structures for $\mathbf{1}^{\bullet+}$ with C_{2v} symmetries, one with a compressed benzene ring ($\mathbf{1c}^{\bullet+}$; $^2A_2$ state) and the other with an elongated one ($\mathbf{1e}^{\bullet+}$; $^2B_1$ state), as has been predicted for the parent benzene radical cation ($^2B_{2g}$ and $^2B_{3g}$ states of the D_{2h} symmetry). Subsequent vibrational frequency calculations proved $\mathbf{1c}^{\bullet+}$ to be a first-order saddle point and $\mathbf{1e}^{\bullet+}$ to be a global minimum (0.62 kcal/mol lower than $\mathbf{1c}^{\bullet+}$) at the UHF/6-31G* level of theory. This situation is reversed at the UB3LYP/6-31G* level of theory and $\mathbf{1c}^{\bullet+}$ is found to be 0.03 kcal/mol below $\mathbf{1e}^{\bullet+}$.

There have been various attempts to observe the Jahn−Teller distortion in radical cations of unsubstituted and symmetrically

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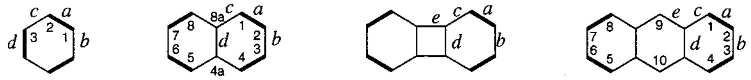
(29) Inclusion of 1,1,2,2-tetrachloroethane in the crystal has been confirmed by NMR analysis.

Table 3. Experimental and Calculated π-Bond Lengths (Å)[a] of **1**−**4**, Corresponding Parent Arenes, and Radical Cations $\mathbf{1}^{\bullet+}$−$\mathbf{4}^{\bullet+}$



compd[b]	method	*a*	*b*	*c*	*d*	*e*
benzene	electron diffraction	1.397				
1	X-ray	1.400(2)	1.389(2)			
	HF	1.406	1.381			
	B3LYP	1.413	1.396			
$\mathbf{1}^{\bullet+}$	X-ray	1.442(8)	1.429(11)	1.414(7)	1.404(10)	
$\mathbf{1c}^{\bullet+}$	UHF	1.445	1.354	1.424	1.371	
	UB3LYP	1.449	1.374	1.428	1.392	
$\mathbf{1e}^{\bullet+}$	UHF	1.400	1.442	1.381	1.464	
	UB3LYP	1.410	1.447	1.392	1.470	
naphthalene	X-ray	1.378	1.415	1.426	1.426	
2 (C_{2h})	X-ray	1.381(2)	1.405(3)	1.431(2)	1.449(3)	
	HF	1.370	1.412	1.435	1.435	
	B3LYP	1.392	1.413	1.435	1.461	
2 (D_2)	HF	1.369	1.415	1.435	1.424	
	B3LYP	1.391	1.414	1.435	1.450	
$\mathbf{2}^{\bullet+}$ (D_2)	X-ray	1.407(4)	1.399(6)	1.417(4)	1.459(8)	
	UHF	1.416	1.375	1.417	1.452	
	UB3LYP	1.422	1.392	1.427	1.454	
$\mathbf{2}^{\bullet+}$ (C_{2h})	UHF	1.416	1.373	1.418	1.458	
	UB3LYP	1.422	1.390	1.429	1.458	
biphenylene	X-ray	1.423	1.385	1.372	1.426	1.514
3	X-ray	1.428(2)	1.386(3)	1.366(2)	1.419(3)	1.512(3)
	HF	1.433	1.371	1.353	1.421	1.509
	B3LYP	1.437	1.390	1.372	1.429	1.509
$\mathbf{3}^{\bullet+}$	X-ray	1.420(2)	1.411(3)	1.374(2)	1.446(4)	1.470(4)
	UHF	1.405	1.416	1.374	1.435	1.466
	UB3LYP	1.424	1.420	1.380	1.454	1.470
anthracene	X-ray	1.361	1.428	1.434	1.436	1.401
4	X-ray	1.371(2)	1.416(3)	1.428(2)	1.443(3)	1.396(2)
	HF	1.358	1.433	1.440	1.429	1.391
	B3LYP	1.383	1.426	1.436	1.449	1.402
$\mathbf{4}^{\bullet+}$	X-ray (planar)	1.406(4)	1.401(5)	1.421(4)	1.439(5)	1.403(3)
	X-ray (bent)	1.405(4)	1.402(5)	1.421(3)	1.437(5)	1.406(3)
	UHF	1.398	1.394	1.408	1.439	1.405
	UB3LYP	1.409	1.406	1.422	1.447	1.407

[a] E.s.d's of mean values given in parentheses are calculated from the experimental esd's by the following equation.; $\sigma(l) = (\Sigma(1/\sigma_i^2))^{-1/2}$. [b] Thick lines denote the endocyclic bonds with respect to the bicyclic annelation.

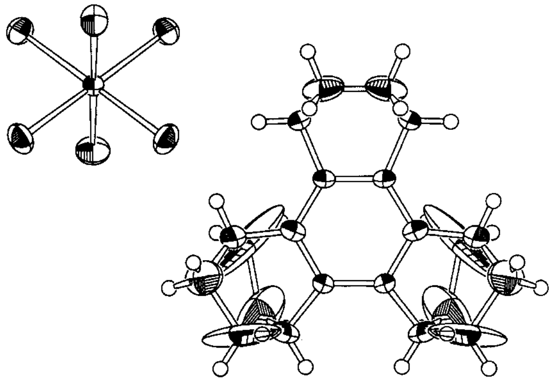


Figure 1. X-ray structure of $\mathbf{1}^{\bullet+}SbCl_6^-$. Thermal ellipsoids are drawn at the 50% probability level.

substituted benzenes. The ESR spectrum of the parent benzene radical cation shows evidence for the static distortion only at temperatures below 4.2 K.[30] ESR spectroscopic investigations of the hexamethylbenzene radical cation generated by γ-irradiation in $CFCl_3$ indicated that the Jahn−Teller distortion occurs at 77 K.[31] On the other hand, no Jahn−Teller distortion was observed in the crystalline radical cation of perfluorobenzene, $C_6F_6^{\bullet+}AsF_6^-$, at 143 K.[32] More recently, Lindner et al. have provided, for the benzene radical cation, definitive experimental proof based on the high-resolution threshold photoionization method that the elongated D_{2h} (B_{2g} in their designation) is lower by 8 cm^{-1} in energy (“only 2% of the zero-point energy of the pseudorotation coordinate alone”) than the compressed D_{2h} (B_{3g} in their designation).[33] Most theoretical studies for the benzene radical cation have indicated small energy differences between the two electronic states ($<\sim$2 kcal/mol), although the order of energy highly depends on the methods of calculations.[34] In the present case, too, these two structures are calculated to be only 0.6 kcal/mol apart, even with the neglect of electron correlation,[35] and the dynamic Jahn−Teller effect is very likely to occur even in the crystal at −100 °C.

A comparison of the experimental bond lengths of $\mathbf{1}^{\bullet+}$ with the theoretical values for $\mathbf{1e}^{\bullet+}$ shows that bond *d* is too short, whereas bond *a* is too long. On the other hand, the lengths of

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[30] Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 320.

[31] Rhodes, C. J. *J. Chem. Soc., Chem. Commun.* **1989**, 327.

[32] Richardson, T. J.; Tanzella, F. L.; Batlett, N. *J. Am. Chem. Soc.* **1986**, *108*, 4937.

[33] Lindner, R.; Müller-Dethlefs, K.; Wedum, E.; Haber, K.; Grant. E. R. *Science* **1996**, *271*, 1698.

[34] (a) Raghavachari, K.; Haddon, R. C.; Miller, T. A.; Bondybey, V. E. *J. Chem. Phys.* **1983**, *79*, 1387. (b) Kato, H.; Hirao, K.; Sano, M. *J. Mol. Struct. (THEOCHEM)* **1983**, *104*, 489. (c) Huang, M.-B.; Lunell, S. *J. Chem. Phys.* **1990**, *92*, 6081. (d) Takeshita, K. *J. Chem. Phys.* **1994**, *101*, 2192.

[35] It has been shown that the inclusion of full π-space configuration interaction (CI) gets two states to be nearly degenerate. See ref 34a,b.

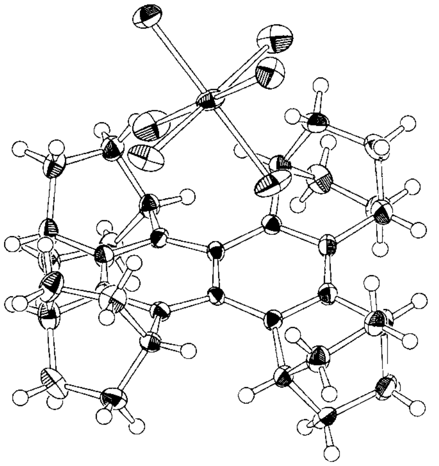
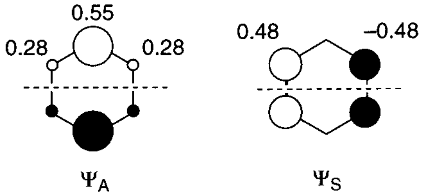


Figure 2. X-ray structure of $\mathbf{2}^{\bullet+}\mathrm{SbCl_6}^-$. Thermal ellipsoids are drawn at the 50% probability level.

Chart 1

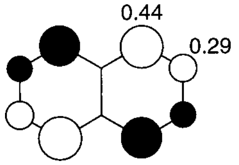


bonds *a*, *c*, and *d* are in *relatively* good agreement with the calculated values for $\mathbf{1c}^{\bullet+}$. However, bond *b* is significantly longer than the calculated values as well as the experimental value of the neutral molecule. Examination of HOMO's of **1** (Chart 1: the values given are the B3LYP/6-31G* calculated orbital coefficients) reveals that Ψ_A is expected to become a SOMO by the skeletal distortion to $\mathbf{1c}^{\bullet+}$. Since removal of an electron from Ψ_A decreases the antibonding nature of bonds *b* and *d*, these bonds should be shortened compared to the neutral molecule, which is not consistent with the experimental observations. Thus, the structural features of the benzene ring in $\mathbf{1}^{\bullet+}$ do not resemble those of the statically distorted cations in either electronic state, $\mathbf{1c}^{\bullet+}$ or $\mathbf{1e}^{\bullet+}$. From these results, although the benzene ring of $\mathbf{1}^{\bullet+}$ is distorted from the original D_{3h} symmetry,[36] there seems to be little reason to regard the observed geometry as one of the Jahn−Teller distorted (static) structures. The deviation from the ideal symmetry of the benzene ring in $\mathbf{1}^{\bullet+}$ could be due to a special crystal environment, or the crystal packing forces.

The Structure of the Naphthalene Radical Cation, $\mathbf{2}^{\bullet+}$. The crystal structure was found to consist of infinite stacks of alternating cations and anions in the columns along the crystallographic *c* axis in the unit cell. The shortest nonbonding distance between the chlorine atom of $\mathrm{SbCl_6}^-$ and the aromatic carbon atom (3.6 Å) is longer than the sum of the van der Waals radii of carbon and chlorine, as in the case of $\mathbf{1}^{\bullet+}\mathrm{SbCl_6}^-$.

The most noticeable geometrical change upon one-electron oxidation is the alteration of the symmetry of the naphthalene framework. The neutral molecule **2** was found to have approximate C_{2h} symmetry with a bent acene core, whereas the radical cation $\mathbf{2}^{\bullet+}$ has D_2 symmetry with a twisted acene core in the crystalline state. Theoretical calculations at the HF level as well as the B3LYP level of theory indicate that both the neutral molecule and the radical cation have two potential minima with C_{2h} and D_2 symmetry; the former is 2−3 kcal/mol less stable than the latter in both the neutral and radical cation states. In the crystalline state, the geometry of the molecule is expected to be highly sensitive to the environmental factors such as the crystal packing force. In the case of $\mathbf{2}^{\bullet+}$, the observed torsion angle C1−C8a−C4a−C4 is 15.6(3)°, and the overall twist in the naphthalene nucleus is 15.0 °.[37]

Chart 2



The calculated bond lengths of **2** and $\mathbf{2}^{\bullet+}$ (each with C_{2h} and D_2 symmetry) are given in Table 3. A comparison of the corresponding bond lengths between the two geometries shows that, for bonds *a*, *b*, and *c*, the differences are quite minute (only within 0.003 Å), whereas the differences are greater in the case of cross-linking bond *d* (longer by 0.004−0.011 Å in the C_{2h} symmetry). However, the conformational change has little effect on the π-bond lengths, which permits a reliable assessment of the changes in π-bond lengths upon one-electron oxidation even though the neutral and the radical cation adopt different conformations.

In the experimental structure, upon going from the neutral to the radical cation, bond *a* is significantly elongated by 0.026 Å to an averaged value of 1.407(6) Å. On the other hand, bond *b* is slightly shortened by 0.006 Å to an averaged value of 1.399(4) Å, although the difference is hardly significant on the 3σ level. These changes in the π-bond lengths are rationalized in terms of the coefficients of the HOMO of the neutral molecule **2** (Chart 2) from which an electron has been removed. In the HOMO of **2**, bond *a* is strongly bonding and bond *b* is moderately antibonding while there is a node along the C4a and C8a atoms. This indicates that electron removal should cause an elongation of bond *a* and a shortening of bond *b* whereas the lengths of the bonds *c* and *d* should be relatively unaffected. For the moment, we have no good explanation for the observed shortening of bond *c* and elongation of bond *d*.[38] Such a discrepancy between experimental observation and prediction is also seen in a comparison of the theoretical bond lengths of the neutral and the radical cation; such phenomena are most likely due to the concomitant strain imposed by the geometrical changes in adjacent bonds.

The Structure of the Biphenylene Radical Cation, $\mathbf{3}^{\bullet+}$. The unit cell was found to contain two dichloromethane molecules which are located on each side of the aromatic core, directing their chlorine atoms toward the aromatic core. The shortest nonbonding distance between the chlorine atom and the aromatic carbon atom (the four-membered ring carbon with the largest positive charge) is slightly larger (3.53 Å) than the sum of the van der Waals radii of carbon and chlorine (3.50 Å). The counteranion is located farther away from the cationic π-system. Not unexpectedly, the π-system retains its planarity.

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[36] The dynamic Jahn−Teller effect causes rapid interconversion between each of three manifolds of the $^2A_2$ or the $^2B_1$ structures, which should lead to the D_{3h} symmetric $\mathbf{1}^{\bullet+}$. Under certain crystal packing conditions, however, some of the Jahn−Teller distorted geometries may be more effectively stabilized than others. In this regard, Miller et al. have previously pointed out that static Jahn−Teller distortions strongly depend on the crystal environment: see ref 8e

[37] Determined by the definition used by Pascal et al. See: Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660.

[38] It should be noted that the same tendency is also observed in a comparison of the structures of naphthalene and its radical anion.[12b] Since naphthalene is an alternant hydrocarbon, removal of electron(s) from its HOMO is expected to have the same structural effect as the addition of electron(s) to its LUMO (i.e., the formation of the radical anion).

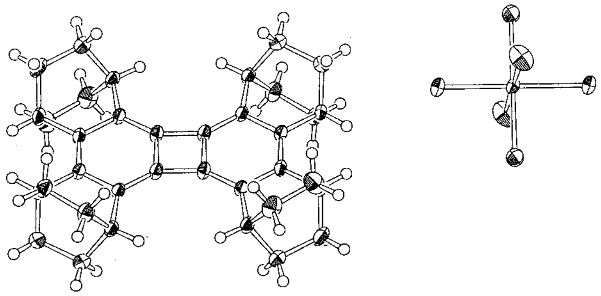
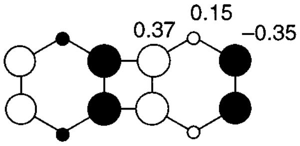


Figure 3. X-ray structure of $3^{\bullet+}SbCl_6^-$. Thermal ellipsoids are drawn at the 50% probability level.

Chart 3



As shown in Table 3, a comparison of the experimental structures of **3** and $\mathbf{3}^{\bullet+}$ indicates that not only the directions of the changes in bond lengths but also the magnitude of the changes are in good agreement with the prediction from the orbital coefficients of the HOMO of **3** (Chart 3). The absolute values of the MO coefficients of the relevant atoms are very similar in bonds *a* and *c*; the length of bond *a* increases by 0.008 Å, while that of bond *c* decreases by 0.008 Å. This is also the case in bonds *b* and *d* (increase by 0.025 and 0.027 Å, respectively). Bond *e* linking two benzene rings is subjected to the most notable change, i.e., decrease by 0.042 Å. Consequently, the four-membered ring in the radical cation is closer to a square rather than a rectangle.

It is generally accepted that biphenylene can be regarded as a weakly coupled benzenoid system rather than a dibenzo derivative of cyclobutadiene, as has been demonstrated by a substantially long *e* bond and pronounced bond alternation in the benzene ring and along the periphery,[39] which can be rationalized by the tendency of the molecule to avoid the antiaromatic nature arising from the conjugation of the $4n\pi$ circuits. Therefore, the observed contraction of bond *e* as well as reduction of the bond alternation would be due to a decrease of the unfavorable contributions from the $4n\pi$ circuits[40] caused by removal of one electron.

The calculated bond lengths of **3** and $\mathbf{3}^{\bullet+}$ are given in Table 3. When we compare the magnitude of changes in the bond lengths upon going from a neutral molecule to the radical cation (Δr), the B3LYP method gives better fit to the experimental results than the HF method.

As the only other structural study on biphenylene radical cation, Kochi and co-workers have reported the X-ray structure of the dimer radical cation of octamethylbiphenylene.[10b] In this case, a positive charge should be equally delocalized over two biphenylene moieties, and the magnitude of Δr's is expected to be roughly half of those found in $\mathbf{3}^{\bullet+}$. However, a structural comparison with the neutral octamethylbiphenylene reveals that the magnitude of Δr's is not consistent to this expectation; it is neither in accord with the prediction by the MO coefficient of its HOMO. Especially, it is to be noted that bond *d* undergoes the smallest change despite the largest coefficients of the relevant atoms.[41] Thus, the structures of dimer radical cations are less appropriate as models for the evaluation of the structural changes accompanied by electron removal than that of the radical cation $\mathbf{3}^{\bullet+}$ in the present study.

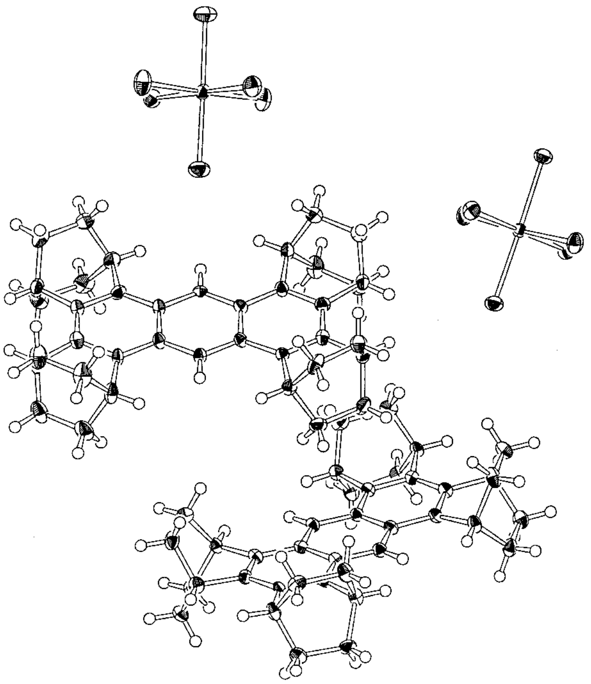


Figure 4. X-ray structure of $4^{\bullet+}SbCl_6^-$. Thermal ellipsoids are drawn at the 50% probability level.

The Structure of the Anthracene Radical Cation, $\mathbf{4}^{\bullet+}$. The crystal structure was found to contain two independent molecules of $\mathbf{4}^{\bullet+}$ ($\mathbf{4a}^{\bullet+}$ and $\mathbf{4b}^{\bullet+}$) in the asymmetric cell. The shortest nonbonding distance between the chlorine atom of $SbCl_6^-$ and the C9 (or the C10) atom carrying the largest charge is again longer (3.87 Å) than the sum of the van der Waals radii (3.5 Å).

The π-system of $\mathbf{4a}^{\bullet+}$ is essentially planar, as in the case of the 1,2,3,4,5,6,7,8-octamethylanthracene radical cation,[9c] whereas that of $\mathbf{4b}^{\bullet+}$ is slightly bent; the dihedral angles between the mean plane of the central six-membered ring and those of the outer planes are 2.04 and 3.97°, respectively. The overall folding angle[42] in the anthracene nucleus is 7.11°. This distortion of the π-system of $\mathbf{4b}^{\bullet+}$ would be ascribed to the crystal packing forces.[43]

The averaged lengths of the corresponding π-bonds in $\mathbf{4a}^{\bullet+}$ and $\mathbf{4b}^{\bullet+}$ are the same within 3σ. In $\mathbf{4a}^{\bullet+}$, bond *a*, which is

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[39] (a) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967. (b) Rabinovitz, M.; Willner, I.; Minsky, A. *Acc. Chem. Res.* **1983**, *16*, 298.

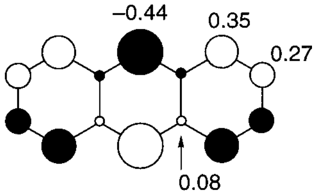
[40] The importance of a peripheral conjugation in the resonance structure of biphenylene dication has been stressed from both the theoretical and experimental point of view: see ref 39 and: (a) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **1988**, *110*, 4634. (b) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 6045. (c) Benken, R.; Finneiser, K.; von Puttkamer, H.; Günther, H.; Eliasson, B.; Edlund, U. *Helv. Chim. Acta* **1986**, *69*, 955. (d) Benken, R.; Günther, H. *Helv. Chim. Acta* **1988**, *71*, 694.

[41] For this reason, several factors could be proposed that would cause structural deformation, e.g., close contact to the chlorine atom in the counteranion or a partial overlap of the aromatic rings in the dimeric pair in the crystal.

[42] Defined as the dihedral angle between the mean planes comprised of the atoms C1, C2, C3, and C4 and that comprised of C5, C6, C7, and C8.

[43] According to Rhine, the nonplanarity of the dianion of naphthalene[13j] and anthracene[13k] is mostly due to the coordination of the lithium cation to the anionic carbon centers. This notion is reinforced by the planarity of the solvent-separated naphthalene and antharcene radical anions.[12b] These observations suggst that the divergence from aromaticity has little effect on the planarity of aromatic systems. The same should hold for the corresponding radical cation, when no significant coordination with the counteranion is present. Thus, it can be concluded that the acene core of the anthracene radical cation is intrinsically planar.

Chart 4



strongly bonding in the HOMO of **4** (Chart 4), is elongated by 0.035 Å to an averaged value of 1.406(4) Å, while bond *b*, which is moderately antibonding in the HOMO, is shortened by 0.015 Å to an averaged value of 1.401(5) Å. Although the changes in the lengths of bonds *c*, *d*, and *e* are not significant on the 3σ criterion, both the direction and magnitude of the changes are qualitatively in accordance with what can be expected from the orbital coefficients of the HOMO of **4**, as in the cases of **2**$^{\bullet+}$ and **3**$^{\bullet+}$. These subtle changes are also well reproduced by theoretical calculations.

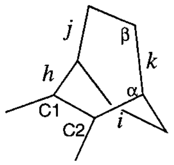
The calculated bond lengths of **4** and **4**$^{\bullet+}$ are given in Table 3, and once again, the B3LYP method gives better fit of Δr's to the experimental results. In particular, the direction of the change of bond *d* in the HF geometry (+0.010 Å) is opposite to the experimental observation (−0.004 Å for **4a**$^{\bullet+}$ and −0.006 Å for **4b**$^{\bullet+}$), whereas that in the B3LYP geometry (−0.002 Å) agrees well with the experiment, which is also consistent with the anticipation from its weak antibonding character of this bond in the HOMO of **4**.

Common Features of Radical Cations, 2$^{\bullet+}$−4$^{\bullet+}$. Besides the changes in the lengths of π-bonds, characteristic changes in the σ-bond lengths of the bicyclic frameworks involved in σ−π conjugation (C−C hyperconjugation)[44] are observed in **2**$^{\bullet+}$−**4**$^{\bullet+}$. Thus, the C_{ar} −C_{α} bonds (antibonding in the HOMO's of the neutral molecules) are shortened, except for bond *h* in **3**$^{\bullet+}$, while all of the C_{α}−C_{β} bonds (bonding in the HOMO's) are lengthened compared to those of the corresponding neutral molecules. The averaged lengths of these bonds together with the theoretical values are listed in Table 4. Such hyperconjugative changes are reproduced by both the HF and the B3LYP calculations, although the magnitude of the changes is generally smaller than the experimental values.

UV−vis−NIR Spectra of the Radical Cations. The electronic absorption spectra of these radical cations are shown in Figure 5 and are summarized in Table 5. All measurements were carried out in dichloromethane under ambient conditions, except for **1**$^{\bullet+}$SbCl$_6^-$ which was taken under vacuum. During the measurements, the spectra did not show any decrease in intensity over several hours in all cases, which can be taken as another piece of evidence of unusual stability of these radical cations.

All the spectral features of **2**$^{\bullet+}$−**4**$^{\bullet+}$ are similar to those of the parent radical cations, which indicates that the electronic natures inherent in the parent radical cations are retained. Hence, the characteristic long-wavelength absorption bands could safely be assigned to the HOMO-1 → SOMO transitions on the basis of the previous interpretation made for the parent radical cations,[45] but these bands are red-shifted by 50−200 nm, undoubtedly due to the hyperconjugative effect of the BCO frameworks.[46] As for the benzene radical cation **1**$^{\bullet+}$, the HOMO → SOMO transition is presumably too low an energy to be observed, since the energy difference between these orbitals, which are degenerate in the neutral state, would be expected to vanish due to the dynamic Jahn−Teller effect at room temperature; therefore, the lowest energy absorption can reasonably be assigned to the HOMO-1 → SOMO transition.

Table 4. Experimental and Calculated σ-Bond Lengths (Å)[a] of **2**−**4** and Their Radical Cations



compd	method	*h*	*i*	*j*	*k*
2 (C_{2h})[b]	X-ray	1.518(2)	1.513(1)	1.537(2)	1.534(2)
	HF	1.526	1.518	1.544	1.541
	B3LYP	1.525	1.517	1.553	1.550
2$^{\bullet+}$ (D_2)[b]	X-ray	1.508(5)	1.508(5)	1.541(4)	1.542(4)
	UHF	1.517	1.514	1.546	1.541
	UB3LYP	1.512	1.511	1.556	1.551
3	X-ray	1.498(2)	1.508(2)	1.533(2)	1.535(2)
	HF	1.509	1.516	1.542	1.543
	B3LYP	1.509	1.515	1.550	1.552
3$^{\bullet+}$	X-ray	1.505(2)	1.507(2)	1.545(2)	1.540(2)
	UHF	1.508	1.513	1.543	1.546
	UB3LYP	1.506	1.507	1.553	1.557
4	X-ray	1.510(2)	1.509(2)	1.531(2)	1.533(2)
	HF	1.517	1.516	1.543	1.543
	B3LYP	1.515	1.515	1.552	1.552
4$^{\bullet+}$	X-ray (planar)	1.496(4)	1.501(4)	1.544(3)	1.540(3)
	X-ray (bent)	1.496(4)	1.506(3)	1.546(3)	1.538(3)
	UHF	1.514	1.514	1.544	1.543
	UB3LYP	1.509	1.511	1.555	1.553

[a] Esd's of mean values are given in parentheses. [b] Although there are two kinds of chemically nonequivalent bonds for bonds *j* and *k* in the crystalline state of **2** and **2**$^{\bullet+}$, the values of these bond lengths are averaged for convenience.

Concluding Remarks

The most essential benzenoid aromatics, namely, benzene, naphthalene, biphenylene, and anthracene annelated with rigid bicyclic frameworks, were shown to have higher oxidizability than the corresponding methyl-substituted analogues by cyclic voltammetry. Actually the quite stable radical cation salts were obtained by chemical one-electron oxidation, which allowed the successful determination of the molecular structures by single-crystal X-ray diffraction. Such endowment of enhanced thermodynamic and kinetic stability is ascribed to the steric as well as electronic effects of the rigid bicyclic frameworks that surround the π-systems.

The present study demonstrates that, even without the aid of n- or π-donor substitituents, the proper structural modification only with σ-frameworks can enable us to obtain remarkably stable aromatic hydrocarbon radical cations that otherwise are not stable enough to be isolated. The detailed investigation of the π-system of the radical cations determined experimentally

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[44] The changes in the length of σ-bonds involved in C−C hyperconjugation have been experimentally and theoretically demonstrated. See ref 18b and: (a) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3990. (b) Laube, T. *Acc. Chem. Res.* **1995**, *28*, 399 and references therein. (c) Laube, T.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1997**, *119*, 3087.

[45] For naphthalene see: (a) Bally, T.; Carra, C.; Fülscher, M. P.; Zhu, Z. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1759. (b) Niederalt, C.; Grimme, S.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1995**, *245*, 455. (c) Salama, F.; Allamandola, L. J. *J. Chem. Phys.* **1991**, *94*, 6964. For biphenylene see: Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1972**, *95*, 3473. For antharcene see ref 45a,b and: Negri, F.; Zgierski, M. Z. *J. Chem. Phys.* **1994**, *100*, 1387.

[46] If we make the reasonable assumption that the σ-orbitals that are involved in hyperconjugative interactions with π-orbitals have nearly identical levels of energy, the lower energy π-MO should be more effectively lifted, which would lead to a narrowing of the gaps between the SOMO and the lower occupied π-orbitals. However, this is not always the case because the degree of the energy lift depends on the substitution patterns.

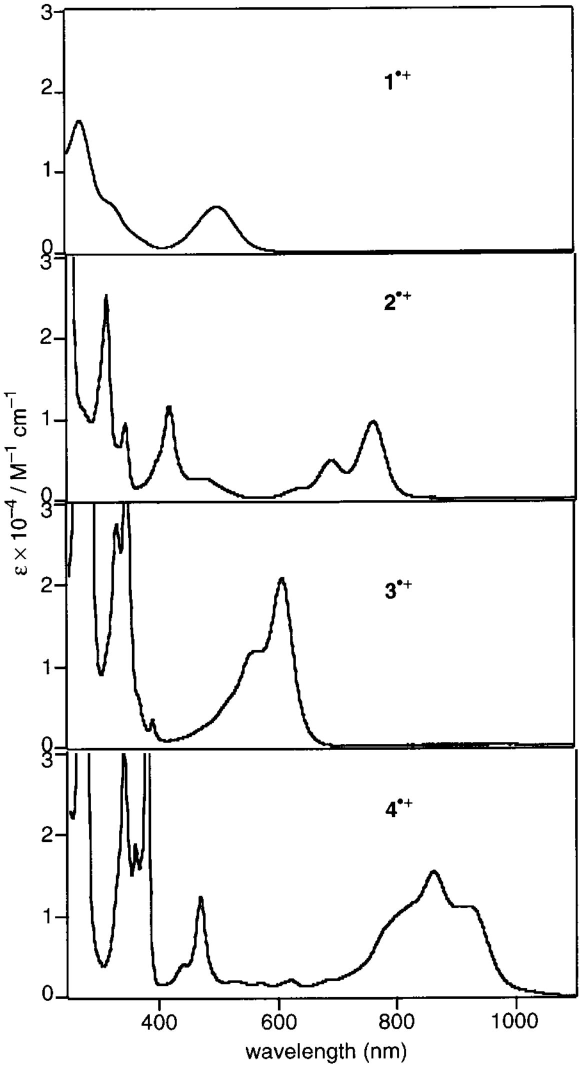

Figure 5. Electronic absorption spectra of the radical cations $1^{\bullet+}-4^{\bullet+}$ in dichloromethane.

Table 5. Absorption Maxima (nm) (ϵ, cm^{-1} M^{-1}) of the Radical Cations $1^{\bullet+}-4^{\bullet+}$ in Dichloromethane

$1^{\bullet+}$	$2^{\bullet+}$	$3^{\bullet+}$	$4^{\bullet+}$
270 (16500)	313 (25300)	274 (67800)	276 (92800)
501 (5700)	344 (9500)	284 (78500)	341 (30200)
	418 (11700)	329 (27500)	359 (19000)
	475 (2700)	346 (35800)	379 (50800)
	690 (5000)	390 (3500)	440 (4000)
	761 (9700)	563 (11800)	469 (12300)
		608 (20900)	862 (15500)
			920 (11100)

not only contributes to the significant understanding of the structures of hydrocarbon radical cations, but also provides important experimental support for the validity of modern computational methods.

Experimental Section

Materials and Instruments. Octamethylnaphthalene,[47] octamethylbiphenylene,[47] and 1,2,3,4,5,6,7,8-octamethylanthracene[48] were prepared according to the literature procedures. Hexamethylbenzene was purchased from TCI and used as received. Dichloromethane was distilled twice over P_2O_5. Carbon disulfide, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and hexane were distilled over P_2O_5. Benzene was distilled over Na. TCNQ and $SbCl_5$ (0.1 M in dichloromethane) were purchased from Aldrich and used as received. Tetrabutylammonium perchlorate (TBAP) was recrystallized from hexane and ethyl acetate. Electronic spectra were taken on a Shimadzu UV-3101(PC)S spectrometer. Cyclic voltammetry was performed on a BAS-50W electrochemical analyzer. The CV cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and a Ag/$AgNO_3$ reference electrode. The measurements were carried out in 1.0 mM solutions of substrate using TBAP as supporting electrolyte (0.1 M), and the oxidation potential values were calibrated with ferrocene.

Computational Methods. All calculations were carried out with the GAUSSIAN 98 series of electronic structure programs,[49] using extended basis sets, including d-type polarization functions on carbon (6-31G*). The geometries were optimized with the restricted Hartree–Fock (RHF) and Becke hybrid (RB3LYP) methods for the neutral compounds, and the unrestricted HF (UHF) and UB3LYP methods for the radical cations, respectively. The symmetries of the molecules are imposed throughout the calculations for **1** (D_{3h}), **2** (C_{2h} and D_2), and **3**–**4** (D_{2h}), and these symmetries are reasonably assumed to be preserved in the radical cations $2^{\bullet+}-4^{\bullet+}$. In the case of $1^{\bullet+}$, anticipated Jahn–Teller distortion should lower the molecular symmetry, and both symmetry-constraint and -nonconstraint approaches converged to essentially the same minima (C_{2v}).

General Procedures for the Isolation of Radical Cation Salts. Compound **1** (79 mg, 0.25 mmol) was dissolved in anhydrous carbon disulfide (6 mL) under an argon atmosphere in a 25 mL flask equipped with a glass filter and a rubber septum. The solution was cooled to 0 °C in an ice–water bath, and a dichloromethane solution of $SbCl_5$ (0.38 mL, 0.38 mmol) was added dropwise via a syringe. The solution immediately turned deep red and a large amount of solid precipitated. The precipitate was filtered and washed thoroughly with anhydrous carbon disulfide (4 × 2 mL). Drying at room temperature in vacuo afforded $1^{\bullet+}SbCl_6^-$ as a ruby red solid (158 mg, 98%). The radical cation salt was dissolved in the mixture of anhydrous 1,2-dichloroethane and 1,1,2,2-tetrachloroethane under an argon atmosphere, and anhydrous hexane was carefully layered. After standing at 5 °C for a week, single crystals suitable for X-ray analysis were obtained.

The radical cation salts of **2**–**4** were prepared as described above ($2^{\bullet+}SbCl_6^-$: dark green, 97% yield; $3^{+\bullet}SbCl_6^-$: dark blue, 99% yield; $4^{\bullet+}SbCl_6^-$: dark green, 94% yield.), and single crystals suitable for X-ray analysis were obtained by the slow diffusion of hexane for $3^{\bullet+}SbCl_6^-$ and benzene for $2^{\bullet+}SbCl_6^-$ and $4^{\bullet+}SbCl_6^-$ into their solutions in dichloromethane at room temperature under an argon atmosphere.

X-ray Crystallographic Analysis. In the case of **1**–**4**, measurements were carried out under ambient conditions on a Rigaku AFC7R diffractometer with Cu Kα radiation. In the case of $1^{\bullet+}SbCl_6^- - 4^{\bullet+}SbCl_6^-$, the crystals were covered with a layer of silicone oil, and a suitable crystal was selected, mounted on a glass fiber, and immediately placed in the low-temperature nitrogen stream. Measurements were carried out on a Rigaku RAXIS-IV imaging area plate detector with Mo Kα radiation at −100 °C to suppress the expected large thermal motions in hexachloroantimonate anion.

The crystal structures were solved by direct methods for all the compounds except for $4^{\bullet+}SbCl_6^-$ (heavy-atom Patterson method) and refined by full-matrix least-squares procedures using the teXsan program package. 1,1,2,2-Tetrachloroethane in the crystal of $1^{\bullet+}SbCl_6^-$ was found to be highly disordered, and could not be well modeled as a chemically reasonable molecule throughout the refinement. All non-hydrogen atoms were refined anisotropically, except those of the

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[47] Hart, H.; Teuerstein, A. *Synthesis*. **1979**, 693.

[48] Meador, M. A.; Hart, H. *J. Org. Chem*. **1989**, *54*, 2336.

[49] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challocombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.5*; Gaussian, Inc.: Pittburgh, PA, 1998.

benzene molecule included in the crystal of **4**$^{\bullet+}$SbCl$_6^-$ which were maintained isotropic. Hydrogen atoms in **1**−**4** were refined isotropically, and those in **1**$^{\bullet+}$SbCl$_6^-$−**4**$^{\bullet+}$SbCl$_6^-$ were included in the refinement at calculated positions, but not refined. Some details of the data collection and refinement are given in Table 2. Full details are provided in the Supporting Information.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 10146102) and a Grant-in-Aid for Scientific Research (A) (No. 09304060) from the Ministry of Education, Science, Sports and Culture, Japan. We thank Professor K. Tamao for the use of the X-ray diffractometer and Dr. S. Yamaguchi for helpful discussions.

Supporting Information Available: Tables of data-collection parameters, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters and selected figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0014436