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Radical Cation and Dication of Fluorene Fully Annelated with Bicyclo[2.2.2]octene Units: Importance of the Quinoidal Resonance Structure in the Cationic Fluorene

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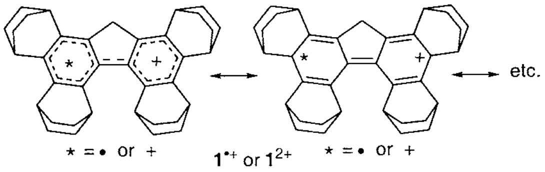
ABSTRACT



Fluorene 1 fully annelated with bicyclo[2.2.2]octene units was newly synthesized and oxidized to stable cationic species. The structure of radical cation salt $1^{•+}SbCl_6^-$ was determined by X-ray crystallography, while the first fluorene dication 1^{2+} was characterized by ^1H and ^{13}C NMR at −80 °C. Combined with the results of theoretical calculations, an important contribution of a quinoidal structure to the resonance hybrid was demonstrated in both $1^{•+}$ and 1^{2+}.

Fluorene is regarded not only as a dibenzo derivative of cyclopentadiene but also as a derivative of biphenyl whose conformation is planarized by a methano bridge connecting the ortho carbons of the two phenyl rings. From such a viewpoint, a number of derivatives of poly(2,7-fluorene)s have been synthesized, and their application to electronic devices has been tested.[1] Through these studies, the electrical conductivity of the electrochemically hole-doped poly(2,7-fluorene)s ($10^{-4} - 10^{-5}$ S/cm)[2] was found to be considerably lower than that of the electrochemically hole-doped poly(*p*-phenylene) (10^2 S/cm).[3] The reason for such a difference in conductivity is still not clear because of the complexity of the conduction mechanism. As an important factor in the conduction mechanism, a possible structural change from a benzenoid to a quinoidal structure upon hole-doping was implied in the cases of biphenyl[4] and poly(*p*-phenylene)[5] on the basis of the combined studies of vibrational spectra and theoretical calculations. However, to the best of our knowledge, neither the X-ray crystallographic study of the radical-cation salt nor the NMR observation of the dication of biphenyl derivatives has been reported due to the intrinsic instability of these cationic species.[6] Furthermore, the occurrence of such a structural change from benzenoid to quinoidal form in the cationic states has not been investigated for fluorene as a planarized model of biphenyl.

In our previous studies, the annelation of cyclic π-conjugated systems with bicyclo[2.2.2]octene (abbreviated as BCO) units[7] has been shown to be quite effective for

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[1] For a review, see: Leclerc, M. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2867−2873.

[2] Waltman, R. J.; Bargon, J. *J. Electroanal. Chem.* **1985**, *194*, 49−62.

[3] Tabata, M.; Satoh, M.; Kaneto, K.; Yoshino, K. *J. Phys. Soc. Jpn.* **1986**, *55*, 1305−1310.

[4] Furuya, K.; Torii, H.; Furukawa, Y.; Tasumi, M. *J. Mol. Struct. (THEOCHEM)* **1998**, *424*, 225−235.

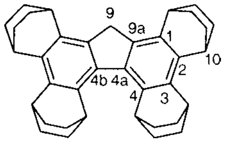
[5] Cuff, L.; Cui, C.; Kertesz, M. K. *J. Am. Chem. Soc.* **1994**, *116*, 9269−9274.

[6] In some polymethoxy derivatives, stable radical cations were generated but were not isolated: Grant, B.; Clecak, N. J.; Oxsen, M.; Jaffe, A.; Keller, G. S. *J. Org. Chem.* **1980**, *45*, 702−705.

[7] Komatsu, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 407−419.

10.1021/ol026841n CCC: $22.00

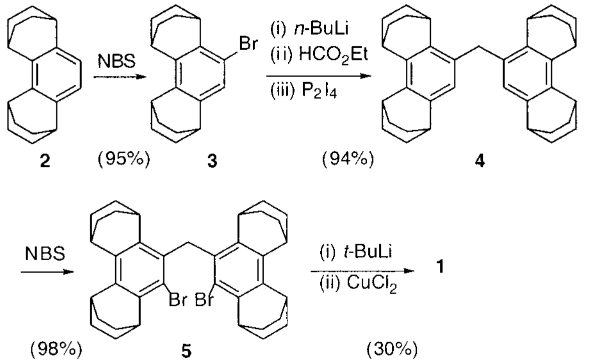
stabilization of their radical cations[8] and dications.[9] One of the advantages of the structural modification by annelation with alkyl sustituents such as BCO units is that the intrinsic electronic properties of a cationic π-system can be examined without significant perturbation of the π-electron systems. In the present paper, we describe the first X-ray structural study of a fluorene radical-cation salt and the first NMR observation of the fluorene dication using a derivative **1** fully annelated with BCO units.



1

For the synthesis of fluorene **1**, bromobenzene **3** was converted to diphenylmethane **4**, as shown in Scheme 1: then, after dibromination, the dilithiation of dibromide **5** and subsequent intramolecular oxidative coupling with $CuCl_2$ was employed successfully. Fluorene **1** is a novel 1,2,3,4,5,6,7,8-octa-substituted derivative, and the π-system of **1** was anticipated to be twisted due to the steric repulsion of the substituents at the 4- and 5-positions as observed in other octa-substituted derivatives.[10,11] In fact, the X-ray crystallography of **1**[12] demonstrated that the π-system of fluorene **1** was twisted with a dihedral angle of 12° between the mean planes of the two benzene rings.

Scheme 1



The redox properties of **1** were examined by cyclic voltammetry in CH_2Cl_2 at room temperature, which exhibited a reversible first oxidation wave ($E_{1/2} = +0.56$ V vs Fc/Fc$^+$) and a quasi-reversible second oxidation wave ($E_{pa} = +0.88$ V). The first oxidation potential of **1** is remarkably lower than the oxidation potential of parent fluorene measured in acetonitrile ($E_{pa} = +1.28$ V vs Fc/Fc$^+$).[13] This is apparently due to the elevated HOMO level caused by inductive and $\sigma-\pi$ conjugative effects of annelation with BCO units.[7−9] Also, the enhanced stability of the radical cation $\mathbf{1}^{\bullet+}$ is clearly demonstrated by the reversibility of the first oxidation wave.

When chemical one-electron oxidation of **1** was conducted with 1.5 equiv of $SbCl_5$ in CH_2Cl_2, the yellow solution of **1** immediately turned to a green solution that showed a broad single-line ESR signal ($g = 2.003$) persistent at room temperature (Figure 1a), indicating the generation of a stable radical species. As concerns the stability of a fluorene radical cation, it has been reported that the proton at the 9-position is prone to be released to give the neutral fluorenyl radical.[13] If such deprotonation takes place for $\mathbf{1}^{\bullet+}$, a two-line ESR signal due to the coupling with a single proton at the 9-position of $\mathbf{6}^{\bullet}$ should be observed, as shown in Figure 1c.[14]

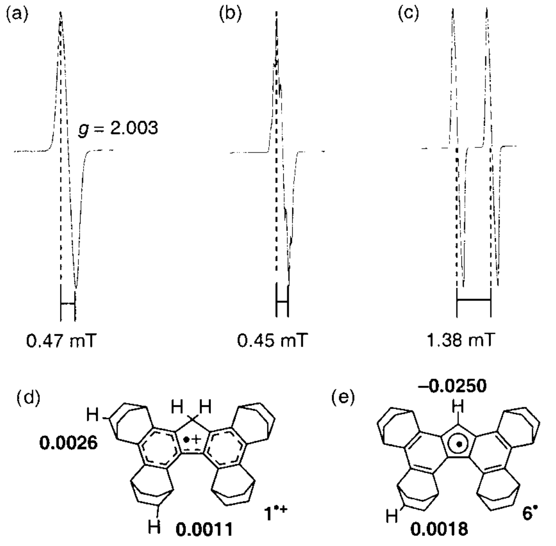


Figure 1. (a) Observed and (b) calculated ESR spectra for $\mathbf{1}^{\bullet+}$, (c) calculated ESR spectrum for $\mathbf{6}^{\bullet}$, and selected spin densities by B3LYP/6-31G(d) for (d) $\mathbf{1}^{\bullet+}$ and (e) $\mathbf{6}^{\bullet}$.

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[11] Marks, V.; Gottlieb, H. E.; Melman, A.; Byk, G.; Cohen, S.; Biali, S. E. *J. Org. Chem.* **2001**, *66*, 6711−6718.

[12] Crystal data for **1**: $C_{37}H_{42}$, triclinic; space group P-1; a =10.3419(10) Å, b = 22.206(2) Å, c = 12.4509(16) Å, α = 90.042(3)°, β = 114.478(2)°, γ = 89.959(2)°, V = 2602.4(5) Å^3, Z = 4. The final R values and GOF were $R_1 = 0.0802$, w$R_2 = 0.1704$ ($I > 2s(I)$), and GOF = 1.211.

[13] Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867−2872.

[14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; 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,

Table 1. Observed and Calculated Bond Lengths (Å)[a] of **1**, **1**$^{\bullet+}$, and **1**$^{2+}$

compd	method	C1−C2	C2−C3	C3−C4	C4−C4a	C4a−C9a	C1−C9a	C4a−C4b	C9−C9a	C2−C10
1	X-ray[a]	1.409(3)	1.393(3)	1.414(3)	1.404(3)	1.415(3)	1.378(3)	1.499(5)	1.500(3)	1.499(3)
	calcd[b]	1.409	1.397	1.417	1.408	1.421	1.386	1.495	1.509	1.515
1$^{\bullet+}$	X-ray[a]	1.419(3)	1.406(3)	1.409(3)	1.417(3)	1.443(3)	1.377(3)	1.449(3)	1.486(3)	1.498(2)
	calcd[b]	1.425	1.412	1.403	1.433	1.445	1.373	1.447	1.505	1.503
1^{2+}	calcd[b]	1.447	1.426	1.394	1.458	1.472	1.361	1.407	1.502	1.481

[a] Averaged values are shown. Estimated standard deviations of mean values given in parentheses are calculated from the following equation: $\sigma(l) = (\Sigma(1/\sigma_i^2))^{-1/2}$. [b] B3LYP/6-31G(d).

Totally different from such an expectation, a single-line signal was observed, with the peak-to-peak width in good agreement with that for the calculated signal for **1**$^{\bullet+}$ (Figure 1b).[14]

Hence, the observed ESR signal should be assigned to the fluorene radical cation **1**$^{\bullet+}$, although no hyperfine coupling could be observed.

The radical cation salt **1**$^{\bullet+}SbCl_6^-$ was precipitated as a green solid when the one-electron oxidation was conducted with 1.5 equiv of $SbCl_5$ in a CS_2 solution of **1**. A single crystal was grown by very slow diffusion of hexane into a solution of **1**$^{\bullet+}SbCl_6^-$ in CH_2Cl_2, and X-ray crystallography[15] was conducted. The obtained molecular structure is shown in Figure 2, and the averaged bond lengths are given in Table 1 together with those for neutral **1** and its dication **1**$^{2+}$. In the X-ray structure of **1**$^{\bullet+}SbCl_6^-$, the π-system of **1**$^{\bullet+}$ was also found to be twisted with a dihedral angle of 17° between the mean planes of the two six-membered rings. The twisting angle is larger than that of neutral **1** due to the enhanced steric repulsion between the bridgehead protons in radical cation **1**$^{\bullet+}$ caused by the shortening of the C4a−C4b bond upon one-electron oxidation of **1** (1.499 Å) to **1**$^{\bullet+}$ (1.449 Å).

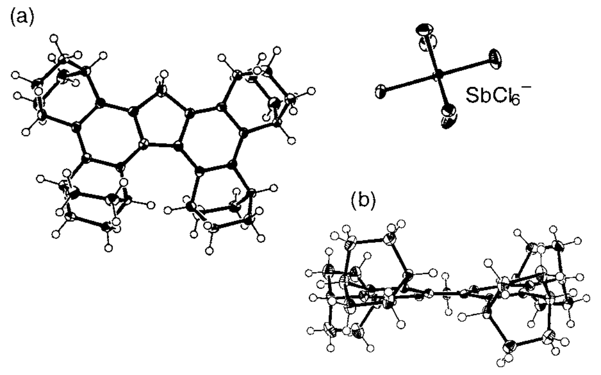

Figure 2. ORTEP drawings showing (a) **1**$^{\bullet+}$ $SbCl_6^-$ and (b) the side view of the **1**$^{\bullet+}$ moiety.

This change of the bond length can be qualitatively explained on the basis of the shape of HOMO in neutral **1**.[8c] As shown in Figure 3, the nature of the bond C4a−C4b (1.499(5) Å in **1**) is strongly antibonding in the HOMO of neutral **1**. This antibonding character is weakened upon removal of one electron from the HOMO, causing the shortening to 1.449(3) Å in **1**$^{\bullet+}$. The tendency in the changes in the other C(sp^2)−C(sp^2) bond lengths can be interpreted in a similar way. Upon one-electron oxidation, the bonds C3−C4 and C1−C9a that are antibonding in the HOMO become slightly shortened, and conversely the bonds C1−C2, C2−C3, C4−C4a, and C4a−C9a that are bonding in the HOMO become elongated, as shown in Table 1. Concerning the C(sp^2)−C(sp^3) bond length, the C9−C9a and C2−C10 bonds were found to become slightly shortened upon going from **1** to **1**$^{\bullet+}$: from 1.500(3) to 1.486(3) Å for C9−C9a and from 1.499(3) to 1.498(2) Å for C2−C10. This bond shortening might be taken as evidence for the presence of the $\sigma-\pi$ conjugation (hyperconjugation) between the electron-deficient 2p orbital of the π-system and the C−H or C−C σ-bonds.[16]

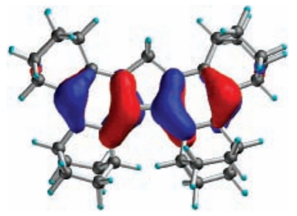

Figure 3. HOMO of **1** calculated by B3LYP/6-31G(d).

The observed changes in bond length upon one-electron oxidation, described above, are well reproduced by theoretical calculations (B3LYP/6-31G(d)),[14] proving the reliability of these calculations. The calculation on **1**$^{\bullet+}$ also indicated that the spin density is mainly localized on C2 and C7 (0.265), supporting the substantial contribution of the resonance

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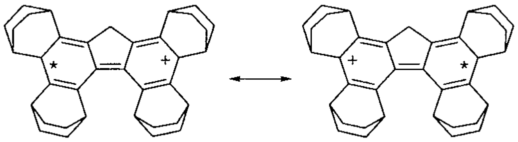
I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Crystal data for **1**$^{\bullet+}\cdot SbCl_6^-\cdot(CH_2Cl_2)_2$: $C_{39}H_{46}Cl_{10}Sb$, orthorhombic; space group $P2(1)2(1)2(1)$; a =10.5029(8) Å, b = 19.6289(15) Å, c = 20.4634(15) Å, V = 4218.7(6) Å^3, Z = 4. The final R values and GOF were $R_1 = 0.0392$, $wR_2 = 0.0942$ ($I > 2s(I)$), and GOF = 1.106.

(16) For the more detailed discussion, see ref 8c.

structure **A**↔**B** (* = •) for $\mathbf{1}^{\bullet+}$.[17] Accordingly, it would be reasonable to conclude that the quinoidal resonance structure involving the $\sigma-\pi$ conjugation is quite important in the enhanced stability in the radical cation salt $\mathbf{1}^{\bullet+}SbCl_6^-$.



A **B**

When fluorene **1** was reacted with an excess (28 equiv) of $SbCl_5$ in CD_2Cl_2 at −80 °C, a purple-colored solution was obtained that was ESR-silent and exhibited the ^1H and ^{13}C NMR spectra shown in Figure 4. It is to be noted that the NMR signals for the sp^2 carbons are considerably downfield shifted, and this spectrum is most reasonably assigned to the dication $\mathbf{1}^{2+}$ on the basis of the comparison of the observed and calculated (GIAO/HF/6-31G(d)//B3LYP/6-31G(d)) chemical shifts shown in Table 2. Also shown are the values of the calculated Mulliken charge. This dication was stable only at −80 °C in CD_2Cl_2, and when the temperature was raised to −60 °C, it underwent gradual decomposition. Diarylmethanes are known to react with $SbCl_5$, causing ready deprotonation at the benzyl position to give diarylmethyl cations.[18] In the case of fluorene **1**, such deprotonation did not take place due to probably unfavorable antiaromatic instability of the fluorenyl cation.[19]

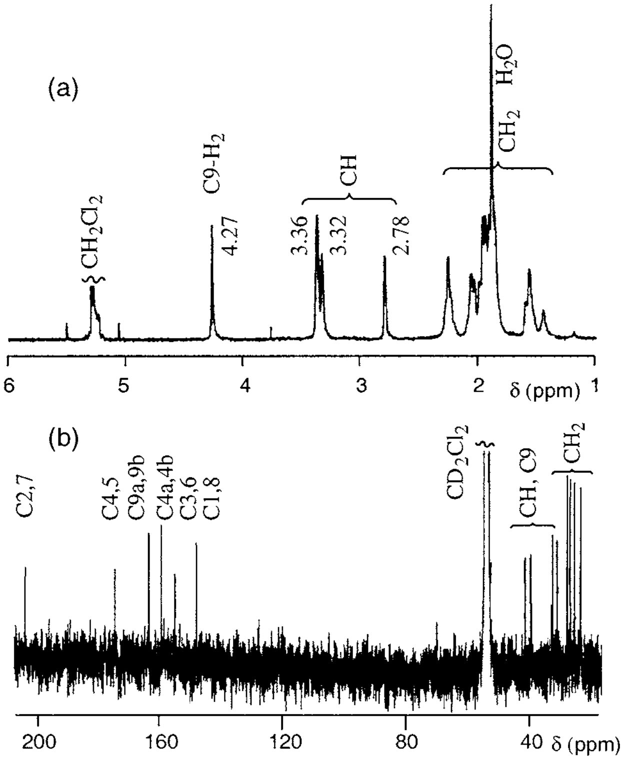


Figure 4. (a) ^1H NMR and (b) ^{13}C NMR spectra for $\mathbf{1}^{2+}$.

Table 2. Observed and Calculated[a] ^{13}C NMR Chemical Shifts and Charge Densities[b] for sp^2 Carbons of $\mathbf{1}^{2+}$

	C1	C2	C3	C4	C4a	C9a
δ (obsd)/ppm	148.0	202.7	154.9	174.0	159.2	163.3
δ (calcd)/ppm	140.3	221.5	148.9	181.5	159.1	159.3
calcd charge	0.089	0.158	0.069	0.135	0.029	0.062

[a] GIAO/HF/6-31G(d)//B3LYP/6-31G(d). [b] B3LYP/6-31G(d).

The signal for C2 is particularly downfield shifted in agreement with the calculated positive charge (+0.158) residing on this carbon. This fact, combined with the calculated results on the structure of dication $\mathbf{1}^{2+}$, that is, definite shortening of bonds C1−C9a, C3−C4, and C4a−C4b and elongation of bonds C1−C2, C2−C3, C4−C4a, and C4a−C9a (Table 1), clearly indicates that a quinoidal structure such as **A** (= **B**) (* = +) is greatly contributing also to the resonance hybrid of the dication $\mathbf{1}^{2+}$.

In summary, we succeeded in the first X-ray structural study of the radical cation salt of fluorene derivative $\mathbf{1}^{\bullet+}SbCl_6^-$ and also the first NMR observation of fluorene dication $\mathbf{1}^{2+}$, taking advantage of a structural modification with BCO units. From the experimental observations and theoretical calculations of $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$, it was concluded that the quinoidal resonance structure is greatly contributing in these cationic fluorenes as calculated for cationic biphenyl.[4] Such a quinoidal structure is also supposed to be contributing in hole-doped poly(2,7-fluorene)s. Thus, the rather low electrical conductivity observed for poly(2,7-fluorene)s[2] might be attributed not to the electronic structure of the hole-doped poly(2,7-fluorene)s but to other factors such as rather poor intermolecular interaction.

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Supporting Information Available: Detailed experimental procedures and CIF data of **1** and $\mathbf{1}^{\bullet+}SbCl_6^-\cdot(CH_2Cl_2)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] In comparison, the spin density on C1 is −0.051; C3, −0.056; C4, 0.100; C4a, 0.124; C9a, 0.095.

[18] Holmes, J.; Pettit, R. *J. Org. Chem.* **1963**, *28*, 1695−1696.

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