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Short nonbond and long C–C bond in naphthalene-1,8-diylbis(10-methylacridinium) and the corresponding hexaphenylethane derivative: a new electrochromic pair exhibiting dynamic redox properties

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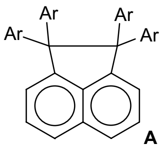
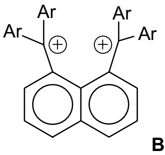
Abstract—The extremely long C–C bond [1.696(3) Å] in the colorless dispiroacenaphthene-type hexaphenylethane is cleaved readily upon electrochemical transformation into the orange colored naphthalene-1,8-diylbis(acridinium), in which the two cationic units are forced to overlap in a face-to-face manner exhibiting the shortest $C^+ \cdots C^+$ interatomic contact of 2.927(7) Å among the values ever reported.

Polyarylated C_{sp^3}–C_{sp^3} bonds are more elongated than the standard[1] due to the steric repulsion[2] between bulky aryl substituents, thus exhibiting special properties[3] related to their reduced bond energy.[4] In general, they undergo easy bond fission under homolytic[5] or mesolytic[6] conditions, the latter of which makes the central point of our novel design for the electrochromic systems based on dynamic redox properties of hexaphenylethane (HPE)-type electron donors.[7] Their weakened 'ethane' bonds are cleaved to give the bond-dissociated dications upon two-electron oxidation, and the starting material was regenerated accompanied by C–C bond formation upon two-electron reduction of the dications with an arylene spacer. The long C–C bonds in the neutral HPE-donors as well as the short $C^+ \cdots C^+$ nonbonded contacts in the dications are intriguing structural features often observed in these redox systems, which prompted us to exploit one of the extreme cases by using the naphthalene-1,8-diyl skeleton.[8]



A



B^{2+}

The central 'ethane' bond of 1,1,2,2-tetraarylacenaphthene **A** would be longer than any other HPE-type compounds due to the torsional fixation that increases the 'front' strain[9] between aryl substituents, whereas the two cationic parts in the dication $\mathbf{B}^{2+}$ are forced to arrange in a proximity to induce the very short $C^+ \cdots C^+$ nonbonded contact. Before the completion of this work, Gabbaï and co-workers reported very recently[10] the preparation of some derivatives of **A** (Ar = 4-$MeOC_6H_4$) and $\mathbf{B}^{2+}$ (Ar = 4-$MeOC_6H_4$; C_6H_5), whose geometrical features are in accord with our prediction described above. Here we report our own results on **1** and $\mathbf{2}^{2+}$ containing the acridine-type skeletons that exhibit much enhanced geometrical features. The former donor possesses one of the longest C–C single bonds (1.70 Å),[2e] and the latter dication exhibits the shortest $C^+ \cdots C^+$ interatomic contact (2.93 Å) ever reported between the two cationic moieties. Furthermore, this pair can be interconverted reversibly thus demonstrating the electrochromic response with vivid change in color (Scheme 1).

9,9′-(Naphthalene-1,8-diyl)bis(acridine) **3** was chosen as a key synthon, which would be transformed into the corresponding dication $\mathbf{2}^{2+}$ by double quaternization. Although many 9-arylacridines could be readily

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Keywords: Long bond; Hexaphenylethane; Short contact; π–π Interaction; *peri*-Interaction; Carbocation; Acridan; Acridinium.

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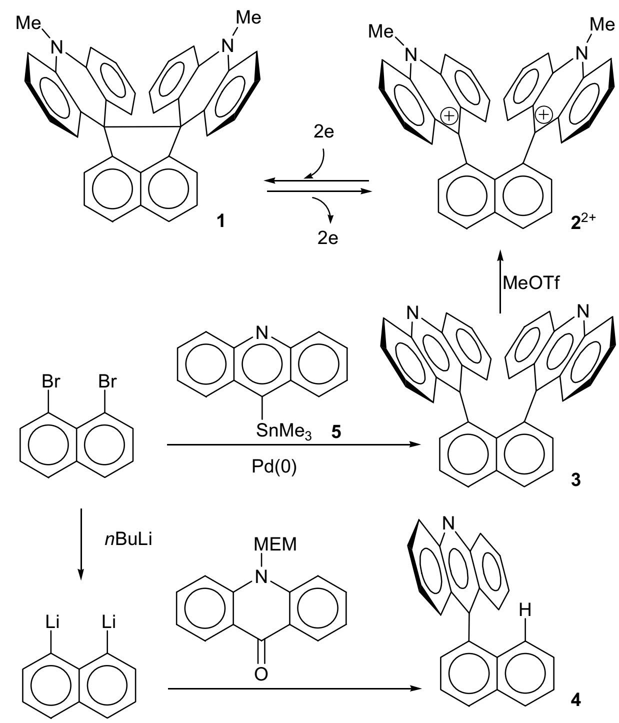

Scheme 1.

obtained by the reactions of aryllithiums and 10-protected 9-acridone,[11] this protocol failed to afford **3** probably due to its severe steric repulsion. As shown in Scheme 1, the reaction of 1,8-dilithionaphthalene and 10-methoxyethoxymethyl-9-acridone[12] did not give the desired 1:2 adduct **3** but the 1:1 adduct, 9-(1-naphthyl)acridine **4**,[13] as a major product.[14] Finally, by the CuO-promoted Stille reaction[15] [30 mol% of Pd(PPh$_3$)$_4$, 200 mol% CuO in DMF at 100–140 °C] between 1,8-dibromonaphthalene and 9-trimethylstannylacridine **5**,[16] we succeeded in obtaining **3**[17] in 23% yield.

The newly prepared bis(acridine) **3** is a stable yellow crystalline material exhibiting strong green fluorescence (536 nm in CH$_2$Cl$_2$), which is red-shifted by more than 100 nm compared with that of the corresponding mono(acridine) **4** (423 nm). The large Stokes shift in **3** (145 nm) is responsible for the observed red shift, suggesting that the two acridine units are arranged in a face-to-face manner suitable for excimer formation. In fact, the X-ray analysis[18] of **3** revealed the parallel arrangement of the chromophores (Fig. 1) with the closest nonbonded contact of 2.993(3) Å between the two C9 carbons of acridine units. This value is much shorter than the sum of vdW radii (3.40 Å),[19] although much closer C_π–C_π contacts were found between the bridgehead carbons in the highly strained cyclophanes.[20]

Upon treatment with a large excess amount of MeOTf in the presence of 2,6-di-*tert*-butyl-4-methylpyridine in CH$_2$Cl$_2$ at room temperature, **3** was transformed into orange crystals of $\mathbf{2}^{2+}$ (OTf$^-$)$_2$ salt[17] in 65% yield. In contrast to 10-methylacridinium that emits fluorescence with very high quantum yield ($\Phi_f = 1.00$),[21] $\mathbf{2}^{2+}$ does not act as a fluorophore. This observation is in accord with the very low Φ_f of 10-methyl-9-(1-naphthyl)acridinium PF$_6^-$ (0.015 in CH$_2$Cl$_2$),[22] in which the fluorescence of acridinium unit is quenched by the intramolecular charge-shift from the electron donating naphthalene unit.[22] Thus, the fluorescence spectroscopy is less informative for the electronic interaction between the two acridinium units in $\mathbf{2}^{2+}$, however, such interaction is indicated by the longer-wavelength absorptions of $\mathbf{2}^{2+}$ (end absorption: 550 nm) compared with $\mathbf{6}^{+}$ (500 nm).[23] Furthermore, the enhanced electron-accepting properties of $\mathbf{2}^{2+}$ [$E_p^{red} = -0.07$ V (irrev.)] than $\mathbf{6}^{+}$ [−0.57 V (rev.)] clearly show the strong electronic interaction[8d] between the two cationic parts in $\mathbf{2}^{2+}$.

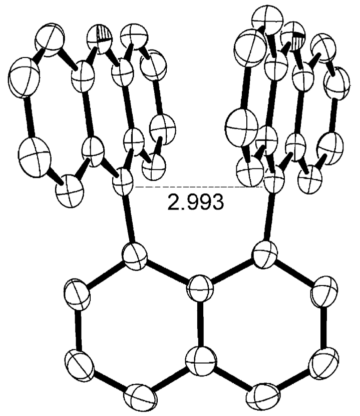

Figure 1. Molecular structure of **3** determined by X-ray analysis at –120 °C. This molecule is C_2-symmetric in crystal and the twisting angle about the naphthalene and acridine units is 75.6°. The averaged interplanar distance between the two acridine units is 3.29 Å (dihedral angle: 14.5°).

The X-ray analyses on the dication salts[18] demonstrate that the naphthalene-1,8-diyl skeleton in $\mathbf{2}^{2+}$ forces the two acridinium units in a surprising proximity (Fig. 2). Despite the electrostatic repulsion between the positive charges, the closest contacts between the two C9 carbons of acridiniums [2.927(7) Å in $\mathbf{2}^{2+}$ (SbCl$_6^-$)$_2$; 3.019(3) Å in $\mathbf{2}^{2+}$ (OTf$^-$)$_2$] are comparable with or marginally shorter than that in the precursor **3**. The former value is the shortest $C^+ \cdots C^+$ nonbonded contact ever reported,[24–26] thus demonstrating the validity of our molecular design.

Such a short contact in $\mathbf{2}^{2+}$ ensures the facile C–C bond formation between them upon 2e-reduction. Treatment of $\mathbf{2}^{2+}$ (OTf$^-$)$_2$ with Zn in THF–Et$_3$N (10:3) afforded dispiroacenaphthene-type HPE **1**,[17] which was isolated as stable colorless crystals in 95% yield. The X-ray analysis has revealed that the newly made C$_1$–C$_2$ bond is extremely long [1.696(3) Å],[27] which is expanded by 10% compared with the standard (C_{sp^3}–C_{sp^3}: 1.54 Å).[1] The small torsion angle of C$_{8a}$–C$_1$–C$_2$–C$_{2a}$ in the acenaphthene skeleton [18.1(3)°] is indicative of nearly eclipsed arrangement of substituents through this bond. On the other hand, all of the franking bonds [C$_1$–C$_{Ar}$ and C$_2$–C$_{Ar}$: 1.509(4)–1.520(4) Å] are similar to or marginally longer than the standard (C_{sp^2}–C_{sp^3}: 1.51 Å).[1] These results clearly show that the observed expansion of C$_1$–C$_2$ bond is mainly caused by steric factors rather

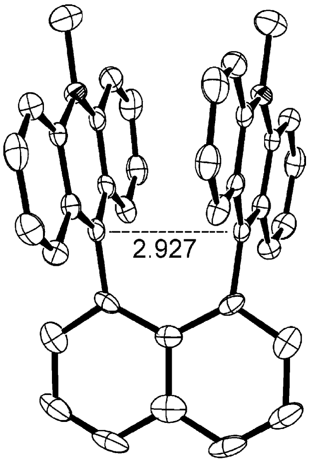

Figure 2. Molecular structure of C_2-symmetric **2**$^{2+}$ determined by X-ray analysis of $SbCl_6^-$ salt at −120 °C. The twisting angle about the naphthalene and acridinium units is 89.5°. The averaged interplanar distance between two acridinium units is 3.16 Å (dihedral angle: 11.8°). The corresponding parameters of **2**$^{2+}$ in the TfO^- salt are 85.9 and 84.3°, 3.28 Å, and 16.8°, respectively.

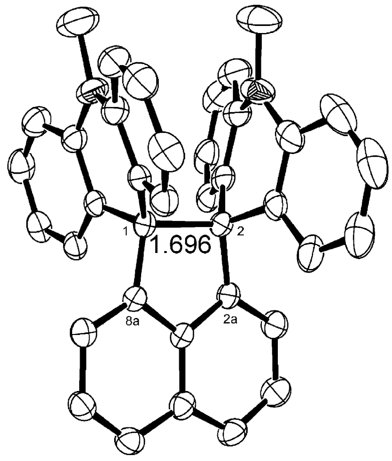

Figure 3. Molecular structure of **1** determined by X-ray analysis at −120 °C. The torsion angles of C_{Acr}–C_1–C_2–C_{Acr} are 23.9(3) and 26.0(3)°. Two 10-methylacridan units adopt the butterfly form with the dihedral angle between two benzene rings of 19.3 and 29.4°, respectively.

than by π–σ* through-bond interaction.[28] Structural optimization by the ab initio calculation (B3LYP/6-31G*)[29] converged to the geometry similar to the X-ray structure (torsion angle: 18.1° for C_{8a}–C_1–C_2–C_{2a}; franking bonds: 1.521–1.531 Å) although a much longer length of 1.719 Å is predicted for the C_1–C_2 bond (Fig. 3).

According to the voltammetric analysis, HPE **1** exhibits very strong donating properties [$E_p^{ox} = +0.14$ V (irrev.)] similar to *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, and regenerated dicationic dye **2**$^{2+}$ upon treatment with 2 equiv of $(p\text{-}BrC_6H_4)_3N^+ \cdot SbCl_6^-$ in CH_2Cl_2, which was isolated as $SbCl_6^-$ salt[17] in 85% yield. The interconversion could be also realized under electrochemical conditions, and clean electrochromic behavior was observed as shown in Figure 4. Highly reversible transformation between **1** and **2**$^{2+}$ accompanied by C–C bond making/breaking is quite important in understanding the reactivities involving such long bonds and short nonbonds, and we are now trying to shed the light on the half-bonded intermediates and their related species.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 247043-247046. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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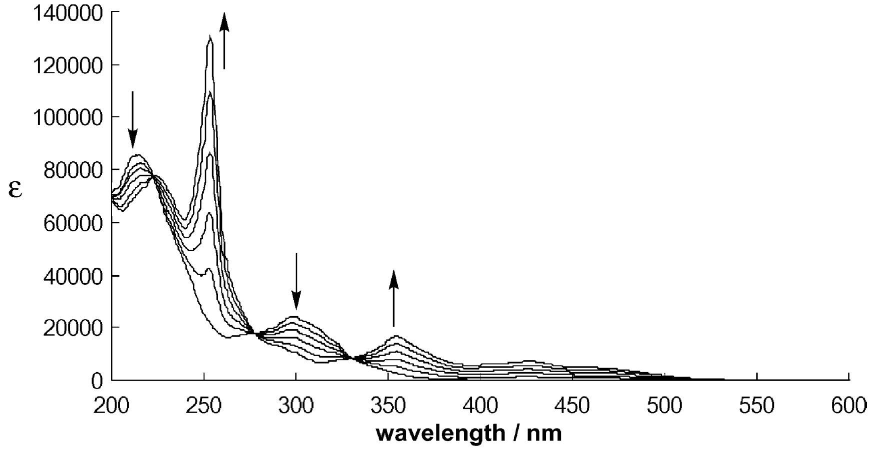

Figure 4. Changes in UV–vis spectra of **1** to **2**$^{2+}$ (3 mL, 2.00×10^{-5} mol dm^{-3}) upon constant-current electrochemical oxidation (20 μA, every 3 min) in MeCN containing 0.05 mol dm^{-3} $n\text{Bu}_4\text{NBF}_4$. Reversal of current caused complete conversion of **2**$^{2+}$ to **1**. Presence of several isosbestic points in both transformations indicates the negligible steady-state concentration of the intermediary cation radicals during the two-electron transfer.

University) for use of the X-ray structure analysis system. MS spectra were measured by Dr. Eri Fukushi and Mr. Kenji Watanabe at the GC–MS NMR Laboratory (Faculty of Agriculture, Hokkaido University).

References and notes

1. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
2. (a) Baldridge, K. K.; Battersby, T. R.; VernonClark, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 7048; (b) Ósawa, S.; Sakai, M.; Ósawa, E. *J. Phys. Chem. A* **1997**, *101*, 1378; (c) Baldridge, K. K.; Kasahara, Y.; Ogawa, K.; Siegel, J. S.; Tanaka, K.; Toda, F. *J. Am. Chem. Soc.* **1998**, *120*, 6167; (d) Toda, F.; Tanaka, K.; Watanabe, M.; Tamura, K.; Miyahara, I.; Nakai, T.; Hirotsu, K. *J. Org. Chem.* **1999**, *64*, 3102; (e) Tanaka, K.; Takamoto, N.; Tezuka, Y.; Kato, M.; Toda, F. *Tetrahedron* **2001**, *57*, 3761; (f) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 1757; (g) Kaupp, G.; Boy, J. *Angew. Chem., Int. Ed.* **1997**, *36*, 48; (h) Suzuki, T.; Ono, K.; Nishida, J.; Takahashi, H.; Tsuji, T. *J. Org. Chem.* **2000**, *65*, 4944.
3. (a) Ball, L.-J.; Dickie, A. P.; Mair, F. S.; Middleton, D. A.; Pritchard, R. G. *Chem. Commun.* **2003**, 744; (b) Suzuki, T.; Nagasu, T.; Kawai, H.; Fujiwara, K.; Tsuji, T. *Tetrahedron Lett.* **2003**, *44*, 6095.
4. Zavitsas, A. A. *J. Phys. Chem. A* **2003**, *107*, 897.
5. (a) Stein, M.; Winter, W.; Rieker, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 692; (b) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.
6. Maslak, P.; Narvaez, J. N.; Vallombroso, T. M., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 12373.
7. Review: (a) Nishida, J.; Suzuki, T.; Tsuji, T. *J. Synth. Org. Chem. Jpn.* **2002**, *60*, 40; (b) Suzuki, T.; Higuchi, H.; Tsuji, T.; Nishida, J.; Yamashita, Y.; Miyas, T. In *Chemistry of Nanomolecular Systems, Dynamic Redox Systems*; Nakamura, T., Matsumoto, T., Tada, H., Sugiura, K., Eds.; Springer-Verlag: Heidelberg, 2003; Chapter 1, p 3.
8. (a) Schweizer, W. B.; Procter, G.; Kaftory, M.; Dunitz, J.; *D. Helv. Chim. Acta* **1978, *61***, 2783; (b) Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567; (c) Komatsu, K.; Abe, N.; Takahashi, K.; Okamoto, K. *J. Org. Chem.* **1979**, *44*, 2712; (d) Tsuji, R.; Komatsu, K.; Inoue, Y.; Takeuchi, K. *J. Org. Chem.* **1992**, *57*, 636; (e) Cozzi, F.; Cinquini, M.; Annunziata, R.; Dwyer, T.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 5729; (f) Katoh, T.; Ogawa, K.; Inagaki, Y.; Okazaki, R. *Tetrahedron* **1997**, *53*, 3557; (g) Elschenbroich, C.; Wolf, M.; Schiemann, O.; Harms, K.; Burghaus, O.; Pebler, J. *Organometallics* **2002**, *21*, 5810; (h) Kawai, H.; Nagasu, T.; Takeda, T.; Fujiwara, K.; Tsuji, T.; Ohkita, M.; Nishida, J.; Suzuki, T. *Tetrahedon Lett.* **2004**, *45*, 4553.
9. (a) Hounshell, W. D.; Dougherty, D. A.; Hummel, J. P.; Mislow, K. *J. Am. Chem. Soc.* **1977**, *99*, 1916; (b) Suzuki, T.; Ono, K.; Kawai, H.; Tsuji, T. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1798.
10. (a) Wang, H.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 184; (b) Wang, H.; Webster, C. E.; Pérez, L. M.; Hall, M. B.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2004**, *126*, 8189.
11. Zimmerman, S. C.; Sainz, K. W.; Zeng, Z. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 1190.
12. Tanaka, T.; Tasaki, T.; Aoyama, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12453.
13. Koshima, H.; Kutunai, K. *Heterocycles* **2002**, *57*, 1299.
14. A small amount of abnormal 1:2 adduct, [4-(9-acridinyl)-9-(1-naphthyl)acridine], was also isolated, which would be produced via the intramolecular lithium transfer from the 8-position of naphthalene unit to the 4-position of acridine unit in the intermediate.
15. Wolf, C.; Mei, X. *J. Am. Chem. Soc.* **2003**, *125*, 10651.
16. Compound **5** was prepared as yellow crystals from 9-bromoacridine and Me_3SnCl according to the established procedure (Ref. 15): mp 86–87 °C ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (dd, 2H, $J = 8.6$, 1.3 Hz), 8.14 (dd, 2H, $J = 8.6$, 1.3 Hz), 7.76 (ddd, 2H, $J = 8.6$, 6.6, 1.3 Hz), 7.53 (ddd, 2H, $J = 8.6$, 6.6, 1.3 Hz), 0.68 (s, 9H); IR (KBr) 2360, 2337, 1533, 1515, 1460, 1394, 1196, 1141, 1127, 1011, 859, 832, 782, 761, 745, 670, 660, 604, 537, 523, 514 cm^{-1}.
17. Selected data for new compounds are as follows: Compound **1**: mp 265–266 °C (decomp.); ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, 2H, $J = 8.3$, 0.6 Hz), 7.68 (dd, 2H, $J = 8.3$, 6.9 Hz), 7.17 (dd, 2H, $J = 6.9$, 0.6 Hz), 6.92 (ddd, 4H, $J = 8.3$, 7.2, 1.4 Hz), 6.59 (dd, 4H, $J = 8.3$, 0.8 Hz), 6.33 (ddd, 4H, $J = 7.8$, 7.2, 0.8 Hz), 6.04 (dd, 4H, $J = 7.8$, 1.4 Hz), 3.08 (s, 6H); IR (KBr) 2924, 1590, 1474, 1358, 1274, 1133, 1055, 784, 747, 700 cm^{-1}. Compound $\mathbf{2}^{2+}$ $(OTf^-)_2$: mp 258–260 °C (decomp.); ^1H NMR (300 MHz, CD_3CN) δ 8.62 (dd, 2H, $J = 8.4$, 1.2 Hz), 8.10 (ddd, 4H, $J = 9.4$, 5.4, 1.7 Hz), 8.07 (dd, 4H, $J = 9.4$, 2.1 Hz), 7.95 (dd, 2H, $J = 8.4$, 7.0 Hz), 7.44 (dd, 2H, $J = 7.0$, 1.2 Hz), 7.28 (dd, 4H, $J = 8.5$, 1.7 Hz), 7.21 (ddd, 4H, $J = 8.5$, 5.4, 2.1 Hz), 4.42 (s, 6H); IR (KBr) 1610, 1551, 1264, 1221, 1143, 1027, 634 cm^{-1}. Compound $\mathbf{2}^{2+}$ $(SbCl_6{}^-)_2$: mp 255–258 °C (decomp.); ^1H NMR spectrum is identical to that of TfO^- salt. Compound **3**: mp 245–247 °C (decomp.); ^1H NMR (300 MHz, CD_2Cl_2) δ 8.24 (dd, 2H, $J = 8.4$, 1.4 Hz), 7.67 (dd, 2H, $J = 8.4$, 6.9 Hz), 7.52 (dd, 4H, $J = 8.4$, 1.2 Hz), 7.29 (ddd, 4H, $J = 8.4$, 6.6, 1.4 Hz), 7.19 (dd, 2H, $J = 6.9$, 1.4 Hz), 6.72 (dd, 4H, $J = 8.4$, 1.4 Hz), 6.61 (ddd, 4H, $J = 8.4$, 6.6, 1.2 Hz); IR (KBr) 3045, 1558, 1540, 1517, 1436, 1145, 1014, 866, 827, 785, 752, 601 cm^{-1}.
18. Crystal data for **1**: $C_{38}H_{28}N_2$, M 512.65, monoclinic, $P21/n$, $a = 10.415(5)$, $b = 18.582(8)$, $c = 13.744(6)$ Å, $\beta = 102.12(1)°$, $V = 2601(2)$ Å^3, D_c $(Z = 4) = 1.309\ g\,cm^{-3}$, $\mu = 0.76\ cm^{-1}$, $T = 153\ K$. The final R value is 0.057 for 2379 independent reflections with $I > 2\sigma I$ and 390 parameters. For $\mathbf{2}^{2+}$ $(TfO^-)_2$: $C_{40}H_{28}F_6N_2O_6S_2$, M 810.78, monoclinic, $P21/n$, $a = 17.602(4)$, $b = 10.715(2)$, $c = 19.766(4)$ Å, $\beta = 112.712(3)°$, $V = 3439.0(12)$ Å^3, D_c $(Z = 4) = 1.566\ g\,cm^{-3}$, $\mu = 2.42\ cm^{-1}$, $T = 153\ K$. The final R value is 0.043 for 5536 independent reflections with $I > 2\sigma I$ and 617 parameters. For $\mathbf{2}^{2+}$ $(SbCl_6{}^-)_2$: $C_{38}H_{28}Cl_{12}N_2Sb_2$, M 1181.59, orthorhombic, F ddd, $a = 11.952(4)$, $b = 37.446(6)$, $c = 42.984(7)$ Å, $V = 19238(6)$ Å^3, D_c $(Z = 16) = 1.632\ g\,cm^{-3}$, $\mu = 18.61\ cm^{-1}$, $T = 153\ K$. The final R value is 0.046 for 3612 independent reflections with $I > 2\sigma I$ and 262 parameters. For **3**: $C_{36}H_{22}N_2$, M 482.58, orthorhombic, $Pbcn$, $a = 15.480(8)$, $b = 10.560(6)$, $c = 14.222(7)$ Å, $V = 2325(2)$ Å^3, D_c $(Z = 4) = 1.379\ g\,cm^{-3}$, $\mu = 0.80\ cm^{-1}$, $T = 153\ K$. The final R value is 0.058 for 1238 independent reflections with $I > 2\sigma I$ and 217 parameters.
19. Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.
20. 2.38 Å in the kinetically stabilized [1.1]paracyclophane derivative: (a) Kawai, H.; Suzuki, T.; Ohkita, M.; Tsuji, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 817; 2.78 Å in [2.2]paracyclophane: (b) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204.
21. Jonker, S. A.; Ariese, F.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 109.
22. van Willigen, H.; Jones, G., II; Farahat, M. S. *J. Phys. Chem.* **1996**, *100*, 3312.

23. Orange crystals of $\mathbf{6}^{+}$OTf^{-} salt were obtained by *N*-methylation of **4** with MeOTf: mp 226–228 °C (decomp.); ^{1}H NMR (300 MHz, CD$_3$CN) δ 8.64 (d, 2H, $J = 9.3$ Hz), 8.36 (ddd, 2H, $J = 9.3$, 6.3, 1.9 Hz), 8.30 (dd, 1H, $J = 8.3$, 1.3 Hz), 8.15 (dd, 1H, $J = 8.1$, 1.3 Hz), 7.83 (dd, 1H, $J = 8.3$, 7.0 Hz), 7.77 (dd, 2H, $J = 8.8$, 1.9 Hz), 7.72 (dd, 2H, $J = 8.8$, 6.3 Hz), 7.61 (dd, 1H, $J = 7.0$, 1.3 Hz), 7.59 (ddd, 1H, $J = 8.1$, 7.0, 0.7 Hz), 7.32 (ddd, 1H, $J = 8.4$, 7.0, 1.3 Hz), 6.94 (dd, 1H, $J = 8.4$, 0.7 Hz), 4.88 (s, 3H); IR (KBr) 1610, 1581, 1551, 1272, 1222, 1160, 1030, 809, 781, 759, 636, 517 cm^{-1}.
24. Previously observed values in $\mathbf{B}^{2+}$ [3.076(2) (Ref. 10a) and 3.112(4) Å (Ref. 10b)] are slightly larger than those found in this work probably due to the propeller-like geometry of the cation units in $\mathbf{B}^{2+}$, which prevents the face-to-face overlap between the two cation units.
25. Strong C–H acidity of the 9-methyl group directly bound to the 10-methylacridinium unit clearly shows that the considerable positive charge on the C9 of acridinium: Suzuki, H.; Tanaka, Y. *J. Org. Chem.* **2001**, *66*, 2227.
26. Close interatomic contact of 2.73 Å was found between the bridgehead carbons in the [2.2]paracyclophane derivative with two *N*-methylpyridinium units: Hasselbach, H.-J.; Krieger, C.; Decker, M.; Staab, H. A. *Liebigs Ann. Chem.* **1986**, 765.
27. Previously observed value in **A** [1.670(3) (Ref. 10a)] is slightly smaller than that in **1**. Typical values for the dispiro-type HPEs with a 9,10-dihydrophenanthrene skeleton are in the range of 1.61–1.65 Å (Ref. 10a). On the other hand, several 1,1,2,2-tetraarylbenzocyclobutenes exhibit longer bond lengths (1.71–1.73 Å) than the present molecule (Ref. 2c,f).
28. Battersby, T. R.; Gantzel, P.; Baldridge, K. K.; J. S. Siegel *Tetrahedron Lett.* **1995**, *36*, 845.
29. Gaussian98. 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.; 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.; Challacombe, 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, Pittsburg, PA, 1998.