JOC*Article*

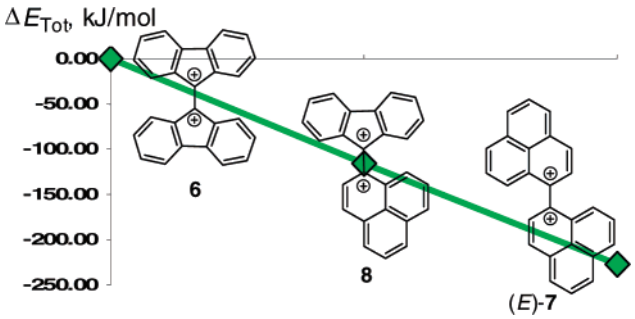
Theoretical Notions of Aromaticity and Antiaromaticity: Phenalenyl Ions versus Fluorenyl Ions

Sergey Pogodin and Israel Agranat*

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

isria@vms.huji.ac.il

Received September 4, 2007



The dications **6**, **7**, and **8** and dianions **9**, **10**, and **11** of the bistricyclic aromatic enes bifluorenylidene (**1**), 1,1′-biphenalenylidene (**2**), and 9-(9*H*-fluoren-9-ylidene)-1*H*-phenalene (**4**), as well as monocations **12a** and **13a** and monoanions **14a** and **15a** of phenalene (**3**) and fluorene (**5**), were subjected to a systematic DFT and ab initio study. B3LYP and MP2 methods were employed to estimate the relative aromaticity/antiaromaticity of these ions, using energetic, magnetic, and structural criteria. The couplings of monoions **12a**−**15a** to give the respective diions **6**−**11** result in a similar destabilization in both the fluorene and phenalene series. The interactions between the $C_{13}H_8$ units in diions **6**−**11** are weak and are not expected to result in a significant loss of aromaticity/gain of antiaromaticity, as compared with the respective monoions. The antiaromaticity of bifluorenylidene dication (**6**), relative to that of two fluorenyl cations (**12a**), is only slightly enhanced as compared with the aromaticity of biphenalenylidene dication ((*E*)-**7**)) relative to that of two phenalenyl cations (**13a**). In particular, the homodesmotic reaction **6** + 2·**13a** = (*E*)-**7** + 2·**12a** is only slightly exothermic, $\Delta E_{Tot} = -6.0$ kJ/mol. The energetic effect of the analogous reaction involving anions **9** + 2·**15a** = (*E*)-**10** + 2·**14a** is even smaller, $\Delta E_{Tot} = -3.4$ kJ/mol. Bifluorenylidene dianion (**9**) and 1,1′-biphenalenylidene dianion ((*E*)-**10**) are aromatic, but the employed criteria disagree about their relative aromaticity. The electronic and structural properties of heteromerous dication **8** and dianion **11** lie between those of the homomerous diions. Thus, dications **6**−**8** and dianions **9**−**11** form *a continuum of aromaticity/antiaromaticity*.

Introduction

Aromaticity is considered one of the most intriguing yet controversial problems in Chemistry. Ever since Kekulé's intuitive and brilliant idea on the structure of benzene in 1865,[1,2] aromaticity has been a challenge both to the theoreticians and to the experimentalists, providing an ideal and fruitful testground for the interaction of theory and experiment.[3−17] The basic tenet of the present study is the proposition submitted two score years

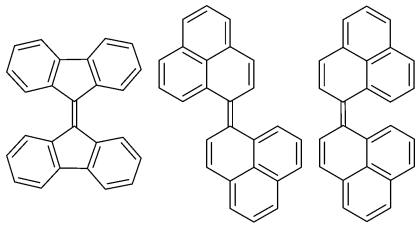
(1) Kekulé, A. *Bull. Soc. Chim. Fr.* **1865**, *3*, 98.
(2) Kekulé, A. *Liebigs Ann. Chem.* **1866**, *137*, 129.
(3) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*: *Electronic and Structural Aspects*; Wiley: New York, 1994.
(4) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: Cambridge, UK, 1969.
(5) Breslow, R. *Sci. Am.* **1972**, *227* (August), 32.
(6) *Aromaticity, Pseudoaromaticity and Antiaromaticity*; Bergmann, E. D., Pullman, B., Eds.; Proceeding of an International Symposium held in Jerusalem, March 31−April 3, 1970; The Israel Academy of Sciences and Humanities: Jerusalem, Isreal, 1971.
(7) Agranat, I. *Theoretical Aromatic Chemistry*; Zollinger, H., Ed.; MTP International review of Science, Organic Chemistry, Series One, Aromatic Compounds; Butterworths: London, UK, 1973; Vol. 3, pp 139−177.
(8) Agranat, I.; Barak, A. *The Controversial Notion of Aromaticity*; Zollinger, H., Ed.; MTP International review of Science, Organic Chemistry, Series Two, Aromatic Compounds; Butterworths: London, UK, 1976; Vol. 3, pp 1−177.

10.1021/jo701939c CCC: $37.00
Published on Web 11/17/2007

ago,[7,18] that aromaticity is a *theoretical notion*, and as such, its meaning is theory dependent. Any attempt to define explicitly the notion of aromaticity should take into consideration the following general statement made by the logician Ernst Nagel:[19] "In these cases in which a given theoretical notion is made to correspond to two or more experimental ideas, it would be absurd to maintain that the theoretical concept is explicitly defined by each of the two experimental ones in turn."

By the same token, antiaromaticity should also be considered a theoretical notion.

Conventional wisdom has classified aromaticity into energetic, structural (geometric), and magnetic descriptors of aromaticity, as well as reactivity measures.[9,10,20] Recently, Cyraňski et al. have raised the old question "to what extent can aromaticity be defined uniquely?"[13] These authors adopted a statistical analysis of quantitative criteria of aromaticity, concluding that "the various manifestations of aromaticity are related" and that aromaticity "from a philosophical point of view...can be regarded as a one-dimensional phenomenon". This conclusion was qualified: "in practical applications energetic, geometric and magnetic descriptors of aromaticity...do not speak with the same voice. Thus, in this sense the phenomenon of aromaticity can be regarded essentially as being *statistically multidimensional*"[13] (emphasis added). The statistical approach is in contradiction to the proposition that aromaticity is a theoretical notion. The article of Cyraski et al.,[13] which is read as a report of a committee, with a majority and a minority opinion, is reminiscent of the plot of the Japanese film *Rashomon*, where the audience is left with the buffing feeling of the relativity of truth.[8,21] The present study applies criteria of aromaticity and antiaromaticity to the novel aromatic/antiaromatic phenalenyl ions and fluorenyl ions and the doubly charged bistricyclic aromatic enes 9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene (bifluorenylidene, **1**) and 1-(1*H*-phenalen-1-ylidene)-1*H*-phenalene (biphenalenylidene, **2**).



Bifluorenylidene (**1**) is the parent of the bistricyclic aromatic enes (BAEs)[22−24] (Figure 1). These systems have fascinated chemists since **1** (Figure 1; X, Y = −) was synthesized in 1875, and thermochromism[25] and photochromism[26] were revealed in bianthrone (Figure 1; X, Y = C═O).[27,28] They can be classified into *homomerous* BAEs (Figure 1; X = Y) and *heteromerous* BAEs (Figure 1; X ≠ Y).[29] These systems are attractive substrates for the study of the ground state conformations and dynamic stereochemistry of overcrowded polycyclic aromatic enes (PAEs).[24] Thermochromic and photochromic polycyclic

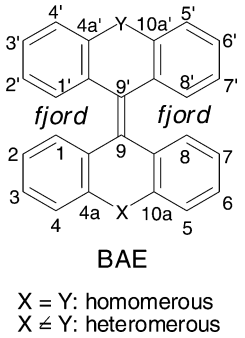


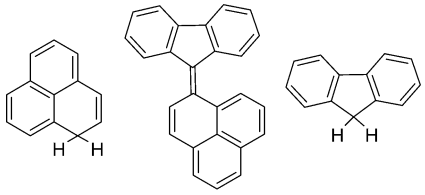
FIGURE 1. 1. Bistricyclic aromatic enes.

aromatic enes are candidates for potential molecular switches.[30] A tetradehydrodianthracene unit, topologically related to BAEs, is a beltlike pyramidalized component of the first Möbius annulene.[31]

Bifluorenylidene (**1**) is a fullerene fragment and serves as a starting material for the preparation of buckybowls,[32,33] undergoing aromatization into the fullerene fragment diindeno[1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*]chrysene.[34,35] Biphenalenylidene (**2**), a constitutional isomer of **1**, has attracted little attention from the explorers.[36,37] Formally, **2** is a bistricyclic aromatic ene, but has

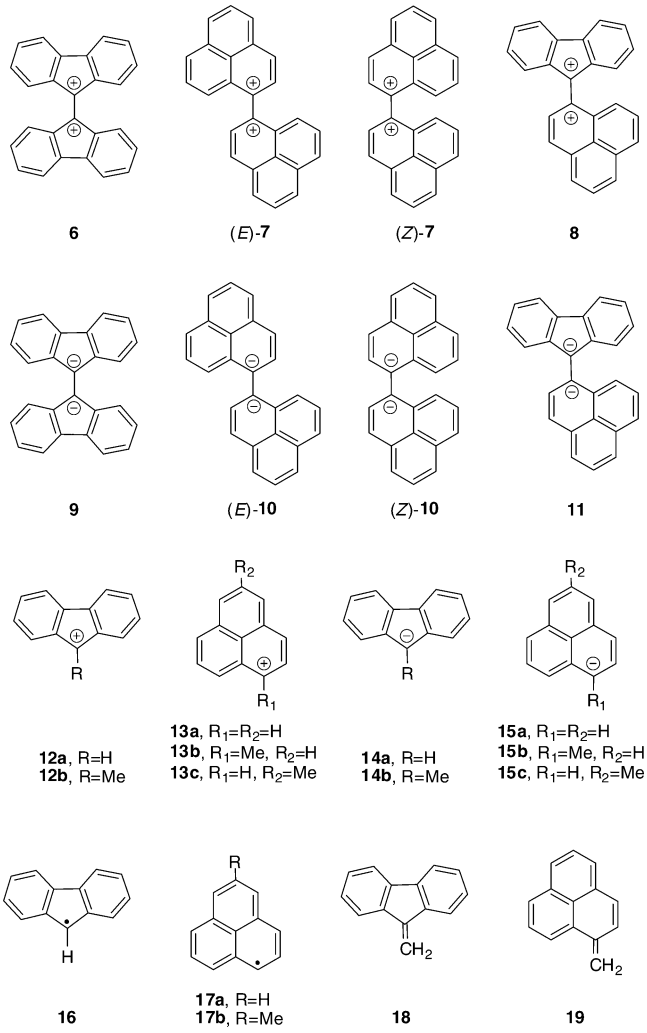
(9) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132−136.
(10) Krygowski, T. M.; Cyraňski, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783−1796.
(11) Schleyer, P. v. R., Ed. *Chem. Rev.* **2001**, *101*, 1115−1118.
(12) Krygowski, T. M.; Cyraňski, M. K. *Chem. Rev.* **2001**, *101*, 1385−1419.
(13) Cyraňski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333−1338.
(14) Schaad, L. J.; Hess, B. A., Jr. *Chem. Rev.* **2001**, *101*, 1465−1476.
(15) Balaban, A. T.; Oniciu, D. C.; Katritzky, A. R. *Chem. Rev.* **2004**, *104*, 2777−2812.
(16) Tarko, L.; Filip, P. *Rev. Roum. Chim.* **2003**, *48*, 745−758.
(17) Bergmann, E. D.; Agranat, I. In ref 6, pp 9−24.
(18) Agranat, I. Ph.D. Thesis, The Hebrew University of Jerusalem, Jerusalem, 1966.
(19) Nagel, E. *The Structure of Science−Problems in the Logic of Scientific Explanation*; Routledge and Kegan Paul: London, UK, 1961.
(20) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209−218.
(21) Anderson, J. I.; Richie, D. *The Japanese Film*: *Art and Industry*; Charles E. Tuttle Company: Tokyo, Japan, 1959; p 223.
(22) Shoham, G.; Cohen, S.; Suissa, R. M.; Agranat, I. In *Molecular Structure*: *Chemical Reactivity and Biological Activity*; Stezowski, J. J., Huang, J.-L., Shao, M.-C., Eds.; IUCr Crystallographic Symposia 2; Oxford University Press: Oxford, UK, 1988; pp 290−312.
(23) Biedermann, P. U.; Stezowski, J. J.; Agranat, I. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Stamford, CT, 1988; Vol. 4, pp 245−322.
(24) Biedermann, P. U.; Stezowski, J. J.; Agranat, I. *Eur. J. Org. Chem.* **2001**, 15−34.
(25) Biedermann, P. U.; Stezowski, J. J.; Agranat, I. *Chem. Eur. J.* **2006**, *12*, 3345−3354.
(26) Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639−665.
(27) Meyer, H. *Ber. Dtsch. Chem. Ges. B* **1909**, *42*, 143−145.
(28) Meyer, H. *Monatsh. Chem.* **1909**, *30*, 165 −177.
(29) Biedermann, P. U.; Levy, A.; Stezowski, J. J.; Agranat, I. *Chirality* **1995**, *7*, 199−205.
(30) Feringa, B. L. *Acc. Chem. Res.* **2001**, *34*, 504−513.
(31) Herges, R. *Chem. Rev.* **2006**, *106*, 4820−4842.
(32) Pogodin, S.; Biedermann, P. U.; Agranat, I. In *Recent Advances in the Chemistry of Fullerenes and Related Materials;* Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1998; Vol. 6, pp 1110−1116.
(33) Bronstein, H. E.; Choi, N.; Scott, L. T. *J. Am. Chem. Soc.* **2002**, *124*, 8870−8875.
(34) Hagen S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycycl. Aromat. Compd.* **1995**, *4*, 209−217.
(35) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.
(36) The formation of 7-(7*H*-benz[*de*]anthracen-7-ylidene)-7*H*-benz[*de*]-anthracene, an annelated derivative of **2**, has been reported briefly in the literature, but the product has not been characterized: Zinke, A.; Ott, R.; Weinhardt, E.; Wiesenberger, E. *Monatsh. Chem.* **1950**, *81*, 878−886.

a different topology than **1** and can exist as two diastereomers, (*E*)-**2** and (*Z*)-**2**. It is constructed of two units of the novel aromatic 1*H*-phenalene (**3**), known for its unusual chemistry.[38−40] BAEs (*E*)-**2** and (*Z*)-**2** have not been isolated, but have been claimed as intermediates undergoing a facile *E*,*Z*-isomerization and aromatization, giving the PAH peropyrene.[37,41] The unknown heteromerous bistricyclic aromatic ene fluorenylidenephenalene (9-(9*H*-fluoren-9-ylidene)-1*H*-phenalene, **4**), constructed of the two isomeric tricyclic moieties 1*H*-phenalene (**3**) and 9*H*-fluorene (**5**), may also be considered. BAEs **1**, **2**, and **4** are overcrowded and cannot adopt planar conformations due to prohibitively close contacts between nonbonded atoms in the regions on both sides of the central double bond. BAE **1** possesses two *fjords*, (*E*)-**2** possess two *coves*, (*Z*)-**2** has *fjord* and *bay* regions, while **4** has *fjord* and *cove* regions. Indeed, these BAEs adopt twisted conformations as their global minima with pure twist ranging from 34° to 59° (vide infra).



3 **4** **5**

BAEs **1**, **2**, and **4** can be potentially transformed to the respective dications [9,9′-bifluorene]-9,9′-diylium (**6**), [1,1′-biphenalene]-1,1′-diylium (**7**), and [9-fluorene-1′-phenalene]-9,1′-diylium (**8**) and the respective dianions 9,9′-bi-9*H*-fluorene dianion (**9**), 1,1′-bi-1*H*-phenalene dianion (**10**), and 9-(9*H*-fluorene)-1′-(1*H*-phenalene) dianion (**11**). The aromaticity/antiaromaticity of these diions would depend not only on the aromaticity/antiaromaticity of the respective monoions, but also on the degree of interactions between them, including charge delocalization and $\sigma-\pi$ donation. Dication **6**, which is formally constructed of two units of 9-fluorenyl cation (**12a**), is an interesting species that has been studied extensively by Mills et al. and claimed to be an antiaromatic species due to $\sigma-\pi$ conjugation between antiaromatic **12a** moieties.[42−44] The antiaromaticity of **12a** has been disputed (vide infra). By contrast, dication **7**, which is constructed of two units of aromatic 1-phenalenyl cation (**13a**),[45−48] is expected to be aromatic. 1-Phenalenyl anion (**15a**)[47−49] is also regarded as an aromatic species. Topological resonance energy per electron[50] (TREPE) values, calculated for **13a** and **15a**, are positive and almost identical, indicating similar aromatic stabilization.[46,51] Fluorenyl anion (**14a**)[52−55] and bifluorenylidene dianion (**9**)[56] are unanimously considered to be aromatic species. The elegant concept of *aromaticity/antiaromaticity continuum*, based on **6** and **9**, has recently been submitted.[43]



6 (*E*)-**7** (*Z*)-**7** **8**

9 (*E*)-**10** (*Z*)-**10** **11**

12a, R=H
12b, R=Me

13a, R_1=R_2=H
13b, R_1=Me, R_2=H
13c, R_1=H, R_2=Me

14a, R=H
14b, R=Me

15a, R_1=R_2=H
15b, R_1=Me, R_2=H
15c, R_1=H, R_2=Me

16

17a, R=H
17b, R=Me

18 **19**

The antiaromaticity of fluorenyl cation (**12a**) is a controversial issue. Recently, Herndon and Mills, using aromatic stabilization energy calculations, showed convincingly a substantial destabilization of **12a** (68.2 kJ/mol), supporting its categorization as an antiaromatic species.[57] However, the state of the art of the antiaromaticity of **12a** reflects varying

(37) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH Publishers: New York, 1988; pp 119−121.
(38) Reid, D. H. *Tetrahedron* **1958**, *3*, 339−352.
(39) Reid, D. H. *Q. Rev.* **1965**, *19*, 274−302.
(40) Murata, I. In *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Breslow R., Hafner, K., Itô, S., Murata, I., Eds.; Wiley: Tokyo, Japan, 1973; Vol. 1, pp 159−190.
(41) Pogodin, S.; Agranat, I. *J. Am. Chem. Soc.* **2003**, *125*, 12829−12835.
(42) Malandra, J. L.; Mills, N. S.; Kadlecek, D. E.; Lowery, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 11622−11623.
(43) Mills, N. S.; Benish, M. *J. Org. Chem.* **2006**, *71*, 2207−2213.
(44) Allen, A. D.; Tidwell, T. T. *Chem. Rev.* **2001**, *101*, 1333−1348.
(45) Hess, B. A., Jr.; Shaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1471−1494.
(46) Randić, M. *J. Phys. Chem.* **1982**, *86*, 3970−3977.
(47) Sethson, I.; Johnels, D.; Edlund, U. *J. Chem. Soc., Perkin Trans.* 2 **1990**, 1339−1341.
(48) Small, D.; Zaitsev, V.; Jung, Y.; Rosokha, S. V.; Head-Gordon, M.; Kochi, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 13850−13858.
(49) Hempenius, M. A.; Heinen, W.; Mulder, P. P. J.; Erkelens, C.; Zuilhof, H.; Lugtenburg, J.; Cornelisse, J. *J. Phys. Org. Chem.* **1994**, *7*, 296−302.
(50) Schaad, L. J.; Hess, B. A., Jr. *Pure Appl. Chem.* **1982**, *54*, 1097−1114.
(51) Ilić, P.; Trinajstić, N. *J. Org. Chem.* **1980**, *45*, 1738−1748.
(52) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075−7083.
(53) Hou, Y.; Meyers, C. Y. *J. Org. Chem.* **2004**, *69*, 1186−1195.
(54) Kinoshita, T.; Fujita, M.; Kaneko, H.; Takeuchi, K.; Yoshizawa, K.; Yamabe, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1145−1149.
(55) Yoshizawa, K.; Yahara, K.; Taniguchi, A.; Yamabe, T.; Kinoshita, T.; Takeuchi, K. *J. Org. Chem.* **1999**, *64*, 2821−2829.
(56) Shenhar, R.; Beust, R.; Hagen, S.; Bronstein, H. E.; Willner, I.; Scott, L. T.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **2002**, 449−454.
(57) Herndon, W. C.; Mills, N. S. *J. Org. Chem.* **2005**, *70*, 8492−8496.

TABLE 1. The DFT and MP2 Relative Energies and HOMO−LUMO Separation Energies (kJ/mol) of Neutral and Singly Charged $C_{13}H_8$ Fluorenyl and Phenalenyl Species

		B3LYP 6-311G(d,p)			B3LYP 6-311++G(d,p)		B3LYP 6-311+G(3df,2p)	MP2 6-31G(d)		MP2 6-311G(d,p)	
		a	ΔE	Δ_{HL}	ΔE	Δ_{HL}	ΔE	*a*	ΔE	ΔE	Δ_{HL}
12a	C_{2v}	M	111.1	109.5	111.1	109.4	111.6	M	123.9	121.7	353.9
13a	C_{2v}	M	0.0	173.2	0.0	173.0	0.0	M[b]	0.0	0.0	414.6
16	C_{2v}	M	59.7	199.9	59.3	195.7	59.6	M[b]	20.1	17.1	527.9
17a	C_{2v}	M	0.0	196.9	0.0	193.0	0.0	M[b]	0.0	0.0	566.5
14a	C_{2v}	M	16.4	165.3	15.8	133.8	15.5	M[b]	1.3	0.8	406.1
15a	C_{2v}	M	0.0	167.5	0.0	111.8	0.0	M[b]	0.0	0.0	409.3

[a] M = minimum (at B3LYP/6-31(d) and MP2/6-31G(d)). [b] C_s symmetry.

opinions (the discussion concerning the antiaromaticity of **12a** can be found in the Supporting Information).[52,53,58−69]

The diions **6**−**11** derived from BAEs **1**, **2**, and **4** are attractive substrates for the theoretical evaluation of different criteria of aromaticity and antiaromaticity. We report here a theoretical study of aromaticity/antiaromaticity of dications and dianions of BAEs **1**, **2**, and **4** as well as of the related monoions. The objective of the present study is to evaluate by computational methods the relative aromaticity/antiaromaticity of ions and diions of the phenalene series as compared with the respective ions and diions of the fluorene series, employing energetic, magnetic, and structural criteria. Special emphasis is given to the question of aromaticity of bifluorenylidene dication (**6**).

Results and Discussion

Energetic Criterion. DFT can be successfully used to probe the aromaticity of large molecular systems, in a cost-effective way, using the different energetic, structural, and magnetic criteria of aromaticity.[70] Lately, B3LYP hybrid functional was successfully employed to treat BAEs,[71] LPAHs,[41] fullerenes, and fulvalenes.[72] The B3LYP/6-311++G(d,p) and B3LYP/6-311G(d,p) were the models of choice for computing the energy and the magnetic properties of the systems under study, respectively (the full discussion can be found in the Supporting Information). Table 1 presents the DFT and MP2 relative energies of $C_{13}H_8$ fluorenyl and phenalenyl species. The respective total energies are presented in Tables S1 and S2 of the Supporting Information. All the species listed in Table 1 adopt planar C_{2v} or C_s conformations as their global minima. Fluorenyl cation (**12a**) is less stable than phenalenyl cation (**13a**) by 111.1 kJ/mol (at B3LYP/6-311++G(d,p)). The differences in stabilities of the fluorenyl versus the phenalenyl species decrease with increasing number of electrons. The 13 π-electron system 9-fluorenyl radical (**16**) is less stable than the 1-phenalenyl radical (**17a**) by 59.3 kJ/mol, while the 14 π-electron fluorenyl anion (**14a**) is less stable than the phenalenyl anion (**15a**) by 15.8 kJ/mol. At MP2/6-311G(d,p), this trend is even more pronounced: the differences between the phenalene and fluorene series are 121.7, 17.1, and 0.8 kJ/mol for cations, radicals, and anions, respectively. Thus, **12a** appears to be highly destabilized, as compared with **13a**, which points to its antiaromatic character, whereas **14a** and **15a** have comparable thermodynamic stabilities.

Table 2 shows the relative DFT energies of $C_{26}H_{16}$ fluorenyl and phenalenyl dimeric species together with their pure twist angles[24] and the lengths of their central bonds. The respective total energies are presented in Tables S3 and S4 of the Supporting Information. Coupling of species **12**−**17** to give the respective dimeric species **1**, **2**, **4**, and **6**−**11** introduces overcrowding in the regions around the central double bond of the resulting species. Neutral hydrocarbons adopt twisted conformations (**t**) with pure twists of 34.0° (**1**), 45.1° ((*E*)-**2**), 59.0° ((*Z*)-**2**), and 33.9° (**4**), at B3LYP/6-311++(d,p). Converting BAE **1** into its diions **6** and **9** removes the central π-bond and allows a greater degree of twist, i.e., 65.1° in **6** and 58.8° in **9**. The twist angles of (*E*)-**7** (67.5°), (*E*)-**10** (71.8°), and (*Z*)-**10** (73.3°) also increase relative to those of BAEs (*E*)-**2** and (*Z*)-**2**. The pure twist angles of the heteromerous species **4** (33.9°), **8** (62.9°), and **11** (60.4°) resemble those of the fluorene series rather than those of the phenalene series.

Consider diions **6**−**11** formed by coupling of the respective monoions **12a**−**15a**. Dication **6** is 228.2 kJ/mol less stable than (*E*)-**7** (or 114.1 kJ/mol per a single $C_{13}H_8$ unit), while dianion **9** is 35.0 kJ/mol higher in energy than (*E*)-**10** (or 17.5 kJ/mol per a $C_{13}H_8$ unit). The energy differences per $C_{13}H_8$ unit between homomerous diions in the fluorene and phenalene series are very similar to the differences between the respective monoions (Table 1). The relative energy of heteromerous dication **8** (111.7 kJ/mol) lies between the energies of the homomerous

(58) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393−398.
(59) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 4485−4492.
(60) Amyes, T. L.; Richard, J. P.; Novak, M. *J. Am. Chem. Soc.* **1992**, *114*, 8032−8041.
(61) Cowell, G.W.; Ledwith, A. *J. Chem. Soc. B* **1967**, 695−697, 697−700, 700−701.
(62) Friedrich, E. C.; Taggart, D. B. *J. Org. Chem.* **1978**, *43*, 805−808
(63) Allen, A. D.; Sumonja, M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 2371−2375.
(64) Dietz, F.; Tyutyulkov, N.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 157−164.
(65) Rodriquez, C. F.; Vucković, D. L.; Hopkinson, A. C. *J. Mol. Struct.* (*THEOCHEM*) **1996**, *363*, 131−138.
(66) Mills, N. S. *J. Am. Chem. Soc.* **1999**, *121*, 11690−11696.
(67) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.
(68) Buck, H. *Int. J. Quant. Chem.* **2000**, *78*, 179−185.
(69) Courtney, M. C.; MacCormack, A. C.; O'Ferrall, R. A. M. *J. Phys. Org. Chem.* **2002**, *15*, 529−539.
(70) De Proft, F.; Geerlings, P. *Chem. Rev.* **2001**, *101*, 1451−1464.
(71) Biedermann, P. U.; Stezowsky, J. J.; Agranat, I. *Chem. Commun.* **2001**, 954−955.
(72) Scott, A. P.; Agranat, I.; Biedermann, P. U.; Riggs, N. V.; Radom, L. *J. Org. Chem.* **1997**, *62*, 2026−2038.

TABLE 2. The DFT Relative Energies and HOMO−LUMO Separation Energies of Neutral and Doubly Charged $C_{26}H_{16}$ Fluorenyl and Phenalenyl Derived Species

			B3LYP/6-311G(d,p)					B3LYP/6-311++G(d,p)				
		a	Δ*E*, kJ/mol	S^2 [b]	pure twist	C−C,[c] pm	Δ_{HL}, kJ/mol	Δ*E*, kJ/mol	S^2 [b]	pure twist	C−C,[c] pm	Δ_{HL}, kJ/mol
t-6	D_2	M	229.4		64.3	146.0	84.1	228.2		65.1	146.1	84.6
(*E*)-**7**	C_2	M	0.0		67.1	149.3	156.3	0.0		67.5	149.3	156.3
t-8	C_1	M	112.4		62.3	147.4	94.6	111.7		62.9	147.4	95.0
t-21	D_2	M	−23.7		49.1	149.2	154.8	−23.4		49.0	149.3	154.4
$\mathbf{t}_\perp$-**6**	D_{2d}	TS	231.1		90.0	146.6	101.4	229.5		90.0	146.6	101.3
$\mathbf{t}_\perp$-**7**	C_2	TS	1.2		90.0	149.8	169.8	1.2		90.0	149.8	169.5
$\mathbf{t}_\perp$-**21**	D_{2d}	TS	−20.4		90.0	150.1	166.6	−20.8		90.0	150.1	166.2
t-1	D_2	M	19.6		33.9	137.8	136.6	18.9		34.0	137.8	135.5
(*E*)-**2**[d]	C_2	M	0.0	0.188	44.8	145.1	87.5	0.0	0.187	45.1	145.1	86.6
(*Z*)-**2**[d]	C_2	M	7.3	0.624	57.8	147.7	88.8	6.4	0.630	59.0	147.8	87.9
t-4	C_1	M	12.0		33.9	139.6	106.2	11.4		33.9	139.6	105.5
t-20[d]	D_2	M	−2.0	0.863	41.1	148.7	91.6	−2.2	0.846	42.0	148.8	90.5
$\mathbf{t}_\perp$-**1**[d]	D_{2d}	TS	107.3	0.377	90.0	146.2	98.1	104.6	0.374	90.0	146.2	97.5
$\mathbf{t}_\perp$-**2**[d]	C_2	TS	10.3	0.792	87.5	149.3	90.3	9.4	0.778	87.9	149.3	89.2
$\mathbf{t}_\perp$-**20**[d]	D_{2d}	TS	4.2	0.759	90.0	149.5	90.9	2.9	0.739	90.0	149.6	89.8
t-9	D_2	M	38.2		58.0	147.7	131.3	35.0		58.8	147.6	74.3
(*E*)-**t-10**	C_2	M	0.0		64.9	149.9	149.0	0.0		71.8	150.0	75.0
(*Z*)-**t-10**	C_2	M	0.3		72.3	150.0	157.6	0.3		73.3	149.9	78.7
t-11	C_1	M	18.1		59.3	148.6	124.2	16.9		60.4	148.6	67.2
t-22	D_2	M	−38.3		39.2	149.6	148.5	−36.1		40.1	149.6	88.4
$\mathbf{t}_\perp$-**9**	D_{2d}	TS	40.5		90.0	148.3	157.3	37.4		90.0	148.2	94.1
$\mathbf{t}_\perp$-**10**	C_2	TS	0.9		92.2	150.2	158.4	0.7		93.3	150.1	81.3
$\mathbf{t}_\perp$-**22**	D_{2d}	TS	−29.7		90.0	150.3	162.6	−29.2		90.0	150.2	83.9

[a] M = minimum, TS = transition state, at B3LYP/6-31G(d). [b] The eigenvalues of S^2 after annihilation of the first spin contaminant. [c] The length of the central cMarbon−carbon bond between the fluorenyl/phenalenyl moieties. [d] Singlet states.

dications **6** and (*E*)-**7**: **8** is 2.4 kJ/mol more stable than the average energy of **6** and (*E*)-**7** (114.1 kJ/mol). Analogously, dianion **11** is more stable than **9** but less stable than (*E*)-**10**: its relative stability (16.9 kJ/mol) is very close to the average energy of **9** and (*E*)-**10** (17.5 kJ/mol). BAE (*E*)-**2** is more stable than **1** by only 18.9 kJ/mol, due to the diradical character of the former,[41] while heteromerous BAE **4** is more stable than **1** by 7.5 kJ/mol. The stepwise replacement of phenalenyl moieties with fluorenyl moieties in BAEs **1**, **2**, and **4** (Figure S1, Supporting Information), dications **6**−**8** (Figure S2, Supporting Information), and dianions **9**−**11** (Figure S3, Supporting Information) causes nearly a linear decrease in the relative energies of the species, indicating the independent effect of each $C_{13}H_8$ unit on the stability of the whole molecule. Note that dianion **10** exists as two diastereomers, (*E*)-**10** and (*Z*)-**10**, and the former is more stable than the latter by only 0.3 kJ/mol. The potential energy surface scan of dication **7** revealed no (*Z*)-**7** diastereomer.

The relative stabilities of the dications and dianions of the fluorene and phenalene series can be estimated from the homodesmotic reactions 1−6 (ΔE_{Tot} calculated at B3LYP/6-311++G(d,p), Schemes 1 and 2). The small energetic effects reflected in these reactions support the existence of interactions between charged $C_{13}H_8$ moieties in diions **6**−**11**. Replacing only one fluorenyl moiety in dication **6** by the phenalenyl moiety to give **8** lowers the energy of the system by 5.4 kJ/mol (reaction 2). Replacing the fluorenyl moiety in **8** by the phenalenyl moiety stabilizes the resulting dication (*E*)-**7** by only 0.6 kJ/mol (reaction 3). Analogous stepwise replacements of fluorenyl moieties in dianion **9** to give **11** and (*E*)-**10** leads to stabilization of the resulting systems by 2.3 and 1.1 kJ/mol, respectively (reactions 5 and 6). Thus, the "couplings" of two cations **12a** and of two anions **14a** to give dication **6** and dianion **9**, respectively, introduce only a minor additional destabilization of these diions as compared with the respective phenalene series.

$$\mathbf{6} + 2\cdot\mathbf{13a} = (E)\text{-}\mathbf{7} + 2\cdot\mathbf{12a}, \qquad \Delta E_{Tot} = -6.0 \text{ kJ/mol} \quad (1)$$

$$\mathbf{6} + \mathbf{13a} = \mathbf{8} + \mathbf{12a}, \qquad \Delta E_{Tot} = -5.4 \text{ kJ/mol} \quad (2)$$

$$\mathbf{8} + \mathbf{13a} = (E)\text{-}\mathbf{7} + \mathbf{12a}, \qquad \Delta E_{Tot} = -0.6 \text{ kJ/mol} \quad (3)$$

$$\mathbf{9} + 2\cdot\mathbf{15a} = (E)\text{-}\mathbf{10} + 2\cdot\mathbf{14a}, \qquad \Delta E_{Tot} = -3.4 \text{ kJ/mol} \quad (4)$$

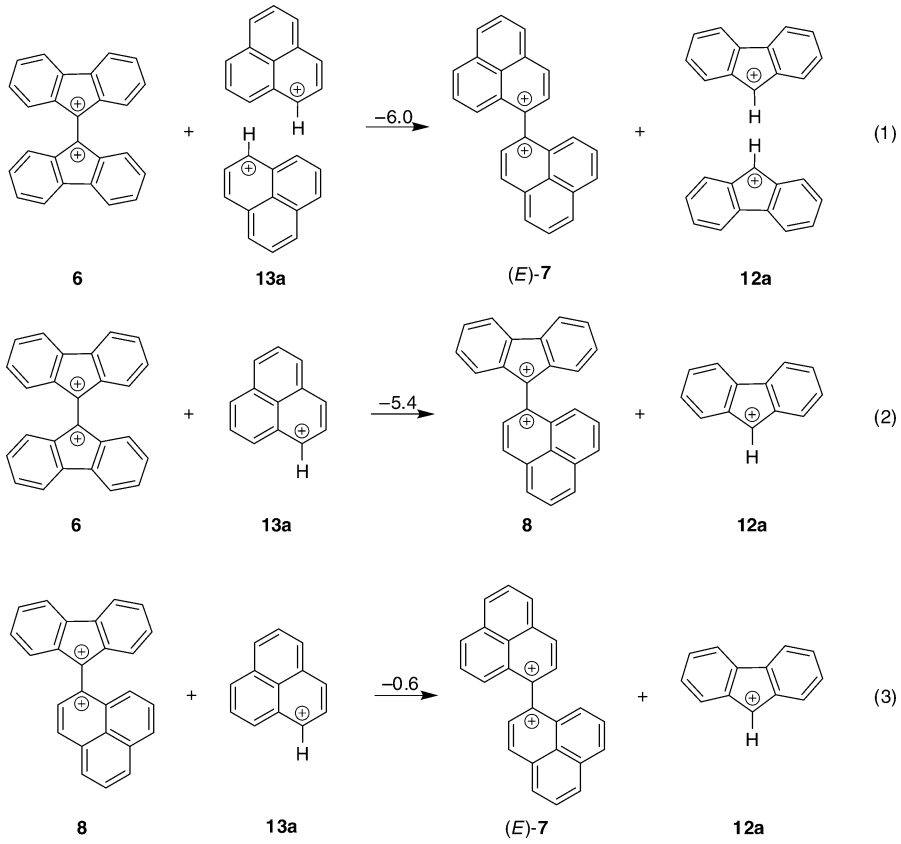
$$\mathbf{9} + \mathbf{15a} = \mathbf{11} + \mathbf{14a}, \qquad \Delta E_{Tot} = -2.3 \text{ kJ/mol} \quad (5)$$

$$\mathbf{11} + \mathbf{15a} = (E)\text{-}\mathbf{10} + \mathbf{14a}, \qquad \Delta E_{Tot} = -1.1 \text{ kJ/mol} \quad (6)$$

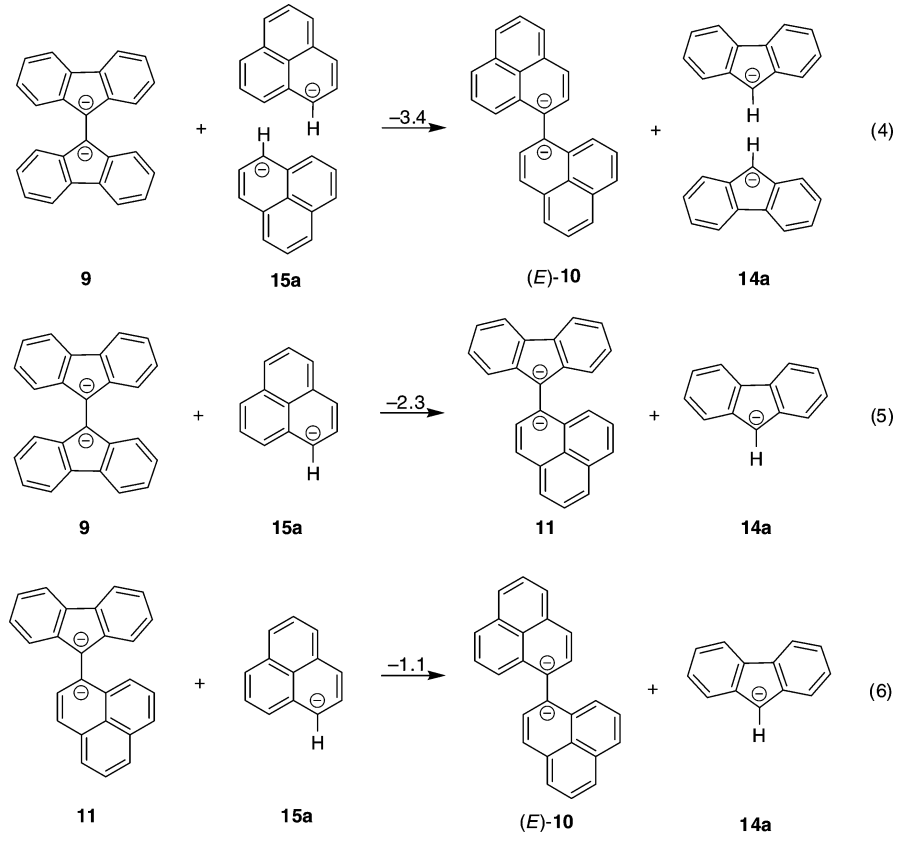
The mode of coupling of two phenalenyl units, however, has a significant impact on the relative stabilities of the resulting diions. Joining two phenalenyl radicals at the 2,2′ positions yields the non-Kekulé hydrocarbon 2,2′-biphenalenylidene (**20**),[73] a constitutional isomer of BAEs **1** and **2**. In spite of its diradical character, it is more stable than **1** by 21.1 kJ/mol (Table 2). Hydrocarbon **20** adopts the D_2 twisted conformation as its global minima, with a twist angle of 42.0°. The pure twist angles of dication **21** and dianion **22** are 49.0° and 40.1°, respectively. These values are smaller than the pure twist angles of diions **6**−**11** relative to those of their respective neutral hydrocarbons **1**, **2**, and **4**, due to the diradical character of the **20** and its lack of a central double bond. Dication **21** and dianion **22** are more stable than **6** and **9** by 251.6 and 71.1 kJ/mol, respectively. The homodesmotic reactions 7 and 8 (Scheme 3), unlike reactions

(73) Baumgarten, M.; Karabunarliev, S. *Chem. Phys.* **1999**, *244*, 35−47.

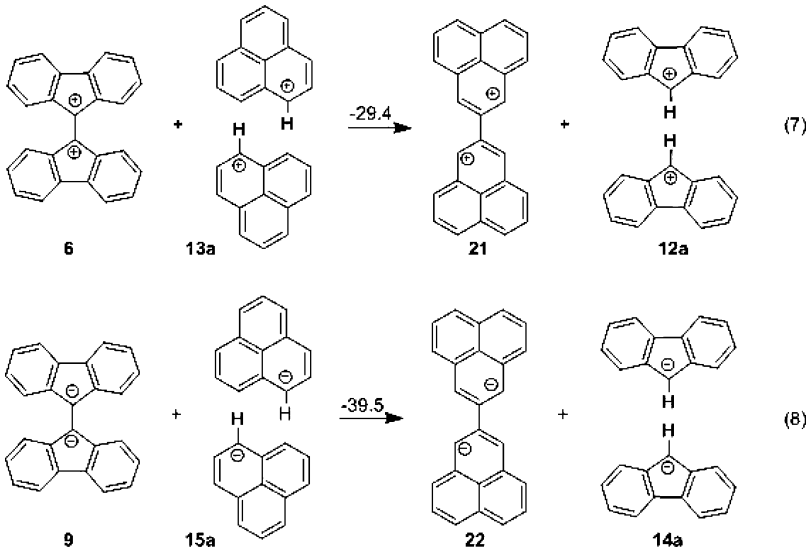
SCHEME 1. Homodesmotic Reactions between Dications 6−8 and Their ΔE_{Tot} (kJ/mol) Values



SCHEME 2. Homodesmotic Reactions between Dianions 9−11 and Their ΔE_{Tot} (kJ/mol) Values



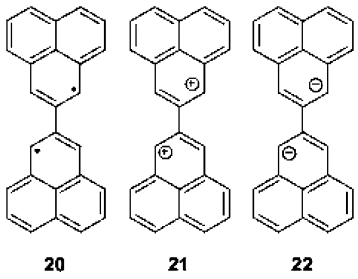
SCHEME 3. Homodesmotic Reactions of 2,2'-Biphenalenyl Diions and Their ΔE_{Tot} (kJ/mol) Values



1 and 4, demonstrate that formations of bifluorenylidene diions from cation **12a** or anion **14a** are clearly unfavorable processes as compared with the formations of the respective 2,2′-biphenalenylidene diions.

$$\mathbf{6} + 2\cdot\mathbf{13a} = \mathbf{21} + 2\cdot\mathbf{12a}, \qquad \Delta E_{Tot} = -29.4 \text{ kJ/mol} \qquad (7)$$

$$\mathbf{9} + 2\cdot\mathbf{15a} = \mathbf{22} + 2\cdot\mathbf{14a}, \qquad \Delta E_{Tot} = -39.5 \text{ kJ/mol} \qquad (8)$$



The increased stabilities of the diions **21** and **22** relative to the isomeric (*E*)-**7** and (*E*)-**10**, like the increased stability of the parent hydrocarbon **20** over **2**,[41] can be explained by their different topologies. Since the charges in a phenalenyl moiety are mostly localized at the α-positions, there are high equal positive or negative charge densities at the bridgehead C^1 and $C^{1'}$ positions of (*E*)-**7** and (*E*)-**10**, but low equal positive or negative charge densities at the bridgehead C^2 and $C^{2'}$ positions of **21** and **22**. Consequently, the "communication" between the two 2-phenalenyl units of **21** and of **22** is greatly reduced. Thus, the coupling of two fluorenyl or two 1-phenalenyl charged $C_{13}H_8$ units to give the respective diions **6**−**11** leads to destabilizing interactions between them, unlike the coupling of two 2-phenalenyl charged units to give diions **21** and **22**. The reduced overcrowding in **20**, **21**, and **22** as compared with (*E*)-**2**, (*E*)-**7**, and (*E*)-**10**, respectively, also contributes to the enhanced stabilities of the 2,2′-biphenalenyl species relative to the 1,1′-biphenalenyl species.

The degree of destabilization stemming from the coupling of two $C_{13}H_8$ cations to give $C_{26}H_{16}$ dications could also be estimated from the following homodesmotic reactions 9−16, (Scheme S1 and S2 in the Supporting Information):

$$2\cdot\mathbf{18} = \mathbf{1} + C_2H_4, \qquad \Delta E_{Tot} = 51.1 \text{ kJ/mol} \qquad (9)$$

$$2\cdot\mathbf{19} = (E)\text{-}\mathbf{2} + C_2H_4, \qquad \Delta E_{Tot} = 17.4 \text{ kJ/mol} \qquad (10)$$

$$\mathbf{18} + \mathbf{19} = \mathbf{4} + C_2H_4, \qquad \Delta E_{Tot} = 36.1 \text{ kJ/mol} \qquad (11)$$

$$2\cdot\mathbf{17b} = \mathbf{20} + C_2H_6, \qquad \Delta E_{Tot} = -3.0 \text{ kJ/mol} \qquad (12)$$

$$2\cdot\mathbf{12b} = \mathbf{6} + C_2H_6, \qquad \Delta E_{Tot} = 294.9 \text{ kJ/mol} \qquad (13)$$

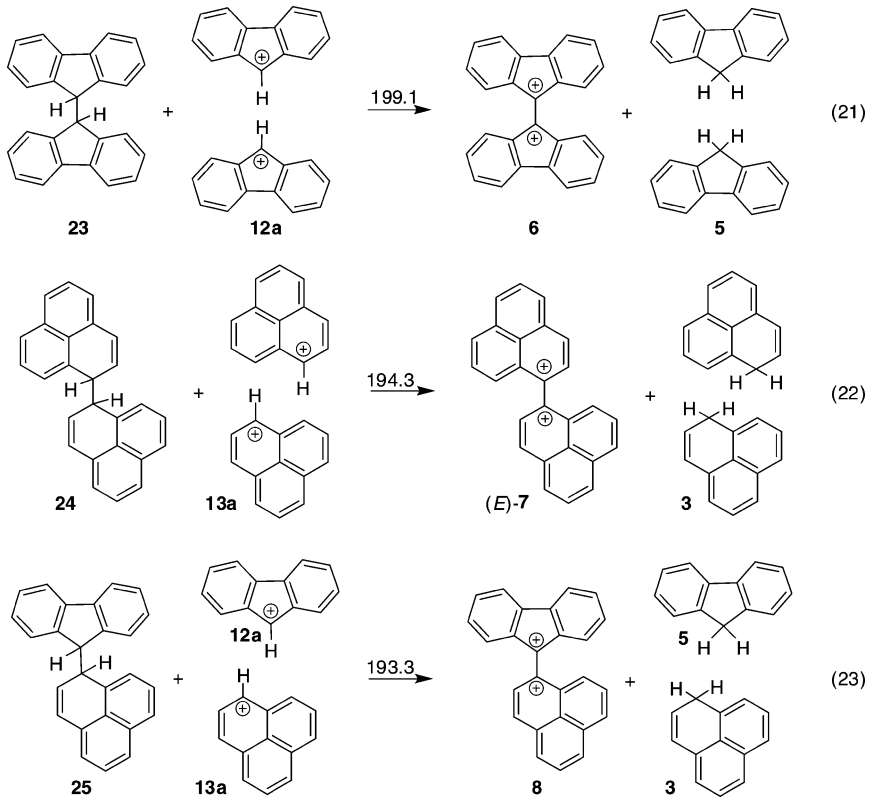
$$2\cdot\mathbf{13b} = (E)\text{-}\mathbf{7} + C_2H_6, \qquad \Delta E_{Tot} = 242.1 \text{ kJ/mol} \qquad (14)$$

$$\mathbf{12b} + \mathbf{13b} = \mathbf{8} + C_2H_6, \qquad \Delta E_{Tot} = 266.1 \text{ kJ/mol} \qquad (15)$$

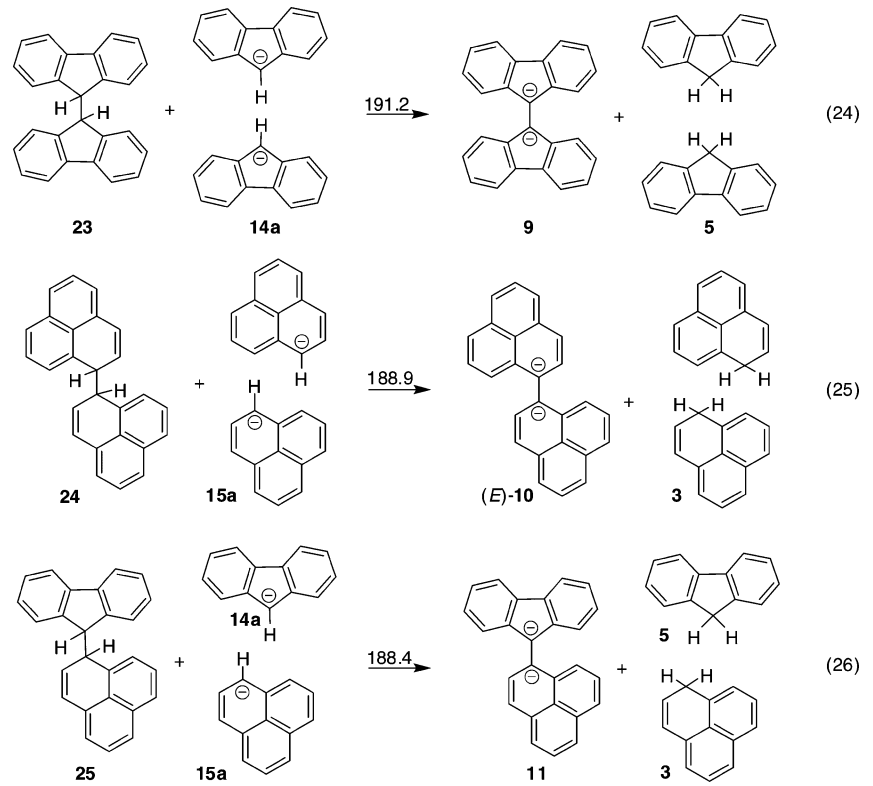
$$2\cdot\mathbf{13c} = \mathbf{21} + C_2H_6, \qquad \Delta E_{Tot} = 212.2 \text{ kJ/mol} \qquad (16)$$

The energetic effects of reactions 9−11 correspond mainly to the steric strain that exists in BAEs **1**, **2**, and **4** due to overcrowding at the two *fjords* (**1**), two *coves* ((*E*)-**2**), and *cove* and *fjord* regions (**4**), respectively. The high exothermicities of reactions 13−16 are ascribed to both steric strain due to overcrowding and electronic effects such as electron delocalization and charge repulsion in the dications **6**−**8** and **21**. Subtracting the energies of reactions 13−16 from the energies of the corresponding reactions 9−12 provides estimates of destabilization caused by connecting two (anti)aromatic charged fluorenyl or phenalenyl units to form the respective diions relative to destabilization caused by coupling of two fluorenylidene or phenalenylidene units into the respective neutral hydrocarbons. Thus, dications **6**, (*E*)-**7**, **8**, and **21** are destabilized relative to their monocations by $\Delta\Delta E_{Tot}$ = 243.8, 224.7, 230.0, and 215.2 kJ/mol, respectively. From the above values it follows that formation of dication **6** from monocation **12b** is hence more energetically unfavorable by 243.8 − 224.7 = 19.1 kJ/mol than formation of (*E*)-**7** from **13b** (reactions 9, 10, 13, and 14). Formation of heteromerous dication **8** from monocations **12b** and **13b** is less energetically unfavorable by 243.8 − 230.0 = 13.8 kJ/mol than formation of **6** from **12b** (reactions 9, 11, 13,

SCHEME 4. Steric Strain Balanced Homodesmotic Reactions for Formation of Dications 6−8 from the Respective Monocations (ΔE_{Tot}, kJ/mol)



SCHEME 5. Steric Strain Balanced Homodesmotic Reactions for Formation of Dianions 9−11 from the Respective Monocations (ΔE_{Tot}, kJ/mol)



and 15), but more energetically unfavorable by 230.0 − 224.7 = 5.3 kJ/mol than formation of (*E*)-**7** from **13b** (reactions 10, 11, 14, and 15).

Similarly, the relative destabilization of dianions **9**−**11** and **22** can be calculated from the following reactions (Scheme S3, Supporting Information):

$2\cdot$**14b** = **9** + C_2H_6, ΔE_{Tot}=208.1 kJ/mol (17)

$2\cdot$**15b** = (*E*)-**10** + C_2H_6, ΔE_{Tot}=207.1 kJ/mol (18)

14b + **15b** = **11** + C_2H_6, ΔE_{Tot}=208.5 kJ/mol (19)

$2\cdot$**15c** = **22** + C_2H_6, ΔE_{Tot}=173.9 kJ/mol (20)

Subtracting the energy terms of reactions 17−20 from the energies of the corresponding reactions 9−12 provides estimates of the destabilization of dianions **9**, (*E*)-**10**, **11**, and **22** relative to their correspondent monoanions: $\Delta\Delta E_{Tot}$ = 157.1, 189.7, 172.4, and 176.9 kJ/mol, respectively. Formation of dianion **9** from monoanion **14b** is less energetically unfavorable by 189.7 − 157.1 = 32.6 kJ/mol than formation of (*E*)-**10** from **15b**, and by 176.9 − 157.1 = 19.8 kJ/mol than formation of **22** from **15c**. Formation of heteromerous dianion **11** from monocations **14b** and **15b** is more energetically unfavorable by 172.4 − 157.1 = 15.3 kJ/mol than formation of **9** from **14b**, but less energetically unfavorable by 189.7 − 172.4 = 17.3 kJ/mol than formation of (*E*)-**10** from **15b**. Thus, diions **6**−**11** may be considered as a part of an aromaticity/antiaromaticity continuum,[43] where replacement of the phenalenyl unit by the fluorenyl unit causes gradual destabilization of dications (by 5.3 and 13.8 kJ/mol for the series (*E*)-**7** → **8** → **6**) but gradual stabilization of dianions (by 17.3 and 15.3 kJ/mol for the series (*E*)-**10** → **11** → **9**).

The energies derived from the homodesmotic reactions 9−20 include both steric and electronic effects and may be overestimated. The homodesmotic reactions 21−26 (Schemes 4 and 5) between diions **6**−**11** and their dihydrogenated derivatives 9,9′-bi-9*H*-fluorene (**23**), 1,1′-bi-1*H*-phenalene (**24**),[74] and 1-(9′*H*-fluorenyl)-1*H*-phenalene (**25**) were also considered (the energies of these species are provided in Table S5 in the Supporting Information). In these reactions the type and number of the overcrowding regions are equivalent on both sides of the equations:

23 + $2\cdot$**12a** = **6** + $2\cdot$**5**, ΔE_{Tot}=199.1 kJ/mol (21)

24 + $2\cdot$**13a** = (*E*)-**7** + $2\cdot$**3**, ΔE_{Tot}=194.3 kJ/mol (22)

25 + **12a** + **13a** = **8** + **5** + **3**, ΔE_{Tot}=193.3 kJ/mol (23)

23 + $2\cdot$**14a** = **9** + $2\cdot$**5**, ΔE_{Tot}=191.2 kJ/mol (24)

24 + $2\cdot$**15a** = (*E*)-**10** + $2\cdot$**3**, ΔE_{Tot}=188.9 kJ/mol (25)

25 + **14a** + **15a** = **11** + **5** + **3**, ΔE_{Tot}=188.4 kJ/mol (26)

The homodesmotic reactions 21−26 indicate considerable degrees of destabilization of diions **6**−**11** relative to their respective monoions, albeit smaller than the estimates based on reactions 9−20. However, the magnitudes of this destabilization are similar for the coupling of two cations **12a**, which has been claimed to be antiaromatic[57] (vide supra), and for the coupling of aromatic **13a**−**15a**. The formation of dication **6** from two cations **12a** and of dianion **9** from two anions **14a** are only marginally less favorable processes (by 4.8 and 2.3 kJ/mol, respectively) than the formation of dication (*E*)-**7** and of dianion (*E*)-**10** from the respective monoions **13a** and **15a** (reactions 21−22 and 24−25). The "communication" between fluorenyl and phenalenyl moieties in diions is not essential: the formation of heteromerous dication **8** and dianion **11** is more exothermic than the formation of dication (*E*)-**7** and of dianion (*E*)-**10** by only 1.0 and 0.5 kJ/mol, respectively (reactions 22−23 and 25−26).

Tables 1 and 2 also present the HOMO−LUMO energy separations Δ_{HL} (calculated as $(E_{LUMO} - E_{HOMO})/2$), which approximates the absolute hardness, an index of structural stability and reactivity.[75] The linear correlation between Δ_{HL} and resonance energy per electron for a range of carbocyclic molecules has been demonstrated.[76] The value of Δ_{HL} of dication **6** (84.6 kJ/mol) is lower than that of neutral BAE **1** (135.5 kJ/mol) by 50.9 kJ/mol. Dication **6** is also destabilized as compared with both dications (*E*)-**7** (156.3 kJ/mol), **8** (95.0 kJ/mol), and **21** (154.4 kJ/mol), by $\Delta\Delta_{HL}$ = 71.7, 10.4, and 69.8 kJ/mol, respectively. On the other hand, Δ_{HL} of **6**, (*E*)-**7**, and **21** decreases relative to their respective monocations **12a** (109.4 kJ/mol) and **13a** (173.0 kJ/mol) by moderate and comparable amounts, 24.8, 16.7, and 18.6 kJ/mol, respectively, with dication **6** being more destabilized than the others. Dianion **9** (Δ_{HL} = 74.3 kJ/mol) is less stable than **1**, (*Z*)-**10** (78.7 kJ/mol), and **22** (88.4 kJ/mol) by 61.2, 4.4, and 14.1 kJ/mol, respectively, but less destabilized than **11** (67.2 kJ/mol) by 7.1 kJ/mol. The Δ_{HL} gap of **9**, (*Z*)-**10**, and **22** relative to the respective monoanions **14a** and **15a** is lower by 59.5, 33.1, and 23.4 kJ/mol, respectively. The HOMO−LUMO energy separation predicts dications **6** and (*E*)-**7** to be less destabilized than the respective dianions **9** and (*E*)-**10**.

Orthogonally twisted conformations (**t**) of **6**, **7**, **9**, **10**, **21**, and **22**, which serve as transition states for the rotation around the central bond, may also be considered. The rotation barriers for dications $\mathbf{t}_\perp$-**6**, $\mathbf{t}_\perp$-**7**, and $\mathbf{t}_\perp$-**21** are 1.3, 1.2, and 2.6 kJ/mol and those for dianions $\mathbf{t}_\perp$-**9**, $\mathbf{t}_\perp$-**10**, and $\mathbf{t}_\perp$-**22** are 2.4, 0.7, and 6.9 kJ/mol. The Δ_{HL} gap of these orthogonally twisted conformations (excluding $\mathbf{t}_\perp$-**22**) is 2.6−19.8 kJ/mol higher than Δ_{HL} of the respective minima conformations, implying an increase in stability of these orthogonal diions due to the absence of "communication" between two tricyclic moieties.

The application of the energetic criterion of aromaticity/antiaromaticity shows that the transition from monoions **12a**−**15a** to the respective diions **6**−**11** results in a considerable destabilization (188−199 kJ/mol, reactions 21−26) for both dications and dianions. On the basis of the homodesmotic reaction analysis, the coupling of two molecules of cation **13a** to give biphenalenylidene dication ((*E*)-**7**) is more favorable by 4.8 (reactions 21−22) or 6.0 (reaction 1) kJ/mol than the coupling of two molecules of cation **12a** to give bifluorenylidene dication (**6**). Analogously, the formation of biphenalenylidene dianion ((*E*)-**10**) from anion **15a** is more favorable by only 2.3 (reactions 24−25) or 3.4 (reaction 4) kJ/mol than the formation of bifluorenylidene dianion (**9**) from **14a**. The magnitudes of destabilization are very similar for the coupling of antiaromatic monocation **12a** into dication **6**, and for the coupling of aromatic **13a**−**15a** into the respective diions, as well as for the coupling leading to the fluorenyl, phenalenyl, and the respective heteromerous diions. There are only weak interactions between the $C_{13}H_8$ units in diions **6**−**11**.

Magnetic Criterion. The DFT B3LYP/6-311G(d,p) method was employed to compute the chemical shifts of the systems

(74) Small, D.; Rosokha, S. V.; Kochi, J. K.; Head-Gordon, M. *J. Phys. Chem. A* **2005**, *109*, 11261−11267.

(75) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423−1430.

(76) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371−7379.

TABLE 3. The Comparative Calculated (B3LYP/6-311G(d,p)) and Experimental ^{13}C and ^{1}H Chemical Shifts (ppm) of Neutral and Charged Fluorenyl and Phenalenyl Derived Species

	calcd/ exptl	^{13}C mean shift total	^{13}C mean shift arom[a]	^{1}H mean shift total	^{1}H mean shift arom[a]	NICS5[b]	NICS6[c]	NICS6[c]	NICS6[c]	mean NICS6[c]	NICS12[d]	ref
12a	calcd	155.2	151.1	6.83	6.76	18.8	4.4					
12b	calcd	154.3	148.1	6.15	7.06	15.6	1.6					
	exptl	148.1	141.4	6.46	7.33							59
13a	calcd	147.8		9.14			−7.8				−18.1	
	exptl	142.8		9.00								47
6	calcd	156.2	152.6	6.59		20.7	7.7					
	exptl	148.1	144.7	5.31								42
(*E*)-**7**	calcd	149.1	147.7	9.21			−7.6	−7.5	−6.9	−7.3	−17.5	
8[e]	calcd	156.6	152.3	6.63		20.5	6.2	6.0		6.1		
8[f]	calcd	148.2	147.5	9.25			−8.6	−7.6	−6.9	−7.7	−17.9	
21	calcd	149.2	149.2	9.40			−8.2	−7.2	−7.2	−7.5	−17.8	
3	calcd	127.1	134.5	6.58	7.17		2.0	−11.1	−9.5	−6.2	−15.3	
	exptl			6.29	6.89							77
5	calcd	129.4	136.7	6.90	7.64	−2.8	−10.3					
	exptl	123.3	130.5	6.83	7.54							
1	calcd	137.8	136.7	7.74		−0.5	−8.2					
	exptl	131.2	130.4	7.68								
(*E*)-**2**	calcd	136.2	135.3	7.52			−3.4	−7.9	−7.8	−6.4	−15.4	
(*Z*)-**2**	calcd	136.0	135.1	7.34			−4.5	−6.8	−6.4	−5.9	−15.1	
4[e]	calcd	136.0	135.0	7.69		−1.9	−8.6	−8.1		−8.4		
4[f]	calcd	137.3	136.3	7.77			−0.7	−9.3	−8.7	−6.2	−15.5	
14a	calcd	121.4	124.2	6.96	7.07	−14.3	−11.0					
	exptl	116.7	119.5	7.19	7.32							77
15a	calcd	125.4		5.38			−3.9				−11.9	
	exptl	121.4		5.31								47,49
9	calcd	122.1	123.5	7.02		−13.5	−10.4					
	exptl	118.0	119.8	7.08								56
(*E*)-**10**	calcd	126.7	126.7	5.38			−4.6	−3.6	−2.4	−3.5	−11.5	
(*Z*)-**10**	calcd	126.7	126.6	5.37			−4.7	−3.9	−2.7	−3.8	−11.7	
11[e]	calcd	122.3	123.3	6.98		−13.8	−10.3	−11.0		−10.7		
11[f]	calcd	126.6	126.8	5.45			−4.4	−3.5	−2.2	−3.4	−11.4	
22	calcd	126.7	124.5	5.31			−5.1	−3.0	−3.0	−3.7	−11.8	

[a] Excluding chemical shifts of C^1 (**2**, **3**, **4**, **7**, **8**, **10**, **11**), C^2 (**21**, **22**), C^9 (**1**, **4**, **5**, **6**, **8**, **9**, **11**, **12**, **14**), H^9 (**5**, **12**, **14**), and H^1 (**3**). [b] NICS value of a five-membered ring. [c] NICS value of a six-membered ring. [d] NICS value of the 12-carbon atom perimeter of a phenalenyl moiety. [e] Fluorenyl moiety only. [f] Phenalenyl moiety only.

under study. The choice of this level was based on the comparison between the calculated and experimental shifts and reflects a sufficient accuracy of the 6-311G(d,p) basis set and a better precision of B3LYP over MP2 (vide infra). Table 3 and the Supporting Information Tables S6−S8 present the calculated and experimental[42,47,49,56,59,77−79] ^{13}C and ^{1}H chemical shifts as well as NICS values of neutral and charged species of the phenalene (**3**) and fluorene (**5**) series. Both the five- and six-membered rings of the fluorenyl cation (**12a**) are notably more antiaromatic as compared with neutral **5** (the respective NICS values are 18.8 vs −2.8 and 4.4 vs −10.3). The five-membered ring of anion **14a** (−14.3) is much more aromatic than that of **5**, while the six-membered rings have similar NICS values (−11.0). However, the signals of the aromatic protons of both **12a** and **14a** demonstrate paratropic shifts relative to those of **5** by 0.88 and 0.57 ppm, respectively (the mean aromatic shifts are 6.76, 7.07, and 7.64 ppm (calculated) and 7.33, 7.32, and 7.54 ppm (experimental), respectively).

Coupling of two fluorenyl units does not affect significantly the NICS values of the resulting $C_{26}H_{16}$ species **1**, **6**, and **9**, which are increased by 0.6−3.3, indicating a mildly reduced aromaticity (**1** and **9**) or mildly increased antiaromaticity (**6**). This effect is most noticeable in bifluorenylidene dication (**6**), relative to **12a** (ΔNICS5 = 1.9, ΔNICS6 = 3.3 ppm). The mean proton chemical shift of dication **6** is 6.59 and that of dianion **9** is 7.02 (the value of 5.94 ppm for **6**, reported earlier,[43] apparently stems from using the eclipsed T_d conformation of TMS as the reference compound, which is a fourth order saddle point). They are shifted upfield relative to **1** (7.74) by 1.15 and 0.72 ppm, respectively, being slightly more paratropic than the aromatic protons of monoions **12a** and **14a**. Note that H^1 of **6** exhibits an upfield shift relative to **12a**, whereas H^1 of **9** shows a downfield shift relative to **14a**. The opposite would be expected if H^1 of **6** and **9** were located in the diatropic and paratropic shielding cones, respectively, of the five-membered ring of the opposite moieties. The aromatic protons of **1** are also shifted upfield relative to **4** (except for the overcrowded H^1 and H^8).

In the phenalene series, the phenalenyl cation (**13a**) is more aromatic than neutral **3** with a more negative mean NICS6 value (−7.8 vs −6.2 ppm) and large diatropic (9.14 vs 7.17 ppm) shifts of its aromatic protons, whereas the phenalenyl anion (**15a**) seems to be significantly less aromatic having a less negative mean NICS6 value (−3.9 ppm) and upfield shifted aromatic protons (5.38 ppm). The experimental data (Table 3) are in agreement with the calculated results. A transition from **3**, **13a**, and **15a** to the respective $C_{26}H_{16}$ species has only a minor influence on the aromaticity of the phenalenyl moieties in diions **7** and **10**. The mean shifts of the aromatic protons are 9.21 ((*E*)-**7**), 5.38 and 5.37 ((*E*)-**10** and (*Z*)-**10**) ppm. On the other hand, the protons of BAE **2** exhibit a diatropic shift to

(77) Kasmai, H. S. *J. Chem. Educ.* **1999**, *76*, 830−834
(78) Prinzbach, H.; Freudenberger, V.; Scheidegger, U. *Helv. Chim. Acta* **1967**, *50*, 1087−1107.
(79) Shannon, R. L.; Cox, R. H. *Tetrahedron Lett.* **1973**, *14*, 1603−1605.

7.52 ((*E*)-**2**) and 7.34 ((*Z*)-**2**) ppm. Dication (*E*)-**7** is more aromatic than BAE **2** (mean NICS6 = −7.3), while dianion (*E*)-**10** appears to be close to a nonaromatic species (mean NICS6 = −3.5). Dication **21** and dianion **22** demonstrate chemical shifts and NICS values which are close to those of **7** and **10**, respectively. The NICS12 values, computed for the 12-carbon perimeter of a phenalenyl unit, behave similarly to the NICS6 values, predicting a decrease in aromaticity in the series cation/dication > neutral hydrocarbon > anion/dianion.

Each tricyclic half of the heteromerous systems **4**, **8**, and **11** has magnetic properties which are similar to the properties of the respective $C_{13}H_8$ halves of the homomerous neutral and charged systems. The mean ^{13}C and ^{1}H chemical shifts and NICS values of the fluorenyl moieties of **4**, **8**, and **11** are very close to the respective values of **1**, **6**, and **9**. Analogously, the mean ^{13}C and ^{1}H chemical shifts and NICS values of the phenalenyl moieties of **4**, **8**, and **11** are very close to the respective values of **2**, **7**, and **10**. The biggest differences are observed in the chemical shifts of the bridgehead C^9 and $C^{1'}$ atoms (see below) and of the overcrowded H^1, H^8, $H^{2'}$, and $H^{9'}$ atoms.

Thus, the comparison between the fluorene and phenalene series shows that dication **6** is antiaromatic contrary to its aromatic constitutional isomer (*E*)-**7**, dianion **9** is considerable more aromatic than its constitutional isomers (*E*)-**10**, while the aromaticity of the neutral BAEs **1** and **2** is similar (based on the NICS values). However, relative to the respective monoions **12a**−**15a**, the aromaticity/anitaromaticity of dications **6** and (*E*)-**7** and dianions **9** and **10** is only marginally lower. The aromaticity of the heteromerous systems **4**, **8**, and **11** lies in between that of the respective homomerous species. The fluorenyl and phenalenyl moieties in **4**, **8**, and **11** do not notably affect the magnetic properties of each other and therefore should not affect significantly the aromaticity/antiaromaticity of diions **6**−**8** and **9**−**11** relative to the respective monoions.

Structural Criterion. The harmonic oscillator model of aromaticity (HOMA) is a popular and successful aromaticity index of aromatic/antiaromatic species based on structural parameters.[12] The HOMA index was claimed to be an insensitive measure of structural effects in substituted bifluorenylidene cations.[80] Nevertheless, it can be a very valuable measure of aromaticity for comparison between different polycyclic aromatic systems. Tables S9 and S10 in the Supporting Information present the bond elongation (EN), bond length alternation (GEO), and total HOMA terms for the aromatic rings of hydrocarbons **1**, **2**, and **4** and **20** and their dications and dianions, based on experimental and calculated geometries. The fluorenyl radical (**16**)[81] has aromatic six-membered rings (HOMA6 = 0.89) and a marginally aromatic five-membered ring (HOMA5 = 0.29). Its oxidation to **12a** lowers somewhat the aromaticity of both the five-membered (0.20) and six-membered (0.85) rings. The X-ray derived HOMA5 of **12a** is even lower, −0.70, due to the contributions of both EN and GEO, contrary to the calculations based on HOMA5, which show mainly a bond elongation effect. The reduction of radical **16** to anion **14a** raises the aromaticity of the central ring (0.35) but lowers somewhat the aromaticity of the six-membered rings (0.74). Dication **6** has slightly lower aromaticity than cation **12a** (HOMA5 = 0.17, HOMA6 = 0.84). The net decrease of aromaticity of the five-membered ring of **6** is the result of a combination of increasing the bond elongation term EN5 and decreasing the bond length alternation term GEO5. Dianion **9** (HOMA5 = 0.29, HOMA6 = 0.72) is slightly less aromatic than anion **14a**. The aromaticity loss of the central ring of dianion **9** is also caused by an increase of the bond elongation term EN5. The HOMA5 indices of **6** (0.17) and **9** (0.29) are larger than that of neutral **1** (−0.26), mainly due to a lesser bond elongation, suggesting a mild aromaticity of their central five-membered rings as compared with the antiaromatic 5-membered ring in **1**. The aromaticity of the six-membered rings of **6** (0.84) and **9** (0.72) is slightly lower than that in **1** (0.95). The net result is the slight increase of aromaticity of both dication **6** and dianion **9** relative to **1**. Note that according to the NICS calculations, the antiaromaticity of both five-membered and six-membered rings of **6** (NICS5 = 20.7, NICS6 = 7.7) is greatly increased, and the aromaticity of **9** (NICS5 = −13.5, NICS6 = −10.4) is notably increased as compared with that of BAE **1** (NICS5 = −0.5, NICS6 = −8.2).

In the phenalene series, the mean HOMA6 indices of the neutral species **17a** (0.78), (*E*)-**2** (0.71), (*Z*)-**2** (0.74), and **20** (0.79) are smaller than the indices for the respective positive charged species **13a** (0.85), (*E*)-**7** (0.82), and **21** (0.85), and larger than the indices for the respective anions **15a** and **22** (0.66), and (*E*)-**10** and (*Z*)-**10** (0.61), implying higher aromaticity of phenalene-based cations and lower aromaticity of phenalene-based anions. Coupling of two molecules of **13a** or **15a** together does not cause a significant decrease in the aromaticity of the resulting dication (*E*)-**7** or dianions (*E*)-**10** and (*Z*)-**10**, respectively.

The 5-membered ring of the heteromerous **4** is less antiaromatic than that in **1** (HOMA5 = −0.17 vs −0.26), whereas the phenalenyl unit of **4** is less aromatic than that in (*E*)-**2** (mean HOMA6 = 0.62 vs 0.71). The benzene rings of the phenalenyl and fluorenyl units of both dication **8** and dianion **11** have HOMA indices very similar to those of the respective rings in the homomerous diions, indicating similar aromaticity.

The structural criterion predicts both dication **6** and dianion **9** to be slightly more aromatic than the neutral **1** but slightly less aromatic than the respective monocation **12a** and monoanion **14a**. Dication **6**, dianion **9**, and neutral BAE **1** of the fluorene series have more aromatic six-membered rings (larger HOMA6 values) than the corresponding members of the phenalene series, but the overall aromaticity of the former species is lower as compared with the latter due to the presence of a low aromatic (**9**, 0.29), nonaromatic (**6**, 0.17), or antiaromatic (**1**, −0.26) five-membered ring.

Conclusions

From the energetic criterion point of view, the coupling of monoions **12a**−**15a** to give the respective diions **6**−**11** leads to a considerable destabilization (188−199 kJ/mol, reactions 21−26) for both dications and dianions. It is similar for the coupling of antiaromatic and aromatic monocations, as well as for the coupling giving the homomerous and heteromerous species. Thermodynamically, the species derived from phenalene (**3**) are much more stable than the corresponding species derived from fluorene (**5**). However, the formation of phenalenylidene dication ((*E*)-**7**) from cation **13a** is only −6.0 kJ/mol more favorable than the formation of fluorenylidene dication (**6**) from cation **12a** (reaction 1), suggesting only a slight destabilization

(80) Mills, N. S. *J. Org. Chem.* **2002**, *67*, 7029−7036.
(81) Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota, M.; Kobayashi, T.; Yakusi, K.; Ouyang, J. *J. Am. Chem. Soc.* **1999**, *121*, 1619−1620.

of bifluorenylidene dication **6** relative to dication (*E*)-**7**. The analogous reaction 4 involving dianions **9** and (*E*)-**10** is even less exothermic, $\Delta E_{Tot} = -3.4$ kJ/mol. Eliminating the effect of the changes in steric strain further reduces these differences in stabilities: (*E*)-**7** is more stabilized than **6** by 4.8 kJ/mol (reactions 21−22) while (*E*)-**10** is more stabilized than **9** by 2.3 kJ/mol (reactions 24−25). The dication **6** and dianion **9** appear to be more destabilized when dication **21** of a different topology is chosen as a reference. The hardness index predicts dication **6** to be less stabilized than (*E*)-**7** by 71.2 kJ/mol and dianion **9** to be less stable than (*Z*)-**10** by only 4.4 kJ/mol.

Application of the magnetic criterion shows that dication **6** is significantly antiaromatic contrary to aromatic (*E*)-**7**, while dianion **9** is significantly more aromatic than (*E*)-**10**. The antiaromaticity of **6** is slightly higher and aromaticities of **7**−**11** are slightly lower than those of their respective monoions **12a**−**15a**.

Application of the structural criterion demonstrates that diions **6**−**11** have slightly lower HOMA indices than the respective monoions, mainly because of the contribution of bond elongation. Due to the presence of the five-membered rings, the diions **6** and **9** of the fluorene series are less aromatic, according to the calculation based on HOMA5 and HOMA6, than the corresponding diions **7** and **10** of the phenalene series.

It should also be mentioned that dication **21** and dianion **22**, while being thermodynamically more stable than their constitutional isomers **7** and **10**, do not exhibit a greater aromaticity than the latter species.

All three criteria of aromaticity suggest that coupling of the monoions **12a**−**15a** to give their respective diions **6**−**11** results in a loss of aromaticity/gain of antiaromaticity. However, the magnitude of the effect is similar for coupling of antiaromatic and aromatic moieties as well as for fluorenyl, phenalenyl, and heteromerous series. In particular, the mildly antiaromatic fluorenyl cation (**12a**)[57] leads to a mildly antiaromatic dication **6**. The destabilizing interactions between the two $C_{13}H_8$ halves of diions **6**−**11** are very weak, reaching the maximum for bifluorenylidene dication (**6**), 5.4 kJ/mol (reaction 2). Charge transfer in these diions is also limited and affects the bridgehead atoms C^9 and C^1 rather than the whole conjugated $C_{13}H_8$ moieties. The mild antiaromaticity of dication **6**, concluded in the present study, is in contradiction to the characterization of **6** as highly antiaromatic, based on notably upfield ^{1}H chemical shifts of **6**.[42,43,66] The results of the comparison between the fluorene and phenalene series are not straightforward. While dication **6** has been found mildly antiaromatic and more destabilized relative to the corresponding aromatic dication (*E*)-**7** by all three criteria of aromaticity/antiaromaticity, these criteria do not speak with the same voice regarding dianions **9** and (*E*)-**10**. The aromaticity of dianion **9** is nearly the same as that of (*E*)-**10** by the energetic criterion, is higher than that of (*E*)-**10** by the magnetic criterion, and is lower than that of (*E*)-**10** by the structural criterion.

The results of the comparative theoretical study of the aromaticity/antiaromaticity of the bifluorenylidene and biphenalenylidene dications and dianions **6**, (*E*)-**7**, **9**, and (*E*)-**10** show that application of energetic, magnetic, and structural criteria of aromaticity/antiaromaticity may or may not lead to the same conclusions. Thus, all three criteria of aromaticity should be examined separately, whereas combining them into a single "statistical" measure would limit our understanding of the nature of the species under study.

Methods

The quantum mechanical calculations of the neutral and charged species under study were performed with the Gaussian03[82] package. The HF, DFT, and MP2 Hamiltonians were employed. Becke's three-parameter hybrid density functional B3LYP,[83] with the nonlocal correlation functional of Lee, Yang, and Parr,[84] was used. The basis sets STO-3G, 6-31G(d), 6-311G(d,p), 6-311+G(d), 6-311++G(d,p), and 6-311++G(3df,2p) were employed. All structures were fully optimized, using symmetry constrains as indicated. Vibrational frequencies were calculated to verify minima at B3LYP/6-31G(d) and MP2/6-31G(d) (MP2 vibrational frequencies were computed with frozen core electrons). Nonscaled thermal energy corrections calculated at the above levels were used. The chemical shifts of ^{13}C, ^{1}H, and NICS[67] values (calculated 1 Å above and below the ring plane and averaged) were computed with the Gauge Independent Atomic Orbital (GIAO) method[85] and calculated relative to TMS (*T* point group). No counterions were considered for charged species.

Supporting Information Available: HF, DFT, and MP2 calculated and experimental structural parameters, chemical shifts and atomic charges, DFT and MP2 total energies, Cartesian coordinates or **Z**-matrices of the species under study, schemes of homodesmotic reactions, figures illustrating the relative energies of the dimeric species, and discussions concerning the antiaromaticity of fluorenyl cation (**12a**) and the choice of the computational model. This material is available free of charge via the Internet at http://pubs.acs.org.

JO701939C

(82) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford CT 2004.

(83) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(84) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(85) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260.