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Quantification of the (Anti)Aromaticity of Fulvalenes Subjected to π-Electron Cross-Delocalization

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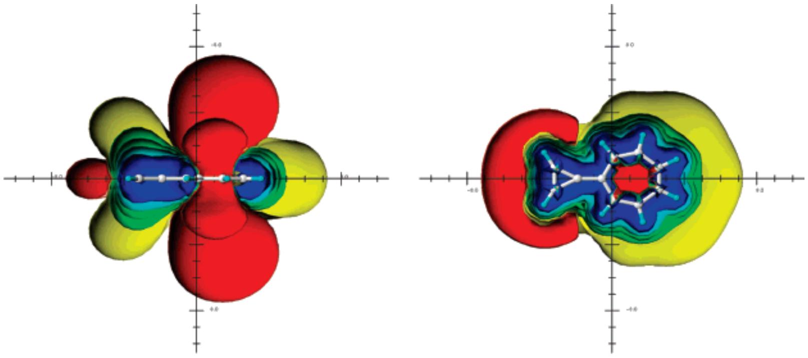
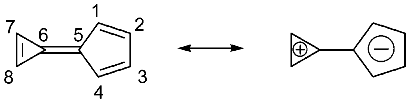


Fulvalenes **3**−**12** were theoretically studied at the ab initio level of theory. For the global minima structures, the occupation of the bonding $\pi_{C=C}$ orbital of the interring C═C double bond obtained by NBO analysis quantitatively proves π-electron cross-delocalization resulting in, at least partially, 2- or 6π-electron aromaticity and 8π-electron antiaromaticity for appropriate moieties. The cross-conjugation was quantified by the corresponding occupation numbers and lengths of the interring C═C double bonds, while the aromaticity or antiaromaticity due to cross-delocalization of the π-electrons was visualized and quantified by through-space NMR shielding surfaces.

Introduction

Fulvalene molecules with two unsaturated ring systems that cross-conjugate through a common exocyclic double bond[1] (e.g., calicene **1**) can exhibit bond polarization generating two separate (4*n* + 2) π-electron aromatic moieties (cf. **2** in Scheme 1). Depending on the number of π-electrons in the two moieties of fulvalenes **3**−**12** (see Scheme 2), dipolar mesomeric electronic structures such as **2** can be attained, resulting in partial (anti)aromatic character, which then subsequently also affects the excited state properties of the molecules.[2]

SCHEME 1



1 **2**

As simple criteria for estimating the extent of the π-electron cross-delocalization in the five-membered ring of the substituted pentafulvalenes **4**−**6** and **11**, the differences in the vicinal H,H coupling constants $^3J_{1,2}$ and $^3J_{2,3}$ and the differences in the ^{13}C chemical shifts $\Delta\delta(1,2)$ and $\Delta\delta(2,3)$ have both been employed.[3,4] For example, if $^3J_{1,2} = {}^3J_{2,3} = 3.4$ Hz, aromaticity of the five-membered ring has been suggested.[3] Otherwise, ^{1}H chemical shifts residing in the aromatic region, ^{13}C chemical shifts resonating at ca. 110 ppm, or large $^3J_{H,H}$ coupling

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* Corresponding author. Fax: 00493319775064.

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[2] Möllerstedt, H.; Piqueras, M. C.; Crespo, R.; Ottosson, H. *J. Am. Chem. Soc.* **2004**, *126*, 13938.

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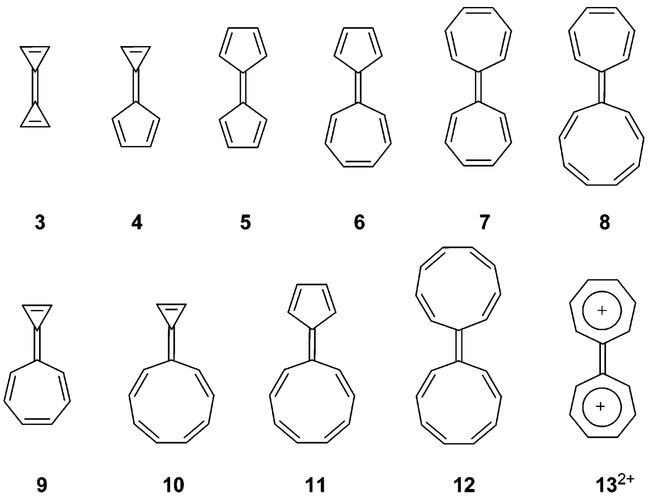
10.1021/jo701520j CCC: $40.75

SCHEME 2



constants of similar size have all been used for assessing the extent of delocalization.[5−8]

Since, in polarized structures such as **2**, the interring C=C double bond is formally a single bond, rotation about this bond can be anticipated, although it is likely to be restricted and thus potentially slow on the NMR time scale. However, experimental dynamic NMR studies have not yet been reported, although theoretical calculations at various levels of theory have been published.[9−11] In this respect, **1** is the best studied molecule, where the barriers to rotation calculated at the MP2 level in the gas phase (40−41 kcal mol^{-1}), in benzene (37 kcal mol^{-1}), and in water (33 kcal mol^{-1}) have been reported.[11] For sesquifulvalene **6**, a similar value at the same level of theory has been obtained (41.5 kcal mol^{-1}).[12a] These rotational barriers are lower than those for ethylene (65 kcal mol^{-1}) or stilbene (46 kcal mol^{-1}),[12b] thus corroborating the reduced double bond character of the interring C=C double bond. Still, the barriers are not low enough to be observed experimentally by dynamic NMR spectroscopy. Significant zwitterionic character, when present in **3**−**12**, has been evident by high dipole moments, either measured for their derivatives or calculated.[11,13] In a comprehensive theoretical study of fulvenes and fulvalenes, Scott et al.[13] addressed the problem of their aromaticity/antiaromaticity in light of bond alternation, energy comparisons, and dipole moments. Recently, Halton reviewed[14] the information available on fulvalenes from research published at the end of 2004.

The major aim of the present study was to investigate fulvalenes **3**−**12** by the application of NBO analysis to the global minima structures obtained from ab initio calculations at the MP2 level of theory. Examination of the occupation numbers of the bonding $\pi_{C=C}$ orbital of the interring C=C double bond permits quantification of the shift of π-electrons from this bond to the fulvalene moieties aspiring to aromaticity. The ratio $\pi_{C=C}/\pi^*_{C=C}$, which usually appears to be the most general criterion for quantifying the push−pull effect in push−pull alkenes,[15] was similarly examined but proved to be not sensitive. In addition, the through-space NMR shielding surfaces (TSNMRS) for fulvalenes **3**−**12** were calculated employing the NICS (nucleus independent chemical shift) concept of Paul v. R. Schleyer[18] and used to visualize the anisotropic effect of the functional groups and the ring current effect of aromatic moieties by isochemical-shielding surfaces (ICSS) of various size and sign[16] to thereby quantify the aromaticity and/or antiaromaticity present.[17] This new approach to both quantify and visualize the partial aromaticity/antiaromaticity in the ring moieties of **3**−**12** is expected to not only deliver a comprehensive picture of this topic but also to complete and prove the results of the quantum chemical study of Scott et al.[13] on fulvalenes **3**−**7** and **10** from different directions, and, finally, to offer a new method to be applied for the study of similar phenomena in physical organic chemistry (e.g., in fullerenes, in fulvenes, or in their metaloorganic isoelectronic analogues).

Of significant note, there have been some recent developments of NICS[18] showing that none of the various methods can safely assign aromaticity,[19] and nonmeasurable parameters have proven generally to be unsuitable for the quantitative evaluation of aromaticity.[20] In addition, the conventional interpretation of deshielded ^{1}H chemical shifts for aromatic protons has proven to be due to reasons other than deshielding ring current effects,[21] and thus, they are not reliable indicators of aromaticity as well.[22] For example, NICS analysis was shown to lead to an incorrect prediction of aromaticity for the cyclopropenyl anion.[23]

Results and Discussion

Ab initio MO calculations were performed using the Gaussian 03 program package.[24] Geometry optimization was performed at the MP2/6-31G** level of theory without restrictions, and the resulting geometries are collected in Table S1 in the Supporting Information and are depicted in Figures 2, 4, and 5. Generally, the global minima structures only are given and have been employed in the present discussions; in the case of folded and/or twisted seven- and nine-membered ring moieties, the corresponding planar conformer proved to be 6−30 kcal mol^{-1} less stable than the preferred conformer under discussion.

The chemical shieldings surrounding the molecules were calculated based on the NICS concept of Schleyer et al.,[25] whereby the molecule was placed in the center of a grid of ghost atoms ranging from −10.0 to +10.0 Å in all three dimensions with a step width of 0.5 Å resulting in a cube of 68 921 ghost

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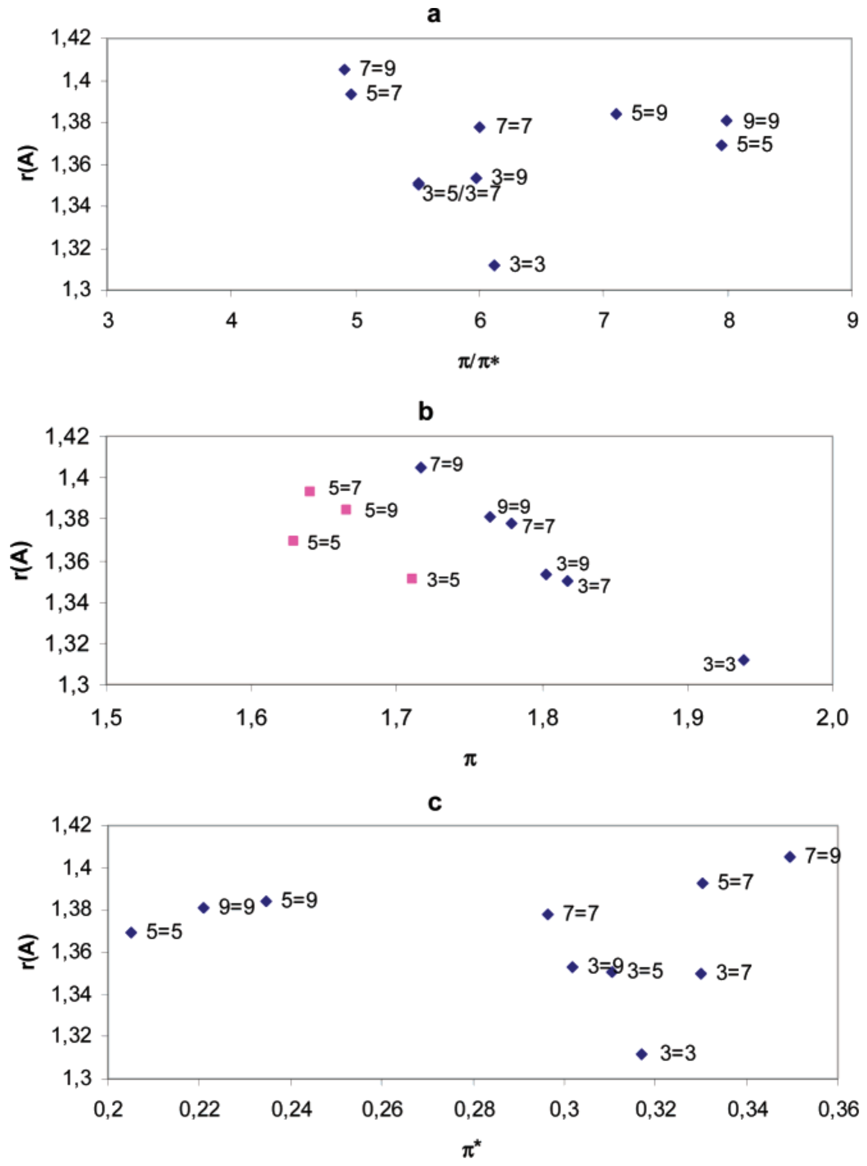

FIGURE 1. Correlation of bond length of the central C═C double bond in fulvalenes **3**−**12** with corresponding occupation quotient $\pi_{C=C}/\pi^*_{C=C}$ (a) and with the occupation of the bonding π-orbital (b) and the antibonding π^*-orbital (c).

TABLE 1. Bond Lengths (r (Å)) and Occupation Numbers of Bonding $\pi_{C=C}$ Orbital of Interring C═C Double Bond in Symmetrical Fulvalenes 3, 5, 7, and 12

compound	r (Å)	$\pi_{C=C}$
3 [3-3]	1.312	1.938
5 [5-5]	1.369	1.629
7 [7-7]	1.378	1.779
12 [9-9]	1.381	1.764

atoms. The chemical shielding calculations were performed using the GIAO[26] method at the HF/6-31G* level of theory. Since GIAO is a coupled HF method that uses gauge-independent atomic orbitals for the calculation of shielding values, it can be applied to the calculation of NICS. Starting structures were generated by the SYBYL modeling software.[27] From the GIAO calculations, the coordinates and isotropic shielding values of the ghost atoms were extracted. After transformation of the tabulated chemical shieldings into the SYBYL[27] contour file, the TSNMRSs were visualized in Figures 2−6 as ICSSs, providing a 3-D view of spatial extension, sign,

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(24) 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, B.; 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.: Pittsburgh, PA, 2004.

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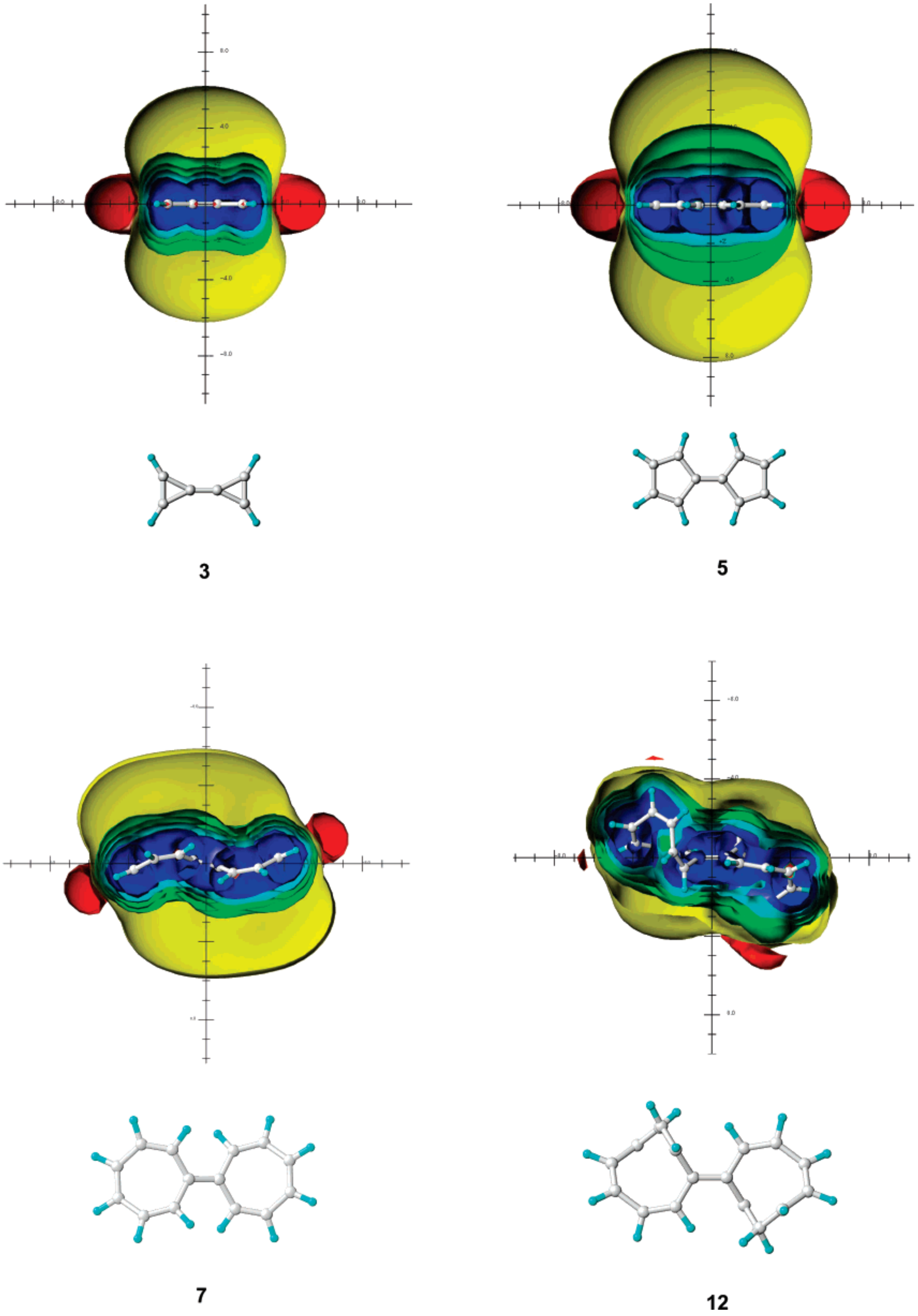
3

5

7

12

FIGURE 2. Structures and TSNMRS surfaces of **3**, **5**, **7**, and **12** (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, and red −0.1 ppm deshielding).

and scope of the aromaticity/ring current effects of the fulvalenes at each point in space.

The occupations of the bonding and antibonding orbitals of the fulvalene interring C═C double bonds were calculated using the NBO option[28] as implemented in the Gaussian 03 package with MP2/6-31G**. The keyword density = current was

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(28) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

TABLE 2. Distances (Å) of ICSS ±0.1 ppm from Center of Respective Ring Moiety (cf. Ref 17)

compound		ICSS −0.1 ppm; in plane (Å)	ICSS 0.1 ppm; perpendicular-to-center (Å)
3	3	4.9	5.9
	3	4.9	5.9
4	3	5.2	7.4
	5	6.0	7.9
5	5	5.4	7.9
	5	5.4	7.9
14	6	5.4	5.6
	6	5.4	5.6
6	5	5.3	6.9
8	7	3.8[a,b]	4.0[b,c]
9	3	4.5	4.3
	7	6.0[a,b]	7.5[b,c]
10	3	4.9	6.3
11	5	5.0	7.0
Benzene		7.2	8.9
Cyclopropenylium cation		5.9	7.2
Cyclobutadiene		5.5[a,b]	6.2[b,c]

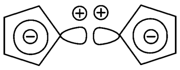
[a] ICSS 0.1 ppm. [b] Sign changed, moiety being antiaromatic.[17] [c] ICSS −0.1 ppm.

included in the Gaussian route cards to verify that the NBO software program analyzes the MP2 densities. The densities, and also the occupations of the various other conjugated double bonds in **3**−**12**, are given in Table S2 in the Supporting Information.

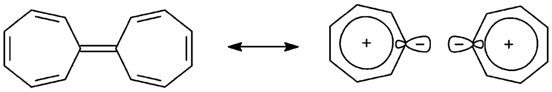
Up to now, only lone double bonds in push−pull alkenes have been studied by this methodology, and in all cases, a strict linear dependence of the quotient $\pi_{C=C}/\pi^*_{C=C}$ to the bond length of the partial C═C double bond was obtained. However, in the case of the fulvalenes **3**−**12**, similar correlations were not evident (cf. Figure 1a). Obviously, due to conjugation along the entirety of the molecules, any accepted/donated π-electron density could potentially be spread over the whole ring moieties and thereby located in much more than just two orbitals. For this reason, the two correlations $\pi_{C=C}$ versus bond length and $\pi^*_{C=C}$ versus bond length for **3**−**12** were also examined (cf. Figures 1b,c). These examinations revealed the following: (i) the occupation of the bonding π-orbital displays two correlations, one for the fulvalenes with five-membered ring moieties and another one for the rest of the set; (ii) obviously, the interplay of bonding π-orbital occupation/bond length in these fulvalenes (**4**−**6** and **11**) is stronger than in the case of the others (corroborating the outstanding position of the five-membered ring moiety, which requires the 2-π-electrons of the connecting C═C double bond to attain, at least partly, aromaticity); and (iii) there is no dependence in the case of the antibonding π^*-orbital. The reason for the insensitivity of the occupation of the $\pi^*_{C=C}$ orbital proves to be conjugation of this orbital. Donation into $\pi^*_{C=C}$ from one ring moiety does not increase its occupation but, due to conjugation, shifts the π-electron density gained into the conjugated $\pi^*_{C=C}$ orbitals of the other ring moiety (cf. Figure S1 in the Supporting Information). Thus, in the ensuing text, the quotient $\pi_{C=C}/\pi^*_{C=C}$ cannot be discussed, but rather the occupation of the $\pi_{C=C}$ orbital only will be addressed in terms of present acceptor properties of the various different fulvalene ring moieties.

Comparison of Symmetrical Fulvalenes 3, 5, 7, and 12. The occupations of the bonding π-orbital of the cross-conjugated C═C double bond connecting the two fulvalene moieties (synonymous for the acceptor activity of the two ring systems) are given, together with the corresponding bond lengths, in Table 1 (the occupancy of two can be established as a "norm" for systems in which changes in the occupancy of $\pi_{C=C}$ would not result in the creation of aromatic or antiaromatic systems); the structures of **3**, **5**, **7**, and **12** are given in Figure 2, and the corresponding TSNMRS surfaces are visualized by ICSSs of different size and direction (partial aromaticities in **3** and **5**, calculated by our method, described in ref 17, are given in Table 2).

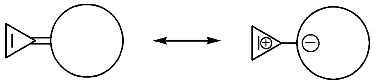
SCHEME 3



SCHEME 4



SCHEME 5



15 **16**

The two small fulvalenes **3** and **5** are planar molecules.[13,29] In [3-3]-fulvalene **3**, the acceptance by the bonding $\pi_{C=C}$ is lowest (cf. Table 1), clearly because 2π-electron aromatic moieties are already present and do not require more π-electrons. In contrast to **3**, in [5-5]-fulvalene **5**, the electron acceptor demands of the two five-membered rings are strongest, again in accordance with the proclivity of the two rings to attract additional 2π-electrons from the interring C═C double bond to complete, at least partly, 6π-electron aromaticity. The canonical structure that reflects this tendency to aromatization is given in Scheme 3. The TSNMR surfaces of **3** and **5**, given in Figure 2, visualize the corresponding anisotropic effects of the central C═C double bond and of the terminal moieties. Because of the cross-conjugation in **3** and **5**, these effects contribute to strong shielding areas above and below the planes (cf. Table 2: ICSS +0.1 ppm, yellow at 5.9 and 7.8 Å, respectively) and deshielding in plane (ICSS −0.1 ppm, red at 4.9 and 5.4 Å, respectively). However, bond alternation in both the three- and the five-membered ring moieties still indicates the olefinic nature of the two fulvalenes and the very small, if any, aromaticity (cf. Figure 2 and Figure S2 in the Supporting Information). If conjugation of the four cross-conjugated C═C double bonds in **5** is interrupted, as in **14** (cf. Figure 3), the extension of both the shielding area (ICSS +0.1 ppm, yellow at 5.6 Å) and deshielding areas (ICSS −0.1 ppm, red at 5.4 Å) is reduced.

In between the two extremes of **3** and **5** are the [7-7]- and [9-9]-fulvalenes **7** and **12**, respectively. They are sterically hindered, and while **7** shows the antifolded C_{2h} structure,[13,30] **12** is highly twisted.[14] Thus, cross-conjugation between the two rings is restricted, and the interring C═C double bond anisotropic effects cannot add effectively as they do in **3** and **5**, thereby excluding any aromatization effects[31] (cf. Figure 2). The acceptor power of the ring moieties in **7** and **12** should be similar (cf. Table 1), and indeed, it is shown to be. Also, the donor

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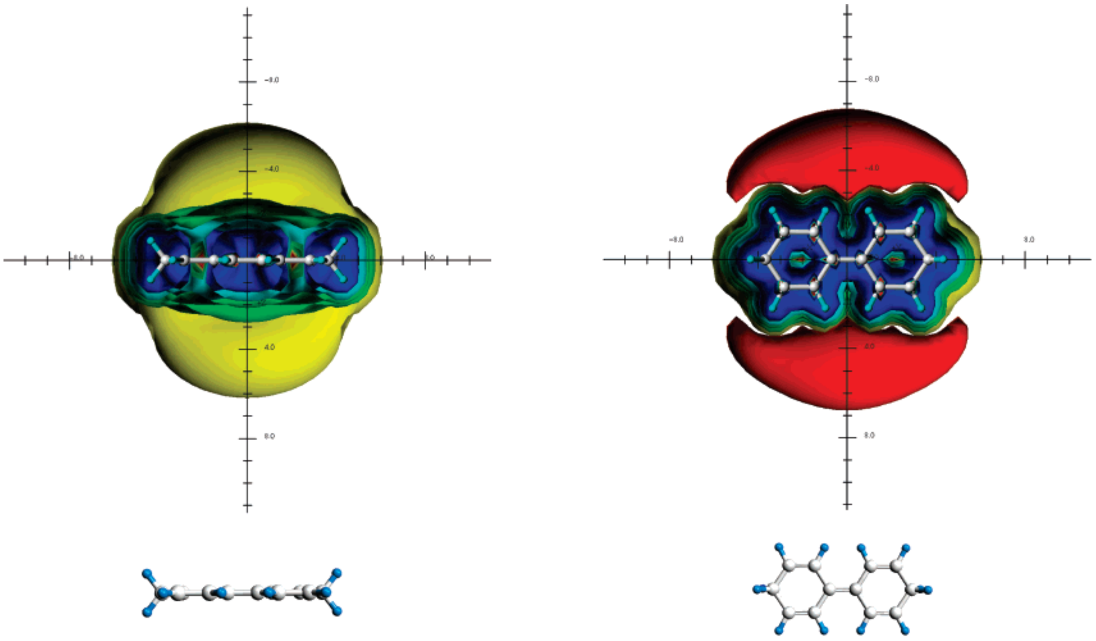


FIGURE 3. Structure and TSNMRS surfaces of compounds **14** (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, and red −0.1 ppm deshielding).

TABLE 3. Bond Lengths (r (Å)) and Occupation Numbers of Bonding $\pi_{C=C}$ Orbital of Interring C=C Double Bond in Symmetrical Fulvalenes 4, 9, and 10

compound	r (Å)	$\pi_{C=C}$
4 [3-5]	1.351	1.711
9 [3-7]	1.350	1.818
10 [3-9]	1.353	1.803

TABLE 4. Bond Lengths (r (Å)) and Occupation Numbers of Bonding $\pi_{C=C}$ Orbital of Interring C=C Double Bond in Symmetrical Fulvalenes 6, 8, and 11

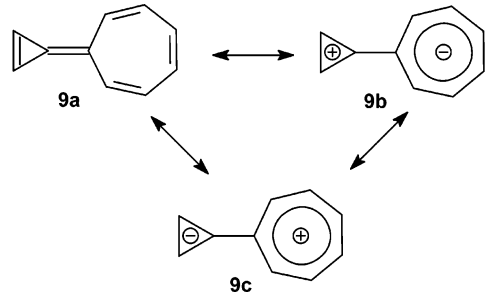
compound	r (Å)	$\pi_{C=C}$
6 [5-7]	1.393	1.640
8 [7-9]	1.405	1.717
11 [5-9]	1.384	1.665

TABLE 5. Bond Lengths (r (Å)) and Occupation Numbers of Bonding $\pi_{C=C}$ Orbital for Asymmetrical Fulvalenes 4, 6, and 8−11

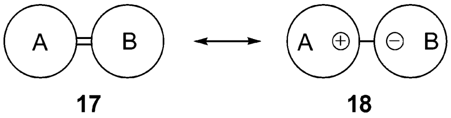
compound	r (Å)	$\pi_{C=C}$
4 [3-5]	1.351	1.711
6 [5-7]	1.393	1.640
8 [7-9]	1.405	1.717
9 [3-7]	1.350	1.818
10 [3-9]	1.353	1.803
11 [5-9]	1.384	1.665

activities of the two rings should be similar because of the propensity of the ring moieties in **7** to repulse the π-electrons of the interring C=C double bond. Although the aromatic π-electron sextet is potentially available, aromaticity does not develop due to both the folded structure of **7** and the bond alternation in this fulvalene (cf. Figure 2). The canonic structure that reflects potentially a tendency to aromatization is depicted in Scheme 4. However, its contribution must be very small, and although it does not result in significant aromaticity overall, it can at least reflect the tendency.

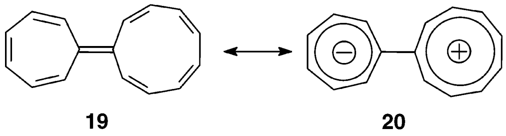
SCHEME 6



SCHEME 7



SCHEME 8



The [9-9]-fulvene **12** is heavily twisted, and therefore, any conclusions regarding partial aromaticity from the participation of the 2-π-electrons of the central C=C double are inappropriate.

Comparison of Fulvalenes 4, 9, and 10 with One Three-Membered Ring Moiety. While **4** and **9** are planar molecules,[11,13,14] **10** proved to be highly twisted in the nine-membered ring segment. The corresponding occupations of the $\pi_{C=C}$ orbitals and the bond lengths of the interring C=C double bond of **4**, **9**, and **10** are given in Table 3, while structures and TSNMRS surfaces are presented in Figure 4 (ICSS values at ±0.1 ppm are given in Table 2). The three-membered ring moiety in these three compounds (cf. **15** in Scheme 5) can

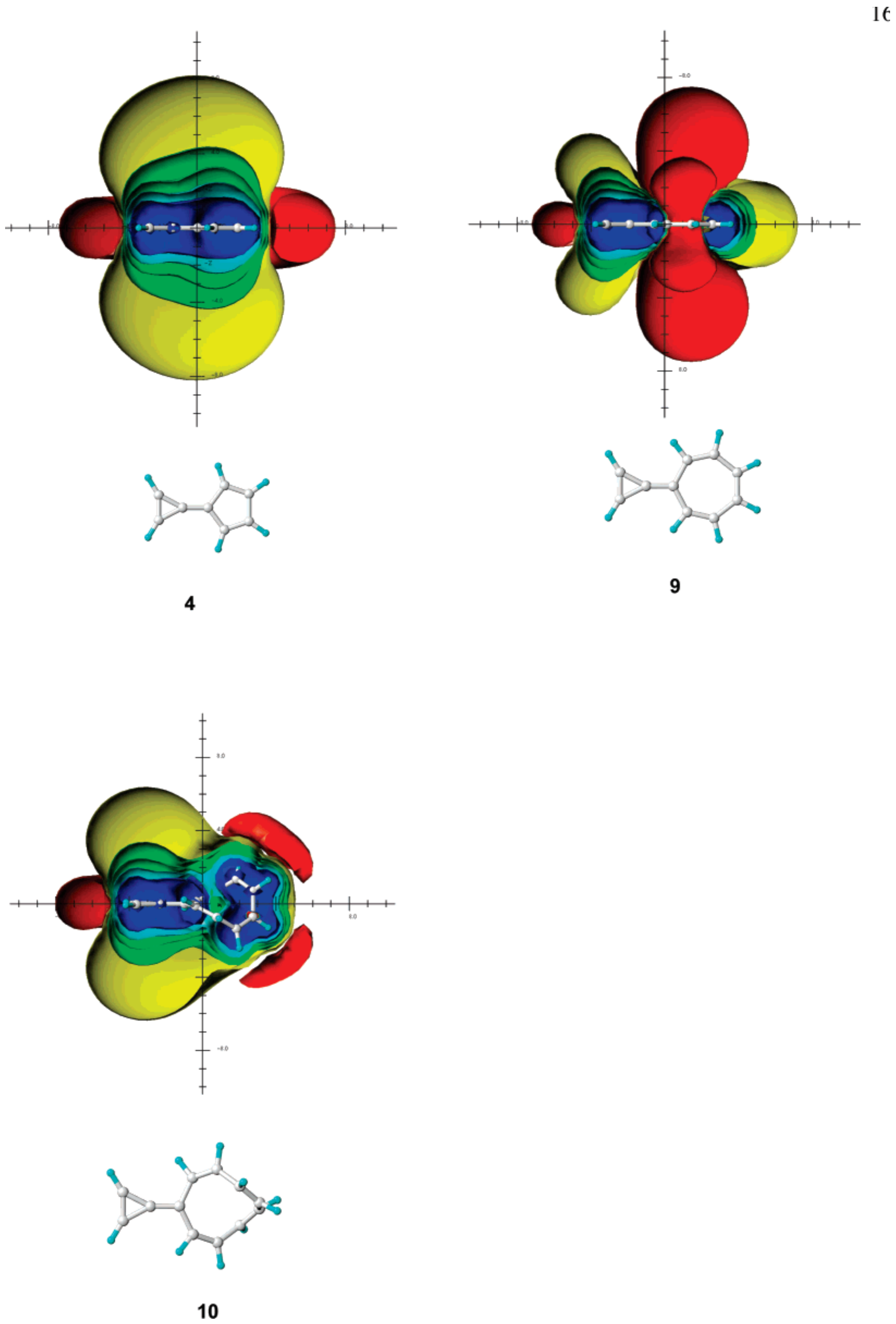
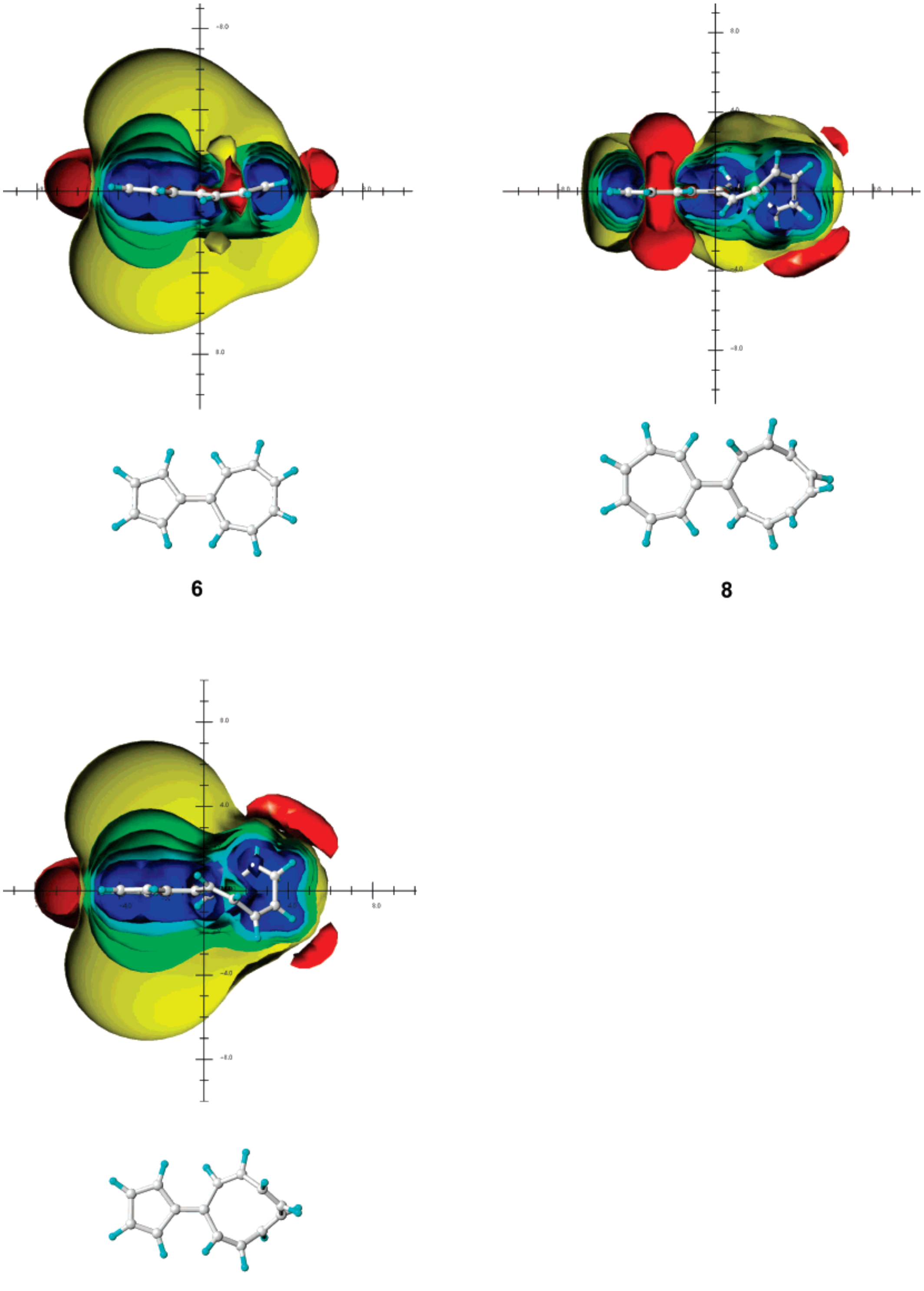


FIGURE 4. Structures and TSNMRS surfaces of **4**, **9**, and **10** (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, red −0.1 ppm deshielding, and dark red −1 ppm deshielding).

potentially transfer to the aromatic cyclopropenylium cation (**16** in Scheme 5) by shifting the 2π-electrons of the cross-conjugated double bond to the second ring moiety. That it obviously happens, at least partly, can be concluded from the corresponding ICSS values given in Table 2 and seen in Figure 4: the three-membered ring moieties in **4**, **9**, and **10** proved to be partly aromatic (**4** (5.2 Å (−0.1 ppm) and 7.9 Å (+0.1 ppm), **9** (4.5 Å (−0.1 ppm) and 4.3 Å (+0.1 ppm), and **10** (4.9 Å (−0.1 ppm) and 6.3 Å (+0.1 ppm)) near to the values of the single cyclopropenylium cation (5.9 Å (−0.1 ppm) and 7.2 Å (+0.1 ppm), cf. Table 2). Two partially aromatic moieties in one molecule (**4**) obviously strengthen each other.

Actually, both bond lengths and occupations of the bonding π-orbitals (cf. Table 3) are rather similar. The attraction of



6

8

11

FIGURE 5. Structure and TSNMRS surfaces of **6**, **8**, and **11** (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, red −0.1 ppm deshielding, and dark red −1 ppm deshielding).

π-electron density from the bonding π-orbital of the interring C═C double bond can be readily understood: the five-membered ring in **4** becomes partly aromatic if the common 2π-electrons are attracted (cf. Figure 4; partial aromaticity of the five-membered ring 6.0 Å (−0.1 ppm)/7.8 Å (+0.1 ppm)); thus, the $\pi_{C=C}$ orbital occupation proves to be the lowest (cf. Table 3). The seven-membered ring in **9**, due to the 8π-electrons potentially available, becomes partially antiaromatic[13] (cf. Figure 4; partial antiaromaticity of the seven-membered ring 6.0 Å (+0.1 ppm)/7.5 Å (−0.1 ppm). Thus, the dominating canonical structure **9b** (cf. Scheme 6) for fulvalene **9**, as found by Scott et al.,[13] is confirmed (the contribution of **9c** is negligible).

Finally, the nine-membered ring in **10**, due to the strong twist in the global minimum structure, cannot employ the additional

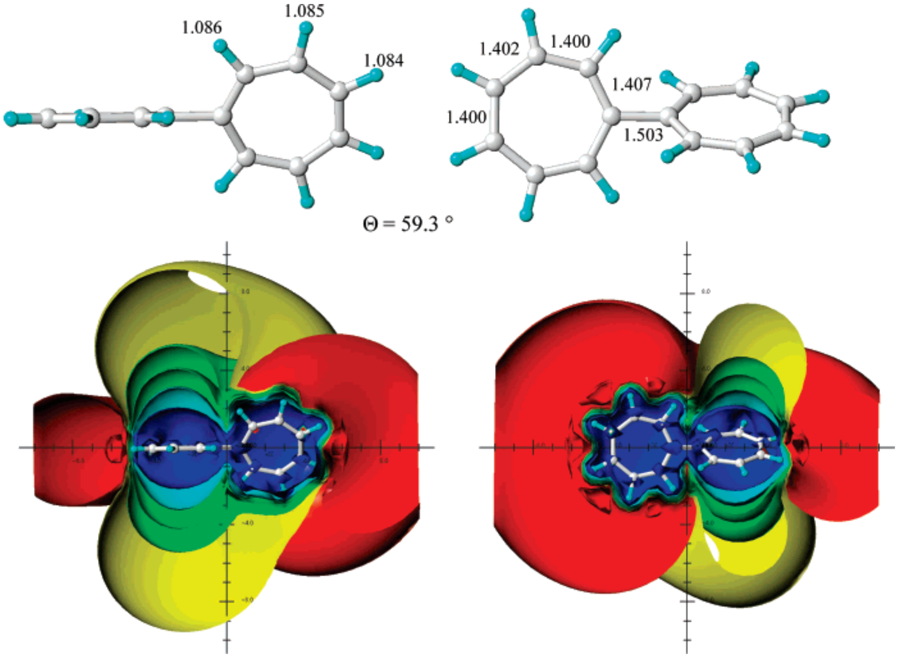


FIGURE 6. Structure and TSNMRS surfaces of the ditropylium dication **13**$^{2+}$ (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, green−blue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding, and red −0.1 ppm deshielding).

2π-electrons to obtain partial 10π-electron aromaticity (cf. Figure 4). Thus, partial aromaticity, suggested for the whole molecule **10**,[4,8,31−33] is limited to the three-membered ring moiety only, and the $\pi_{C=C}$ orbital occupation proves to be of intermediate nature.

Further interesting conclusions regarding the behavior of **4**, **9**, and **10** are (i) the partial 6π-electron aromaticity is stronger than 2π-electron aromaticity (in **4**: 6.0 Å (−0.1 ppm) and 5.2 Å (−0.1 ppm), respectively, and 7.9 Å (+0.1 ppm) and 7.4 Å (+0.1 ppm), respectively, as already determined and visualized by the TSNMRS surfaces of benzene and cyclopropenylium cation, respectively; cf. Table 2);[17] (ii) the partial 2π-electron aromaticity in **4** and **10** (ICSS +0.1 ppm at 7.4 and 6.3 Å, respectively) is larger than in **9** (ICSS +0.1 ppm at 4.5 Å only; apparently, partial antiaromaticity in the seven-membered ring moiety weakens the partial aromaticity in the three-membered ring); and (iii) among the set of the fulvalenes studied, the [3-5]-fulvalene **4** is best suited to achieve partial aromaticity in the two cross-conjugated ring systems (cf. Scheme 1, vide supra).

Comparison of Fulvalenes 6, 8, and 11. The five-membered ring moieties in **6** and **11** and the seven-membered ring in **8** are all planar. For the second ring systems of each, the seven-membered ring in **6** is folded,[13] while the nine-membered rings in both **8** and **11** are highly twisted (cf. Figure 5). Occupations and bond lengths of these three fulvalenes are given in Table 4. Low occupation numbers of $\pi_{C=C}$ equal to 1.640 and 1.665 for the [5-7]- and [5-9]-fulvalenes **6** and **11**, respectively, are indicative of the highest acceptor power of the five-membered ring moiety, which is indicative of attaining partial 6π-electron aromaticity (cf. also Figure 1b). The same conclusion can be drawn from analysis of the five-membered ring TSNMRS surfaces (ICSS +0.1 ppm ca. 7 Å in both cases; cf. Figure 5 and Table 2).

The acceptance from the bonding $\pi_{C=C}$ orbital is not much different in the [7-9]-fulvalene **8** (cf. Table 4), but it is significantly lower than in **6** and **11**. Obviously, the seven-membered ring makes no arrangements to repulse the 2π-electrons of the C═C double to attain partial aromaticity, and actually, the opposite is true: it attracts partial π-electron density from the connecting C═C double bond to attain partial 8π-antiaromaticity (cf. Figure 5).

Comparison of Fulvalenes 4, 6, and 8−11. Finally, fulvalenes **4**, **6**, and **8**−**11** are compared since they are capable of cross-delocalizing the 2π-electrons of the interring C═C double bond leading to partial aromatic (for **4**, **6**, **8**, and **10**) or antiaromatic (for **9** and **11**) structural elements (cf. Scheme 7). Structures and TSNMR surfaces are given in Figures 4 and 5, the corresponding ICSS values are given in Table 2, and occupations and bond lengths, already presented in Tables 3 and 4, are collected again for comparative purposes in Table 5.

The best acceptor potential is observed in the fulvalenes with five-membered ring moieties: highest in the [5-7]- and [5-9]-fulvalenes, **6** and **11**, respectively, and a bit smaller in the [3-5] analogue **4**. These are the fulvalenes of highest partial 6π-electron aromaticity (vide supra and cf. Figures 4 and 5). The [7-9]-fulvalene **8** occupies the middle position with respect to acceptor ability ($\pi_{C=C}$ = 1.717), and no attempt to attain partial aromaticity can be found. Actually, the seven-membered ring, being planar, proved to be partly antiaromatic (3.8 Å (+0.1 ppm)/4.0 Å (+0.1 ppm)), although the nine-membered ring moiety is highly twisted to show local C═C double bond anisotropy only.

Finally, the fulvalenes with one three-membered and one seven- and nine-membered ring, **9** and **10**, respectively, show the lowest degree of π-electron transfer from the interring C═C double bond ($\pi_{C=C}$ > 1.8, Table 5). In each case, the three-membered ring has still some aromaticity (in **9**: 4.5 Å (−0.1 ppm)/4.3 Å (+0.1 ppm) and in **10**: 4.9 Å (−0.1 ppm)/6.3 Å (+0.1 ppm)), although weakened by the partial antiaromaticity

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of the seven-membered ring in **9** but strengthened by the twisted nine-membered ring moiety in **10** (vide supra).

TSNMRS Surfaces of the Ditropylium Dication $\mathbf{13^{2+}}$. This dication was first synthesized in 1964 and was shown to be stable in strongly acidic media as the di-PCl_6^- salt.[34] The proton chemical shift resonated at a value characteristic for aromatic protons, viz. 9.55 ppm. This compound was included in this study because the seven-membered ring moieties in fulvalenes **6**−**9** were found to possess either partial antiaromaticity (if planar as in **8** and **9**) or be folded (as in **6** and **7**). In the case of $\mathbf{13^{2+}}$, however, 6π-electron aromaticity was forced to be present: the two planar seven-membered conjugated cationic moieties are twisted by 59.3°, the connecting bond is elongated to 1.5 Å, and both moieties are completely aromatic (cf. Figure 6, ICSS 0.1 ppm at 9.7 Å is even larger than in benzene at 8.9 Å).[17] Thus, 6π-electron aromaticity of seven-membered rings, if conjugated, is readily possible and, from the extension of both ICSSs at ±0.1 ppm, seems to be even larger than that of benzene itself. In the seven-membered ring moieties of fulvalenes **6**−**9**, this possibility, although in principle available for **6**−**9**, is not attained for steric reasons in **6** and **7**, nor realized in **8** and **9**. Instead, they demonstrate partial antiaromaticity by including the π-electrons from the interring C=C double bond as evident from Figures 4 and 5.

Conclusion

The π-electron distribution in fulvalenes **3**−**12** has been studied by occupation numbers of the bonding $\pi_{C=C}$ (synonymous for the acceptor activity of the two cross-conjugated ring moieties) and by their TSNMRS surfaces quantified by ICSS values at ±0.1 ppm. It was found that the three- and five-membered ring moieties always remained planar and attained partial aromaticity via cross-conjugation. Regarding the seven-membered ring moieties, they demonstrate different behavior in this respect: in [5-7]- and [7-7]-fulvalenes (**6** and **7**, respectively), no aromaticity at all is attained due to steric hindrance, whereas in [3-7]- and [7-9]-fulvalenes (**9** and **8**, respectively), they become partly antiaromatic. Finally, the nine-membered ring moieties proved to be twisted due to steric hindrance and did not exhibit any partial aromaticity or antiaromaticity at all.

The symmetrical fulvalenes **3**, **5**, **7**, and **12** proved to have no aromaticity at all.[13,14] However, the antiaromaticity of **3** as reported by Scott et al.[13] could not be confirmed. The [3-5]-fulvalene **4** proved to have the highest aromaticity in complete agreement with results obtained by other methods.[11,13] Furthermore, the dominant canonical structure **18** (cf. Scheme 7) of [3-7]-fulvalene **9**[13] was able to be impressively confirmed where the molecule is planar with aromatic (three-membered) and antiaromatic (seven-membered) ring moieties (cf. Figure 4). The three-membered ring moiety 2π-electron aromaticity of the [3-9]-fulvalene **10**[5,8,14,32,33] was also confirmed. However, the related nine-membered ring moiety is so strongly twisted that the expected 10π-electron aromaticity was not able to be developed.

Both [5-7]- and [5-9]-fulvalenes, **6** and **11**, respectively, corroborated the bond polarization expected: the five-membered ring moiety is partly aromatic; both the corresponding seven- and five-membered rings cannot develop aromaticity and antiaromaticity, respectively, due to steric hindrance. This is in complete disagreement with Neuenschwander et al.[4,6,7] but also in partial disagreement with Scott et al.[13] because the aromaticity of the seven-membered ring moiety in **6** could not be confirmed.

Another interesting result of the study is the dominating canonical structure of the [7-9]-fulvalene **8**, viz. **20** (cf. Scheme 8). This is because the seven-membered ring moiety proves to be planar and partly antiaromatic (cf. Figure 4). This result has not yet been reported before but throws light on the tendency of seven-membered rings with three conjugated endocyclic double bonds and one exocyclic C=C double bond to behave similarly.

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Supporting Information Available: Coordinates and absolute energies at the MP2/6-31G** level of theory, occupation numbers of bonding $\pi_{C=C}$ and antibonding $\pi^*_{C=C}$ orbitals for fulvalenes **3**−**12**, visualization of π-electron density shifts in the compounds, and complete set of calculated structures together with both bond lengths and TSNMRS shieldings. This material is available free of charge via the Internet at http://pubs.acs.org.

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