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Quantification of the (anti)aromaticity of fulvenes subject to ring size

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Abstract

Tria-, penta-, hepta- and nonafulvenes (**1**–**4**) have been studied theoretically at the MP2 ab initio level of theory. For the global minimum structures, the occupation of the bonding $\pi_{C=C}$ orbital of the exocyclic C=C double bond, obtained by NBO analysis, quantitatively proves π-electron delocalization which can reveal partial 2-, 6- and 10-π-electron aromaticity, and 4-, 8- and 12-π-electron antiaromaticity of the ring moieties. Beside the corresponding occupation number, this conjugation was quantified by the length of the exocyclic C=C double bond whilst the (anti)aromaticity of the ring moieties of **1**–**4** was visualized and quantified by through space NMR shielding surfaces (TSNMRS).

Keywords: Fulvenes; Through space NMR shieldings; MP2 ab initio calculations; GIAO, NICS; Aromaticity; Antiaromaticity

Fulvenes, conjugated ring systems with one exocyclic C=C double bond, attract continuous interest due to their unique cross conjugated structure which can generate $(4n+2)$ π-electron aromatic and $4n$ π-electron antiaromatic moieties via bond polarization (cf. Scheme 1). Depending on the number of conjugated π-electrons in fulvenes **1**–**4**, dipolar mesomeric electronic structures **1a**,**b**–**4a**,**b** can be attained resulting in partial (anti)aromatic character of the compounds.

Fulvenes **1**–**4** have previously been synthesized (triafulvene **1**,[1–3] pentafulvene **2**,[4] heptafulvene **3**[5] and nonafulvene **4**),[6] and were studied with respect to their dipole moments[7–9] and NMR spectra.[1,3,10–14] The ^1H and ^{13}C NMR spectra of triafulvene **1** (both protons and carbon atoms of the 3-membered ring moiety display resonances in the region of aromatic compounds) evidence a significant contribution of the resonance form **1b**;[1,3] the corresponding NMR spectra of **2**–**4**, however, display typical olefinic compounds with strongly alternating bond lengths and only a small extent of charge separation[10–14] (corroborated by the relatively small dipole moments).

In addition, extensive theoretical studies of fulvenes **1**–**3** have been reported; concerning (anti)aromaticity, the contributions of dipolar canonical structures to overall structures were calculated[15–17] [**1b** (19–22%), **2a** (7–8%) and **3b** (5–8%)], intensity [**1** (1.90 ± 0.02 D),[7] **2** (0.42 D)[8] and **3** (0.27 D),[9] calc. 0.48 D][18] and direction of the corresponding dipole moments were determined, and several energetic, magnetic and geometric criteria[17,19,20] were employed. Also **1**–**3** were compared with analogues which are differently substituted at the exocyclic C=C double bond or have the terminal CH_2 group replaced by potential hetero atoms.[17,19–23] Dependent on the criterion employed, **1**–**4** were reported as partially aromatic, non- or even antiaromatic. Also, the calculated molecular polarizabilities of **1**–**4** were not helpful in this respect.[24]

The major aim of the present study is to investigate fulvenes **1**–**4** by the application of NBO analysis to the global minimum 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 exocyclic C=C double bond permits quantification of the shift of π electrons from this bond to the fulvene moieties aspiring to (anti)aromaticity. The ratio $\pi_{C=C}/\pi^*_{C=C}$, which appears to be the most general criterion for quantifying the

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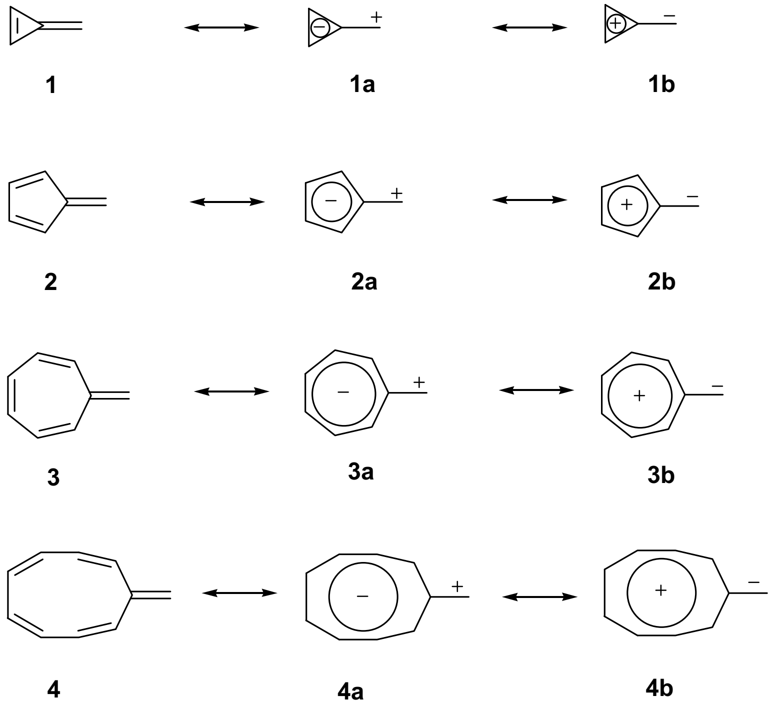


Scheme 1. Canonical structures of the compounds studied.

push–pull effect in push–pull alkenes,[25] was similarly examined but proved not to be sensitive.

In addition, the through space NMR shielding surfaces (TSNMRS) for fulvenes **1**–**4** were calculated employing the NICS concept of Schleyer and co-workers;[26] TSNMRS values can be used to visualize the *anisotropic effect* of functional groups and the *ring current effect* of aromatic moieties by iso-chemical-shielding surfaces (ICSS) of various sizes and signs[27] to quantify the aromaticity or antiaromaticity present.[28] This new approach to quantify and visualize the partial aromaticity/antiaromaticity of **1**–**4** ring moieties is expected to offer a comprehensive picture of this situation and a new successful method to be applied for the study of similar phenomena in physical organic chemistry.

The concept of employing spatial NICS[29] for the quantitative analysis of (anti)aromaticity[28,29] was meanwhile extended to solid state systems[30] and applied to fulvalenes,[31,32] fullerenes[33] and a large variety of aromatic compounds.[28]

Of significant note though, there have been some recent developments of NICS[34] showing that none of the various methods can safely assign aromaticity[35] and these parameters not measurable have proven to be generally unsuitable for the quantitative evaluation of aromaticity.[36] 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[37] and thus they are not reliable indicators of aromaticity either.[38] For example, NICS analysis was shown to lead to an incorrect prediction of aromaticity for the cyclopropenyl anion.[39]

Ab initio MO calculations were performed using the GAUSSIAN 03 program package.[40] Geometry optimization was performed at the MP2/6-31G** level of theory without restrictions and the resulting geometries are depicted in Figures 1–3. Generally, only the global minimum structures are given and have been employed in the present discussions; in the case of the *twisted* 9-membered ring moiety in **4**, the corresponding *planar* conformer proved to be ca. 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 Paul von Rague Schleyer[26] whereby the molecule was placed in the centre of a grid of ghost atoms ranging from -10.0 to $+10.0$ Å in all the three dimensions with a step width of 0.5 Å resulting in a cube of 68,921 ghost atoms. The chemical-shielding calculations were performed using the GIAO[41] method at the HF/6-31G** level of theory.[42] At the same level of theory and on the basis of the MP2/6-31G** structures, both ^{1}H and ^{13}C chemical shifts of fulvenes **1**–**4** were calculated; the corresponding values together with the experimental chemical shifts are given in Table 1. Excellent agreement in the NMR shielding of both nuclei proved the correctness of the present estimations. In addition, the ^{13}C chemical shift of C-2 in **1**, not yet published, was obtained.

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 modelling software.[43] From the GIAO calculations, the coordinates and isotropic shielding values of the ghost atoms were

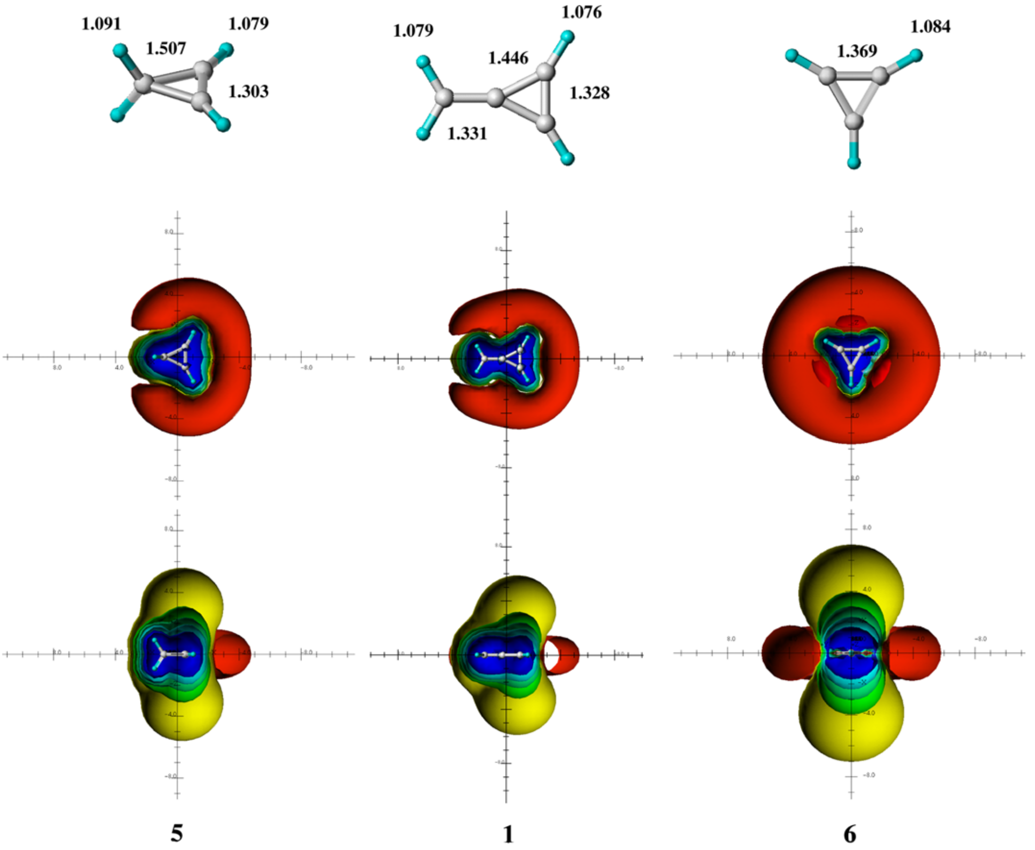


Fig. 1. Visualization of the TSNMRSs (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of triafulvene **1** in comparison with cyclopropene **5** and the cyclopropenylium cation **6**.

extracted. After transformation of the tabulated chemical shieldings into the SYBYL[43] contour file, the TSNMRSs are visualized in Figures 1–3 as ICSSs, providing a 3D view of spatial extension, sign and scope of the anisotropic/(ring current) effects of the fulvenes at each point in space; for comparison, the TSNMRS values of cyclopropene **5**, of the aromatic compounds cyclopropenylium cation **6** and benzene **7** and of the antiaromatic cyclobutadiene **8** are involved in Figures 1 and 2.

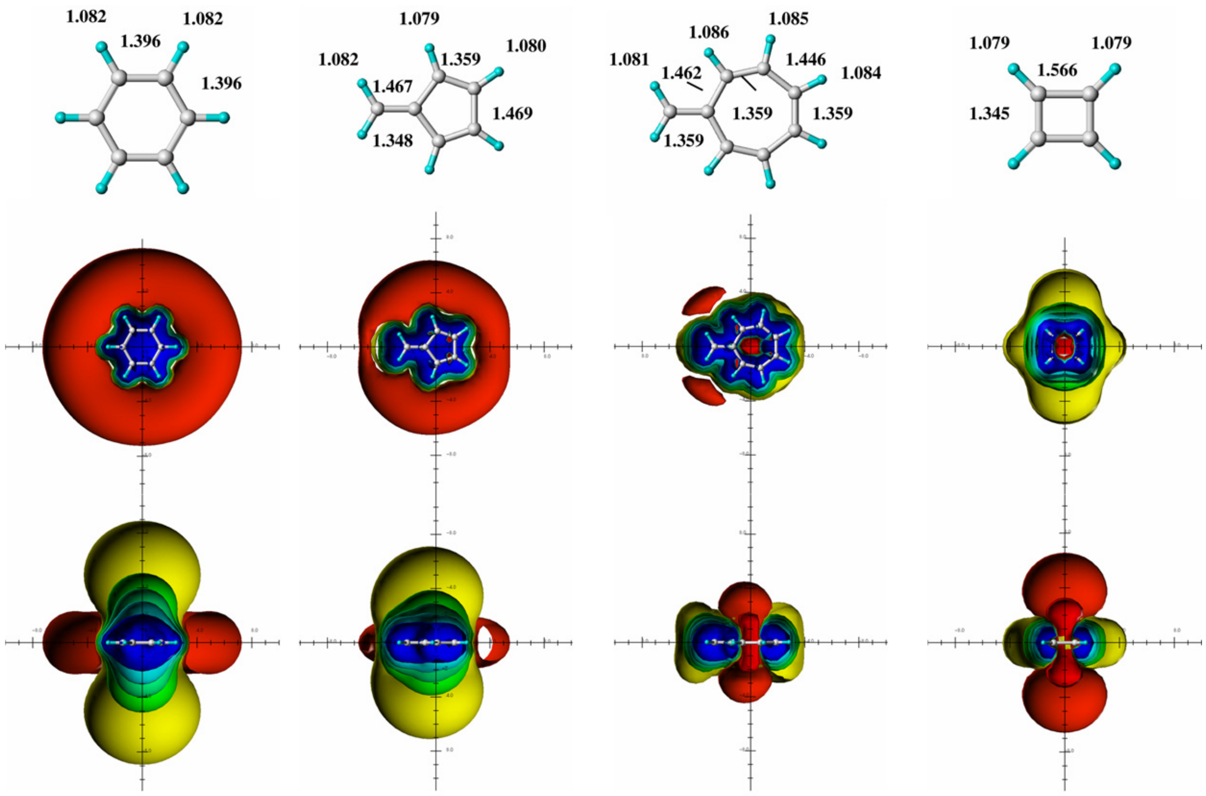
The occupations of the orbitals (especially of the bonding orbital of the fulvenes exocyclic $C{=}C$ double bonds) were calculated using the NBO option[44] as implemented in the GAUSSIAN 03 package with MP2/6-31G**. The keyword density = current was included into the Gaussian route cards to verify that the NBO software program analyses the MP2 densities.

The occupations of the bonding π orbital of the exocyclic conjugated $C{=}C$ double bond (synonymous for the acceptor activity of the ring system)[25a] are given in Table 2 together with the corresponding bond lengths (the occupancy of 2 electrons can be established as a 'norm' for systems in which no changes in the occupancy of $\pi_{C=C}$ happen to create aromatic or antiaromatic systems). The structures of **1**–**4** are given in Figures 1–3 and the corresponding TSNMRS are visualized as ICSSs of different sizes and directions. The partial aromaticities in **1**–**8**, calculated by our method described in Ref. 28 are given in Table 2. Fulvenes **1**–**3** are planar, however with strong bond alternation as expected for typically olefinic structures (cf. Figs. 1–3).

If the contribution of resonance structure **1b** is significant, then **1** would be aromatic (due to the cyclopropenylium ring system). That this contribution is not significant can be concluded from the corresponding ICSS values given in Table 2 and seen in Figure 1: the 3-membered ring moiety in **1** proved to be only very slightly aromatic [**1**—4.6 Å (−0.1 ppm) and 5.8 Å (+0.1 ppm)] because both ICSSs at ±0.1 ppm are close to the values of cyclopropene **5** [4.8 Å (−0.1 ppm) and 5.6 Å (+0.1 ppm)] but far away from the corresponding ICSSs of the aromatic cyclopropenylium cation (5.9 Å (−0.1 ppm) and 7.2 Å (+0.1 ppm), cf. Table 2).

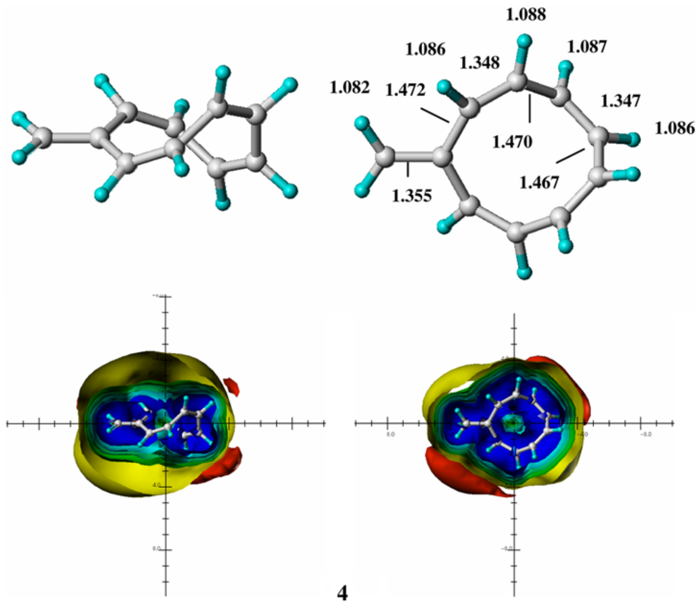
Actually, the length of the exocyclic $C{=}C$ double bond in **1** is shortest and the occupation of the corresponding bonding π orbital highest (cf. Table 2) corroborating the contribution of **1b** as reported previously.[8,15,17] However, the expected partial aromaticity of the 3-membered ring moiety of **1** was not observed (vide supra).

Similar conclusions can be drawn for the presence of partial aromaticity in **2**: even if the occupation of $\pi_{C=C}$ of the exocyclic double bond is lowest in the series (which can be realized with the participation of **2a**, corroborated by the correct direction of the dipole moment),[7] both ICSSs at



7 2 3 8

Fig. 2. Visualization of the TSNMRSs (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of pentafulvene **2** and heptafulvene **3** in comparison with benzene **7** and cyclobutadiene **8**.



4

Fig. 3. Visualization of the TSNMRSs (ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of nonafulvene **4**.

±0.1 ppm [**2**: ICSS = −0.1 ppm (5.0); ICSS = +0.1 ppm (6.2)] are far away from reference benzene **7** [**7**: ICSS = −0.1 ppm (7.2); ICSS = +0.1 ppm (8.9)] or even from cyclopropenylium cation **6** [**6**: ICSS = −0.1 ppm (5.9); ICSS = +0.1 ppm (7.2)]—pointing to 2π electron aromaticity (see Table 2 and Figs. 1 and 2). Again, if there

Table 1
Experimental ^{1}H and ^{13}C chemical shifts δ/ppm of fulvenes **1**–**4** and ab initio calculation at the HF/6-31G** level of theory on the basis of MP2/6-31G** structures

Compound	δ(^{1}H) exp. (calc.)					δ(^{13}C) exp. (calc.)						Ref.
	Exocyclic $C^2{=}C^1H_2$	Endocyclic CH=CH				Exocyclic $C^2{=}C^1H_2$		Endocyclic CH=CH				
	C^1H_2	C^3H	C^4H	C^5H	C^6H	C^1H_2	C^2H	C^3H	C^4H	C^5H	C^6H	
1[a]	3.47	8.61	—	—	—	59.6	—	132.9	—	—	—	1–3
	(3.83)	(8.60)	—	—	—	(59.7)	(119.3)	(133.5)	—	—	—	This work
2[b]	5.85	6.22	6.53	—	—	123.4	152.6	124.9	134.3	—	—	10
	(6.09)	(6.62)	(6.85)	—	—	(126.7)	(148.2)	(126.7)	(135.4)	—	—	This work
3[b]	4.45	5.95	5.2–5.7		—	111.9	146.6	138.3	129.9	130.8	—	11
	(4.71)	(6.24)	(5.59)	(5.79)	—	(112.5)	(148.0)	(140.0)	(128.7)	(132.4)	—	This work
4[c]	5.11	5.12	5.63	5.99	5.82	122.0	143.5	130.4	127.2	128.7	126.7	14b
	(5.42)	(5.43)	(5.93)	(6.40)	(6.28)	(124.1)	(145.2)	(133.8)	(128.7)	(131.9)	(129.4)	This work

[a] At −98 °C in THF-d_8.
[b] At rt in $CDCl_3$.
[c] At −20 °C to −30 °C in acetone-d_6.

Table 2
Bond length r/Å and occupation number of the bonding $\pi_{C=C}$ orbital of the exocyclic C=C double bond in **1**–**4** together with distances d/Å of the ICSS = ±0.1 ppm from the centre of the respective ring moiety (cf. Ref. 28)—the corresponding values of cyclopropene **5**, cyclopropenylium cation **6**, benzene **7** and cyclobutadiene **8** are involved for comparison

Compound	r/Å	$\pi_{C=C}$	d/Å ICSS = −0.1 ppm (in plane)[a]	d/Å ICSS = +0.1 ppm (perpendicular to centre)[a]
1	1.331	1.9442	4.6	5.8
2	1.348	1.7792	5.0	6.2
3	1.359	1.8441	<4.0[b,d]	4.1[c,d]
4	1.355	1.8421	<4.0	<4.0[e]
5	—	—	4.8	5.6
6	—	—	5.9	7.2
7	—	—	7.2	8.9
8	—	—	5.5[b,d]	6.2[c,d]

[a] For the method, see Ref. 28.
[b] ICSS = +0.1 ppm.
[c] ICSS = −0.1 ppm.
[d] Sign changed; moiety being antiaromatic.
[e] 9-Membered ring moiety is twisted; no ring current effect measurable, cf. Figure 3.

is partial 6π electron aromaticity in **2**, due to the contribution of **2a**, then it is only very small.

The 7-membered ring in **3**, due to 8π electrons being potentially available, proves to be slightly antiaromatic [cf. Fig. 2; partial antiaromaticity of the 7-membered ring 4.1 Å (+0.1 ppm)/<4.0 Å/(−0.1 ppm)]. Thus, the contribution of the canonical structure **3b**, as found by several groups,[8,15,17] which should potentially produce partial aromaticity, did not have the expected influence; actually small antiaromaticity of the 7-membered ring can be concluded [e.g., ICSS = +0.1 ppm (4.1 Å) in **3**] even if it is much smaller than in the antiaromatic cyclobutadiene **8** ICSS = +0.1 ppm (6.2 Å)] (cf. Fig. 2).

Finally, the 9-membered ring in **4**, due to the strong twist in the global minimum structure (cf. Fig. 3), cannot employ the additional 2π electrons to obtain partial 10π electron aromaticity or remain at 8π electron antiaromaticity level. The effects observed (cf. Fig. 3), however, are rather small only and comparable with the anisotropic effect of isolated C–C single and C=C double bonds, calculated by the same method.[27,45] Both bond length of the exocyclic C=C double bond and $\pi_{C=C}$ orbital occupation corroborate the intermediate nature of hepta-(**3**) and nonafulvene (**4**) with respect to the participation of canonical structures and both size and direction of the corresponding dipole moments.

The π-electron distribution in fulvenes **1**–**4** has been studied by the occupation numbers of the bonding orbital $\pi_{C=C}$ of the exocyclic C=C double bond (synonymous for the acceptor activity of conjugated ring moiety)[25a] and by their through space NMR shielding (TSNMRS) surfaces quantified by ICSS values at ±0.1 ppm. It was found that the 3- and 5-membered ring moieties in **1**–**2** are planar, but attain negligibly small partial aromaticity via conjugation with the exocyclic C=C double bond. The 7-membered ring moiety in **3**, planar as well, proves to be slightly antiaromatic; participation of some % of the canonical structure **3b**, which would produce partial aromaticity in the 7-membered ring, as found by several groups,[8,15,17] proves to be not of the influence expected. Finally, the 9-membered ring moiety in **4** is strongly twisted due to steric strain and did not exhibit any partial aromaticity or antiaromaticity at all.

The low-field ^{1}H chemical shift of the endocyclic protons in **1** (δ = 8.61 ppm) proves to be not the result of aromaticity of **1** by participation of **1b** as suggested[1,3] but corroborates the fact that in the aromatic region deshielded δ(^{1}H) values are no reliable indicators of aromaticity.[38]

Compared with the corresponding fulvalenes, studied previously,[32] which are genuine push–pull olefins and exhibit partial (anti)aromaticity in the corresponding 3-, 5- and 7-membered ring moieties (in the latter if structurally planar), the 3-, 5- and 7-membered ring moieties in fulvenes **1**–**4** reveal very small, if not negligible (anti)aromaticity only.

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