Extent of Cyclic π-Electron Delocalization Modification in Exocyclically Substituted Fulvenes

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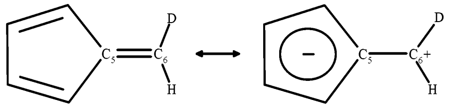
Fulvene derivatives, 20 mono- and 14 di-exocyclically substituted, were optimized at the B3LYP/6-311+G** level of theory. Aromaticity indices include aromatic stabilization energy (ASE), Schleyer's Nucleus Independent Chemical Shift (NICS), ^{3}He chemical shifts, anisotropy and exaltation of magnetic susceptibility, and the Harmonic Oscillator Model of Aromaticity (HOMA), which is a geometry-based descriptor. These indices were used to estimate the extent of a cyclic π-electron delocalization due to the substituent effect. A dramatic variation of these indices was found, indicating great sensitivity of the π-electron structure of the ring. Except for anisotropy of magnetic susceptibility, all other indices exhibited perfect equivalence.

Introduction

Fulvene is a cyclic isomer of benzene and one of the classical nonalternant π-electron systems[1] attracting much interest due to its potential tendency to fulfill the Hückel $4N + 2$ rule.[2] Therefore, a unique cross-conjugated structure is formed when it is substituted exocyclically by electron-donating groups.[3] Structural studies[4] on fulvene and its substituted derivatives, often supported by NMR[5] and UV−vis[6] analyses as well as by reactivity[7] investigations, shed much light for a better understanding of the role of cyclic π-electron delocalization reflected in aromaticities[8] of these systems. Fulvene is a polar molecule with a dipole moment μ equal to 0.42 D.[9] However, because of its highly polarizable moiety, substitution by electron-donating groups may dramatically increase its polarity (see Scheme 1). For instance, in the case of 6-dimethylaminofulvene the dipole moment $\mu = 4.5$ D.[10]

SCHEME 1



Recent detailed studies on structural effects of C_6 substitution in 6-(4-(dimethylamino)phenyl)fulvenes[4a] clearly showed that the through resonance effect may work significantly, even from a substantial distance. Of course, short distance interactions have much more dramatic consequences. For instance, the exocyclic bond length R_{C5-C6} in fulvene is 1.349 Å,[9,11] whereas in pentaheptafulvalene this bond is 1.397 Å.[11] Similarly, a substantial role of the substituent effect on induced current densities in penta- and heptafulvenes has been studied recently.[12] It has also been shown very recently that aromaticities of the rings in exocyclically substituted fulvene and heptafulvene depend strongly on σ^+ and σ^- constants, respectively.[13] Almost perfect linear correlations allowed us to have a new insight into the definition of the substituent through resonance effect.[13]

Aromaticity is a theoretical concept of great practical importance.[8] The exocyclically substituted fulvenes represent a very convenient sample to study the extent of changes of the cyclic π-electron delocalization as a result of substitution. This may be done with the use of three

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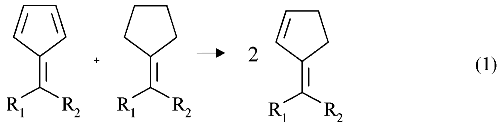
main features of aromaticity: increase of stability, decrease of bond length alternation, and characteristic magnetic properties.

The purpose of this report is to present a comprehensive analysis of the aromatic character of mono- and di-exocyclically substituted fulvene derivatives involving the most reliable descriptors: aromatic stabilization energy (ASE) based on the homodesmotic reaction,[14] Schleyer's Nucleus Independent Chemical Shift (NICS),[15] anisotropy[16] and exaltation[17] of the magnetic susceptibility, and the Harmonic Oscillator Model of Aromaticity (HOMA), which is a geometry-based index of aromaticity.[18] Additionally, we have made use of the idea of applying ^{3}He NMR chemical shifts for estimating the aromaticity of π-electron systems.[19-21]

Methods and Results

The aromatic stabilization energies were calculated according to eq 1



where $R_1 = CH_3$, OCH_3, NH_2, NMe_2, F, CN, NO_2, CMe_3, OH, CF_3, CCH, COMe, $CONH_2$, $SiMe_3$, $B(OH)_2$, O^-, NH^-, CC^-, CH_2^-, COO^-; R_2 = H or $R_1 = R_2$ = H, CH_3, OCH_3, NH_2, NMe_2, F, NO, CN, NO_2, CMe_3, OH, CF_3, CCH, COMe, $CONH_2$, $SiMe_3$, $B(OH)_2$. This equation is a simple extension of the scheme used recently by Schleyer et al.[22] in their studies on aromaticities of monoheteropenta-atomic systems. In fact, this reaction does not fulfill all homodesmotic reaction requirements.[8a,23,24] Nevertheless, the derived values are fully equivalent to the values based on the homodesmotic reaction.[23,24]

The systems with strongly positive ASEs are aromatic, while those with strongly negative ones are considered to be antiaromatic.

The NICS[15] and the anisotropy and exaltation of magnetic susceptibility were used as descriptors of aromaticity from the magnetic point of view. The NICS is defined as a negative value of the absolute magnetic shielding[15] computed at ring centers. Rings with highly negative values of nucleus independent chemical shifts are quantified as aromatic by definition, whereas those with positive NICS values are quantified as antiaromatic. The anisotropy of magnetic susceptibility is defined as the difference between the perpendicular and average in-plane diamagnetic susceptibilities. Another important magnetism-based quantitative criterion of aromaticity is the exaltation of magnetic susceptibility (Λ). It is defined as the difference between the magnetic susceptibilities of a given system and a reference one that does not display cyclic delocalization. In our case, it is also estimated with use of eq 1.[25]

Geometry is another very important source of information on aromaticity. Among many easily accessible quantitative definitions of aromaticity based on the geometric criterion, the HOMA model has been shown to be the most reliable one.[8c,26,27] The HOMA is defined in eq 2.

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_i)^2 \qquad (2)$$

In eq 2, n is the number of bonds taken into the summation; α is a normalization constant (for CC bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system[18a] and HOMA = 1 for the system with all bonds equal to the optimal value R_{opt}, assumed to be realized for fully aromatic systems (for CC bonds R_{opt} is equal to 1.388 Å);[28] R_i stands for running bond lengths.[28]

Molecular geometries of fulvene and 20 mono- and 14 di-exocyclically substituted derivatives were optimized[29] at the DFT B3LYP/6-311+G** level of theory, while the energies for calculation of ASE were corrected by the B3LYP/6-311+G** zero point energies. All structures correspond to the minima at the B3LYP/6-311+G** level, with no imaginary frequencies. CSGT calculations employing B3LYP/6-311+G** optimized geometries and the 6-311+G** basis set were selected for the calculations of the anisotropy and exaltation of magnetic susceptibility. The GIAO/HF/6-31+G* method was used for the NICS and $\Delta\delta$ ^{3}He calculations. The $\Delta\delta$ ^{3}He values were calculated for ^{3}He 1 Å above the molecular planes. The HOMA values were based on molecular geometries optimized at the B3LYP/6-311+G** level. Tables 1 and 2 present all data for quantitative measures of aromaticity which are the subject of discussion. Additionally presented are the exocyclic bond lengths $R_{\mathrm{C5-C6}}$, given as potentially important descriptors of electronic structure.

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TABLE 1. Calculated ASE (kcal/mol), Exaltation of Magnetic Susceptibility Λ, Anisotropy of Magnetic Susceptibility Δχ, NICS, Δδ ^{3}He (ppm), HOMA, and Bond Lengths R_{C5-C6} (Å) for Fulvene and 6-Monosubstituted Derivatives[13]

	ASE	NICS	Λ	Δχ	Δδ ^{3}He	HOMA	R_{C5-C6}
−H	−2.90	−0.68	−2.93	19.59	60.50	−0.286	1.342
$-CH_3$	−0.11	−1.77	−3.71	24.29	61.33	−0.169	1.348
$-OCH_3$	3.40	−3.96	−4.75	24.8	62.57	0.072	1.351
$-NH_2$	7.62	−6.00	−6.20	25.16	64.17	0.246	1.364
$-CMe_3$	−0.51	−1.71	−3.43	23.33	61.27	−0.217	1.351
$-NMe_2$	7.42	−7.48	−8.52	26.59	65.30	0.259	1.374
−F	0.02	−2.53	−3.36	19.27	61.16	−0.119	1.337
−CN	−6.80	2.28	−0.09	20.68	58.13	−0.321	1.351
$-CONH_2$	−4.24	0.33	−2.04	22.07	59.74	−0.313	1.349
$-NO_2$	−8.90	3.77	−0.84	23.5	56.61	−0.490	1.343
−OH	2.75	−3.72	−4.53	21.48	62.31	0.043	1.348
$-CF_3$	−5.76	1.24	−1.30	19.32	58.91	−0.428	1.343
−CCH	−3.64	0.46	−1.40	22.47	59.63	−0.189	1.356
$-COCH_3$	−5.56	1.16	−1.30	31.51	58.93	−0.370	1.353
$-B(OH)_2$	−5.57	1.48	−1.39	21.81	59.09	−0.388	1.352
$-SiMe_3$	−3.22	0.01	−2.65	22.90	60.23	−0.319	1.352
$-CC^-$	9.60	−6.99	−5.05	31.18	65.35	0.369	1.386
$-CH_2^-$	22.72	−12.32	−12.90	31.61	68.92	0.745	1.427
$-NH^-$	21.9	−12.02	−14.75	28.73	68.72	0.704	1.426
$-O^-$	18.74	−11.92	−12.68	30.88	68.70	0.672	1.423
$-COO^-$	2.13	−4.50	−5.06	26.79	63.49	0.101	1.360

TABLE 2. Calculated ASE (kcal/mol), Exaltation of Magnetic Susceptibility Λ, Anisotropy of Magnetic Susceptibility Δχ, NICS, Δδ ^{3}He (ppm), and HOMA for 6,6-Disubstituted Fulvene Derivatives

	ASE	NICS	Λ	Δχ	Δδ ^{3}He	HOMA
$-CH_3$	0.25	−2.32	−3.90	23.53	61.82	−0.131
$-OCH_3$	−0.87	−4.70	−4.89	27.74	62.89	0.088
$-NH_2$	1.34	−8.36	−7.33	24.32	65.51	0.416
$-NMe_2$	8.26	−8.48	−7.18	26.98	65.81	0.419
−F	0.77	−3.96	−3.47	18.66	61.69	0.000
−CN	−11.86	5.68	2.38	14.34	55.44	−0.387
$-NO_2$	−12.93	5.25	2.50	25.59	54.95	−0.548
−OH	2.97	−4.67	−4.48	21.24	62.61	0.110
$-CF_3$	−9.61	3.76	0.05	18.20	56.46	−0.648
$-COCH_3$	−9.89	1.91	−0.75	30.27	58.61	−0.424
$-B(OH)_2$	−6.13	1.67	−1.78	18.49	59.14	−0.459
$-SiMe_3$	−4.66	1.28	−1.14	20.60	59.02	−0.506
$-CONH_2$	−5.96	−2.58	−0.89	23.32	58.12	−0.453
−CCH	−6.42	2.06			58.43	−0.136

Discussion

Even a superficial inspection of the data in Tables 1 and 2 gives very important information: the substituent effect on the aromatic character of the ring in fulvene is enormously large! In the case of monosubstituted species, the range in aromatic stabilization energies is over 30 kcal/mol, the NICS varies by about 16 ppm, and the HOMA varies by more than 1.2 units. These three independent estimations demonstrate that the aromaticity of the fulvene ring is extremely sensitive to the effect of substituent at C_6, much more so than in the case of benzene derivatives![30] The differences for disubstituted species are smaller only because of the absence of the negatively charged substituents such as O^-, CC^-, NH^-, CH_2^-, and COO^-. Nevertheless, despite this, the differences are still substantial: 21 kcal/mol for ASE, 12 ppm for NICS, and 1.1 for HOMA. If the same sets of substitents are considered for mono- and disubstituted fulvenes, the changes of the aromaticity descriptors are obviously much larger for the latter case. It is clear that the π-electron intramolecular charge transfer is responsible for the above effects. For electron-donating substituents, aromaticity of the ring is significantly and in a regular way enlarged. Electron-attracting substituents decrease the number of π electrons in the ring and hence induce the antiaromatic character of such systems. This is nicely illustrated by Figure 1a, where the HOMA is plotted against R_{C5-C6}. A similar trend was observed by Staley et al.[31] for 6-arylfulvenes in the case of the dependence of experimental C5−C6 bond lengths on σ_p. From our recent report,[13] it is known that aromaticity indices depend on substituent constants. Note that for electron-accepting substituents there is practically no dependence of the HOMA on R_{C5-C6}, while for electron-donating substituents the correlation is much better, as shown in Figure 1b. Also, the dependencies of NICS and Λ on R_{C5-C6} illustrate well the point: the correlations for electron-donating substituents are very good with correlation coefficients 0.991 and 0.942, respectively.

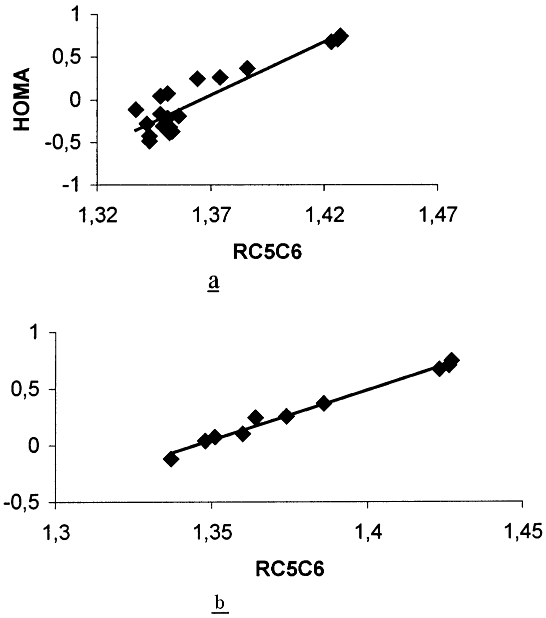

FIGURE 1. Dependence between bond length C5−C6 and HOMA: (a) for all 21 monosubstituted fulvene derivatives (correlation coefficient $r = 0.904$); (b) for 10 electron-donating substituents (correlation coefficient $r = 0.994$).

Moreover, for monosubstituted fulvenes, it is clear that the ASE, NICS, HOMA, and exaltation of magnetic susceptibility (Λ) correlate well with each other, with the lowest value of correlation coefficient equal to −0.948 (for Λ vs HOMA). Figure 2 presents mutual scatter plots of ASE, NICS, HOMA, and exaltation of magnetic susceptibility (Λ). With no surprise, factor analysis[32] applied to these descriptors indicates that there is only one factor which describes over 98% of the total variance. The energy, geometry, or magnetism responds to the changes of substituent almost perfectly in an equivalent way. This demonstrates the crucial importance of the substituents on stability[3] and other physicochemical properties.

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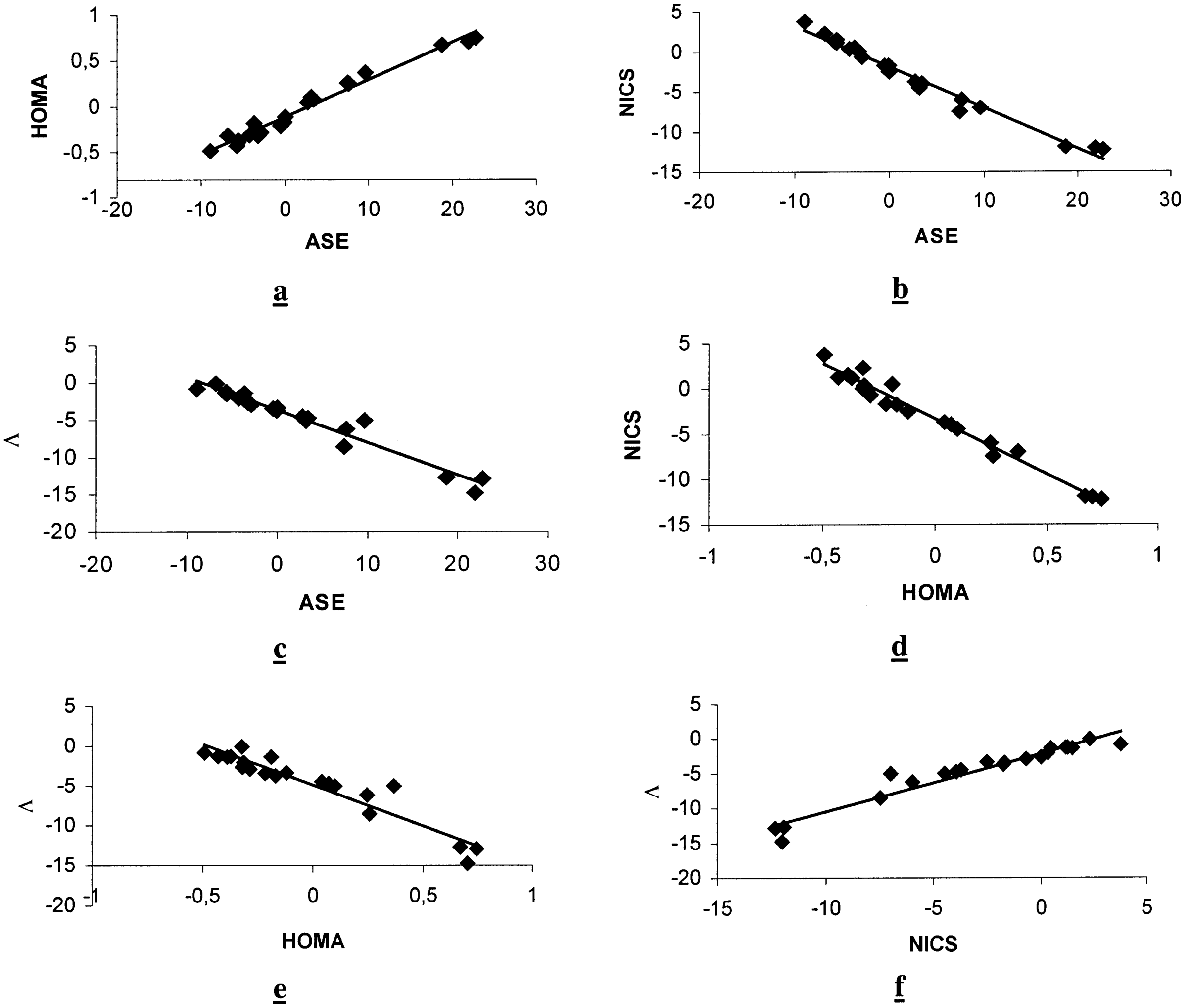


FIGURE 2. Scatter plots of the ASE, NICS, HOMA, and exaltation of magnetic susceptibility (Λ) for monosubstituted fulvene derivatives: (a) HOMA vs ASE (correlation coefficient $r = 0.987$); (b) NICS vs ASE (correlation coefficient $r = -0.989$); (c) Λ vs ASE (correlation coefficient $r = -0.975$); (d) NICS vs HOMA (correlation coefficient $r = -0.988$); (e) Λ vs HOMA (correlation coefficient $r = -0.948$); (f) Λ vs NICS (correlation coefficient $r = 0.966$).

Importantly, the magnetic susceptibility anisotropy correlates markedly worse with other quantitative descriptors of cyclic π-electron delocalization. Since the correlations with the models based on magnetism (NICS and Λ) are poor (correlation coefficients 0.676 and 0.648, respectively), this supports the view[8a] that the above index does not necessarily work reliably in estimating aromaticity. The correlations of anisotropy of magnetic susceptibility with aromatic stabilization energy (ASE) and HOMA may also confirm this point (correlation coefficients 0.691 and 0.701, respectively).

As previously pointed out, the changes of aromatic character in disubstituted species are substantially larger in comparison with those of monosubstituted systems, implying a more significant role of the substituent. Despite this, the correlations between the indices are slightly worse, as shown in Table 3. In fact, this is easy to understand. In the case of monosubstituted fulvenes, the exocyclic groups are almost always coplanar or nearly coplanar with the ring. This is not the case for disubstituted systems, where the torsional angles are much different from zero, as shown in Table 4.

TABLE 3. Coefficients for Correlation between Pairwise Combinations of ASE, NICS, HOMA, and Λ for Disubstituted Fulvene Derivatives

	ASE	HOMA	NICS
HOMA	0.874		
NICS	−0.927	−0.883	
Λ	−0.936	−0.900	0.955

The non-coplanar conformation of the interacting groups with the ring in disubstituted fulvenes is a substantial perturbation for π-electron interactions between the substituents and the ring and finally results in a worse correlation between aromaticity indices. This also means that the perturbation of this kind affects in a slightly different way the properties which are the measure of aromatic character.

^{3}He NMR Chemical Shift as an Index of Aromaticity. The ^{3}He NMR chemical shift was experimentally measured for He@C$_{60}$[19] and supported the conclusion of a substantial aromatic character of fullerene. Schleyer et al. studied theoretically the ^{3}He NMR chemical shifts of He@C$_{60}$ and He@C$_{70}$ at various levels of theory and found a good agreement of theoretical values with

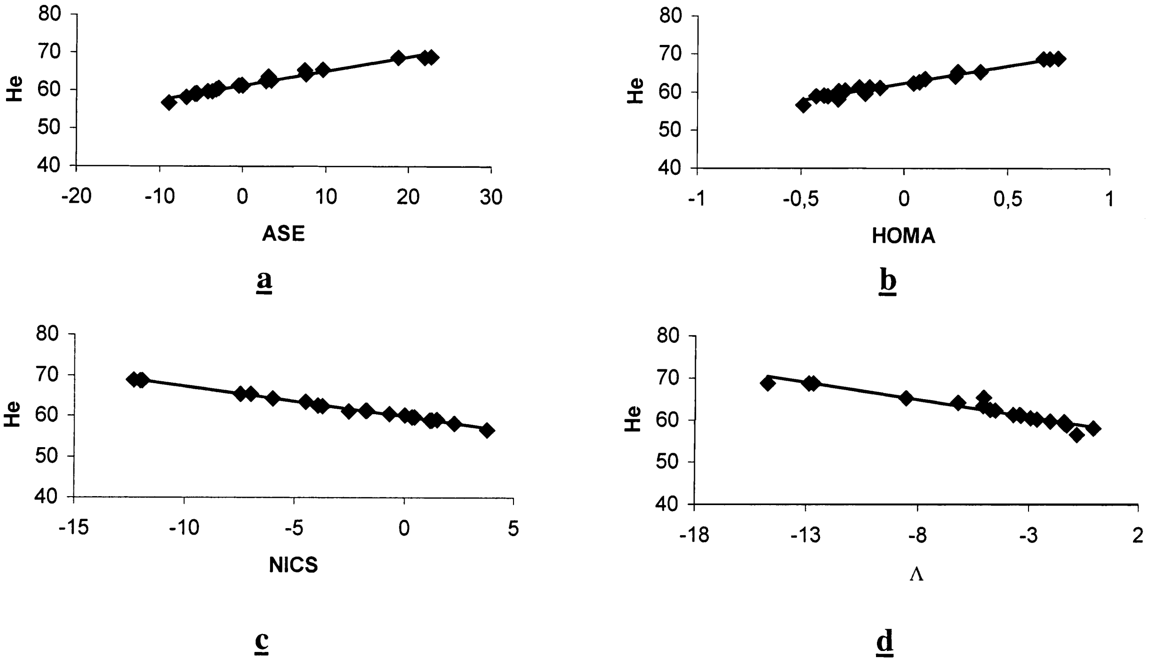
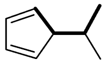
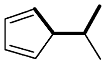
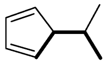


FIGURE 3. Dependences of ^{3}He NMR chemical shift on (a) ASE ($r = 0.986$), (b) HOMA ($r = 0.984$), (c) NICS ($r = -0.998$), and (d) exaltation of magnetic susceptibility ($r = -0.961$) for monosubsituted fulvene derivatives.

TABLE 4. Torsion Angles Defining Coplanarities of Substituents with the Fulvene Ring

	Monosubstituted fulvene derivatives	Disubstituted fulvene derivatives	
			
-H		0.00	0.00
$-CH_3$	0.00	0.01	0.01
$-OCH_3$	0.05	-6.93	-6.93
$-NH_2$	0.79	14.94	14.89
$-CMe_3$	0.00	-19.59	-19.58
$-NMe_2$	-4.97	-27.47	-27.47
-F	0.00	0.00	0.00
-CN	0.00	0.00	0.00
$-CONH_2$	0.15	1.51	0.78
$-NO_2$	0.00	-3.33	-3.32
-OH	0.00	-7.86	-7.89
$-CF_3$	-0.22	0.61	1.31
-CCH	0.00	0.00	0.00
$-COCH_3$	0.00	-0.27	-0.33
$-B(OH)_2$	0.00	2.36	2.35
$-SiMe_3$	0.00	5.17	5.17
$-CC^-$	0.00		
$-CH_2^-$	0.00		
$-NH^-$	-0.02		
$-O^-$	0.00		
$-COO^-$	-5.34		

experimental results. Thus, a ^{3}He NMR chemical shift seems to be a reasonable tool for estimating aromaticity. Figure 3a–d shows the ^{3}He NMR chemical shift plotted against the ASE, NICS, exaltation of magnetic susceptibility, and HOMA for monosubstituted fulvenes. The results are very good with the lowest correlation coefficient equal to 0.961. The dependences for disubstituted fulvenes are only slightly worse. This clearly indicates that $\Delta\delta$ ^{3}He may serve well as a reliable magnetism-based descriptor of cyclic π-electron delocalization.

Conclusions

Apart from the dramatic changes in aromaticity of the ring in exocyclically substituted fulvene, the most important is the conclusion that substituents at C_6 in monosubstituted species bear a uniform perturbation, which modifies dramatically the aromaticity of the ring in an almost perfectly equivalent way, as observed in energetic, magnetic, and geometric properties. Correlation coefficients between ASE, NICS, Λ, and HOMA are exclusively high. As far as the disubstituted species are concerned, the correlations are slightly worse. Noncoplanarity of substituents bears a new kind of perturbation, which acts in a different way for different properties of a molecule. To some extent, it might be compared with the analysis done for five-member heterocyclic π-electron systems.[33] If there was only one heteroatom in the ring for this series, all aromaticity indices correlated with each other reasonably well. For the cases where two or more heteroatoms were present in the ring, the correlations become much worse. Hence, the more differently a π-electron system is perturbed, the less equivalent is the description of the cyclic π-electron delocalization, as expressed by various quantitative definitions of aromaticity.

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[33] Cyrański, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333

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Supporting Information Available: The Cartesian coordinates, absolute electronic energies at B3LYP/6-311+G**, zero point energies at B3LYP/6-311+G**, and magnetic susceptibilities calculated with use of the CSGT method at HF/6-311+G** for molecules used in eq 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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