

Variation of the π -electron delocalization in exocyclically substituted heptafulvene derivatives[†]

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ABSTRACT: Eleven mono- and eight di-exocyclically substituted heptafulvene derivatives were optimized at the B3LYP/6–311+G** level of theory. The aromaticity indices REC (ring energy content), Schleyer's NICS, ³He NMR chemical shift and anisotropy of magnetic susceptibility and the geometry based descriptor HOMA were used to estimate the extent of cyclic π -electron delocalization due to the substituent effect. A dramatic variation of these indices was found for electron-accepting substituents indicating great sensitivity of the π -electron structure of the ring. In the case of monosubstituted derivatives all indices exhibit a perfect or at least very good equivalence, whereas for disubstituted species the mutual correlations are markedly worse. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: substituent effect; aromaticity; heptafulvene; *ab initio* DFT; NICS; HOMA; chemical shift

INTRODUCTION

Since its synthesis,¹ heptafulvene has been one of the classical non-alternant π -electron systems attracting considerable interest.² Because of their potential tendency to fulfil the Hückel $4N + 2$ rule, various properties of heptafulvene and particularly of its derivatives have been the subject of study, including cycloaddition reactions,³ dependence on substituent non-linear optical activity,⁴ through-resonance effect in 8-substituted heptafulvene derivatives,⁵ colour properties,⁶ geometric isomerism of the exocyclic double bond in heptafulvene derivatives and electronic effects on the rotational barrier.⁷ Recently the substituent effect on induced current densities in penta- and heptafulvenes has been studied.⁸

Most of the accumulated information on 8-substituted heptafulvene derivatives suggests great sensitivity of the π -electron structure of the ring. Aromaticity is a theoretical concept of great practical importance,⁹ and the exocyclically substituted heptafulvenes represent an interesting group of systems for a systematic study of the extent of changes in the cyclic π -electron delocalization due to substitution (Scheme 1). This may be done with the use of three main features of aromaticity characterizing the ring: an increase in stability, a decrease in bond

length alternation and characteristic magnetic properties.⁹

The purpose of this paper is to present an analysis of the aromatic character of mono- and di-exocyclically substituted heptafulvene derivatives involving Schleyer's magnetism-based index NICS¹⁰ and anisotropy of magnetic susceptibility,^{11,12} geometry-based index of aromaticity HOMA¹³ and empirical measures of energy of the ring.^{14,15} Additionally, the ³He NMR chemical shifts were used for estimating the aromaticity of π -electron systems.^{16–18}

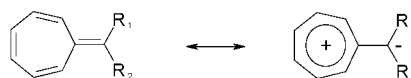
EXPERIMENTAL AND RESULTS

The energies of the ring were calculated by employing two empirical models that allow one to estimate bond energies from C—C bond lengths according to Eqn. (1)¹⁴ and Eqn. (2):¹⁵

$$\text{REC}(1) = -368.15 \sum \exp[2.255(1.533 - R_i)] \quad (1)$$

$$\text{REC}(2) = 530.83 \sum [1 - 5.052(R_i - 1.3549)^2] \quad (2)$$

where R_i represent the running C—C bond length in the ring of heptafulvene derivatives (in Angstroms).



where (a) $R_1 = \text{H}, \text{CH}_3, \text{OCH}_3, \text{NH}_2, \text{N}(\text{CH}_3)_2, \text{F}, \text{NO}, \text{CN}, \text{NO}_2, \text{N}_2^+, \text{NH}_3^+$ and $R_2 = \text{H}$
or (b) $R_1 = R_2 = \text{CH}_3, \text{OCH}_3, \text{NH}_2, \text{N}(\text{CH}_3)_2, \text{F}, \text{CN}, \text{NO}_2$.

Scheme 1

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[†]This paper is dedicated to our friend Shinji Kobayashi on the occasion of his retirement.

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The above equations are based on different models but they both employ the C—C bond lengths to estimate the energy of the ring. The first empirical model gave good agreement between the experimental heats of formation and those obtained by Eqn. (1) for eight benzenoid hydrocarbons.^{14,19} These bond energies also correlate impressively well with the bond energies obtained recently by Exner and Schleyer,²⁰ which are based on the Bader topological analysis.²¹ Equation (2) reproduces very well the atomization energies of a set of 16 benzenoid hydrocarbons.¹⁵ Since in both cases the energies refer to the same structural unit, the ring, the changes are expected to be equivalent to the changes in aromatic stabilization energy (ASE). The energies obtained for the ring by Eqns (1) and (2) are depicted further as ring energy contents REC(1) and REC(2).

The nucleus-independent chemical shift¹⁰ (NICS) and anisotropy of magnetic susceptibility^{11,12} were used as the descriptors of aromaticity from the magnetic point of view. The NICS is defined as the negative value of the absolute magnetic shielding computed at ring centres and NICS (1) if the probe function is located 1 Å over the ring plane. The rings with highly negative values of nucleus-independent chemical shifts are qualified by definition as aromatic and those with positive NICS values as anti-aromatic. The anisotropy of magnetic susceptibility is defined as the difference between the perpendicular and average in-plane diamagnetic susceptibilities.

Variation in geometry is another very important source of information about aromaticity.²² Among many easily available quantitative definitions of aromaticity based on geometric criteria, the HOMA model has been shown to be the most reliable.^{22,23} The HOMA is defined by Eqn. (3):¹³

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum (R_{\text{opt}} - R_i)^2 \quad (3)$$

where n is the number of bonds taken into the summation; α is a normalization constant (for C—C bonds $\alpha = 257.7$)

fixed to give HOMA = 0 for a model non-aromatic system and HOMA = 1 for the system with all bonds equal to the optimum value R_{opt} assumed to be realized for full aromatic systems (for C—C bonds $R_{\text{opt}} = 1.388$ Å); R_i is the running bond length. HOMA may also be presented in such a way that two different contributions to the decrease of aromaticity are shown:^{13b}

$$\begin{aligned} \text{HOMA} &= 1 - \left[\alpha (R_{\text{opt}} - R_{\text{av}})^2 + \frac{\alpha}{n} \sum (R_{\text{av}} - R_i)^2 \right] \\ &= 1 - EN - GEO \end{aligned} \quad (4)$$

where EN describes the decrease in aromaticity due to bond elongation and GEO that due to the increase in bond alternation; R_{av} is the average bond length.

Molecular geometries of heptafulvene and 11 mono- and eight di-exocyclically substituted derivatives were optimized at the DFT B3LYP/6-311+G** level of theory. All species corresponded to minima at the B3LYP/6-311+G** level, with no imaginary frequencies. The GIAO/HF/6-31+G* method was used for the anisotropy of magnetic susceptibility, NICS and $\Delta\delta$ ³He calculations. The $\Delta\delta$ ³He values were calculated at 1 Å above the molecular planes. All calculations were performed with the use of the Gaussian 98 program.²⁴ 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, the exocyclic bond lengths $R_{\text{C7-C8}}$ and $\Delta\delta$ ³He values are given as potentially important descriptors of the electronic structure.

DISCUSSION

The substituent effect on aromaticity of the ring is substantial, as shown by the ranges of variation of the indices in question presented in Tables 1 and 2 for mono-

Table 1. Calculated energies (REC(1) and REC(2)) (kJ mol⁻¹), NICS and NICS (1), $\Delta\delta$ ³He (ppm), anisotropy of magnetic susceptibility $\Delta\chi$, HOMA, EN , GEO and bond lengths $R_{\text{C7-C8}}$ (Å) for heptafulvene and its mono-substituted derivatives

	HOMA	EN	GEO	NICS	NICS (1)	$R_{\text{C7-C8}}$	³ He	REC(1)	REC(2)	$\Delta\chi$
H	0.164	0.142	0.695	8.47	4.24	1.356	54.36	3413.39	3605.23	6.14
CH ₃	0.165	0.147	0.689	8.87	4.60	1.361	53.97	3409.79	3604.75	7.74
OCH ₃	0.146	0.145	0.709	10.73	6.33	1.358	52.24	3411.68	3603.54	12.04
NH ₂	0.095	0.159	0.746	9.62	4.75	1.360	50.80	3404.14	3598.39	6.64
N(CH ₃) ₂	0.147	0.147	0.706	8.42	3.09	1.363	50.84	3410.42	3603.48	6.37
F	0.164	0.138	0.698	8.68	4.59	1.350	54.06	3415.65	3605.60	2.50
NO	0.509	0.086	0.405	4.27	0.43	1.388	58.22	3443.22	3636.71	67.06
CN	0.381	0.105	0.515	4.71	0.79	1.375	57.84	3432.64	3625.08	14.94
NO ₂	0.467	0.096	0.437	2.06	-1.50	1.378	60.18	3436.53	3632.60	28.06
N ₂ ⁺	0.822	0.042	0.136	-3.83	-7.02	1.419	66.02	3477.41	3666.49	36.33
NH ₃ ⁺	0.449	0.094	0.457	2.29	-1.27	1.366	60.06	3428.24	3620.89	22.34
Range	0.727	0.117	0.610	14.56	13.35	0.069	15.22	73.27	68.10	64.56

Table 2. Calculated energies [REC(1) and REC(2)] (kJ mol⁻¹), NICS and NICS (1), $\Delta\delta$ ³He (ppm), anisotropy of magnetic susceptibility $\Delta\chi$, HOMA, *EN*, *GEO* and bond lengths R_{C7-C8} (Å) for heptafulvene and its di-substituted derivatives

	HOMA	<i>EN</i>	<i>GEO</i>	NICS	NICS (1)	R_{C7-C8}	³ He	REC(1)	REC(2)	$\Delta\chi$
H	0.164	0.142	0.695	8.45	4.24	1.356	54.26	3413.39	3605.23	6.14
CH ₃	0.042	0.184	0.774	1.66	-2.78	1.356	55.13	3388.29	3592.27	16.85
OCH ₃	0.137	0.150	0.713	10.46	6.07	1.362	51.82	3408.45	3602.35	9.32
NH ₂	0.042	0.172	0.786	4.93	0.44	1.364	51.80	3397.74	3593.31	4.94
N(CH ₃) ₂	0.107	0.170	0.723	15.45	10.07	1.387	45.38	3396.82	3598.22	29.57
F	0.112	0.145	0.743	8.91	4.99	1.345	53.70	3412.68	3601.37	1.32
CN	0.546	0.077	0.377	1.01	-2.61	1.399	61.40	3449.96	3639.59	20.81
NO ₂	0.552	0.082	0.356	-0.93	-4.38	1.385	62.80	3445.15	3640.43	41.18
Range	0.510	0.107	0.430	16.38	14.44	0.054	11.00	61.67	48.16	39.86

Table 3. Calculated energies [REC(1) and REC(2)] (kJ mol⁻¹), NICS and NICS (1) (ppm), HOMA, *EN* and *GEO* and for benzene and its N₂⁺ derivative

	HOMA	<i>EN</i>	<i>GEO</i>	NICS	NICS (1)	REC(1)	REC(2)
C ₆ H ₆	0.991	0.001	0.000	-10.5	-12.3	3001.69	3082.20
C ₆ H ₅ N ₂ ⁺	0.955	0.021	0.024	-10.6	-11.2	2948.4	3154.98
Range	0.036	0.010	0.024	0.1	1.1	53.29	72.78

and disubstituted derivatives, respectively. Electron-accepting substituents increase the cyclic π -electron delocalization in the ring following the Hückel $4N + 2$ rule. The HOMA values illustrate this point very well. For heptafulvene HOMA = 0.164 whereas for the N₂⁺ derivative it rises to 0.822. The NICS values also illustrate the changes well, but the scale should be shifted. It is important to note that the above changes are dramatically larger than that observed for benzene derivatives. For instance, the difference between the aromatic character of benzene and its N₂⁺ derivative is only Δ HOMA = 0.036. This is also indicated by other aromaticity indices, as illustrated by the data in Table 3.

In some cases the ranges for monosubstituted derivatives (Table 1) are larger than those for the disubstituted derivatives (Table 2) because of the absence of the positively charged substituent N₂⁺. However, if the same substituents are taken into account in both series, then the ranges for disubstituted derivatives are almost twice as large as those for the monosubstituted derivatives.

Comparison with benzene obviously indicates that the aromatic character of the benzene ring is less sensitive to substituent effects than the ring in heptafulvene. This evidently results from the tendency of the benzene ring to maintain its six π -electrons, compared with that of the heptafulvene ring to achieve six π -electrons, i.e. to offer a surplus of electrons to the substituent, thus decreasing the number of electrons in the ring. This can be realized by electron-attracting substituents which increase the π -electron delocalization in the ring.

For monosubstituted derivatives, all descriptors of aromaticity, except anisotropy of magnetic susceptibility,

exhibit very good or at least good mutual correlations, as shown by the correlation coefficients in Table 4. An important point should be made here: in the case of anisotropy, the quantity computed consists of information on the electronic structures of both the ring and the substituents. Hence the high anisotropy of the substituent affects substantially the value for the substituted system. Therefore, the anisotropy of magnetic susceptibility should not be considered as a fully reliable indicator of the extent of cyclic π -electron delocalization in the ring. This may be supported by bad or very bad correlations between anisotropy and other magnetic descriptors with correlation coefficients of about 0.6 or less.

Good correlations exist not only between indices of the same background but also for those describing different properties, e.g. REC(1) vs NICS with $r = -0.966$, NICS vs HOMA with $r = -0.975$ and HOMA vs REC(1) with $r = 0.994$, as shown for typical scatter plots in Fig. 1(a)–(c).

Table 4. Correlation coefficients for correlation between HOMA, NICS, ³He, $\Delta\chi$, REC(1) and REC(2) for monosubstituted heptafulvene derivatives

	HOMA	NICS	NICS(1)	³ He	REC(1)	REC(2)
NICS	-0.975					
NICS (1)	-0.975	0.997				
³ He	0.973	-0.987	-0.982			
REC(1)	0.994	-0.966	-0.965	0.968		
REC(2)	0.988	-0.951	-0.951	0.950	0.986	
$\Delta\chi$	0.614	-0.510	-0.509	0.511	0.571	0.573

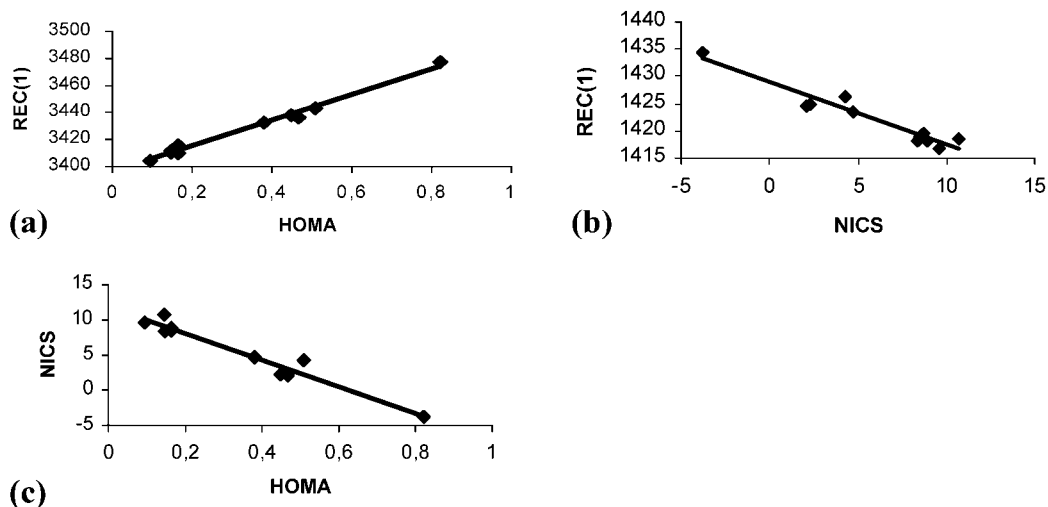


Figure 1. Dependences between HOMA, NICS and REC(1) for monosubstituted heptafulvene derivatives

Table 5. Correlation coefficient for correlation between HOMA, NICS, ^3He , $\Delta\chi$, REC(1) and REC(2) for disubstituted heptafulvene derivatives

	HOMA	NICS	NICS(1)	^3He	REC(1)	REC(2)
NICS	-0.588					
NICS (1)	-0.586	0.999				
^3He	0.693	-0.981	-0.983			
REC(1)	0.971	-0.548	-0.652	0.712		
REC(2)	0.999	-0.583	-0.685	0.739	0.980	
$\Delta\chi$	0.635	-0.298	-0.310	0.381	0.446	0.608

Much worse is the picture for mutual correlations for disubstituted species, as shown by the data in Table 5. Of the physically related quantities presented, such as REC(1) and REC(2) or $\Delta\delta$ ^3He and NICS(1), only REC(1) and REC(2) vs HOMA give acceptable correlations. However, both HOMA and RECs are defined on the basis of the same kind of structural information.

For NICS and $\Delta\delta$ ^3He , some difficulties arise from the fact that for some substituents the ring is not planar, hence finding the center of the ring encounters substantial

Table 6. Mean least-squares deviation of the carbon atoms in the ring from the ring best plane for disubstituted heptafulvene derivatives

	Mean deviation from plane
H	0.0001
CH_3	0.1800
OCH_3	0.0001
NH_2	0.1753
$\text{N}(\text{CH}_3)_2$	0.0024
F	0.0002
CN	0.0000
NO_2	0.0360

problems. Table 6 presents the mean least-squares deviations from the best plane for disubstituted derivatives of heptafulvene.

In the case of dimethyl and diamino derivatives, where the deviation from planarity is large, one can observe a significant decrease in the HOMA value from 0.164 for unsubstituted species to 0.042 for dimethyl and diamino derivatives. This is also associated with a decrease in REC values. Another interesting finding is that for electron-donating substituents, there is no regularity in the variation of the aromaticity indices for the ring. The reason seems to be clear since these substituents increase the number of π -electrons in the ring so that the ring approaches a more anti-aromatic state, i.e. where it would have $4N$ π -electrons. Hence some other factors may strongly influence the observed state of the ring differently characterized by different aromaticity indices.

Application of HOMA in the form of Eqn. (4) allows us to understand better the consequences of substituent effects on the π -electron structure of the ring. It appears that the decrease in aromaticity results mostly from a large bond alternation. The *GEO* term is large and varies considerably over a range of 0.610 for monosubstituted series, whereas the effect of the mean bond elongation is much smaller, the range of the *EN* term being 0.117. Hence the intramolecular charge transfer from the ring to electron-accepting substituents affects mostly the bond alternation. As a result of intramolecular charge transfer, the *EN* term decreases significantly, from 0.142 for the unsubstituted species to 0.042 for the N_2^+ derivative. This means that as a result of delocalization due to charge transfer, the mean bond length becomes smaller.

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