

Aromatic character of heptafulvene and its complexes with halogen atoms

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Received: 6 May 2011 / Accepted: 28 September 2011 / Published online: 19 October 2011
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Abstract Geometry optimization of heptafulvene–halogen complexes (halogens: F, Cl, Br, I, and At) carried out at the B3LYP/6-311+G(d,p) level of theory allowed us to estimate the geometry-based aromaticity index HOMA, the magnetism-based indices NICS, NICS(1), and NICS(1)_{ZZ}, as well as the energy of complex formation. Application of the NBO method allowed us to estimate the pEDA characteristics of the π -electron distribution in complexes (i.e., the electron excess/deficiency of the π -electron system in the ring). All of the characteristics of the complexes were found to be mutually interrelated, exhibiting good or at least acceptable correlation coefficients. It was also noted that halogen atoms with greater radii yielded weaker complexes and lower aromaticities, as shown by the HOMA, NICS, and pEDA indices. The energy of complex formation was observed to be linearly correlated with the degree of aromatization of the heptafulvene ring, as expressed by these indices.

Keywords NBO · DFT · Heptafulvene · Aromaticity · Charge transfer · pEDA · HOMA · NICS

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Introduction

Heptafulvene belongs to the nonalternant class of π -electron hydrocarbons (for details, see [1]), which are characterized by high reactivity [2, 3] and low thermodynamic stability. The Hess–Schaad model for estimating the resonance energy per π electron (REPE) [4] gives the same value for fulvene and heptafulvene (REPE = -0.002), indicating that they both possess nonaromatic character. Schleyer's NICS [5] value for heptafulvene is 8.468 [6], clearly indicating its non- or even antiaromatic character. Since heptafulvene has $4N+3$ π electrons, it becomes more stable when electron-withdrawing substituents are added to it, allowing the number of π electrons in the ring to approach $4N+2$. Indeed, 8,8-diformylheptafulvene is a stable compound with a known crystallographic structure [7] and a high value of the geometry-based aromaticity index HOMA [8, 9], 0.769 (based on the experimental geometry) [7, 10]. Theoretical studies of 8-substituted heptafulvene derivatives have shown [6] that increasing the electron-accepting power of the substituent leads to an increase in the aromaticity of the ring, as documented by several aromaticity indices [11].

Another way to force the π -electron structure of the ring in heptafulvene to approach $4N+2$ π electrons is to form a complex with strongly electronegative atoms. With this in mind, in the work described in this paper, we modeled complexes between heptafulvene and halogen atoms. To estimate the degree of aromatization of the heptafulvene ring, three different aromaticity indicators were employed: the geometry-based HOMA index, the magnetism-based NICS index, and the π -electron distribution based pEDA index. Additionally, to investigate the similarity in aromatic stabilization energy ASE between heptafulvene and fulvene, a similar procedure to that employed for fulvene

(which gave ASE = $-3.1 \text{ kcal mol}^{-1}$) [12] was applied to heptafulvene.

Because of the multidimensional character of aromaticity [13], every index of it has rather limited reliability, and depends on the system. The question of the validity of the NICS index has been raised [14–16]; particularly the reliability of the NICS description of aromaticity in distorted benzene rings [17] and π -stacked polyfluorenes [18]. Not every system with a negative NICS is aromatic [19], while not every system with positive NICS is antiaromatic, as we will also try to show in this paper focusing on heptafulvene.

The geometry-based index of aromaticity HOMA was originally invented for uncharged systems [8, 9], but despite this, it has also been successfully applied to ionic π -electron systems [20–22], and even to excited states [22, 23]. Nevertheless, the application of the HOMA index to these types of system requires some care: the systems should be structurally comparable. Recently, some criticism of HOMA when applied to hetero π -electron systems was presented [24].

The higher stability of aromatics than their olefinic analogs has long been known [25, 26], but this phenomenon was only approached quantitatively much later [27, 28], by introducing the concept of resonance energy (RE), which describes the aromatic system to be more stable than its olefinic analog. In fact, the aromatic stabilization energy, ASE, is most often studied. This is estimated in such a way that energy is (usually) only gained through π -electron delocalization [12, 29, 30].

The pEDA index also has its limitations. It can only be calculated for fully planar systems where the σ/π separation is good. It also has all of the advantages and disadvantages of the NBO method on which it is based; it is important to bear in mind that it uses orbital-based partitioning of the electron density, which is always somewhat arbitrary.

Because fulvenes are often unstable [3], theoretical methods are attractive tools for studying the properties of these molecules. There is increasing interest in studying the structural chemistry of these compounds, and numerous papers have recently been devoted to quantifying the aromaticities and other properties of these compounds [31–36]. The reliability of geometry predictions of heptafulvene obtained through various computational methods has also been assessed [37].

The purpose of the work described in this paper was to investigate the amount of charge that can be transferred from the halogen atoms to the heptafulvene moiety during the formation of the heptafulvene–halogen complex, and—by analogy to fulvene complexes with lithium [38]—how the charge of the ring in each complex is related to its aromatization.

Methods

Geometry optimizations of heptafulvene–halogen complexes were performed at the B3LYP/6-311+G(d,p) level of theory using the Gaussian 03 software package [39]. For the two heaviest halogens, the Stuttgart–Dresden effective core potentials (ECP) were used instead of the inner-core electrons of the halogen, with the accompanying basis sets. In the case of iodine, 46 electrons were replaced, leading to the use of the MWB46 ECP [40] in Gaussian 03, and in the case of astatine, 78 electrons were replaced using the MWB78 ECP [41]. For all other atoms, the all-electron 6-311+G(d,p) basis set was employed. Vibrational frequencies were then determined to evaluate the character of the computed stationary point. The binding energies of the complexes were calculated using a supramolecular approach corrected for basis set superposition error (BSSE) according to the Boys counterpoise method [42], assuming a neutral heptafulvene molecule and a neutral halogen atom as reference. NBO analysis [43] was performed by the NBO 5.G program interfaced to Gaussian. Graphical representations of molecules were obtained using the Chemcraft program [44].

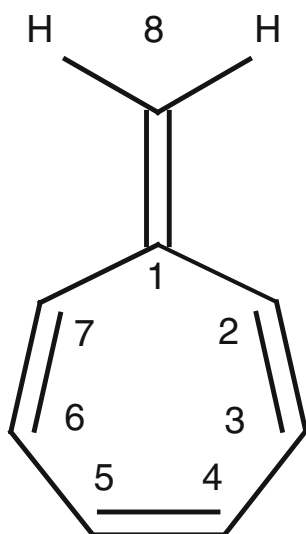
The magnetism-based aromaticity index NICS (nucleus-independent chemical shift) [5] was calculated as the negative of the shielding constant of a ghost atom located at the geometric center of the ring. The NICS(1) values were calculated at a point located 1 Å below the ring (on the other side compared to the halogen atom). NICS(1)_{ZZ}, the component perpendicular to the ring plane, which is mathematically equal to the Z component of the induced magnetic field [45, 46], was also calculated.

The geometry-based aromaticity index HOMA (harmonic oscillator model of aromaticity) was calculated according to [8, 9]. HOMA is defined as the normalized sum of the squared deviations of bond lengths from the values obtained for a system assumed to be fully aromatic. For hydrocarbons, the appropriate expression takes the following form:

$$HOMA = 1 - \frac{\alpha}{n} \sum_i^n (R_{opt} - R_i)^2, \quad (1)$$

where $\alpha = 257.7$ is an empirical normalization constant chosen to make HOMA = 0 for the model nonaromatic system and HOMA = 1 for the system where all bonds are equal to $R_{opt} = 1.388 \text{ \AA}$, n is the number of CC bonds included in the summation, R_{opt} is the optimal aromatic bond length, and R_i are the experimental or computed bond lengths.

The π -electron count based aromaticity index pEDA [47] (π -electron donor acceptor) was calculated by summing the $2p_z$ natural atomic orbital occupancies of the heptafulvene ring carbon atoms and subtracting 6, thus

Fig. 1 Atom labeling for the heptafulvene molecule

indicating how much the π population of the ring deviates from the ideal sextet:

$$pEDA = \sum_{i=1}^7 \pi_{heptafulvene}^i - 6, \quad (2)$$

where π_i is the i th $2p_z$ natural atomic orbital perpendicular to the plane of the molecule. Population analysis done within the NBO methodology is called natural population analysis (NPA) [48], and can be considered an improved Mulliken analysis with more basis set and molecular system type independency. In a study where the aromatization of pentafulvenes via substituents was analyzed, the pEDA index was found to be linearly correlated with HOMA [49].

The ASE (aromatic stabilization energy) values for fulvene and heptafulvene were calculated at the B3LYP/6-

311+G(d,p) DFT level using isodesmic, homodesmotic, and superhomodesmotic reactions. This calculation level is expected to be quite accurate for molecules of this type [50]. The energies used to calculate the ASE were corrected for the B3LYP/6-311+G(d,p) zero-point energies. All species corresponded to minima on the potential energy surface, with no imaginary frequencies.

To estimate the extent to which the halogen atom and carbon atom penetrate their van der Waals spheres, an additional parameter, Δ_{vdw} , was introduced. This is defined as the difference between the sum of the van der Waals radii of the halogen and carbon atoms and the distance between the carbon atom and the halogen atom. This parameter may be treated (by analogy with H bonding [51]) as the approximate strength of the interaction of the halogen atom with the heptafulvene molecule:

$$\Delta_{vdw} = R_{vdw}(\text{halogen}) + R_{vdw}(\text{carbon}) - R(\text{halogen} - \text{carbon}). \quad (3)$$

Results and discussion

We first consider the complexes that form between the heptafulvene molecule and various halogen atoms. The atom numbering scheme for heptafulvene is depicted in Fig. 1, whereas data characterizing these complexes are shown in Table 1.

As shown in Fig. 2, the halogen atom in the halogen–heptafulvene complex is equidistant from the C4 and C5 carbon atoms, as illustrated in this figure by the heptafulvene–iodine complex.

Table 1 Various data for heptafulvene–halogen complexes

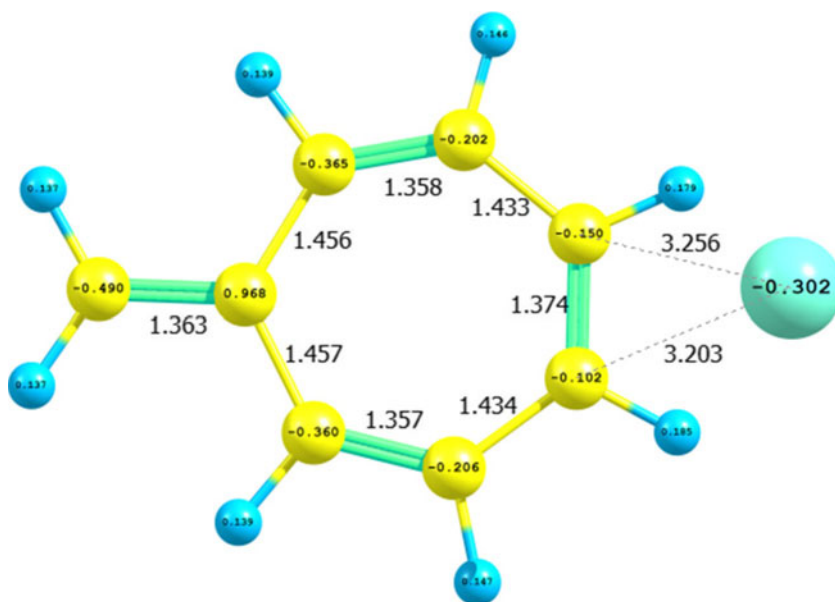
Hal. atom	$q(X)$	$q(C8)$	$R_{vdw}(\text{hal})$ (Å)	R_{CHal} (Å)	Δ_{vdw} (Å)	HOMA	NICS	NICS (1)	NICS (1) _{zz}	pEDA	Stat. point	ΔE_{bind} BSSE corr. (kcal/mol)
F	−0.552	−0.291	1.47	2.129	1.041	0.640	3.791	−0.353	1.716	0.447	TS	−32.250
Cl	−0.460	−0.292	1.75	2.745	0.705	0.553	6.216	1.388	6.381	0.543	TS	−19.193
Br	−0.404	−0.300	1.85	2.925	0.626	0.503	7.080	2.134	8.346	0.592	TS	−14.905
I	−0.318	−0.315	1.98	3.230	0.450	0.428	8.134	3.491	11.757	0.665	Min	−9.052
At	−0.252	−0.327	2.00	3.314	0.386	0.369	8.950	3.940	13.568	0.718	Min	−6.581
*	N/A	−0.386	N/A	N/A	N/A	0.165	10.627	5.856	19.235	0.903	Min	N/A

$q(X)$: NPA charge on the halogen; $q(C8)$: NPA charge on the C8 atom; $R_{vdw}(\text{hal})$: van der Waals radius of the halogen atom; R_{CHal} : average distance between the carbon and halogen atoms; Δ_{vdw} : the difference between the sum of the van der Waals radii of the halogen and carbon atoms and the distance between the carbon atom and the halogen atom; HOMA, NICS, NICS(1): aromaticity indices; pEDA: π -excess/deficiency characteristics; ΔE_{bind} : the nature of the stationary point and the binding energy (computed as the difference between energy of the complex and those of its components for complexes of heptafulvene with halogen atoms)

van der Waals radius of C atom = 1.70 Å [52]; van der Waals radius of astatine is not available in publications and was assumed to be R_{vdw} = 2.00 Å

* Free heptafulvene without halogen

Fig. 2 Geometry characteristics and total NPA charges at atoms of the heptafulvene–iodine complex



From Fig. 2, it is clear that despite the partly aromatic character of the complex, the C–C bonds still possess strongly alternating character; similarly, the NPA charges at the carbon atoms indicate a highly nonuniform distribution of charge transferred from the halogen atom. It should also be mentioned that this kind of complex is known as either a transition state (TS) or a real equilibrium system (a true potential energy minimum). Interestingly, the iodine complex shows unexpected asymmetry in C–I distances (Fig. 2), and this corresponds to the true minimum at which system locates itself during optimization, even if the starting point is a symmetric structure. In all other cases, the two carbon–halogen distances are the same.

Table 1 presents the full characteristics of the complexes. Complexes with more electronegative halogen atoms (F, Cl, Br) are transition states, but those with I and At are true minima. Looking at Table 1, the HOMA, NICS, and pEDA values for the complexes indicate significantly stronger aromatic charac-

ter than observed for free heptafulvene. This aromatization is due to the charge transfer from the heptafulvene moiety towards the halogen atom, as nicely documented by Fig. 3, where HOMA is plotted against the NPA charge at the halogen atom. The correlation coefficient $cc=-0.995$ when the complex with fluorine is excluded, but it is still quite high ($cc=-0.974$) when it is included. Interestingly, an increase in the negative charge in the ring is associated with a decrease in the negative charge at the exocyclic carbon atom C8; see Fig. 4. In principle, changes in almost all of the indicators of aromaticity [NICS, NICS(1), pEDA, and HOMA] are correlated with the binding energy $\Delta E(\text{bind})$ and charge transferred from the halogen atom $q(X)$; see Table 2.

The charge on the C8 carbon atom in heptafulvene is significantly negative because the heptafulvene ring tends to donate electron density in order to achieve an electronic sextet. When the halogen atom accepts part of the charge from the heptafulvene ring, the charge on the C8 atom

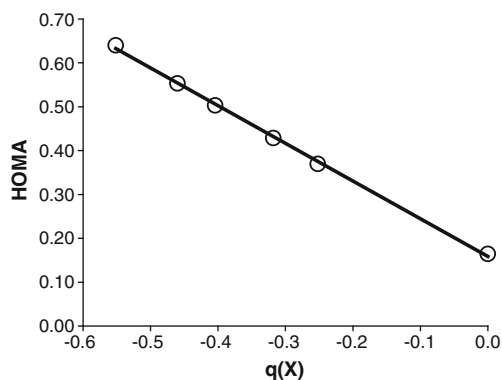


Fig. 3 Linear regression of HOMA vs the NPA charge $q(X)$ on the halogen. Correlation coefficient $cc=-0.999$; regression equation: $y = -0.8585x + 0.159$

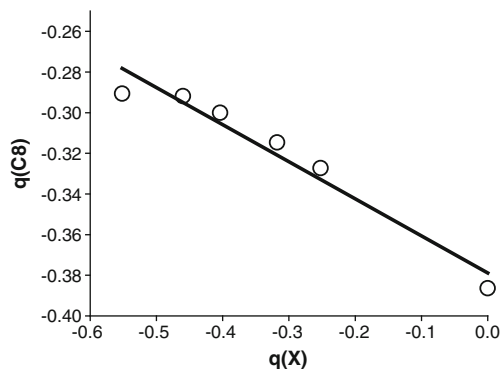


Fig. 4 Linear regression of the NPA charge on C8 carbon atom $q(\text{C8})$ vs natural charge on the halogen atom $q(X)$. Correlation coefficient $cc2=-0.976$; regression equation: $y = -0.1824x - 0.3788$

Table 2 Correlation coefficient (cc) matrix (the cc values obtained for free heptafulvene are also included in parentheses)

	HOMA	NICS	NICS(1)	NICS(1) _{ZZ}	pEDA	q(hal)	ΔE_{vdw}	$\Delta E(\text{bind})$
NICS	0.983 (0.962)	x	x	x	x	x	x	x
NICS(1)	0.992 (0.980)	0.993 (0.994)	x	x	x	x	x	x
NICS(1) _{ZZ}	0.996 (0.988)	0.994 (0.992)	0.999 (0.999)	x	x	x	x	x
pEDA	0.999 (0.999)	0.990 (0.973)	0.996 (0.987)	0.999 (0.993)	x	x	x	x
q(hal)	1.000 (0.999)	0.980 (0.953)	0.990 (0.973)	0.994 (0.982)	0.998 (0.997)	x	x	x
ΔE_{vdw}	0.977 (0.984)	0.997 (0.990)	0.993 (0.994)	0.992 (0.996)	0.985 (0.991)	0.973 (0.979)	x	x
$\Delta E(\text{bind})$	0.973 (0.934)	0.998 (0.995)	0.991 (0.984)	0.989 (0.978)	0.982 (0.948)	0.969 (0.922)	0.999 (0.977)	x
q(C8)	0.951 (0.968)	0.879 (0.863)	0.912 (0.901)	0.922 (0.918)	0.937 (0.957)	0.956 (0.976)	0.865 (0.914)	0.856 (0.815)

becomes less negative, and the linear trend for all halogen atoms except for fluorine has a very high correlation coefficient (Fig. 4).

Charge transfer from the halogen atom to the heptafulvene moiety is achieved by occupying the molecular π orbital, leading to an excellent correlation between the pEDA and HOMA values, as shown in Fig. 5. Moreover, almost all of the variables presented are intercorrelated.

The binding energy of the complex correlates well with all of the aromaticity indices (HOMA, pEDA, and the three types of NICS), but the correlation with NICS yields the best correlation coefficient; see Fig. 6. In this figure, we have added a point representing the free heptafulvene molecule, with $\Delta E_{\text{bind}}=0$ for this point. The overall correlation between NICS and ΔE_{bind} is excellent.

The aromaticity of heptafulvene is usually considered similar to that of fulvene, and their Hess–Schaad REPE values strongly support this notion; they are both -0.002β in the HMO theory [4]. NICS values cannot be used to perform this kind of comparison, since they strongly depend on the area of the ring [53]. When HOMA is applied, it gives -0.286 for fulvene and 0.164 for heptafulvene [6]. In order to investigate this issue at the level of the actual approaches applied to estimate the aromatic stabilization energy, we followed the procedure presented below.

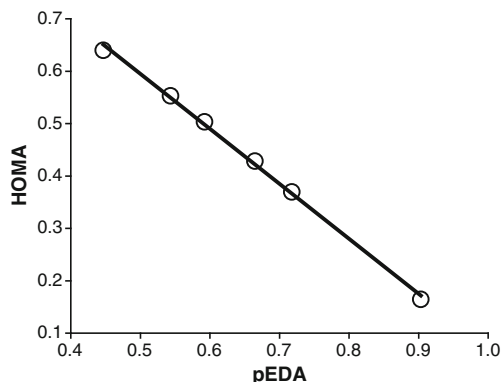


Fig. 5 Regression of HOMA vs pEDA values. Correlation coefficient $cc=-0.999$; regression equation: $y = -1.0494x + 1.1198$

Two kinds of homodesmotic reactions were employed [6, 12]: (i) based on cyclic olefinic and conjugated unsaturated analogs (see Scheme 1a) [13, 54], or (ii) based on acyclic reference systems (see Scheme 1b) [13]. In the former case, fulvene is regarded as consisting of three unsaturated units represented by two 3-methylene-1-cyclopentene reference molecules on the reactant side and methylenecyclopentane unit on the product side. The conjugative interactions in the ring are largely compensated for by considering an analog decomposition of cyclopentadiene. The homodesmotic reaction (Scheme 1b) based on polyene reference molecules is similar to the schemes frequently used to estimate the ASE of benzene [12, 55–58]. This reaction also compensates for conjugative interactions, but unlike the previous approach (Scheme 1a), it does not balance strain effects. Both reactions lead to the same ASE value, $-5.1 \text{ kcal mol}^{-1}$ [13], which indicates that the energies of particular fragments are nearly additive and, as expected, fulvene is a nonaromatic system. For heptafulvene, the ASE can be estimated in a similar way: based on cyclic or acyclic reference systems. The former approach leads to a set of homodesmotic reactions (a few examples are shown in Scheme 1c–g) where heptafulvene and cycloheptatriene consist of unsaturated units that partly compensate for the conjugative interactions in the ring, and the saturated systems

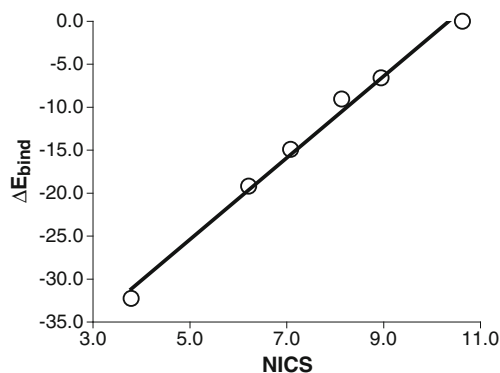
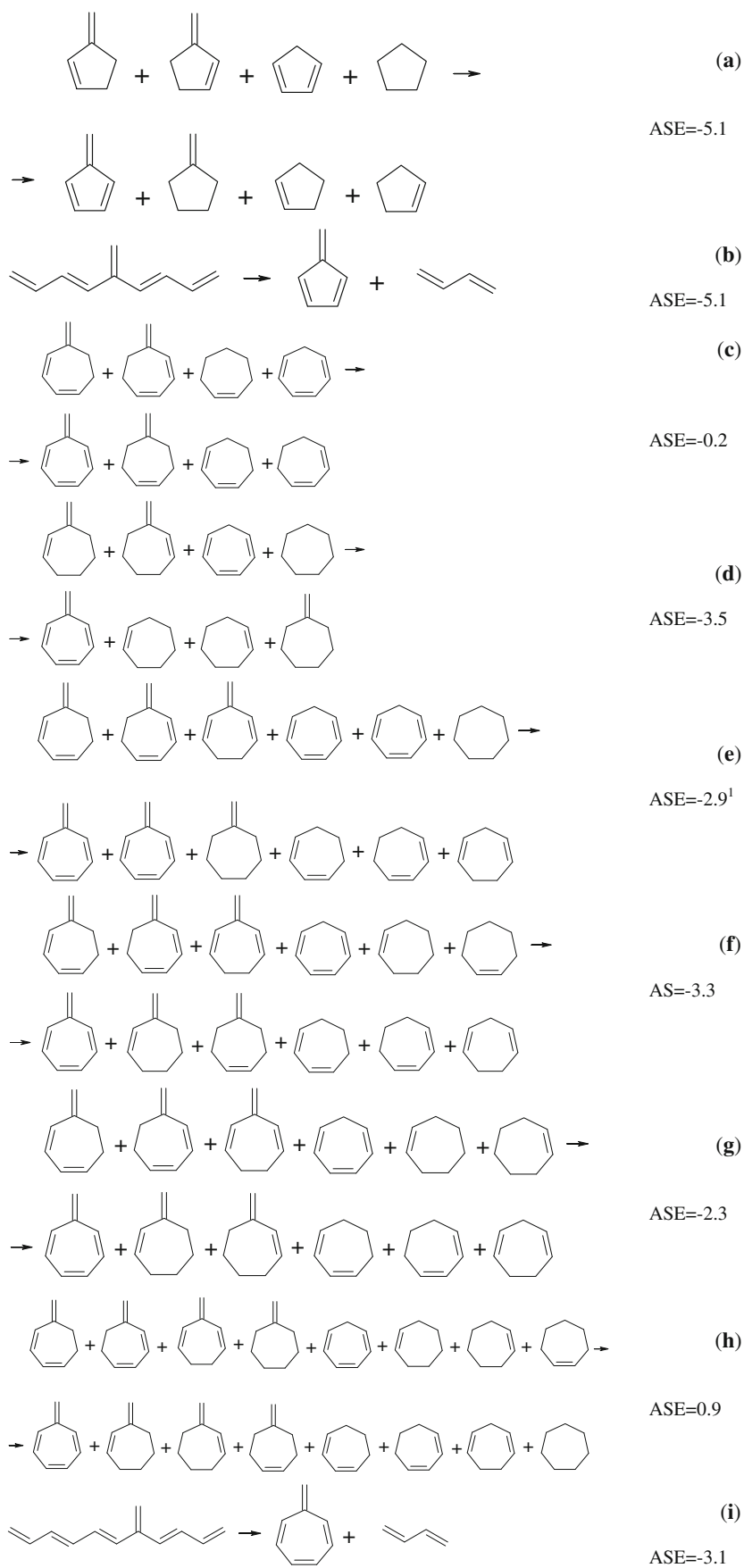


Fig. 6 Regression of ΔE_{bind} vs NICS values. Correlation coefficient $cc=0.995$; regression equation: $y = 4.7556x - 49.171$

Scheme 1 Homodesmotic reactions for evaluating the ASE values of fulvene (**a–b**) and heptafulvene (**c–i**)



¹Per one molecule of heptafulvene

accomplish the obvious homodesmotic reaction requirements. The resulting ASE values fall within a narrow energy interval (from -0.2 to -3.5 kcal mol $^{-1}$), which fits perfectly with the ASE value obtained based on acyclic reference systems (Scheme 1i; ASE = -3.1 kcal mol $^{-1}$). The size of the ring allowed us also to formulate a superhomodesmotic reaction [13, 59, 60] (see Scheme 1h) that compensated for the effects of both strain and conjugative interactions in the best possible way. The estimated ASE is close to zero (ASE = $+0.9$ kcal mol $^{-1}$), indicating that heptafulvene is a nonaromatic system. The π -electron structure is essentially localized, and the system provides a good reference structure for any comparisons with aromatic (delocalized) structures.

Two reactions in Scheme 1 give the same value for fulvene, -5.1 kcal mol $^{-1}$, whereas all of the ASE values for heptafulvene range from ASE = 0.9 (Scheme 1h) to the most negative value of ASE = -3.5 for Scheme 1d. Regardless of the subtle differences between the applied homodesmotic reactions, the conclusion is that heptafulvene is essentially a nonaromatic system. Both the energy-based index (ASE) and the geometry-based (HOMA) index indicate that this property is more pronounced in heptafulvene than in fulvene. The latter is shifted towards antiaromaticity compared with the former.

Conclusions

Heptafulvene is a nonaromatic system. However, it is slightly more aromatic than fulvene, as supported by values of ASE and HOMA.

The π -electron delocalization in the ring of each complex of heptafulvene (equilibrium or transition states) with a halogen atom (F, Cl, Br, I, At), as estimated from the HOMA, NICS, and pEDA values, depends linearly (with a high correlation coefficient) on the charge transferred from heptafulvene to the halogen atom. In all of the linear regressions, the point for fluorine deviates slightly from the linear relation.

The absolute value of the binding energy $\Delta E(\text{bind})$ decreases with increasing distance between the C4 or C5 carbon atom and the halogen atom.

Acknowledgments This paper is dedicated to the memory of our friend Professor Zvonimir B. Maksić (1928–2011) in recognition of his outstanding contribution to theoretical organic chemistry. Computational grant G36-9 from the Interdisciplinary Centre for Mathematical and Computational Modelling at Warsaw University (ICM UW) is gratefully acknowledged.

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