

Aromatic Character and Energy of the Five- and Seven-Membered Rings in Derivatives of Penta- and Heptafulvene Substituted in Exocyclic Position

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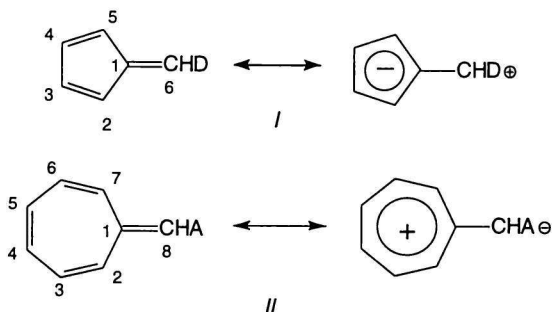
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Application of aromaticity indices to geometries of rings of eleven derivatives of fulvene, two salts of cyclopentadienyl, and nine derivatives of heptafulvene gives a coherent view in line with expectation due to the $(4n + 2)$ rule: electron-donating substituents attached to exocyclic carbon atom in fulvenes and electron-accepting substituents attached to heptafulvenes increase significantly their aromatic character.

Penta- and heptafulvenes have long been a subject of consideration in respect to their partly aromatic character. Delocalization energy estimated by simple HMO, within the original Hückel scheme, is 1.466 for fulvene (I) and 1.994 for heptafulvene (II) [1] or 0.24β and 0.25β per electron π which may be compared to 0.33β for benzene. When the partial delocalization of π -electrons in cyclic polyenes is taken into account, then following the Hess and Schaad procedure [2] one obtains much more reliable results. The numerical values of resonance energy per electron (REPE) for fulvene, heptafulvene, and benzene are now -0.002 , -0.002 , and 0.065 , respectively. These results, being in line with chemical experience [3] and expectations, are much more satisfactory indicating nonaromatic (or even slightly antiaromatic) properties of fulvene and heptafulvene.

From the Hückel $(4n + 2)$ rule it results that π -electron systems in rings of fulvene and heptafulvene tend to contain six π -electrons. Thus fulvene should be stabilized by substitution by electron-donating substituents D (I), whereas heptafulvene by electron-accepting ones A (II).



In most cases information on the aromatic character of fulvene, heptafulvene, and other nonalternant π -electron systems stems from theoretical calculations [3]. However, many of these systems are not stable except when the substituted species are prepared. Then the stability of these systems changes and theoretical calculations are no more the reliable source of information. On the other hand, the stable systems form crystals which have often been studied by X-ray diffraction techniques.

The aim of this paper is to present the application of recently introduced indices of aromaticity estimated from experimental geometries of molecules or their fragments [4] to study the dependence of the aromatic character of rings in penta- and heptafulvene derivatives on the nature of the substituent at the exocyclic carbon atom.

THEORETICAL

Indices of Aromatic Character Derived from Bond Length of π -Electron Systems

Bond lengths of π -electron cyclic systems may readily be used to define indices of aromatic character. The first such investigation was carried out by Julg and Francois [5] who used a degree of differentiation of peripheral (perimeter) bond lengths, estimated as squared differences from the mean value, as a measure of aromatic character. This idea was then improved by replacing the mean bond lengths by the optimal ones which in the case of CC bonds occurred to be very close to the bond lengths in benzene [6]. The index was called HOMA and turned out to be very useful in describing the aromatic character [7] of many differ-

ent systems, including heterocycles with such bonds as CN, CO, CS, CP, and even NN.

Several indices of aromaticity used in this study are described below.

The harmonic oscillator model of aromaticity, HOMA [7], is defined as

$$\text{HOMA} = 1 - \frac{\sum_i^m a_i \sum_j^n (d_i^{\text{opt}} - d_j)^2}{N} \quad (1)$$

where d_i^{opt} is an empirically estimated optimal bond length which is assumed to be realized when full delocalization of π -electrons occurs, a_i is an empirical constant dependent on the kind of bond, and d_j stands for the bond lengths taken into account, N is a number of bonds taken into account. For CC-bond length $d_i^{\text{opt}} = 1.388 \times 10^{-10}$ m and $a_i = 257.7 \times 10^{10}$ m [7].

The bond alternation coefficient (BAC) is a measure of the degree of alternation of bond lengths in the ring. It is normalized in such a way as to obtain 1 for a π -electron system with equal bond lengths, e.g. for benzene, and 0 for the Kekule structure of benzene with single and double bonds, such as in 1,3-butadiene [8], i.e. 1.467×10^{-10} m and 1.349×10^{-10} m for the single and double bonds, respectively. Thus the index reads

$$\text{BAC} = 1 - 3.46 \left\{ \sqrt{\sum_r (d_r - d_{r+1})^2} \right\} \quad (2)$$

where d_r and d_{r+1} are consecutive bond lengths in the ring and summation runs over all bonds of the molecule or its fragment.

LB (the longest bond in the ring) is assumed to be a "magnetic type" index of aromaticity. Following the *Jug* idea [9] the longer is the bond in the ring, the less readily a π -electron current is induced as a result of action of the external magnetic field.

Bond Energy

It has long been known that the energy of the bond depends on its length, nevertheless this relationship has not yet been used explicitly for the systems with bonds of medium lengths. Moreover, the resonance energy was defined as a measure of nonadditivity of bond energy terms for such systems. Recently, a simple way of making use of CC-bond lengths in hydrocarbons to estimate the energy of these molecules has been suggested [4].

Almost half a century ago *Pauling* [10] defined a fractional bond number n as a function of interatomic distance (bond length) $d(n)$ and a standard "single bond" length $d(1)$.

$$d(n) = d(1) - c \ln n \quad (3)$$

where c is an empirical constant.

The usefulness of this idea has been demonstrated widely in the last decades [11].

About thirty years ago *Johnston* and *Parr* [12] applied successfully the idea of bond number to estimate bond energy

$$E(n) = E(1)n^p \quad (4)$$

where $E(1)$ and $E(n)$ stand for the energies of bonds with bond number equal to 1 and n , respectively. When eqns (3) and (4) are combined, the formula for bond energy BE in function of the bond lengths is obtained [4, 13]

$$E(n) = \text{BE} = E(1) \exp \{ \alpha [d(1) - d(n)] \} \quad (5)$$

where $\alpha = p/c$ and may be easily derived from eqn (5) by using reference bond lengths and energies

$$d(1) = 1.533 \times 10^{-10} \text{ m} \quad (6a)$$

$$d(2) = 1.337 \times 10^{-10} \text{ m} \quad (6b)$$

$$E(1) = 357.89 \text{ kJ mol}^{-1} \quad (6c)$$

$$E(2) = 556.84 \text{ kJ mol}^{-1} \quad (6d)$$

For these reference data $\alpha = 2.255 \times 10^{10}$ m. Then the formula (5) with $\alpha = 2.255 \times 10^{10}$ m was fitted to reproduce heat of formation (from atoms) of benzene, 5529.1 kJ mol⁻¹ and the adjustable parameter was $E(1)$. Energies of CH bonds are taken additively $E(\text{CH}) = 420.90$ kJ mol⁻¹. Thus for any molecule of π -electron hydrocarbon or its fragment one can estimate its bond energy (or heat of formation from atoms abbreviated by HtFfA) by use of the following formula [4]

$$\{\text{HtFfA}\} = - \{ 100.53n + 87.99 \sum \exp [2.255(1.533 - d_i)] \} \quad (7)$$

where n is the number of CH bonds in the molecule (or its fragment) and summation runs over all N CC bonds. Formula (7) was tested by comparison of calorimetric HtFfA with those estimated from bond lengths and the obtained results turned out to be in a good agreement with experimental data [4].

DISCUSSION

The above-presented indices of aromatic character were calculated for eleven derivatives of fulvene substituted at exocyclic carbon atoms and two salts of cyclopentadienyl. Table 1 presents all these data. In seven cases C-6 is involved in alicyclic system, in two cases it is substituted by aliphatic substituents. Only in two cases there are one or two electron-donating substituents attached to it (amines). For the first two groups HOMA values are in the range -0.117—0.074

Table 1. Indices of Aromaticity for Fulvene Derivatives

Refcode [17—19]	Compound	Ref.	HOMA	BAC	BE/(kJ mol ⁻¹)	LB/10 ⁻¹⁰ m
GEZKOL	1,4-Bis(2,4-cyclopentadien-1-ylidene)cyclohexane	[20]	0.074	0.255	2440.9	1.465
VARZOD	(2,4-Cyclopentadien-1-ylidene)cyclooctan-5-one	[21]	-0.117	0.138	2456.4	1.466
KEMPAT	3,7-Bis(2,4-cyclopentadien-1-ylidene)bicyclo[3.3.0]octane	[22]	0.059	0.217	2449.7	1.459
KUMRIT*	6-(4-Dimethylaminophenyl)fulvene	[23]	-0.008 -0.106	0.233 0.195	2410.8 2400.3	1.468 1.474
FULHPF	α -(6-Fulvenyl)dibenzo(<i>a,e</i>)-heptafulvene	[24]	0.027	0.204	2467.7	1.464
JEHHEJ	9-(2,4-Cyclopentadien-1-ylidene)-bicyclo[3.3.1]nonane	[25]	0.037	0.220	2456.8	1.467
SENDUK*	1,5-Bis(2,4-cyclopentadien-1-ylidene)cyclooctane	[26]	0.047 0.004	0.187 0.172	2520.9 2503.3	1.455 1.471
KAPBOS	Dimethyl 7-[4-(2,4-cyclopentadien-1-ylidene)cyclohexylidene]-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate	[27]	0.046	0.237	2441.7	1.473
VARYUI	2-(2,4-Cyclopentadien-1-ylidene)adamantane	[28]	-0.050	0.148	2473.1	1.459
NMEFUL	6-Dimethylaminofulvene	[29]	0.669	0.542	2500.4	1.437
QQQACM01	6-Dimethylamino-6-piperidinofulvene	[30]	0.702	0.650	2487.8	1.445
COGWEA	Dicyclopentadienyl beryllium	[31]	0.671	0.719	2396.5	1.445
CPENCA	Dicyclopentadienyl calcium	[32]	0.986	0.929	2542.2	1.402

* Two independent molecules in the unit cell.

with the mean value 0.001 (eleven rings). These results point to nonaromatic properties of the derivatives in which the substituents have no clear donating effect and are in line with the value of REPE = -0.02 close to zero [2]. In a similar way BAC has rather low values in the range 0.148—0.255 with the mean value 0.20. When we look at amine derivatives we find mean HOMA and mean BAC values much higher, amounting to 0.685 and 0.591, respectively. The highest values are observed for cyclopentadienyl anion for which HOMA equals 0.986 and BAC equals 0.929 (Ca salt). The other indices, LB and BE, are less indicative. All these results are in a good agreement with chemical experience and expectation.

Nonequivalence of indices of aromatic character, as mentioned above, may be associated with the well-known fact that the aromatic character is a multidimensional phenomenon [14, 15]. Therefore we have applied factor analysis [16] to study this problem. Application of this analysis to all four indices for 13 geometries discussed above shows that two orthogonal factors describe 97.8 % of the total variance. The first factor explains 80.1 % of the total variance and is strongly correlated with purely geometric index of aromaticity, BAC, whereas the next factor is described mostly by energetic index (BE). These results are at variance with those obtained for benzene rings in benzenoid

hydrocarbons [4], for which the decisive factor was energetic in nature. It may be interpreted as follows. In the case of benzene rings embedded in various environments in benzenoid hydrocarbons, no intramolecular charge transfer is expected. All structural changes of the ring are rather topological in nature. A completely reverse situation occurs in the case of fulvene derivatives and cyclopentadienyl anion in which variation in the structure is due to intra- or intermolecular charge transfer (push-pull effect of amine group or formation of salts). Due to these effects, one might expect a stronger variation of bond lengths due to the change of the ring charge. Hence the energetic effect may be less indicative in comparison with the geometric one. The condition could be also that in the case of fulvene derivatives the parent molecule of fulvene is nonaromatic in nature and changes towards a higher aromaticity due to charge transfer into the ring. In the case of benzene rings in benzenoid hydrocarbons the changes occur from the parent aromatic systems towards the less aromatic ones due to various topological attachments to the other rings. Additionally, in benzene rings there are usually three longer and three shorter CC bonds. As a result of *p*-substitution by groups of different electronegativity a more quinoid structure is formed. Consequently, two longer bonds (C-1—C-6 and C-1—C-2) are in the vicinity thus giv-

Table 2. Indices of Aromaticity for Heptafulvene Derivatives

Refcode [17–19]	Compound	Ref.	HOMA	BAC	BE/(kJ mol ⁻¹)	LB/10 ⁻¹⁰ m
DOXPIP	8-Phenylheptafulvenyl-8-tosylate	[33]	0.191	0.095	3517.7	1.461
HEPFUL 10	Heptafulvene	[34]	0.257	0.152	3520.3	1.460
FAPMUE	1,1-Dicyano-3-(2,4,6-cycloheptatrien-1-ylidene)-2-(4-methoxyphenyl)-prop-1-ene	[35]	0.412	0.309	3682.3	1.451
KESWOU*	5-Cycloheptatrienylidene-2,4-imidazolidinedione	[36]	0.473 0.513	0.274 0.299	3552.1 3585.6	1.442 1.440
SAFGIP	2,4,6-Cycloheptatriene-1-thione	[37]	0.533	0.374	3451.6	1.461
DONCUE	Heptahendecafulvalene	[38]	-0.005	-0.034	3470.0	1.468
TAFFAH	9-[1-(2,4,6-Cycloheptatrienylidene)]-xanthene	[39]	-0.008	-0.001	3499.3	1.466
BETBEH 10	8,8-Diformylheptafulvene	[40]	0.769	0.535	3554.2	1.426

* Two independent molecules in the unit cell.

ing no contribution to a decrease of BAC value, which is accepted as a mostly geometric measure of the aromatic character.

Table 2 presents the values of aromaticity indices of heptafulvene derivatives. There are only nine independent seven-membered rings in derivatives of heptafulvene and only in one case the exocyclic carbon atom is substituted effectively by electron-accepting groups (two formyl substituents). For this case both BAC and HOMA values are the highest: 0.535 and 0.769, respectively. For heptafulvene derivative much better correlation between HOMA and BAC values is observed than it was for fulvenes.

Since this set of data is rather scarce, it is not advisable to draw any stronger conclusion. Nevertheless, similarly as in the case of fulvene derivatives, the observed changes in aromatic character presented by aromaticity indices are in line with chemical expectation.

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