

Relationes

Ground State Properties of Some Nonbenzenoid Hydrocarbons

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Ground state properties including π - and σ -bond energies, resonance energy, and heats of atomization of some nonbenzenoid hydrocarbons have been studied using the method of Dewar and Harget and compared with results obtained by the Dewar-de Llano method. It is seen that the Dewar-Harget method is less effective in correlating the chemical properties.

Key words: Non-benzenoid hydrocarbons

1. Introduction

To synthetic organic chemists and quantum chemists non-benzenoid hydrocarbons play an interesting role. Recently many workers [1–7] have studied the ground state properties, such as heats of atomization, resonance energies, and σ - and π -bond energies for some conjugated hydrocarbons using the methods of Dewar *et al.* [1–4], Lo and Whitehead [5], and Hess and Schaad [8]. Dewar and Harget [4] have developed a method to predict the heats of atomization and other ground state properties using a linear relation to the overlap integral (Mulliken approximation) to estimate the one electron resonance integrals. They have shown that the results agree well with the method of Dewar and de Llano and with experiment. Here we report the results of calculations on some nonbenzenoid hydrocarbons (Fig. 1) using this method [4] and comparisons with other reported results.

2. Method and Parameters

The method used here has been described by Dewar *et al.* [4]. The one centre two electron repulsion integral, γ_{ii} , (11.13 eV) was taken as the difference between the ionization energy (11.16 eV) and electron affinity (0.026 eV) of the carbon atom in its sp^2 valence state [9]. The two electron repulsion integrals, γ_{ij} , were calculated using Ohno's [10] formula. β_{ij} , the resonance integral for two neighbouring centres, was calculated according to the Mulliken formula as used by Dewar *et al.* [4].

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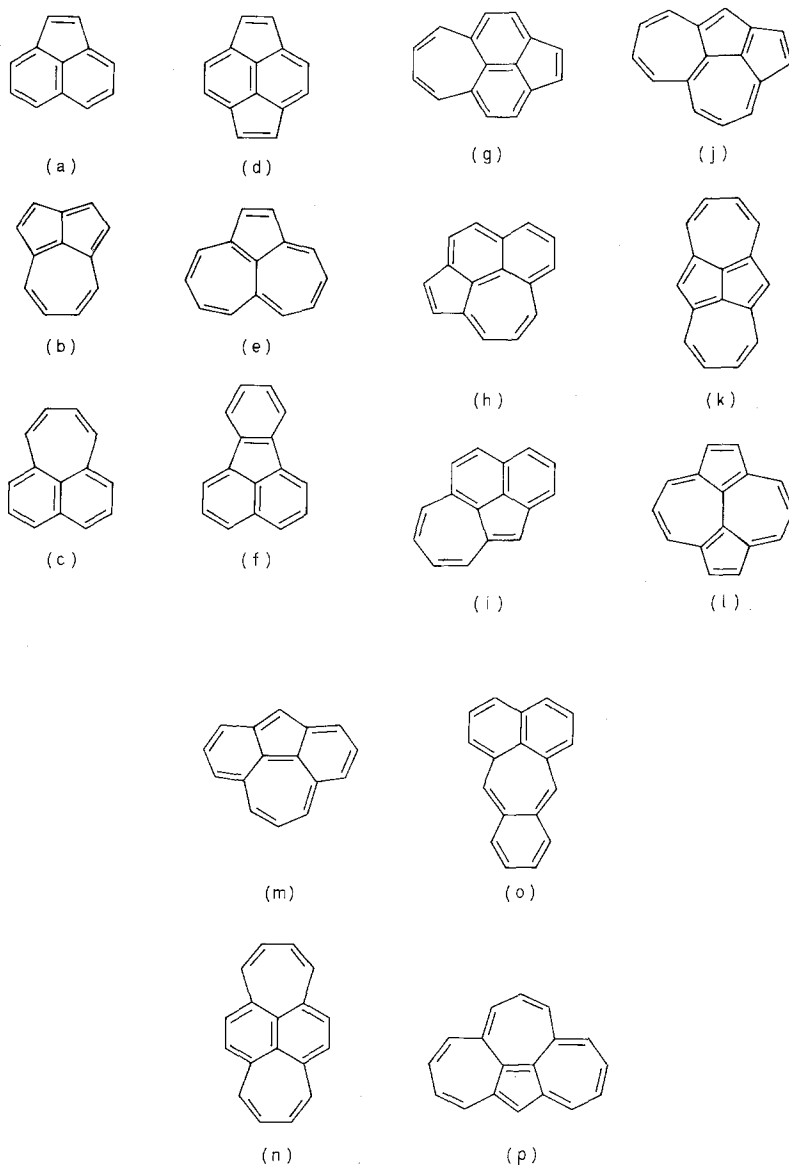


Fig. 1. Molecules listed in Table 1

After each iteration of the SCF procedure, the bond lengths between bonded atoms were recalculated from the relation of bond order and bond length [3]. The β_{ij} and γ_{ij} for neighbouring centres used in the next iteration were those calculated using the new bond lengths. For the initial iteration we used the true geometry of the molecules or their derivatives where available and for others we used assumed geometries as described elsewhere [7].

Table 1. Heats of atomization and bond energies (eV)

Molecule	Bond energy		Heats of atomization	
	$E_{\pi b}$	$E_{\sigma b}$	Dewar-Harget	Dewar-de Llano ^a
(a) Acenaphthylene	17.388	51.953	104.840 ^b	104.607
(b) Aceazulylene	16.411	52.053	103.964	104.021
(c) Pleiadiene	19.961	59.227	123.564	123.212
(d) Pyracylene	20.305	63.203	119.008	118.531
(e) Aceheptylene	18.961	59.357	122.693	122.896
(f) Fluoranthene	23.647	70.670	138.690 ^b	138.447
(g) Acepleiadylene	22.919	70.563	137.857	138.043
(h) Naphth[<i>cde</i>]azulene	22.963	70.569	137.907	137.521
(i) Cyclohept[<i>bc</i>]acenaphthylene	22.939	70.566	137.880	137.667
(j) Pentaleno[<i>de</i>]heptalene	20.046	70.673	137.094	137.126
(k) Dicyclohepta[<i>cd,gh</i>]pentalene	21.944	70.865	137.184	136.895
(l) Azupyrene	21.912	70.960	137.247	137.094
(m) Cyclohept[<i>def</i>]fluorene	21.328	71.043	136.746	136.404
(n) Dipleiadadiene	25.483	77.781	156.514	155.924
(o) Benzopleiadiene	25.519	77.862	156.631	156.142
(p) Azuleno[<i>def</i>]heptalene	24.382	78.131	155.763	155.493

^a Ref. [7]; ^b Ref. [4].

3. Results and Discussion

Table 1 contains the heats of atomization, and π - and σ -bond energies calculated by this method along with the values of heats of atomization calculated by the method of Dewar and de Llano [3]. Table 2 contains the resonance energies of all the molecules studied here. Since resonance energy increases with the increase of number of π -electrons for the same type of molecules, it is not suitable for predicting the aromaticity or stability of molecules. However, resonance energy per carbon-carbon bond has been proposed by Lo and Whitehead [5] as being more useful in this respect. Table 2 also contains the resonance energy per carbon-carbon bond. For comparison we have included the results of calculation using the method of Dewar and de Llano [3]. From Table 2 it is clear that as regards the resonance energy per carbon-carbon bonds ($E_R/C-C$) this method also maintains the same sequence of order i.e. benzenoid (0.111–0.163) > semibenzenoid (0.07–0.105) > nonbenzenoid (0.03–0.048) molecules. Although according to our classification [7] fluoranthene belongs to semibenzenoid systems, its resonance energy per carbon-carbon bonds is higher than other semibenzenoid systems. The higher $E_R/C-C$ of fluoranthene may be due to the fact that there exists little conjugation between the benzene and naphthalene moieties i.e., the bonds connecting them are localized [3].

Although in most cases the results of calculation (Tables 1 and 2) are in good agreement between the Dewar-Harget and Dewar-de Llano methods there are some disagreements which need some comments. It is also interesting to note that in all the cases except aceheptylene $E_R/C-C$ calculated by the Dewar-Harget method is less than that calculated by the Dewar-de Llano method.

Table 2. Resonance energies, E_R (eV) and resonance energy per C-C bond, $E_R/C-C$

	Dewar-Harget method		Dewar-de Llano method	
	E_R^a	$E_R/C-C$	E_R^b	$E_R/C-C$
Benzenoid Systems				
Benzene	0.980	0.163	0.869	0.145
Naphthalene	1.457	0.132	1.323	0.120
Anthracene	1.774	0.111	1.600	0.100
Phenanthrene	2.125	0.133	1.933	0.121
Pyrene	2.294	0.121	1.822	0.096
Chrysene	2.719	0.129	2.483	0.118
Semibenzenoid Systems				
Acenaphthylene	1.464 ^a	0.105	1.081 (1.335)	0.077 0.095
Pleiadiene	1.461	0.091	1.123	0.070
Pyracylene	1.394	0.082	0.767	0.045
Acepleiadylene	1.518	0.080	1.517	0.080
Naphth[cde]azulene	1.568	0.082	0.995	0.052
Cyclohept[bc]acenaphthylene	1.541	0.081	1.141	0.060
Fluoranthene	2.353 ^a	0.124	1.921 (2.141)	0.101 0.113
Cyclohept[def]fluorene	0.407	0.021	-0.122	-0.006
Dipleiadadiene	1.448	0.069	0.635	0.030
Benzopleiadiene	1.566	0.075	0.853	0.041
Nonbenzenoid Systems				
Azulene	0.351 ^a	0.032	0.232 (0.169)	0.021 0.015
Aceazulylene	0.587	0.042	0.495	0.035
Aceheptylene	0.590	0.037	0.807	0.050
Pentaleno[def]heptalene	0.755	0.040	0.600	0.032
Azupyrene	0.908	0.048	0.563	0.030
Dicyclohepta[cd,gh]pentalene	0.844	0.044	0.369	0.019
Azuleno[def]heptalene	0.698	0.033	0.204	0.010

^a For benzenoid systems the values taken from Ref. [4].

^b For benzenoid systems and values in the parentheses taken from Ref. [3], and for others Ref. [7].

According to chemical properties acepleiadylene is more aromatic than pleiadiene [11]. If we consider the resonance energy per carbon-carbon bonds to be a measure of aromaticity then the Dewar-Harget method suggests that pleiadiene is more aromatic than acepleiadylene whereas the reverse is true for the Dewar-de Llano method.

The $E_R/C-C$ for pyracylene (0.082) is comparable to that of other semibenzenoid hydrocarbons and it appears that pyracylene is an aromatic compound. But according to Trost *et al.* [12] it is not aromatic and this is in agreement with the value of $E_R/C-C$ (0.045) calculated by the Dewar-de Llano method [7].

Each of the molecules pentaleno[def]heptalene, dicyclohepta[cd,gh]pentalene and azupyrene contains 16 π -electrons and two azulene nuclei fused together. The $E_R/C-C$ value calculated by the method of Dewar and Harget suggests that all of them are equally aromatic whereas the Dewar-de Llano method

predicts that dicyclohepta[cd,gh]pentalene is not aromatic. Moreover the report of its synthesis has not yet been found in the literature.

Another disagreement is found in predicting aromaticity in the case of aceazulylene and aceheptylene. According to the chemical properties [13, 14] and the Dewar-de Llano method the latter is more aromatic than the former [7]. But the reverse is being predicted by the Dewar-Harget method.

Thus it is seen that prediction of aromaticity for these types of molecules on the basis of $E_R/C-C$ calculated by the Dewar-Harget method is less effective than the Dewar-de Llano method. Moreover it appears that the magnitude of scaling of $E_R/C-C$ calculated by the Dewar-Harget method is less consistent with the chemical properties of these molecules than that calculated by the Dewar and de Llano method.

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