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AROMATICITY OF SOME NONBENZENOID AND SEMIBENZENOID HYDROCARBONS

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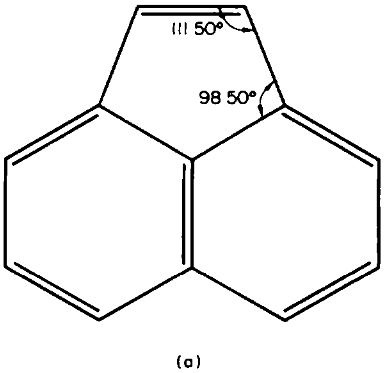
Abstract—Aromaticity of some nonbenzenoid and semibenzenoid hydrocarbons has been studied according to the theories developed by Chung and Dewar, Lo and Whitehead, Dewar and de Llano, and Hess and Schaad. Heats of atomization, σ and π bond energies and resonance energies for these molecules are also reported.

An attempt has been made to classify benzenoid, semibenzenoid and nonbenzenoid molecules according to the resonance energy value per carbon–carbon bond and per π electron.

INTRODUCTION

FOR MANY YEARS, explanations have been sought for the "aromatic nature" associated with benzene and other benzenoid compounds. The discovery of numerous nonbenzenoid compounds with properties similar to those of benzene emphasized the need for more rigorous definition of "aromaticity". A large number of theoretical and experimental studies of these cyclically conjugated nonbenzenoid compounds have contributed much in developing the concept of "aromatic character".[1] Among the earliest theories developed to explain aromaticity were the concept of the "aromatic sextet"[2] and the Huckel $4n + 2$ rule[3] based on quantum mechanical considerations. More recently aromaticity has been associated with delocalization of π electrons and resonance energy. Chung and Dewar,[4] Lo and Whitehead,[5] Dewar *et al.*,[6] and Hess and Schaad[7] have proposed criteria for "aromaticity". We report the results of calculations on some nonbenzenoid and semi-benzenoid (i.e. compounds having five and seven membered rings fused with a benzene or naphthalene nucleus) molecules giving their π and σ bond energies, heats of atomization and resonance stabilization energies along the lines developed by those authors.[4–7] Fig 1 contains the molecules studied. We restrict our discussions of nonbenzenoid



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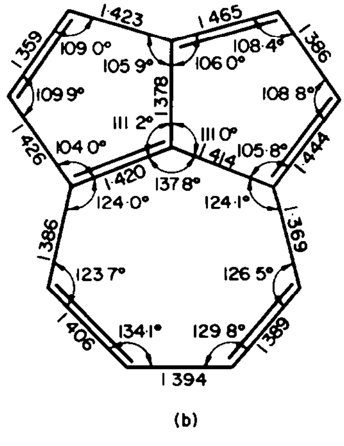

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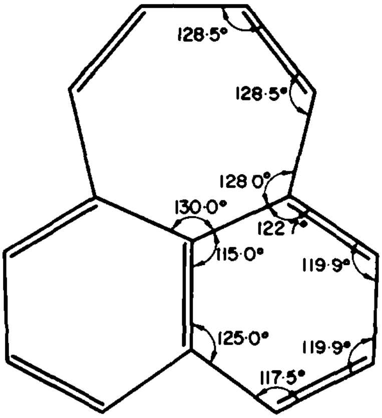
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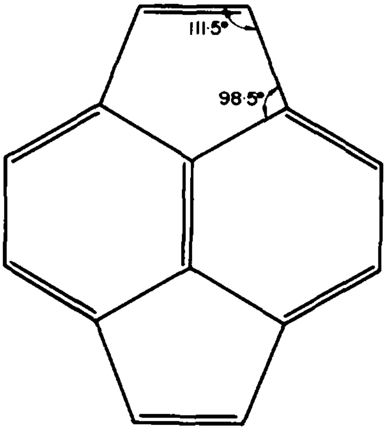
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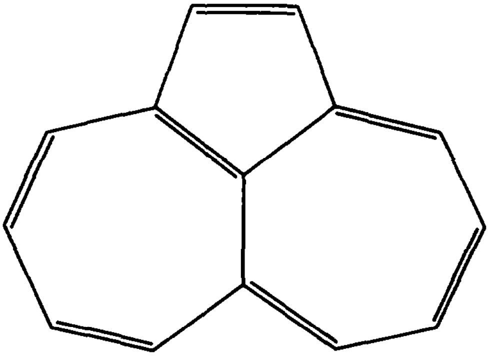

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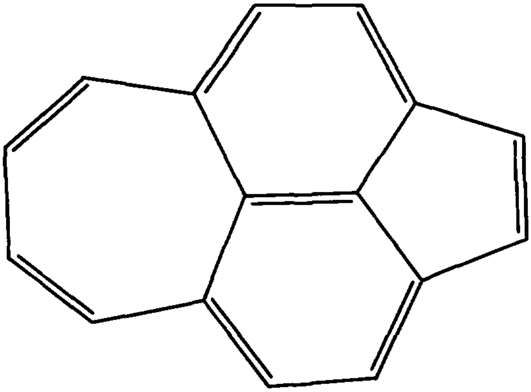

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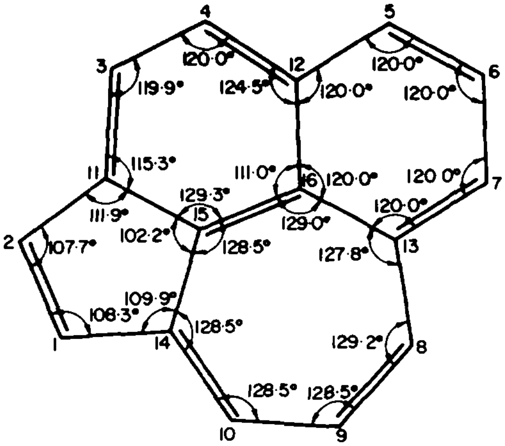
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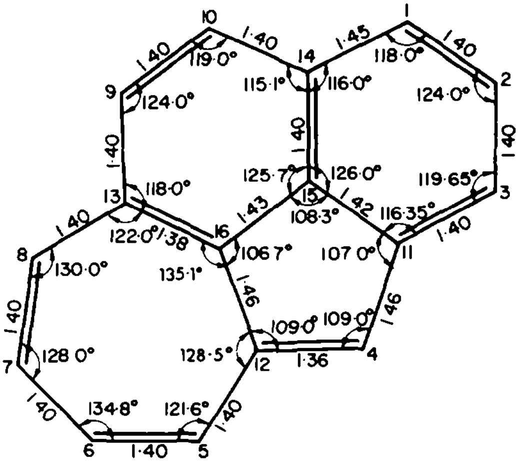
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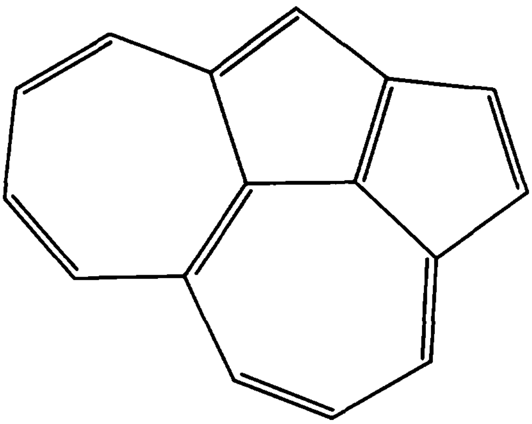

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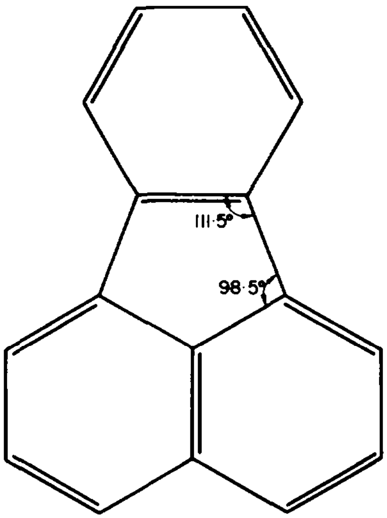
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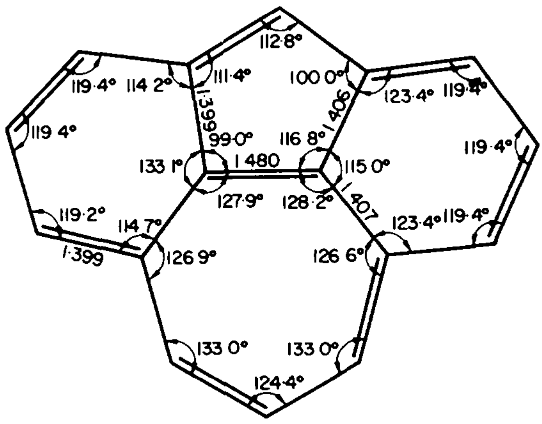
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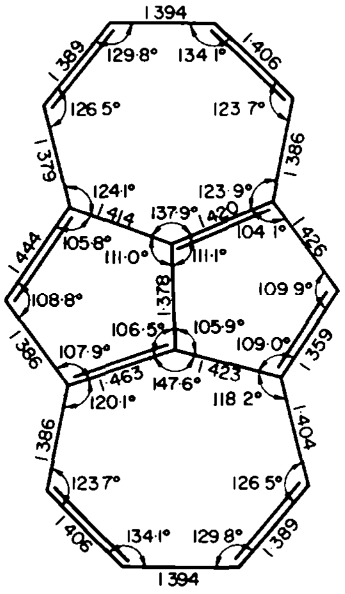
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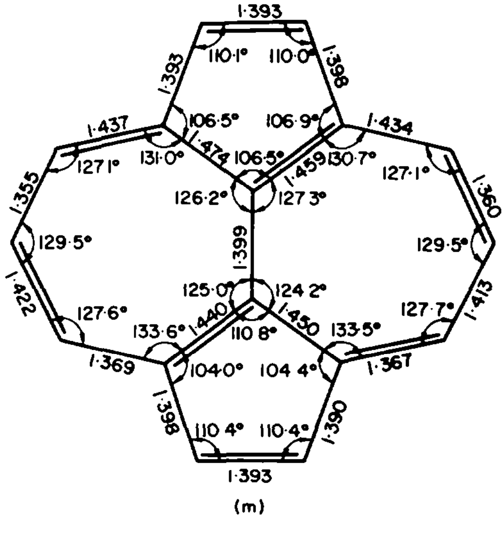
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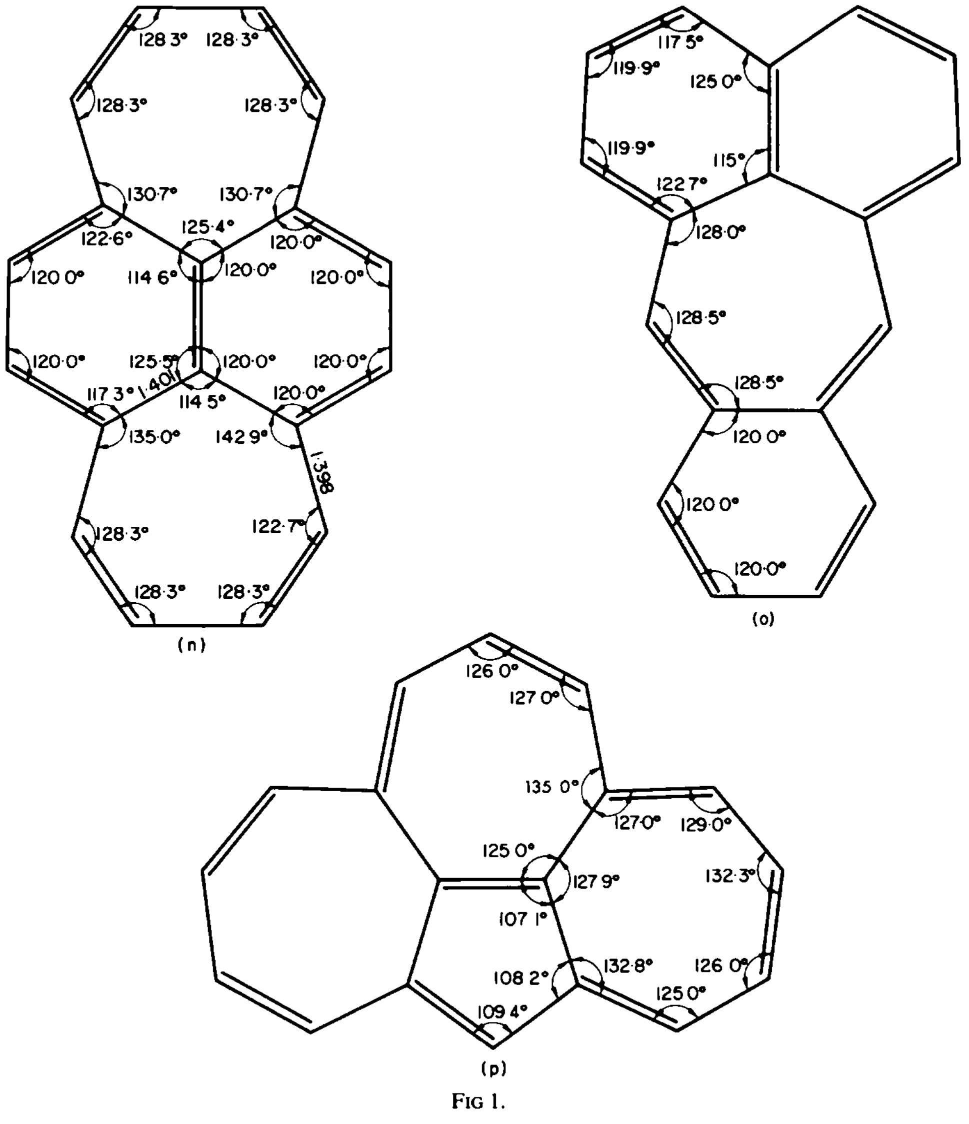

(n)

(o)

(p)

FIG 1.

(a) Acenaphthylene (C_{2v}) (all bonds equal to 1·40 A and bond angles equal to 120° except otherwise mentioned).

(b) Aceazulylene

(c) Pleiadiene (C_{2v}) (All bonds equal to 1·40 A)

(d) Pyracylene (D_{2h}) (All bonds equal to 1·40 A)

(e) Aceheptylene

(f) Acepleiadylene

(g) Naphthazulene

(h) Cycloheptacenaphthylene

(i) Pentalenoheptalene

(j) Fluoranthene (C_{2v}) (All bonds equal to 1·40 A)

(k) Cycloheptfluorene (other bonds equal to 1·40 A)

(l) Dicycloheptpentalene

(m) Azupyrene

(n) Dipleiadadiene (other bonds equal to 1·40 A)

(o) Benzopleiadiene (C_{2v}) (All bonds equal to 1·40 A)

(p) Azulenoheptalene (C_{2v}) (All bonds equal to 1·40 A) hydrocarbons to those compounds with five and seven membered rings fused to the azulene nucleus.

In this paper the molecules pentaleno[def]heptalene, naphth[cde]azulene, cyclohept[bc]acenaphthylene, cyclohepta[def]fluorene, dicyclohepta[cd,gh]pentalene, and azuleno[def]heptalene will be referred to as pentalenoheptalene, naphthazulene, cycloheptacenaphthylene, cycloheptfluorene, dicycloheptapentalene, and azulenoheptalene respectively.

METHOD AND PARAMETER

The calculations were done within the SCF context using the zero differential-overlap approximation so that the method is equivalent to those described by Pariser and Parr[8] and Pople.[9]

The two electron integrals, γ_{rs}, were calculated by the method of Ohno[10]

$$\gamma_{rs} = \frac{14{\cdot}397}{[1{\cdot}328^2 + R_{rs}^2]^{\frac{1}{2}}}\,\text{e.v.} \tag{1}$$

where R_{rs} is the internuclear distance in Å. Thus the one centre two electron integral γ_{rr} is equal to 11·134 e.v., equal to the difference between 11·16 e.v.,[11] the ionization energy of the carbon atom in its sp^2 valence state, and 0·026 e.v.,[11] the electron affinity of the carbon atom in that state.

The values of the resonance integral for two neighbouring centres were calculated in two ways: (i) a value dependent on bond length as proposed by Lo and Whitehead[5] and (ii) a constant value of $-1{\cdot}7901$ e.v.[12] determined by the method of Chung and Dewar.[4] The corresponding SCF results are designated as SCF (a) and SCF (b), respectively. We did not use the β-variable method depending on bond order and bond length, because Lo and Whitehead's method gives proper attention to the value of β depending on the bond length.

For the purpose of evaluating the β and γ integrals, the benzenoid molecules were taken to be planar with all bond lengths equal to 1·40 Å. The structures of azulene[13] and derivatives of aceazulylene,[14] aceheptylene,[15] and pentalenoheptalene[16] are known. All are planar except aceazulylene (almost planar) for which a planar geometry very close to that reported was used in the calculation. For those molecules with no reported structure, a reasonable planar geometry was used as proposed in Fig 1. Moreover we believe that use of a reasonable geometry for the calculation of β and γ for those molecules whose structure has not been determined experimentally is more realistic than using the β variable method.

The total π-bond energy is given by

$$-E_{\pi b} = 2\beta \sum_{r<s} P_{rs} + \tfrac{1}{4}\sum_{r} q_r^{\,2}\gamma_{rr} + \sum_{r<s} [(q_r - 1)(q_s - 1) - \tfrac{1}{2}P_{rs}^2]\,\gamma_{rs} \tag{2}$$

where P_{rs} is the bond order and q_r the charge density.

The heats of atomization, ΔH_a, (at 25°) can be expressed by

$$\Delta H_a = E_{\pi b} + E_{\sigma b} + N_{\text{CH}}E_{\text{CH}}. \tag{3}$$

where E_{CH}(4·4375 e.v.)[17] is the C—H bond energy and N_{CH} is the number of C—H bonds. $E_{\sigma b}$, the total σ bond energy, is assumed to be equal to $\Sigma_k E_k^{CC}$, the sum of all individual σ bond energies determined according to Lo and Whitehead.[5]

Lo and Whitehead[5] proposed the resonance energy as

$$E_R^{(a)} = E_{\pi b} + E_{\sigma b} - (n'E_{C-C} + n''E_{C=C}) \tag{4}$$

where n' and n'' are respectively the number of single and double bonds in a reference valence bond structure, with $E_{\pi b}$ and $E_{\sigma b}$ as defined earlier. E_{C-C}, the single bond energy at 1·505 Å C—C distance, is equal to 3·9115 e.v. and $E_{C=C}$, the double bond energy at 1·334 Å C=C distance, is equal to 5·6033 e.v.

In a series of papers Dewar *et al.*[4, 6] calculated resonance energies for conjugated molecules. In the first paper of the series Chung and Dewar[4] proposed that resonance stabilization energy may be expressed as $E_R^{(b)} = n(A_0 + a_1A_1) + E_{\pi b}$ with $A_0 = -1{\cdot}0871$ e.v., $A_1 = -0{\cdot}1627$ e.v., and $a_1 = 1/n\ (n' - n/2)$ where n and n' are the number of π electrons and number of carbon–carbon single bonds respectively in a reference valence bond structure.

Dewar and de Llano[6b] defined resonance energy "as the difference between the heat of formation of a given conjugated compound and that calculated for a corresponding classical structure with localized bonds." Thus the resonance energy, $E_R^{(c)}$ of any conjugated hydrocarbon is given by

$$E_R^{(C)} = \Delta H_a - \Delta H_a' \tag{5}$$

where ΔH_a is the observed heat of atomization and $\Delta H_a'$ is that calculated for a classical structure. Again $\Delta H_a'$ accordipg to them is given by

$$\Delta H_a' = n'E' + n''E'' + n_{CH}E_{CH} \tag{6}$$

where n' and n'' are defined earlier and E' (4·3499 e.v.)[6b] and E'' (5·5378 e.v.)[6b] are the localized bond energies for a single and a double bond respectively. ΔH_a, the heat of atomization, may be given in the following way[6b]

$$-\Delta H_a = n_{CH}E_{CH} + \Sigma E_{C-C}^r - E_{\pi b} \tag{7}$$

where E_{CH} and n_{CH} have been defined earlier and E_{C-C}^r is the bond energy of a C—C σ bond in an aromatic ring. Again

$$E_{C-C}^r = E_{C-C}^0 - C'$$

where E_{C-C}^0 is the bond energy of a pure σ bond between two sp^2 carbon atoms and c' is the energy to compress a single bond to a bond length r.

Hess and Schaad[7] have recently attacked the problem in a different way. They have calculated π resonance energies from knowledge of the Hückel π-energy, $E_{HMO}(\pi)$, given by

$$E_{HMO}(\pi) = n_{23}E_{23}^\pi + n_{22}E_{22}^\pi + n_{22'}E_{22'}^\pi + n_{21}E_{21}^\pi + n_{20}E_{20}^\pi + n_{12}E_{12}^\pi + n_{11}E_{11}^\pi + n_{10}E_{10}^\pi \tag{8}$$

where E_{ij}^π is the π bond energy in units of β for an ij bond and the coefficients, n_{ij}, are the numbers of bonds of a given type in a molecule. Table 1 contains the various types of E_{ij}^π E_R, the resonance energy, may be calculated as

$$E_R = E_{HMO} - E_{loc} \tag{9}$$

where E_{loc} is the π energy of a reference valence bond structure shown in Fig 1.

TABLE 1*

Types of bond	Calculated π bond energy (β)	
$H_2C{=}CH$	E^{π}_{23}	2·0000
$HC{=}CH$	E^{π}_{22}	2·0699
$H_2C{=}C$	$E^{\pi}_{22'}$	2·0000
$HC{=}C$	E^{π}_{21}	2·1083
$C{=}C$	E^{π}_{20}	2·1716
$HC{-}CH$	E^{π}_{12}	0·4660
$HC{-}C$	E^{π}_{11}	0·4362
$C{-}C$	E^{π}_{10}	0·4358

* Ref. (7).

RESULTS AND DISCUSSION

It is well known that the Hückel delocalization energy increases more or less monotonically with increase in the number of π electrons, which renders it useless as a method of analysis for aromaticity and stability. However, it may be useful to compare the delocalization energy per π electron (DE/e) for molecules with identical numbers of π electrons and with identical ring structures except for the types involved. Table 2 contains the DE/e for the molecules studied here. It is seen that when a benzene or naphthalene ring is replaced by five or seven membered rings, the DE/e decreases consistent with the more sophisticated methods of analysis of stability and aromaticity discussed below. Taking the DE/e as a measure of stability, for the same number of π electrons and rings the stability is in the order benzenoid > semibenzenoid > nonbenzenoid.

TABLE 2. DELOCALIZATION ENERGY PER π ELECTRON*

Molecule	DE/e	Molecule	DE/e	Molecule	DE/e
Naphthalene	0·368			Azulene	0·336
		Acenaphthylene	0·385	Aceazulylene	0·366
Phenanthrene	0·389	Pleiadiene	0·3675	Aceheptylene	0·351
		Pyracylene	0·387		
Pyrene	0·407	Acepleiadylene	0·391	Pentalenoheptalene	0·372
		Naphth(cde)azulene	0·389	Azupyrene	0·378
		Cyclohept(bc) acenaphthylene	0·388	Dicycloheptpentalene	0·377
		Fluoranthene	0·406		
		Cycloheptfluorene	0·375		
Chrysene	0·400	Benzopleiadiene	0·375	Azulenoheptalene	0·356
		Dipleiadadiene	0·363		

* For the calculation of DE/e some of the HMO energies have been taken from the compilation in ref. 30.

Table 3 contains the heats of atomization calculated by Eq. (3) for these molecules along with the π and σ bond energies generated by both SCF(a) and SCF(b) methods. Table 4 contains E_R, the resonance energy, and $E_R/C{-}C$, the resonance energy per

TABLE 3. VALUE OF HEATS OF ATOMIZATION (E.V.) AND σ AND π BOND ENERGIES (E.V.)

Molecule	ΔHa Calculated		σ bond energies		π bond energies	
	SCF(a)	SCF(b)	SCF(a)	SCF(b)	SCF(a)	SCF(b)
Naphthalene	90·618[*]	90·616	40·576[*]	40·608[a]	14·600[*]	14·508[a]
Azulene	89·520	89·294	40·283[a]	40·386[a]	13·736[a]	13·408[a]
Acenaphthylene	104·607	104·715	51·303	51·679	17·804	17·536
Aceazulylene	104·021	103·596	51·270	51·366	17·251	16·730
Phenanthrene	124·250[*]	124·206	59·164[*]	59·066	20·783[*]	20·765
Pleiadiene	123·212	123·444	58·394	59·113	20·444	19·955
Pyracylene	118·531	118·676	62·294	62·754	20·737	20·422
			62·928[b]		20·676[b]	
Aceheptylene	122·896	121·935	58·899	58·372	19·621	19·188
Pyrene	138·644[*]	138·529	70·456[*]	70·141[a]	23·886[*]	24·013[a]
Acepleiadylene	138·043	136·787	70·308[a]	69·274[a]	23·360[a]	23·138[a]
Naphthazulene	137·521	137·668	69·633[a]	70·134[a]	23·512[a]	23·159[a]
Cycloheptacenaphthylene	137·667	137·125	70·133[a]	69·639[a]	23·158[a]	23·111[a]
Fluoranthene	138·447	138·596	69·621	70·138	24·451	24·083
Cycloheptfluorene	136·404	136·371	69·960	69·880	22·069	22·116
Pentalenoheptalene	137·126	135·993	70·231[a]	69·255[a]	22·520[a]	22·364[a]
Azupyrene	137·090	136·463	69·777	69·475	22·938	22·613
Dicycloheptpentalene	136·895	136·760	69·453	69·850	23·067	22·535
Chrysene	157·805[*]	157·719	77·774[*]	77·525	26·869	26·945
Benzopleiadiene	156·142	156·421	76·711	77·572	26·180	25·590
Dipleiadadiene	155·924	156·110	76·928	77·527	25·746	25·333
Azulenoheptalene	155·493	155·675	76·932	77·501	25·310	24·924

[*] Ref. 5
[a] Ref. 12
[b] Ref. 31

carbon–carbon bond, obtained by the method of (a) Lo and Whitehead[5] and (b) Chung and Dewar.[4] The average of all available values for E_R/C—C is given in the last column. Although the scale of values is somewhat different, all the methods agree in that E_R/C—C falls in the order benzenoid > semibenzenoid > nonbenzenoid, with reasonably distinct ranges for these classes of molecules. SCF(b) calculations with E_R/C—C based upon $E_R^{(b)}$, i.e., use of Chung and Dewar's method throughout, offer the clearest distinction between the classes of compounds with ranges 0·32 to 0·33 (or greater) 0·251 or 0·30 and 0·22 to 0·249, respectively. Dewar and de Llano used a "variable β" method outlined in part II[6a] of their series. As we have not used a variable β method we use Eq. (3) for the calculation of ΔH_a using SCF(a) method instead of the Dewar and de Llano[6b] method. Table 5 compares the ΔH_a values of some hydrocarbons calculated by those methods and it is clear from the table that the values of heat of atomization calculated by the Lo and Whitehead[5] method using Eq. (3) are in good agreement with the experimental value and with those calculated by the Dewar and de Llano[6b] method using Eq. (7). The last column contains the % deviation between these two methods. Table 6 contains the resonance energy calculated by the method of Dewar and de Llano and resonance energy per π electron,

TABLE 4. RESONANCE ENERGIES (E.V.) AND RESONANCE ENERGIES PER CARBON–CARBON BOND

Molecule	Resonance Energies				Resonance Energy/C—C bond				
	SCF[a]		SCF[b]		SCF[a]		SCF[b]		Average
	E_R^a	E_R^b	E_R^a	E_R^b	E_R^a /C—C	E_R^b /C—C	E_R^a /C—C	E_R^b /C—C	E_R /C—C
Naphthalene	3·690*	3·566	3·630[a]	3·474[a]	0·336*	0·324	0·330[a]	0·316	0·327
Azulene	2·534[a]	2·701[a]	2·309[a]	2·374[a]	0·230[a]	0·246	0·210[a]	0·216	0·226
Acenaphthylene	4·195	4·433	4·303	4·165	0·300 0·3222[b]	0·317	0·307	0·298	0·306
Aceazulylene	3·609	3·880	3·184	3·359	0·258	0·277	0·227	0·240	0·251
Phenanthrene	5·520*	5·238	5·404	5·220	0·345*	0·327	0·338	0·326	0·334
Pleiadiene	4·411	4·899	4·642	4·410	0·276	0·306	0·290	0·276	0·287
Pyracylene	4·692	5·029	4·838	4·714	0·276 0·3105[b]	0·296	0·286	0·277	0·284
Aceheptylene	4·094	4·076	3·133	3·643	0·256	0·255	0·196	0·228	0·234
Pyrene	6·489*	6·004[a]	6·301[a]	6·131[a]	0·342*	0·316	0·332	0·323	0·328
Acepleiadylene	5·815[a]	5·479[a]	4·559[a]	5·253[a]	0·306[a]	0·288	0·240[a]	0·277	0·278
Naphthazulene	5·292[a]	5·631[a]	5·440[a]	5·277[a]	0·279[a]	0·296	0·286[a]	0·278	0·285
Cycloheptacenaphthylene	5·438[a]	5·277[a]	4·896[a]	5·229[a]	0·286[a]	0·278	0·258[a]	0·275	0·274
Fluoranthene	6·218	6·569	6·368	6·202	0·327	0·346	0·335	0·326	0·334
Cycloheptfluorene	4·176	4·187	4·143	4·235	0·220	0·220	0·218	0·223	0·220
Pentalenoheptalene	4·898[a]	4·638[a]	3·765[a]	4·482[a]	0·258[a]	0·244	0·198[a]	0·236	0·234
Azupyrene	4·861	5·056	4·235	4·732	0·256	0·266	0·223	0·249	0·249
Dicycloheptpentalene	4·667	5·186	4·531	4·653	0·246	0·273	0·238	0·245	0·250
Chrysene	7·275*	6·813	7·101	6·889	0·346*	0·324	0·338	0·328	0·334
Benzopleiadiene	5·524	6·124	5·803	5·543	0·263	0·292	0·276	0·264	0·274
Dipleiadadiene	5·306	5·690	5·492	5·277	0·253	0·271	0·262	0·251	0·259
Azulenoheptalene	4·874	5·255	5·057	4·868	0·232	0·250	0·241	0·232	0·239

* Ref. 5

[a] Ref. 12

[b] Ref. 31

RE/PE, for these molecules and it also maintains the same trend benzenoid (0·114 to 0·138 or higher) > semibenzenoid (0·120 to 0·055) > nonbenzenoid (0·011 to 0·057).

Table 6 also contains the resonance energies and resonance energies per π electron, RE/PE, calculated by the method of Hess and Schaad[7] based on the HMO energy, Eq. (9). The quantities RE/PE exhibit the same trends as E_R/C—C but with a much sharper distinction of the ranges for benzenoid, semibenzenoid and nonbenzenoid molecules, 0·051 to 0·055, 0·030 to 0·039 and 0·009 to 0·023. A more significant feature is that RE/PE decreases sharply among the nonbenzenoid hydrocarbons, azulene with the value 0·023 and azulenoheptalene with the value 0·009. But the change in RE/PE among the semibenzenoids is not so sharp and the value is almost constant for benzenoid molecules.

Now, the question is whether the nonbenzenoid and semibenzenoid molecules studied here are aromatic. If so, to what extent? For the purpose of investigating this

TABLE 5. COMPARISON BETWEEN HEAT OF ATOMIZATION (E.V.)

Calculated by equations 3 and 7 for some hydrocarbons

Molecule	Heat of atomization			Difference between			% Deviation of (a) from (b)
	Eq 3[a] (a)	Eq 7[b] (b)	obs[b]	observed and (a)	observed and (b)	(a) and (b)	
Benzene	57·177	57·157	57·16	0·017	0·00	0·020	0·035
Naphthalene	90·618	90·612	90·61	0·008	0·002	0·006	0·007
Anthracene	123·902	123·889	123·93	−0·028	−0·041	0·013	0·010
Phenanthrene	124·250	124·222	124·20	0·050	0·022	0·030	0·024
Pyrene	138·644	138·624	138·88	−0·236	−0·256	0·020	0·014
3,4 Benzphenanthrene	157·807	157·767	157·48	0·327	0·287	0·040	0·025
1,2 Benzanthracene	157·612	157·580	157·49	0·122	0·090	0·032	0·020
Chrysene	157·805	157·772	157·73	0·075	0·042	0·033	0·021
Naphthacene	157·114	157·112	157·56	−0·446	−0·448	0·002	0·001
Triphenylene	157·977	157·943	157·76	0·217	0·183	0·034	0·022
Perylene	172·173	172·146	172·04	0·133	0·106	0·027	0·016
1,12 Benzperylene	186·911	186·892				0·019	0·010
Pentacene	190·266	190·294				−0·028	0·015
1,2,5,6 Dibenzanthracene	191·267	191·238				0·029	0·015
Coronene	201·510	201·527				−0·017	0·008
Acenaphthylene	104·607[c]	104·861	104·32	0·287	0·641	−0·254	0·242
Fluoranthene	138·447[c]	138·668	138·11	0·337	0·557	−0·221	0·159
Azulene	89·520[c]	89·458	89·19	0·330	0·268	0·062	0·069

[a] Ref. 5, unless otherwise stated

[b] Ref. 6*b*

[c] This work

question we use the three criteria discussed above: the Hückel delocalization energy per π electron, (DE/e), the resonance energy and resonance energy per carbon–carbon bond (E_R/C—C) and the resonance energy per π electron (RE/PE).

The Chung and Dewar[4] and Lo and Whitehead[5] papers are similar in that they define aromaticity as the energy difference between the actual structure and a hypothetical structure of pure single and double bonds which has, of course, zero resonance energy. The Dewar and de Llano[6b] and Hess and Schaad[7] papers use instead a polyene as reference structure. Since polyenes themselves have considerable delocalization,[18] one result is that the resonance energies of the last two papers are lower than those of the first two.

Table 7 contains the resonance energies of some polyenes. Comparison of Table 4 and 7 shows that the resonance energies of the nonbenzenoid hydrocarbons calculated by the method of Lo and Whitehead[5] are greater than those of the polyenes. Moreover, the E_R/C—C of the polyenes lies between the values of 0·1233 and 0·1706 which are much lower than those of nonbenzenoid hydrocarbons studied here (0·23 to 0·25). Hence the nonbenzenoid hydrocarbons may not be polyenes according to these theories.

TABLE 6. RESONANCE ENERGY, E_R, AND RESONANCE ENERGY PER π ELECTRON, RE/PE

	Dewar & de Llano method			Hess and Schaad method		
Molecule	Resonance energy E_R^C, (e.v.)	RE/PE	% of aromaticity	Resonance energy*, E_R, (β)	RE/PE	% of aromaticity
Naphthalene	1·323[a]	0·132		0·55[b]	0·055[b]	
Azulene	0·169[a]	0·017	12·8	0·23[b]	0·023[b]	41·8
	0·232	0·023	17·5			
Acenaphthylene	1·335[a] 1·081	0·111 0·090	81·7[c] 55·9[d]	0·47[b]	0·039[b]	85·5[c] 61·0[d]
Aceazulylene	0·495	0·041	37·4[c] 25·6[d]	0·22	0·018	40·0[c] 28·6[d]
Phenanthrene	1·933[a]	0·138		0·77[b]	0·055[b]	
Pleiadiene	1·123	0·080	58·1	0·46	0·033	60·0
Pyracylene	0·767	0·055	39·7	0·26	0·019	33·8
Aceheptylene	0·807	0·057	41·7	0·23	0·016	29·1
Pyrene	1·822[a]	0·114		0·81[b]	0·051[b]	
Fluoranthene	2·141[a]	0·134		0·77	0·048	
	1·921	0·120				
Acepleiadylene	1·517	0·095	83·3	0·55[b]	0·034[b]	66·7
Naphthazulene	0·995	0·062	54·7	0·52	0·033	64·7
Cycloheptacenaphthylene	1·141	0·071	62·6	0·51	0·032	62·7
Cycloheptfluorene	−0·122	−0·008		0·29	0·018	
Pentalenoheptalene	0·600	0·038	32·9	0·25	0·016	31·4
Azupyrene	0·563	0·035	30·9	0·35	0·022	43·2
Dicycloheptpentalene	0·369	0·023	20·3	0·33	0·021	40·7
Chrysene	2·483[a]	0·138		0·96[b]	0·053[b]	
Benzopleiadiene	0·853	0·047	30·3	0·53	0·030	56·6
Dipleiadadiene	0·635	0·035	25·7	0·30	0·017	31·2
Azulenoheptalene	0·204	0·011	8·2	0·17	0·009	17·0

[a] Ref. 6*b*

[b] Ref. 7

[c] Calculated with reference to naphthalene

[d] Calculated with reference to Phenanthrene

[*] In all these molecules more than one localised structure is possible. Hence E_{loc} is calculated for each structure and an average has been taken. The energy difference between various localised structures of the same molecule is insignificant, the maximum difference being 0·0045.

From the comparison of E_R/C—C calculated by the methods of Chung and Dewar[4] and Lo and Whitehead[5] it appears that the semibenzenoid and nonbenzenoid molecules might be aromatic and stable except for cycloheptfluorene, dipleiadadiene, and benzopleiadiene because the E_R/C—C value is either below the range or on the margin for these three molecules. According to the criterion of Dewar and de Llano these molecules are essentially polyenic in nature. In addition dicycloheptpentalene and azulenoheptalene are probably not aromatic because their resonance energies are sufficiently low.

A comparison of resonance energy between nonbenzenoid and benzenoid molecules with the same number of π electrons and rings will be of much interest. A similar comparison is also made between semibenzenoid and benzenoid molecules. Table 6 also contains the result of such a comparison.

TABLE 7. RESONANCE ENERGIES (E.V.) FOR SOME POLYENES

Molecule	Resonance Energy (e.v.)	Resonance energy per C—C bond
Ethylene	0	0
1,3 butadiene (trans)	0·370	0·1233
1,3 butadiene (cis)	0·404	1·1346
2-Vinylbutadiene	0·762	0·1524
Hexatriene	0·756	0·1512
Octatetraene	1·146	0·1637
Decapentaene	1·535	0·1706

It is well known that azulene is aromatic. But Dewar and de Llano's method predicts 17% aromaticity compared with naphthalene where as Hess and Schaad's method predicts 42%. A similar discrepancy in predicting aromaticity is also found in other molecules such as aceheptylene (42% and 29%), acepleiadylene (83% and 67%), azupyrene (31% and 43%), dicycloheptpentalen (20% and 41%), benzopleiadiene (30% and 57%) and azulenoheptalene (8% and 17%).

A quantitative comparison of computed aromaticities is difficult as no quantitative experimental measure of aromaticity has been generally agreed. There are only the qualitative, but still very useful, ideas that aromatics are especially stable, undergo electrophilic substitution, are planar and can be represented by more than one Kekule structures.

Although the overall picture of prediction of aromaticity for these nonbenzenoid and semibenzenoid molecules is good there are still uncertainties and correlation between theoretical results and chemical properties of these molecules will be of much interest. According to chemical properties pleiadiene is less aromatic than acepleiadylene.[19] From the E_R/C—C values one can find examples which agree and those which disagree with this statement. The use of Lo and Whitehead's method throughout gives the clearest agreement. But Dewar, de Llano[6b] and Hess and Schaad's[7] method clearly indicate that acepleiadylene is more aromatic than pleiadiene because the former has a larger value of RE/PE than the latter in both cases.

The methyl derivative of azulenoheptalene has been synthesized by Hafner *et al.*[20] and some of the properties have been reported. It is thermally stable, forms an adduct with trinitrobenzene, protonates easily and has an unusually high-field proton. The E_R/C—C value predicts that the molecule might be aromatic which, however, is not reflected in its properties,[20] but the low resonance energy per π electron calculated by both methods of Dewar and de Llano[6b] and Hess and Schaad[7] suggest that the molecule might be more a polyene than an aromatic. It has only 8% aromaticity compared with chrysene calculated by Dewar and de Llano's[6b] method.

The properties of azupyrene have been reported by Anderson Jr., *et al.*[21] Its thermal stability at least to the melting point (256–258°), NMR and IR spectra, and diamagnetic susceptibility measurement (3·9 ± 0·3) indicate that the molecule has a definite degree of aromaticity.[21] Craig's rule[22] also predicts that the valence bond ground state of the molecule is totally symmetric and hence it has normal aromatic stability. The resonance energy and resonance energy per C—C bond (Table 4), and resonance energy and resonance energy per π electron also indicate that the molecule is aromatic. It is 31% and 43% aromatic as compared with pyrene calculated by the methods of Dewar and de Llano[6b] and Hess and Schaad[7] respectively. Although the two methods do not agree in the degree of aromaticity, still they agree that the molecule azupyrene has sufficient aromaticity and is not a polyene.

The aromaticity of the molecules cycloheptacenaphthylene, naphthazulene, and pentalenoheptalene has been studied by Birss and DasGupta[12] in the context of the methods of Lo and Whitehead[5] and Chung and Dewar.[4] According to Reid *et al.*[23] the molecule cycloheptacenaphthylene would be azulenic and not a cyclopolyolefin. This is also in agreement with the results of calculation of resonance energy, resonance energy per C—C bond and resonance energy per π electron (Table 4 and Table 6) and it is 63% aromatic with respect to pyrene calculated by both methods.[6b, 7]

The properties of the methyl derivative of pentalenoheptalene have been reported by Hafner *et al.*[24] It is thermally stable, can be hydrogenated, and is surprisingly inert to electrophilic attack. No other reactions such as Friedel–Crafts have been reported. Hence it is very difficult to judge its aromaticity chemically. However, the molecule is planar[16] and can be represented by more than one Kekule structure. According to the method of Lo and Whitehead[5] and Chung and Dewar[4] it may be classed as an aromatic compound.[12] The more sophisticated method of Dewar and de Llano also suggest it to be aromatic. The same conclusion can be drawn by the method of Hess and Schaad.[7] According to these methods it is 33% and 31% aromatic compared with pyrene. The degree of aromaticity predicted by these methods is almost the same for azupyrene and pentalenoheptalene both of which contain 16π electrons and two azulene nuclei, the former having higher symmetry.

Synthesis of dicycloheptpentalene has not been reported. The E_R/C—C value (Table 4) and resonance energy per π electron calculated by the Hess and Schaad method predict that the molecule might be stable. However, the resonance energy and resonance energy per π electron calculated by the method of Dewar and de Llano[6b] is smaller than other nonbenzenoid hydrocarbons and it has 20% aromaticity compared with pyrene predicted by this method.[6b]

Cycloheptfluorene is of interest because all attempts[23, 24] at synthesis have failed. The resonance energy per C—C bond (Table 4) is below the range of aromaticity for a semibenzenoid hydrocarbon. The resonance energy calculated by the method of Hess and Schaad[7] is also low and is negative calculated by the method of Dewar and de Llano.[6b] Thus the failure at synthesis is in agreement with the values of resonance energy per C—C bond and resonance energy per π electron calculated by these methods.

The properties of pyracylene have been reported by Trost *et al.*[2b] to be inconsistent with aromatic character. This is also reflected in the value of the resonance energy and resonance energy per π electron (Table 6) and the values are well below the common semibenzenoid aromatic hydrocarbon such as acenapthylene, acepleiadylene and pleiadiene.

The properties of Hafner hydrocarbons have been described by Hafner *et al.*[27] and Ali and Coulson.[28] Dimethyl aceheptylene forms an adduct with maleic anhydride, it undergoes mild electrophilic attack, e.g. Vilsmeir reaction, and it is thermally stable to the melting point. It undergoes Friedel–Crafts acylation.[28] These properties along with its spectra led Hafner[27] to suggest that aceheptylene might be aromatic. Crystal structure of a dimethyl derivative of aceheptylene shows that it is planer.[15] Ali and Coulson[28] and DasGupta and Ali[29] have proposed aceheptylene to be aromatic: the resonance energy per C—C bond (Table 4) and resonance energy per π electron (Table 6) are also in agreement that it is a genuine aromatic compound. It has 42% aromaticity compared with phenanthrene calculated by Dewar and de Llano.

However, the dimethyl derivative of aceazulylene lacks the stability and aromaticity of the dimethyl derivative of aceheptylene. Neither Hückel's rule[3] nor Craig's rule[22] predicts it to be aromatic. The resonance energy per π electron calculated by the method of Dewar and de Llano also predict it to be aromatic but less aromatic than aceheptylene.

Among all these approaches the prediction of aromaticity and stability by Dewar and de Llano's method is better and more consistent with observed chemical properties for these molecules. But it is not understood why the prediction of aromaticity is less in the case of azulene.

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