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Theoretical Study of Some Non-Benzenoid Hydrocarbons: Benzo[3′,4′]cyclobuta[1′,2′:6,7]cycloocta[1,2,3,4-*def*]biphenylene and Related Compounds

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Benzo[3′,4′]cyclobuta[1′,2′:6,7]cycloocta[1,2,3,4-*def*]biphenylene (**1**), benzo[6,7]cycloocta[1,2,3,4-*def*]biphenylene (**2**), dibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-*f*]cyclooctene (**3**), and biphenyleno[8′,1′:4,5,6,7]cycloocta[1,2-*l*]phenanthrene (**4**) have been studied by semiempirical SCFMO method of Pariser and Parr and Pople. Core resonance intergral values of Lo and Whitehead, Dewar et al. and Yamaguchi et al. have been used. It has been observed that $\pi^*\leftarrow\pi$ spectra predicted by the methods of Lo and Whitehead and Chung and Dewar suitable for the prediction of ground state properties are in good agreement with experimental results and comparable to those predicted by the method of Yamaguchi et al. developed for the prediction of spectral transitions. For comparison values obtained by configuration interaction method has also been included. Resonance stabilization of the molecules has been studied along with other properties such as bond length, ionization potential, electron affinity, and half-wave reduction potential.

The properties of polycyclic hydrocarbons formed by the fusion of $(4n+2)$ π-electron rings have been studied extensively with special reference to six π-electron systems. However, little is known about the properties of hydrocarbons composed of fused $4n$, or of $4n$ and $(4n+2)$, π-electron rings. Few polycyclic compounds have been known with fused $4n$ π-electron rings.[1,2] These molecules are interesting because their properties suggest that it is the nature of the individual $4n$ rings and not the overall number of π-electrons which determine the behavior of such systems. In this paper we report the results of our calculations on benzo[3′,4′]cyclobuta[1′,2′:6,7]cycloocta[1,2,3,4-*def*]biphenylene (molecules **1**), benzo[6,7]cycloocta[1,2,3,4-*def*]biphenylene (molecules **2**), dibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-*f*]cyclooctene (molecules **3**), and biphenyleno[8,′1′:4,5,6,7]cycloocta[1,2-*l*]phenanthrene (molecules **4**) using the method of Pariser and Parr[3] and Pople.[4] The molecules studied here belong to those class of compounds mentioned above and moreover all of them contain bicyclo[6.2.0]decapentaene (**5**) ring in the moiety. Molecule **5**[5] is isomeric to azulene and naphthalene and obeys Huckel's $(4n+2)$ rule. On these grounds it might be aromatic. But actually it is not. Hence it would be worthwhile to theoretically predict the stability, $\pi^*\leftarrow\pi$ spectra, ionization potential, electron affinity, and half-wave reduction potential of the hydrocarbons **1**—**4**.

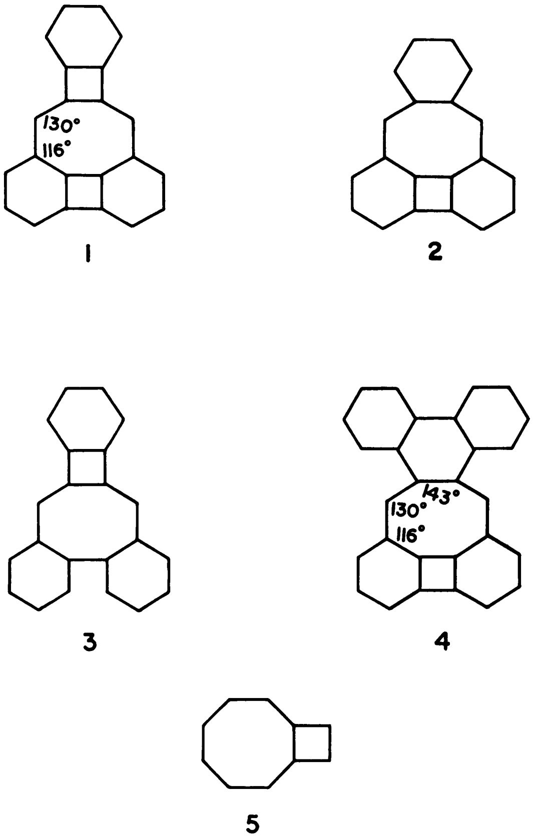

Fig. 1. Molecules studies.
1: Benzo[3′,4′]cyclobuta[1′,2′:6,7]cycloocta[1,2,3,4-*def*]biphenylene (**1**).
2: Benzo[6,7]cycloocta[1,2,3,4-*def*]biphenylene (**2**).
3: Dibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-f]cyclooctene (**3**).
4: Biphenyleno[8′,1′:4,5,6,7]cycloocta[1,2-*l*]phenanthrene (**4**).
5: Bicyclo[6.2.0]decapentaene (**5**).

Methods and Parameter

The method has been described elsewhere.[6] Only the salient features are described herein. The resonance integrals, β_{ij} were calculated by the following methods: (I) In the first method, designated as SCF(a), β_{ij} was estimated using the method of Lo and Whitehead;[7] (II) in the second one, designated as SCF(b), β_{ij} was given a value of -1.7901 eV proposed by Chung and Dewar[8] and modified by Birss and Das Gupta.[9] In the SCF(a) and SCF(b) methods the integrals, β_{ij} were not varied at each iteration; (III) the third method, designated as SCF(c) method was due to Dewar and Harget[10] and (IV) fourth one was due to Yamaguchi et al.[11] In these two methods the integrals, β_{ij}, the bond lengths (r_{ij}) and the two center two electron repulsion integrals (Υ_{ij}) for bonded atoms were adjusted according to the following relations:

In the SCF(c) method[10] the relations used were

$$r_{ij}(\text{Å}) = 1.512 - 0.174\, p_{ij} \tag{1}$$

$$\beta_{ij} = -6.927\, S_{ij} \tag{2}$$

where p_{ij} is the π-bond order and S_{ij} is the overlap integral between $2p_\pi$ Slater-type of orbitals.

In the SCF(d) method[11] the relations used were

$$r_{ij}(\text{Å}) = 1.520 - 0.186\, p_{ij} \tag{3}$$

$$\beta_{ij} = \beta_o \exp[a(r_o - r_{ij})] \tag{4}$$

where r_o=1.397 Å, a=−1.7 Å^{-1} and β_o is the resonance integral of benzene. The value of β_o decreased as the number of ring[12] increased.

For the calculation of bond lengths in the SCF(a) and SCF(b) methods the bond order–bond length relations (Eq. 5), due to Dewar and Gleicher[13] was used.

$$r_{ij}(\text{Å}) = 1.504 - 0.166\, p_{ij} \tag{5}$$

One-center two-electron repulsion integrals Υ_{ii} were calculated using the relation (Eq. 6) of Pariser[14]

$$\Upsilon_{ii} = I_i - A_i \tag{6}$$

where I and A represent the valence state ionization potential and electron affinity of carbon atoms respectively. The values have been taken from the work of Hinze and Jaffe.[15] The values of Υ_{ii} and I for carbon atoms are 11.136 and 11.16 eV respectively.

Except for SCF(d) method the two-center two-electron repulsion integrals, Υ_{ij} were evaluated using the method of Ohno[16] and for SCF(d) method the formula of Mataga and Nishimoto[17] was used. In the SCF(c) and SCF(d) methods the values Υ_{ij} were also not varied for nonbonded centers, but were kept at the values calculated from the initial geometry of the molecules which were assumed to be planar with ideal geometry and bond lengths equal to 1.40 Å.

Spectral transitions have been predicted by both SCF and configuration interaction (CI) methods. The final vectors, resonance integrals and two-center two-electron repulsion integrals obtained at the end of SCF(d) method were transferred in the CI procedure. The value of β_o used in the SCF(d) method was −2.15 eV.[18] In the CI procedure the configurations arising from one-electron excitation has been considered. Except molecule **2** ten highest occupied and ten lowest unoccupied orbitals and for molecule **2** all the occupied and unoccupied orbitals have been considered.

Results and Discussion

Charge Density and Bond Length. All the hydrocarbons **1**—**4** are alternant hydrocarbons. Hence calculated charge densities on each carbon atom is unity. Except molecule **3** all have biphenylene nucleus. The calculated bond lengths of the benzene rings of the biphenylene moiety have aromatic character lying between 1.39 and 1.41 Å. All the hydrocarbons have one eight-membered ring where bond length alternation exists and the bonds have alternately single bond and double bond character. However, the common bonds with the six-membered ring of biphenylene and eight-membered ring have aromatic character. But the common bond between eight-membered ring and six-membered ring other than the biphenylene moiety of molecules **2** and **4** has single-bond character and the predicted bond length is equal to 1.45 and 1.46 Å for these molecules respectively. This suggests that the π-electrons are localized here. In the biphenylene moiety (**1**, **2**, and **4**) the bonds joining the two six-membered rings have single bond character and the length lies between 1.48—1.49 Å same as in the biphenylene itself. The bond length joining the two six-membered rings (molecule **3**) has also single-bond character having length equal to 1.46—1.47 Å. In the molecules **1** and **3** there is a four-membered ring attached in between the eight-membered and six-membered rings. The bond common to the four-membered and six-membered ring has aromatic character with bond length 1.41 Å and the other three bonds of the four-membered ring have single bond character (1.46 Å). Thus π-electrons are not delocalized in this region of the molecules.

$\pi^* \leftarrow \pi$ Spectra. Table 1 presents the theoretical and experimental spectral transitions along with the oscillator strengths (f). The theoretical results have been predicted using the SCF methods and CI procedure. The oscillator strengths were obtained from the relation[19]

$$f = 1.095 \times 10^{-5} \bar{\nu}\, \mu^2 \tag{7}$$

where $\bar{\nu}$ is the transition energy in (cm^{-1}) and μ is the dipole length (in Å) for the corresponding transition.

Literature survey shows that only molecules **1** and **3** have experimental spectral transitions. The experimental spectra of the molecule **1** have a large number of peak maxima many of which are not clearly resolved. Therefore the best one can expect in a comparison of the theoretical and observed transition energies is a general correlation over quite wide spectral regions. Table 1 displays this comparison. In addition to the observed peak maxima included in the table there is a number of observed maxima at low transition energies for which no theoretical counterpart was found. Table 1 also contains the theoretical spectral transitions of molecule **3** along with

Table 1. $\pi^* \leftarrow \pi$ Spectral Transitions [ΔE(eV)] of Molecules **1** and **3**

Symmetry	Exptl. transitions		Present work									
			SCF(a)		SCF(b)		SCF(c)		SCF(d)		CI	
	ΔE	$\log \varepsilon$	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
	Ref. 26						Molecule **1**					
B_2	2.41	3.12	2.20	0.00	2.20	0.00						
	2.79	3.31					2.89	0.01			2.65	0.02
B_2	3.11	4.02									3.06	0.00
	3.30	3.91	3.29	0.29	3.27	0.28	3.69	0.29	3.45	0.18	3.17	0.02
A_1	3.85	4.04	3.86	0.82	3.84	0.82			3.91	0.86	3.95	0.02
B_2	4.27	4.83	4.63	0.00	4.60	0.00	4.27	0.36	4.35	0.39	4.31	0.74
A_1	4.82	4.56	5.13	0.05	5.11	0.05			4.80	0.06	4.82	0.02
B_2	5.56	4.51	5.55	0.47	5.52	0.47	5.41	0.00	5.54	0.51	5.70	1.61
	Ref. 27						Molecule **3**					
A_1	3.52	3.96	3.84	0.99	3.83	0.98			3.88	0.99	3.69	0.002
B_2	4.44	4.66	4.37	0.46	4.36	0.46	4.32	0.41	4.34	0.45	4.42	0.96
B_2	4.71	4.53	5.17	0.09	5.14	0.09	4.66	0.44	4.98	0.08	4.83	0.02

Table 2. $\pi^* \leftarrow \pi$ Spectral Transitions [ΔE(eV)] of Molecules **2** and **4**

Symmetry	SCF(a)		SCF(b)		SCF(c)		SCF(d)		CI	
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
					Molecule **2**					
B_2	2.86	0.08	2.82	0.08	2.21	0.14			2.68	0.00
B_2	3.10	0.24	3.09	0.24	3.32	0.09	3.11	0.27	2.97	0.13
B_2	3.86	0.09	3.85	0.09	3.76	0.26	3.97	0.11	3.80	0.50
A_1	4.19	0.90	4.18	0.90	4.61	0.81	4.29	0.91	4.50	1.61
A_1	5.25	0.01	5.25	0.01	5.51	0.01	5.07	0.01	5.13	0.04
B_2	5.44	0.36	5.41	0.36	5.59	0.36	5.24	0.35	5.40	1.16
					Molecule **4**					
B_2	2.96	0.11	2.94	0.11	2.60	0.07	3.31	0.26	3.11	0.08
A_1	4.00	0.82	3.99	0.81	4.40	0.77	3.98	0.82	3.95	1.57
B_2	4.82	0.00	4.80	0.00	4.45	0.13	4.65	0.00	4.65	0.11
A_1	5.26	0.15	5.24	0.15	5.48	0.14	5.26	0.10	5.30	0.14
B_2	5.38	0.29	5.35	0.29	5.46	0.27	5.38	0.31	5.39	1.36

experimental ones. In all these molecules (**1** and **3**) the results predicted by the CI method is better than those predicted by the SCF methods. Table 2 contains the theoretical transitions of the molecules **2** and **4** for which no experimental transitions are available in the literature.

Molecular Properties such as Ionization Potentials, Electron Affinities, Half-Wave Reduction Potentials, and Stability. According to Koopmans' theorem[20] ionization potential (IP) could be represented by the highest occuopied orbital energy (HOOE). Electron affinity (EA) could also be represented by the lowest unoccupied orbital energy (LUOE). It has been found[21] that the values obtained by this method are 1 or 2 eV higher than the experimental values of IP and EA. Hence a correction term is to be added to the HOOE and LUOE in order to get the correct value of IP and EA respectively. Correction terms are displayed in Table 3. The half-wave reduction potential ($E_{1/2}$) has been evaluated from the relation[22] (Eq. 8) in the context of SCF(c) method

$$E_{1/2} = -0.833\, e_j - 3.46 \tag{8}$$

where e_j is the LUOE. The values of IP, EA, and $E_{1/2}$ are presented in Table 4. For lack of experimental value we can not compare our results with

Table 3. Values of Correction Terms, '*C*' and '*D*'

Method	Value of $C^{a)}$	Value of $D^{a)}$
SCF(a)	$1.29^{b)}$	$1.49^{c)}$
SCF(b)	$1.28^{b)}$	$1.50^{c)}$
SCF(c)	1.88 (Ref. 22)	$1.28^{c)}$
SCF(d)$^{d)}$	1.06	1.90

a) The values are in eV. b) The values are due to difference between the HOOE and experimental value of IP of some standard molecule. Here it is chrysene the value of which is 8.01 eV (Ref. 29). c) The values are due to difference between the LUOE and experimental value of electron affinity of some standard molecule. Here it is chrysene. The value of which is 0.397 eV (Ref. 30). d) Ref. 31.

Table 4. Ionization Potential (IP), Electron Affinity (EA), and Half-Wave Reduction Potential ($E_{1/2}$) of the Hydrocarbons **1**—**4**

Molecule	Method[a)]	IP/eV	EA/eV	$-E_{1/2}$/V
1	a	7.68	0.73	
	b	7.68	0.72	
	c	7.41	0.62	1.88
	d	7.53	0.81	
2	a	7.05	1.36	
	b	7.06	1.34	
	c	6.95	1.08	1.49
	d	6.96	1.35	
3	a	7.66	0.74	
	b	7.67	0.74	
	c	7.40	0.63	1.87
	d	7.51	0.80	
4	a	7.31	1.09	
	b	7.32	1.08	
	c	6.09	0.94	1.61
	d	7.17	1.14	

a) a, b, c, and d represent SCF(a), SCF(b), SCF(c), and SCF(d) methods respectively.

Table 5. Heat of Atomization (ΔH_a) and Bond Energies of the Hydrocarbons **1**—**4**

Molecule	Method[a)]	ΔH_a/eV	Bond energy/eV	
			π-bond	σ-bond
1	a	184.904	32.738	98.916
	b	185.151	32.226	99.675
	c	185.736	32.002	100.484
2	a	169.955	28.780	87.925
	b	170.173	28.323	88.600
	c	170.759	28.415	89.095
3	a	190.043	32.666	95.253
	b	190.264	32.156	95.983
	c	190.624	31.950	96.549
4	a	237.655	42.094	124.561
	b	237.956	41.440	125.516
	c	238.498	40.963	126.535

a) a, b, and c represent SCF(a), SCF(b), and SCF(c) methods respectively.

Table 6. Resonance Energy (E_{R}), Resonance Energy per Carbon-Carbon Bond (E_{R}/C–C), Resonance Energy per π-Electron (RE/PE) of the Molecules Studied Here

Property[a)]	Molecule			
	1	**2**	**3**	**4**
E_{R} (a)	7.533	6.161	7.610	9.879
E_{R} (b)	7.497	5.930	7.589	10.025
E_{R} (c)	2.197	1.457	2.596	3.270
E_{R} (d)	1.239	0.428	1.754	2.128
E_{R} (e)	0.2476	0.0607	0.6551	0.6538
E_{R}/C–C(a)	0.2938	0.2567	0.2927	0.2906
E_{R}/C–C(b)	0.2776	0.2471	0.2919	0.2948
E_{R}/C–C(c)	0.0814	0.0607	0.0998	0.0962
E_{R}/C–C(d)	0.0459	0.0179	0.0675	0.0626
RE/PE(e)	0.0113	0.0028	0.0297	0.0234

a) a, b, c, d, and e represent SCF(a), SCF(b), SCF(c), Dewar-de Llano and Hess, and Schaad method respectively. For a, b, c, and d E_{R} is in eV and for e it is in β.

Table 7. Criteria of Aromaticity or Stability of Hydrocarbons

Method[a)]	Range of E_{R}/C–C or RE/PE for the hydrocarbons to be aromatic
a	0.26—0.31
b	0.25—0.30
c	0.075—0.112
d	0.041—0.095
e	0.03—0.04

a) a, b, c, d, and e represent the SCF(a), SCF(b), SCF(c), Dewar-de Llano and Hess, and Schaad methods respectively. (Refs. 25 and 32).

experimental ones.

Stability or aromaticity of the molecules has been studied using the criteria of resonance energy (E_{R}) and resonance energy per carbon–carbon bond (E_{R}/C–C) or resonance energy per π-electron (RE/PE). The values of E_{R} of the hydrocarbons have been obtained using the methods of Lo and Whitehead,[7)] Chung and Dewar,[8)] Dewar and de Llano,[23)] Dewar and Harget,[10)] and Hess and Schaad.[24)]

The values of heat of atomization (ΔH_a) and bond energies of the hydrocarbons have been presented in Tables 5 and 6 contains the values of E_{R}, E_{R}/C–C, and RE/PE of the molecules. The hydrocarbons belong to semibenzenoid[25)] type of compounds. The criteria for stability of this type of hydrocarbons with respect to E_{R}/C–C or RE/PE have been discussed by Das Gupta and Das Gupta and are displayed in Table 7.

The molecule **1** is thermally stable[26)] and melts without decomposition at 192—193 °C. It exhibits diamagnetic ring current suggesting that it might be aromatic. From Table 6 E_{R} and E_{R}/C–C bond calculated by SCF(a), SCF(b), and SCF(c) methods and Dewar-de Llano method[23)] suggest also that the molecule might be aromatic. On the other hand resonance energy and RE/PE (0.0113) calculated by Hess and Schaad method predict it to be not aromatic. However, stability[25)] predicted by Dewar-de Llano method is better than any other methods.

Resonance energy, E_{R}/C–C bond calculated by all the SCF methods[7,8,10,23)] and RE/PE suggest that the molecule **2** might be unstable one. It predicts paramagnetic ring current[26)] which points it out to be not an aromatic compound. Synthesis of **2** has not yet been found in the literature.

Hydrocarbon **3** has been synthesized by Garratt et al.[27,28] They have also studied the properties. According to them the molecule is an aromatic one which is in agreement with the results obtained from the values of E_R, E_R/C–C bond calculated by the SCF methods and E_R and RE/PE calculated by the Hess and Schaad method.

Molecule **4** is an interesting one. It has not yet been synthesized. However, ring current criteria[26] and E_R, E_R/C–C suggest it to be aromatic and stable compound. As in molecule **1**, RE/PE predicts it to be not aromatic.

Biphenylene is an aromatic compound and hydrocarbon **5** is not. The molecules **1**—**4** either contain biphenylene or molecule **5** or both in their nucleus. But aromatic character or not of these molecules is not governed by the presence of biphenylene or molecule **5**. As for example **1** and **3** contain molecule **5** in their nucleus. From the above discussion it is clear that both the molecules **1** and **3** are aromatic. Again **1**, **2**, and **4** contain biphenylene moiety. But as discussed earlier it is clear that the hydrocarbons **1** and **4** are aromatic and **2** is not. Although molecule **4** has not yet been synthesized still we expect that either it or some of its derivatives will be synthesized in near future.

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