π-Electron Structure of Some Nonbenzenoid Hydrocarbons Using β-Variable Method

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The molecules pentaleno[*def*]heptalene, cyclohept[*fg*]acenaphthylene, naphth[*cde*]azulene and cyclohept[*bc*]-acenaphthylene have been studied using β-variable methods proposed by Dewar *et al.* and Yamaguchi *et al.* The predicted results are compared with experimental values and with other theoretical results.

The Pariser-Parr-Pople (PPP) semiempirical self-consistent antisymmetrized molecular orbital (SCF ASMO) method[1] is very useful in predicting the electronic structure of conjugated systems. From time to time the semiempirical nature of the method has been changed by several authors by changing the mode of evaluation of certain integrals. Among these are Nishimoto and Forster[2], Yamaguchi *et al.*[3] and Dewar and co-worker[4] who used exchange integrals $\beta_{\mu\nu}$ as functions of bond order $p_{\mu\nu}$ or bond length $r_{\mu\nu}$. These methods are known as the "β-variable" method. The former two methods were developed to calculate the electronic transitions and the latter one to calculate the ground state properties of conjugated systems. But we[5] have successfully applied the β-variable technique of Yamaguchi *et al.*[3] and Dewar *et al.*[4] to predict the electronic transitions of many nonbenzenoid hydrocarbons. In this paper we are going to report the results of calculations on some nonbenzenoid hydrocarbons shown in Fig. 1. However, these molecules were studied by several authors[6] using a different set of parameters. Our aim is to see how far the results calculated by the "β-variable" technique are in agreement with the experimental results.

Geometry of the Molecules. Although the β-variable technique is insensitive to the assumed geometry of the molecule, still for molecules **1**[7] and **2**[8] we used the actual structure and for the other two we assigned the

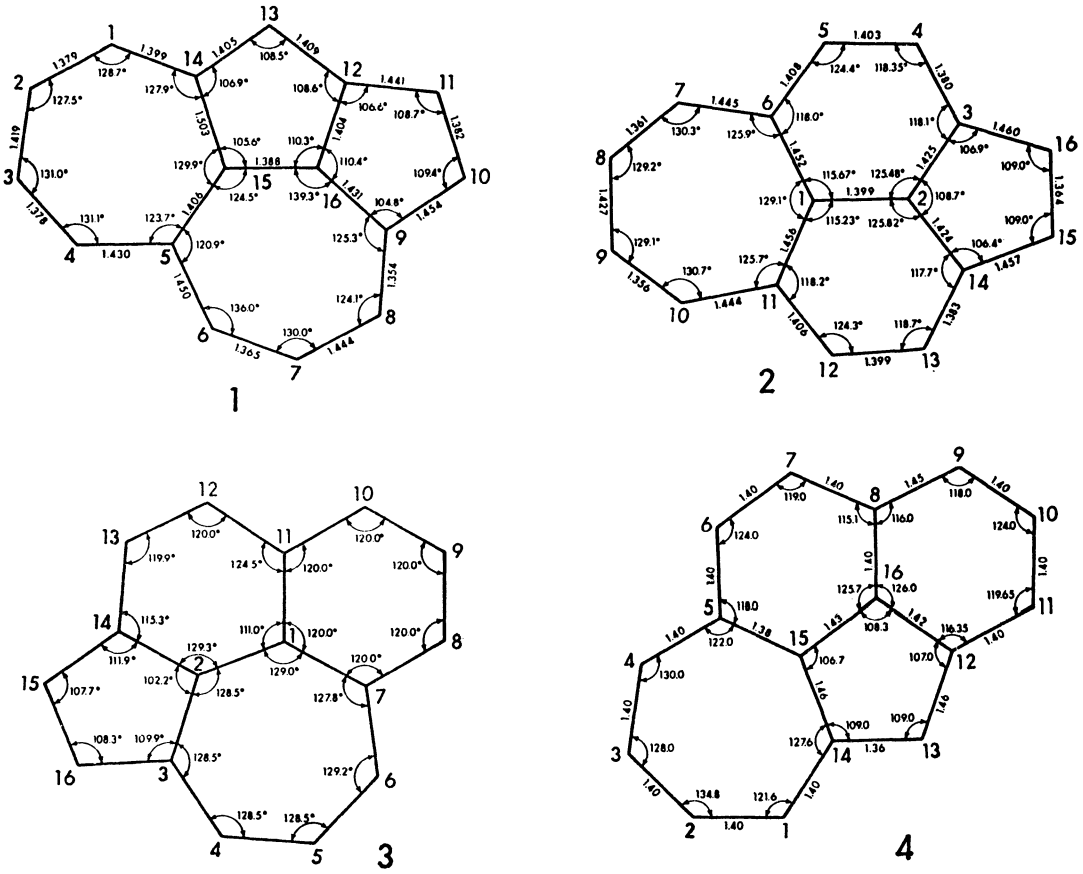

Fig. 1. Molecules.
(**1**) Pentaleno[*def*]heptalene. (**2**) Cyclohept[*fg*]acenaphthylene. (**3**) Naphth[*cde*]azulene.
(**4**) Cyclohept[*bc*]acenaphthylene.

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TABLE 1. $\pi^*\leftarrow\pi$ TRANSITIONS (eV) AND OSCILLATOR STRENGTHS (f)

Molecule	Symmetry	Present work a eV	a f	b eV	b f	Experiment** eV	Experiment** log ε	Other work c eV	c f*	d eV	d f	e eV	e f	g eV	g f
1				1.89	0.06	1.8	2.1			1.81	0.004				
		2.35	0.15			2.2	3.1	2.2	0.016	2.38	0.05				
		3.27	0.36	2.84	0.45	2.8	3.8	2.9	0.21	3.11	0.3				
				3.00	0.39			3.0	0.55						
										3.20	0.09				
		3.32	0.42												
		3.41	0.48	3.47	0.64	3.4		3.4	0.53	3.66	1.1				
		3.62	0.44												
		3.96	0.27	3.97	0.39			3.8	0.37	4.07	0.9				
				4.19	0.36			4.1	0.31	4.30	0.2				
		4.51	0.28	4.24	0.24	4.3		4.3	0.22	4.43	1.1				
		4.93	0.33	4.91	0.46	4.9		5.0	0.20						
2						2.5	3.6			2.59	0.1			2.504	0.002
														2.553	0.056
										2.89	0.04				
	B_2	3.36	0.24	3.18	0.27	3.0		2.9	0.26	3.14	0.3	2.98	0.28	2.986	0.115
								3.1	0.31			3.15	0.026		
								3.3	0.98			3.32	0.066		
	B_2	3.91	0.40	4.06	0.51	3.8	4.6	3.9	0.43	3.45	1.5	3.87	0.025	3.998	1.715
		4.31	0.41	4.28	0.42			4.2	0.39	4.34	0.1			4.187	0.207
								4.4	0.51	4.58	0.03	4.50	0.96		
												4.67	0.16		
	A_1			4.59	0.0			4.6	0.0						
		4.86	0.02	4.83	0.0	4.8	4.3	4.7	0.01	4.76	1.2	5.09	0.87		
		4.94	0.01	5.11	0.0			5.0	0.0			5.13	0.010		
		5.03	0.44									5.26	0.021		
	B_2	5.58	0.23	5.58	0.25			5.4	0.01			5.64	0.021		
	B_2	5.80	0.0	5.92	0.0	5.8		5.84*	0.31			5.68	0.040		
3				2.69	0.42	2.2	2.8	2.6	0.46	2.10	0.08			1.803	
		3.10	0.43	3.17	0.25	3.0	3.4	2.9	0.24	2.89	0.3			2.792	
														3.496	
		3.43	0.21	3.85	0.72	3.6	3.9	3.7	0.73	3.61	0.6			3.722	
		3.92	0.65					3.8	0.35	3.90	0.1				
		4.03	0.33	3.99	0.42	4.0		4.1	0.49					4.153	
								4.2	0.18						
				4.27	0.55					4.31	0.2				
		4.47	0.55	4.40	0.22	4.6	4.5	4.7	0.42	4.51	1.3				
		4.50	0.19												
4						2.4	2.9			2.23	0.1			1.949	
								2.8	0.24						
		3.24	0.68	2.85	0.67	2.9	3.8	2.9	0.77	2.90	0.5			2.746	
		3.39	0.24	3.21	0.32	3.4		3.5	0.21					3.674	
		3.65	0.23	3.69	0.32					3.78	0.3				
		3.98	0.49	4.00	0.51			3.9		3.83	0.07			3.910	
		4.56	0.14	4.35	0.58	4.3	4.5	4.3	0.49	4.18	1.2			4.118	
				4.44	0.15			4.4	0.16						
										4.37	0.8				
		4.67	0.57	4.64	0.31			4.6	0.32						
		4.98	0.25	5.02	0.16	5.0	4.8	5.0	0.11	4.61	0.4				
		5.08	0.11					5.2	0.37						

(a) Present work using the methods of Dewar and Harget.[4] (b) Present work using the method of Yamaguchi *et al.*[3] (c) Ref. 6(a). (d) Ref. 6(b). (e) Ref. 6(d). (g) Ref. 6(c).

* and values of oscillator strengths (f) in Item c not included in Ref. 6(a).

** Experimental spectra: Molecule **1**, Ref. 6(b) and 18(a). **2**, Ref. 6(b) and 18(b). **3**, Ref. 6(b) and 18(c). **4**, Ref. 6(b) and 18(d).

geometry shown in Fig. 1 for our calculation.

Parameters. As usual the two-centre, two-electron repulsion integrals $\gamma_{\mu\nu}$ were computed from the initial geometry of the molecules using the formula of Ohno[9] for the method of Dewar and Harget and for the method of Yamaguchi *et al.* the formula of Mataga and Nishimoto[10] was used. For both the methods the integrals between non-bonded atoms were not varied throughout the calculation.

The one-centre, two-electron repulsion integrals were evaluated from the valence-state ionization energy I_μ (11.16 eV)[11] and electron affinity A_μ (0.026 eV)[11] of the carbon atom using the relation

$$\gamma_{\mu\mu} = I_\mu - A_\mu = 11.134 \text{ eV}.$$

For bonded atoms, $\gamma_{\mu\nu}$ and core resonance integrals $\beta_{\mu\nu}$ were adjusted at each iteration on the basis of bond-order bond length relations. For the method of Yamaguchi *et al.* the relations are

$$r_{\mu\nu}(\text{Å}) = 1.520 - 0.186 p_{\mu\nu}$$

and

$$\beta_{\mu\nu} = \beta_0 \exp\left[a(r_0 - r_{\mu\nu})\right]$$

where r_0 is the bond length of benzene, a is equal to 1.7 Å^{-1} and β_0 has been taken to be equal to -2.15 eV.[5] For the method of Dewar and Harget the relations are

$$\beta_{\mu\nu} = -6.927 S_{\mu\nu}$$

and

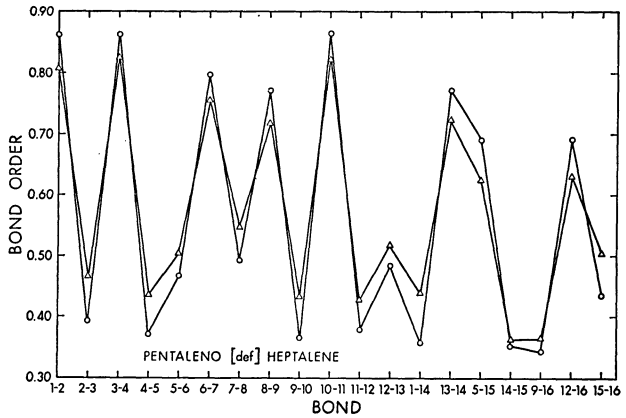
$$r_{\mu\nu}(\text{Å}) = 1.512 - 0.174 p_{\mu\nu}$$

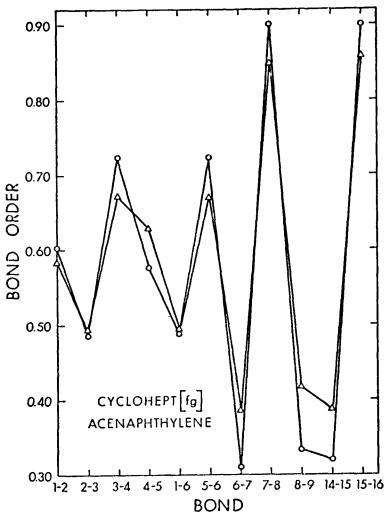
where $S_{\mu\nu}$ is the overlap integral between two π_{2p} orbitals with orbital exponent 1.59. In both the methods $\beta_{\mu\nu}$ for non-bonded atoms was equal to zero.

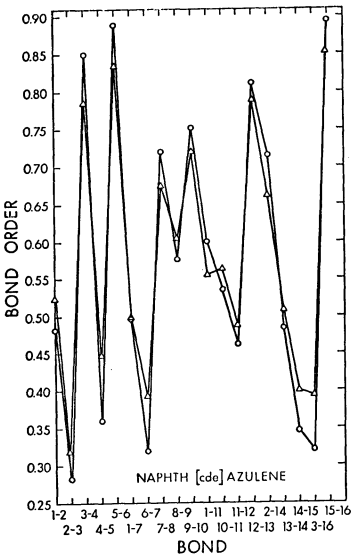
The starting vectors were Hückel MO coefficients and the interation was continued until the self-consistency was achieved within the desired degree of accuracy.

Results and Discussion

Table 1 contains the calculated $\pi^* \leftarrow \pi$ transitions along with the oscillator strengths and experimental results. For comparison we have also included in the table the other theoretical results. Since the molecules are not simple it is very difficult to make point-to-point correlations. However, attempts have been made to do so. It is clear that except for a few cases the present work in which case no configuration interaction was performed is in good agreement with experiment and is also comparable to other theoretical results where, in some cases, configuration interaction was done.







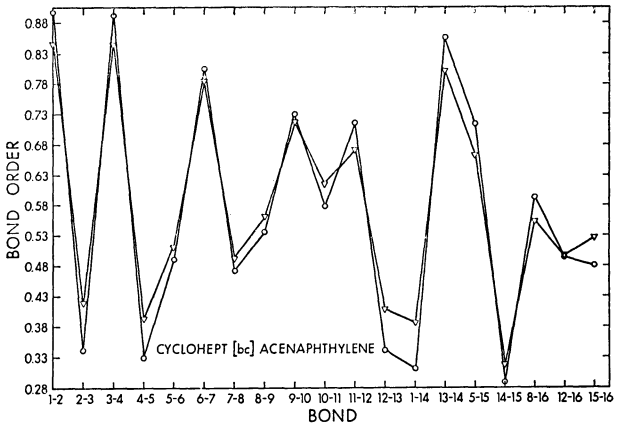


Fig. 2. Variation of bond order with bonds (SCF(a)—○; SCF (b)—△).

Figure 2 represents the variation of bond order with

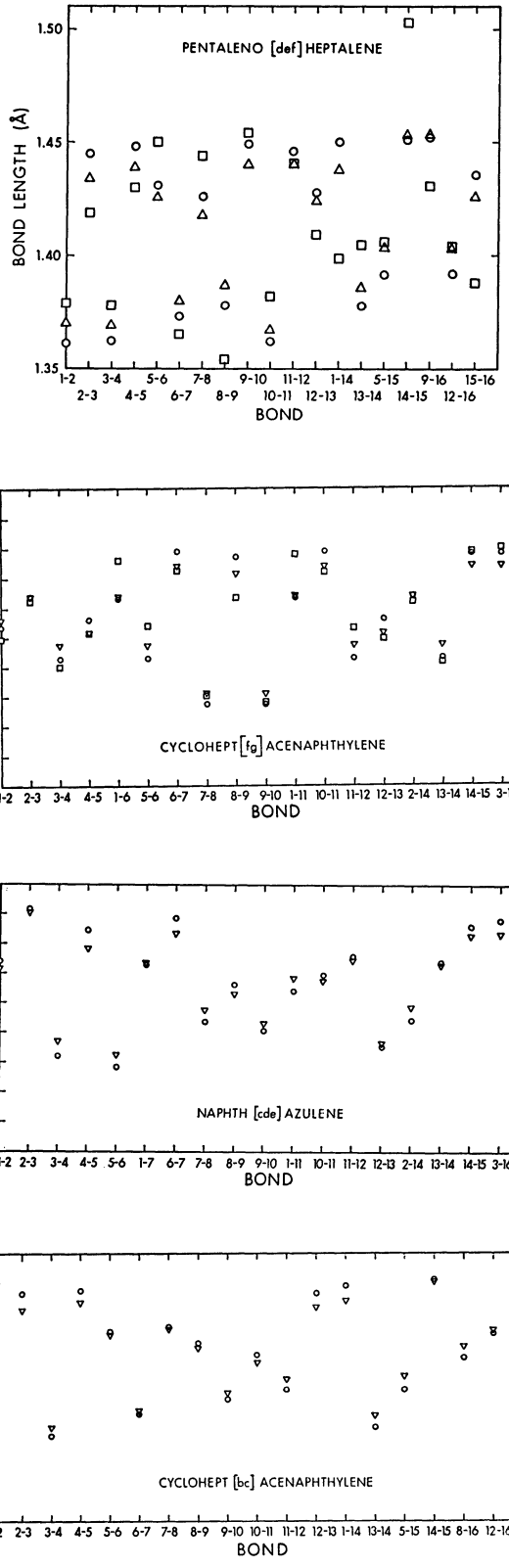


Fig. 3. Comparison between predicted bond lengths and experimental bond lengths (SCF (a)—○; SCF (b)—△; experimental—□).

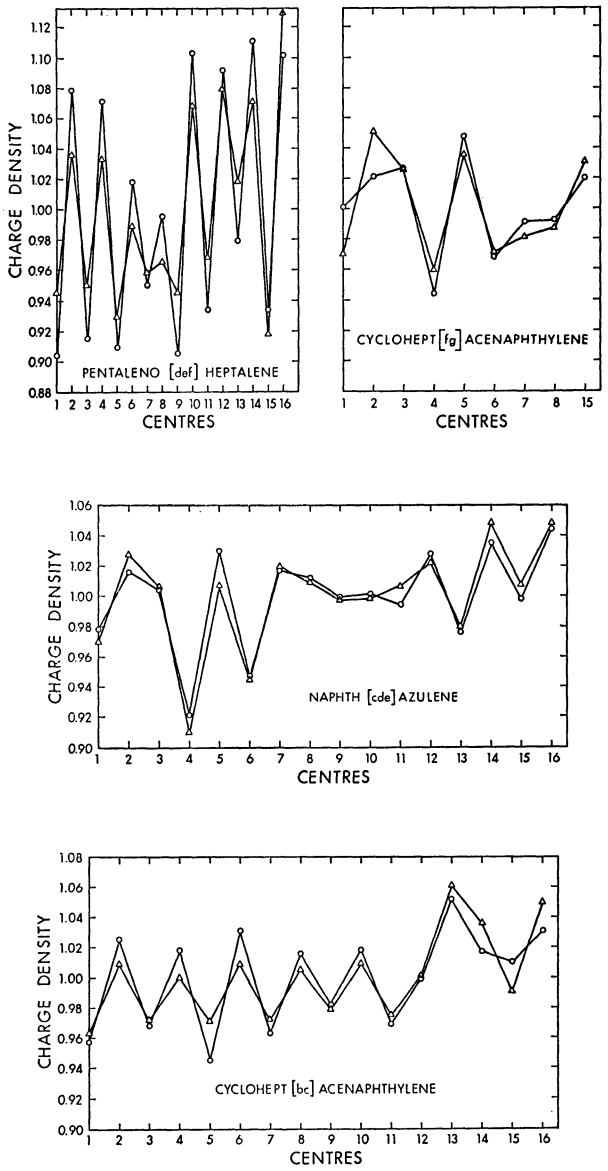


Fig. 4. Variation of charge density with centres (SCF(a) —○; SCF (b)—△).

bond. It is seen that the two methods maintain almost the same trend of variation in all the cases. Figure 3 compares the bond length calculated by the different methods. Experimental values, where available are also included in the figure. It is evident from Fig. 3 that in all the molecules the bond lengths calculated by the two methods are in very good agreement with each other. Except for a few cases, the agreement between the predicted bond lengths and the experimental values are good. Figure 4 represents the variation of charge density with different centres. Here also the two methods maintain the same trend.

It will be clear from the predicted bond lengths that when a bond is common to two different types of rings then the bond has a tendency to have single bond character. This is pronounced when the bond is common to five and seven membered rings and less pronounced when the bond is common to a six membered ring and seven or five membered ring. The range is from 1.43 to 1.46 Å. But the bond C_{15}–C_{16} of the molecule cyclohept[*bc*]acenaphthylene has a value of 1.422 Å calculated by the method of Yamaguchi *et al.* Although the bond is common to two different types of

TABLE 2. CALCULATED VALUES OF IONIZATION POTENTIAL, ELECTRON AFFINITY AND DIPOLE MOMENT

Molecule	Ionization potential (eV)				Electron affinity (eV)				Dipole moment (D)		
	Uncorrected		Corrected		Uncorrected		Corrected				
	a	b	b	c	a	b	b	c*	a	b	c
1	−8.99	−8.16	7.10	7.36	−2.21	−2.96	1.06	−2.45	1.75	2.68	1.51
2	−9.16	−8.45	7.39	7.61	−2.16	−2.82	0.92	−2.44	1.26	2.27	2.06
3	−9.16	−8.47	7.41	7.54	−2.13	−3.01	1.11	−2.23	1.09	1.77	1.70
4	−9.13	−8.34	7.28	7.42	−2.12	−2.81	0.91	−2.48	0.59	1.00	0.87

(a) Present work using the methods of Dewar and Harget. (b) Present work using the method of Yamaguchi *et al.* (c) Ref. 6(a). (* Measure of half-wave reduction potential)

rings, still its single bond nature is not exhibited as much. A similar situation is also seen in the case of C_1–C_2 bond, the value being 1.423 Å calculated by the method of Yamaguchi *et al.* of molecule **3**. This may be due to the fact that these molecules have three consecutive bonds, common to two different types of rings. As a result the tendency of single bond character for the middle one, C_1–C_2 for molecule **3** and C_{15}–C_{16} for molecule **4**, is not so pronounced. Again when a bond is in common to two of the same type of rings such as two seven membered, five membered and six membered rings the bond has a predicted bond length almost equal to that of an aromatic C–C bond. The examples are C_5–C_{15} (1.392, 1.404 Å) and C_{12}–C_{16} (1.392, 1.403 Å) of pentaleno[*def*]heptalene, C_1–C_2 (1.407, 1.412 Å) of molecule **2**, C_1–C_{11} (1.408, 1.417 Å) of naphth[*cde*]-azulene and C_8–C_{16} (1.409, 1.417 Å) of cyclohept[*bc*]-acenaphthylene. Moreover if we examine the predicted peripheral bond lengths of all the molecules, an interesting feature will be observed. The predicted peripheral bond lengths of one of the seven and five membered rings of pentaleno[*def*]heptalene has alternate single bond and double bond character. Thus the bonds C_{14}–C_1, C_2–C_3, C_4–C_5, C_9–C_{10}, and C_{11}–C_{12} have single bond character whereas the bonds C_1–C_2, C_3–C_4, and C_{10}–C_{11} have double bond character. The peripheral bonds of the other seven membered ring (C_5–C_6, C_6–C_7, C_7–C_8, and C_8–C_9) and five membered ring (C_{12}–C_{13} and C_{13}–C_{14}) have more or less bond length equal to an aromatic C–C bond length. Thus the peripheral bonds of this molecule are of two types— in one case the bonds are localized and in the other case they are delocalised. This is more clearly observed in the method of Yamaguchi *et al.* A similar situation is also seen in the case of other molecules. Thus the peripheral bonds of the naphthalene ring of molecule **2** are delocalised whereas those of five and seven membered rings are localized. In the case of naphth[*cde*]-azulene and cyclohept[*bc*]acenaphthylene the peripheral bonds of five and seven membered rings have alternate single and double bond character. Moreover the peripheral bonds of naphthalene moiety of these molecules are not predicted to be of similar type. It is found that the peripheral bonds of one of the benzene rings of the naphthalene nucleus is more delocalised than the other one which is joined with both five and seven membered rings. Thus the peripheral bonds of these molecules are either aromatic or polyolefinic in nature. Hence any definition of aromacity based on the global π-electron properties such as delocalization energy, magnetic properties or the standard deviation of bond length[12] is not adequate for these types of molecules.

Ionization Potential, Electron Affinity and π-Dipole Moment. According to Koopmans' theorem[13] the highest occupied orbital energy and the lowest unoccupied orbital energy represent ionization potential and electron affinity respectively of a molecule. But ionization potential and electron affinity calculated in this way is 1 or 2 eV higher than the true value. Hence we have used a relation of Kunii and Kuroda[14] for the calculation of ionization potential (I.P.) and electron affinity (E.A.). The relations are

$$\text{I.P.} = -(\varepsilon_i + 1.06)\ \text{eV}$$

and

$$\text{E.A.} = -\varepsilon_j - 1.90\ \text{eV}$$

where ε_i and ε_j are respectively the highest occupied and lowest unoccupied orbital energy. Table 2 contains uncorrected and corrected ionization potential and electron affinity respectively along with other theoretical values calculated in a similar way. It is seen that the present work is in good agreement with other theoretical results.

Table 2 also contains calculated values of π-dipole moment of these molecules along with other results. The dipole moment of molecule **2** has been determined experimentally and it is 0.49 D.[15] Theoretical values for the π-dipole moment have been obtained by Birss and Das Gupta,[6a] 1.15 and 2.06 D, by Pullman *et al.*,[16] 1.0 D, and by Francois *et al.*,[17] 0.9 D, compared with the present value of 1.26 and 2.27 D.

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