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Theoretical Study of Phenalenium Systems

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Phenalenium systems have been studied using PPP method modified by Dewar et al. Ground state properties and other properties such as $\pi^*\leftarrow\pi$ spectra, ionization potential, electron affinity, half-wave reduction potential, pi-dipole moment have been predicted and correlated with experimental ones where available. Stability and resonance energy have also been discussed.

In recent years the chemistry of nonbenzenoid aromatic hydrocarbons involving the contribution of a dipolar structure in its ground state has created much interest. Azulene and its derivatives constitute the simplest case belonging to this class and they are recognized as a class of condensed and fully conjugated cyclic hydrocarbons exhibiting aromatic character with effective contribution of dipolar structures in the ground state.[1] Phenalenium systems also belong to this class having dipolar structure and they are very much interesting to synthetic organic chemists and theoretical chemists. In this paper we like to report the results of our calculations based on Pariser and Parr[2] and Pople[3] method modified by Dewar et al.[4] on the molecules (**1**—

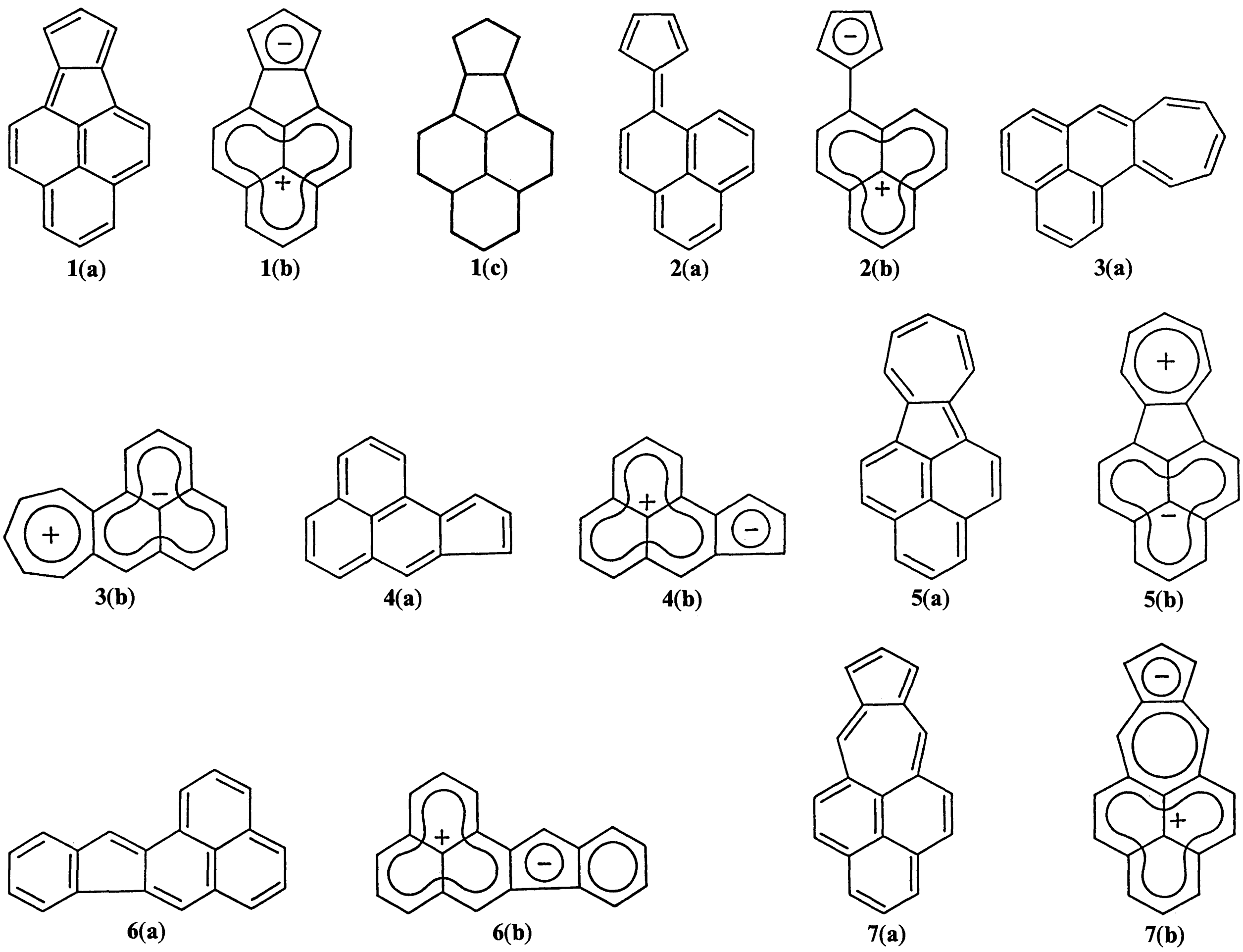
1(a) **1(b)** **1(c)** **2(a)** **2(b)** **3(a)** **3(b)** **4(a)** **4(b)** **5(a)** **5(b)** **6(a)** **6(b)** **7(a)** **7(b)**

Fig. 1. Molecules studied.
Molecule **1.** a) Pentaleno[4,5,6-*cd*]phenalene, b) Dipolar form, and c) Perturbed [16]annulene.
Molecule **2.** a) Pentaphenafulvalene, b) Dipolar structure of (a).
Molecule **3.** a) Cyclohepta[*a*]phenalene, b) Dipolar structure of (a).
Molecule **4.** a) Cyclopenta[*a*]phenalene, b) Dipolar structure of (a).
Molecule **5.** a) Azuleno[1,2,3-*cd*]phenalene, b) Dipolar form of (a).
Molecule **6.** a) Indeno[2,1-*a*]phenalene, b) Dipolar structure of (a).
Molecule **7.** a) Azuleno [5,6,7-*cd*] phenalene, b) Dipolar structure of (a).

7) in Fig. 1 and predicting the ground state properties and other properties such as $\pi^* \leftarrow \pi$ spectra, ionization potential, electron affinity etc. and compare and correlate them with experimental results where available.

Although the molecule **1** has not yet been synthesized, its derivatives5) are known. Their properties suggest that molecule **1** might be treated as a novel example of a peripheral 16π-electron model.5b) Molecule **2**, pentaphenafulvalene is not known but its derivatives have been synthesized by Murata et al.6) The substantial pi-electron delocalization energy (5.83 β)7) of phenalenium cation suggests that the molecule pentaphenafulvalene (**2**) would be specially notable for its significant contribution of the resonance form (dipolar structure) and the molecule would have a high value of dipole moment. The molecules **5** and **7** are very much interesting because they contain azulene and phenalene rings and because of their unique electronic structures and their expected carcinogenic activities. The stable crystalline moss green azuleno[5,6,7-*cd*]phenalene (**7**)8) exhibits considerable carcinogenic activity.9) The molecule **5** has been synthesized and studied by Murata and co-workers.10) The molecules **3** and **4** nor their derivatives are known but the molecule **6** has been synthesized and studied by Reid.11) Some of the molecules have been theoretically studied (**1**,11) **2**,6) and **7**12,13)) with different sets of parameters.

Method and Parameters

The method used here is due to Pariser and Parr2) and Pople3) within the zero-differential overlap approximation. The standard notations are used for the necessary parameters.14) β_{ij} was calculated by the following four methods. SCF(a) due to the method of Lo and Whitehead.15) SCF(b): given a value of −1.7901 eV suggested by Chung and Dewar4a) and modified by Birss and Das Gupta.16) In SCF(a) and (b) β_{ij} was not changed at each iteration. SCF(c): due to Dewar and Harget4b) and SCF(d): due to Yamaguchi et al.17) In SCF(c) and (d) β_{ij}, r_{ij}, and γ_{ij} were adjusted at each iteration according to the following relations:

In SCF(c)4b) the relations used were

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

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

In SCF(d)17) the relations used were

$$r_{ij} = 1.520 - 0.186\,p_{ij}, \tag{3}$$

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

where β_o is the resonance integral of benzene, $a = -1.7\,\text{Å}^{-1}$ and r_o is the bond length of benzene. The value of β_o decreased as the number of rings18) increased.

In the SCF(a) and (b) the bond lengths were calculated using the relation of Dewar and Gleicher19) (Eq. 5)

$$r_{ij}\,(\text{Å}) = 1.503 - 0.166\,p_{ij}, \tag{5}$$

Y_{ii} were calculated using the relation of Pariser.20)

$$Y_{ii} = I_i - A_i. \tag{6}$$

The values of I and A have been taken from Hinze and Jaffe.21) The values of Y_{ii} and I for carbon atom are 11.136 and 11.16 eV respectively.

For SCF(d) Y_{ij} were evaluated using the formula of Mataga and Nishimoto22) and for other methods they were evaluated using the formula of Ohno.23) In SCF(c) and (d) the values Y_{ij} for non bonded centers, were not varied at each iteration but 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.

For the prediction of spectral transitions we have used 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) procedure were transferred in the CI method. The value of β_o used in SCF(d) was −2.15 eV.24) The configuration arising from one-electron excitation was considered. All the occupied and unoccupied orbitals were taken into consideration for the CI method.

Table 1. Correction Terms for IP and EA (in eV)

Method	Correction term for IP	Correction term for EA
SCF(a)	1.29a)	1.49b)
SCF(c)	1.88c)	1.28b)
SCF(d)	1.06d)	1.90d)

a) Difference between the |HOMO| and experimental value of IP of the standard molecule, chrysene (IP=8.01 eV (Ref. 28)). b) Difference between the |LUMO| and the experimental value of electron affinity of chrysene (EA=0.397 eV (Ref. 29)). c) Ref. 27. d) Ref. 30.

Table 2. IP, EA, $E_{1/2}$, and Pi-Dipole Moment of the Molecules Studied

Molecule	Method	IP/eV	EA/eV	$-E_{1/2}$/V	μ/D
1	SCF(a)	7.65	1.77		2.75
	SCF(c)	7.08	1.89	0.828	2.03
	SCF(d)	7.22	2.24		3.04
2	SCF(a)	7.60	1.74		3.84
	SCF(c)	7.30	1.44	1.194	2.14
	SCF(d)	7.49	1.74		3.63
3	SCF(a)	6.85	0.99		1.80
	SCF(c)	6.77	0.82	1.71	0.83
	SCF(d)	6.74	0.97		1.54
4	SCF(a)	7.63	1.48		2.35
	SCF(c)	7.39	1.26	1.344	1.38
	SCF(d)	7.51	1.51		2.33
5	SCF(a)	6.86	1.05		4.12
	SCF(c)	6.51	1.17	1.420	3.42
	SCF(d)	6.68	1.22		4.31
6	SCF(a)	7.45	1.39		1.53
	SCF(c)	7.21	1.20	1.393	0.93
	SCF(d)	7.33	1.40		1.49
7	SCF(a)	7.22	1.17		2.24
	SCF(c)	6.78	1.19	1.406	2.23
	SCF(d)	6.99	1.17		2.83

Results and Discussion

Molecular Properties Such as Ionization Potential, Electron Affinity, Half-Wave Reduction Potential, and π-Dipole Moment: It has been observed[26] that the values obtained from Koopmans' theorem[25] differ from the experimental values of IP and EA by 1 or 2 eV. Hence a correction term is to be added to the HOMO and LUMO so that we can obtain the correct values of IP and EA respectively. Correction terms are presented in Table 1. The half-wave reduction potential has been evaluated from the relation[27] (Eq. 7) in the context of SCF(c).

$$E_{1/2} = -0.833\, e_j - 3.46, \tag{7}$$

where e_j is the LUMO. The values of IP, EA, and $E_{1/2}$ have been presented in Table 2. For lack of experimental values we can not compare these results with experimental ones. The values of π-dipole moment have also been included in Table 2 along with experimental values where available.

$\pi^*\leftarrow\pi$ Spectral Transitions: Theoretical spectral transitions along with oscillator strengths, f, have been presented in Table 3 which contains the experimental transitions for the molecules **1**, **2**, **5**, and **7**. Table 4 contains the theoretical transitions and f values of other molecules for which there are no experimental values. The oscillator strengths, f, were obtained from the relation.[31]

Table 3. $\pi^*\leftarrow\pi$ Spectral Transitions, ΔE (eV) and Oscillator Strength, f, of Molecules **1**, **2**, **5**, and **7**

Experimental			Theoretical						Other works		
		Sym	SCF(a)		SCF(d)		CI				
ΔE	$\log\varepsilon$[a)]		ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE
					Molecule **1**						
Ref. 5b											
2.57	3.95	A_1	2.80	1.39	2.61	1.51	2.44	0.95			
3.44	3.90	B_2	3.37	0.04	3.08	0.03	3.39	0.27			
3.88	4.04	B_2	3.96	0.57	3.78	0.16	3.75	0.01			
4.04	4.45	A_1	3.98	0.16	3.83	0.03	4.09	0.36			
4.23	4.43	A_1	4.17	0.05	4.36	0.60	4.29	0.25			
σ			0.119		0.201		0.092				
					Molecule **2**						
Ref. 6											
2.11	3.95		2.13	0.01	2.44	0.01	1.95	0.01			
3.06	3.66		2.75	1.28	2.74	1.34					
3.20	3.52		3.40	0.05			3.30	0.04			
4.06	3.80		4.06	0.44	3.90	0.37	4.19	0.12			
5.08	3.71		5.06	0.06	5.18	0.03	4.96	0.05			
σ			0.165		0.248		0.115				
					Molecule **5**						
Ref. 10											
1.63	2.52						1.51	0.02			
1.79	2.34	B_2	1.88	0.07	1.77	0.07					
2.60	4.69						2.66	0.46			
2.92	3.90	A_1	2.86	1.42	2.89	1.49					
3.53	4.85	A_1			3.64	0.86	3.63	1.83			
4.36	3.96	B_2	4.35	0.29	4.36	0.01	4.48	0.17			
4.74	4.21	B_2	4.64	0.03	4.76	0.01					
4.85	4.16						4.89	0.26			
5.08	4.12	A_1	5.17	0.07	5.14	0.05	5.17	0.01			
5.48	4.21	A_1	5.48	0.42	5.40	0.28	5.52	0.04			
σ			0.071		0.058		0.088				
					Molecule **7**[a)]						
Ref. 12									Ref. 12		Ref. 13(a)
1.65	0.01	B_2	2.34	0.22	2.19	0.20	1.76	0.03	1.96	0.02	1.80
2.75	0.4	A_1	2.92	1.57	2.93	1.61	2.63	0.45	2.54	0.4	2.90
3.35	w	B_2					3.33	0.02	3.52	0.05	3.31
3.66	0.3	A_1	3.76	1.08	3.80	1.21	3.86	1.83	3.77	0.2	3.33
3.84	1.6	B_2	3.79	0.47	3.71	0.46	3.79	0.25	3.94	0.2	4.28
4.28	?	A_1	4.26	0.05	4.22	0.09	4.17	0.58	3.97	1.4	4.43
4.59	w	B_2	4.60	0.00	4.64	0.09	4.54	0.00	4.09	0.003	4.56
5.08	s	B_2	4.99	0.05	4.95	0.06	5.14	0.01	4.17	0.2	4.79
5.70	?	A_1	5.67	0.19	5.80	0.21	5.71	0.16	4.41	0.3	
σ			0.257		0.222		0.097		0.580		0.239

a) Figures in column 2 are 'f' values. 's' and 'w' stand for strong and weak.

Table 4. $\pi^* \leftarrow \pi$ Spectral Transitions, ΔE (eV) and 'f' of **3**, **4**, and **6**

SCF(a)		SCF(d)		CI	
ΔE	f	ΔE	f	ΔE	f
		Molecule **3**			
2.23	0.71	2.48	0.79	2.15	0.16
2.53	0.43	2.78	0.42	2.80	0.55
4.01	0.36	3.90	0.34	4.00	0.13
4.38	0.36	4.32	0.37	4.38	0.25
4.89	0.31	4.89	0.31	4.86	0.39
5.30	0.44	5.31	0.47	5.38	0.15
		Molecule **4**			
2.35	0.57	2.59	0.63	2.28	0.16
2.80	0.45	3.09	0.47	3.01	0.39
3.90	0.36	3.86	0.36	4.01	0.07
4.46	0.36	4.39	0.38	4.48	0.44
4.75	0.16	4.94	0.13	4.70	0.10
5.29	0.46	5.24	0.17	5.15	0.51
		Molecule **6**			
2.63	1.08	2.77	1.13	2.58	0.58
4.07	0.38	4.00	0.36	4.05	0.20
4.55	0.08	4.65	0.07	4.59	0.51
5.02	0.10	5.07	0.05	5.05	0.32
5.49	0.37	5.55	0.03	5.55	0.08

$$f = 1.085 \times 10^{-5}\, \bar{\nu} \mu^2 \qquad (8)$$

with $\bar{\nu}$ is the transition energy in cm^{-1}) and μ is the dipole length (in Å) for corresponding transition. Results of SCF(a), (d), and CI are included in the table.

From Table 3 it is clear that the correlation between the theoretical transitions and experimental ones for molecules **1** and **2** is good. However agreement between the theoretical transitions predicted by SCF(d) method is not so good. This is evident from the calculation of standard deviation, σ included in the table. For the calculation of σ, point to point correlation has been taken.

The experimental spectral transitions of molecule **5** have a large number of peak maxima many of which are not clearly resolved. Therefore the best one can do in a comparison of the theoretical and observed transitions is a general correlation over quite wide spectral regions. Table 3 displays this comparison for molecule **5**. The value of σ predicted by the SCF and CI methods suggest that the agreement between the theoretical and experimental transitions is good. Table 3 also displays the experimental transitions for molecule **7** where other theoretical works have also been included along with our work. The molecule is rich in experimental transitions and attempt has been made a point to point correlation. The values predicted by the CI method is very good compared to the values predicted by the SCF methods and other workers.[12,13a]

Stability or Aromaticity: Stability of the molecules has been studied according to the criteria of resonance energy (E_R) and resonance energy per bond (E_R/C–C) or resonance energy per π-electron (RE/PE). The values of E_R of the molecules have been calculated using the methods of Whitehead et al.,[15] Chung and Dewar,[4a] Dewar and de Llano,[32] Dewar and Harget,[4b] and Hess and Schaad.[33] The values of heat of atomization, ΔH_a and π-bond energy, resonance energy, E_R, resonance energy per carbon–carbon bond (E_R/C–C) and resonance energy per π-electron of the molecules have been presented in Table 5. Since the hydrocarbons contain benzene rings fused with five or seven membered rings, they belong to semibenzenoid systems.[34] The criteria for stability or aromaticity of this type of hydrocarbons have been discussed by Das Gupta and Das Gupta[34] and are displayed in Table 6.

The hypothetical molecule **1**, pentaleno[4,5,6-*cd*]-phenalene, can be represented by the dipolar structure. Application of Craig's rule[37] to any one of the Kekule' structure of **1** gives the result $f+g=7$ which predicts the valence-bond ground state to be nontotally symmetric and hence the molecule **1** should be pseudoaromatic. The two non-charge separated resonance forms possess a 16 π-electron moiety peripheral to the central ethylene fragment. If it is considered that the cross links are regarded to contribute only negligible perturbation the present hydrocarbon should be antiaromatic.[38] Low resonance energy and low resonance energy per carbon–carbon bond calculated by all the methods and low resonance energy per π-electron also suggest that the molecule should not be an aromatic one. Moreover, the physical properties of the derivatives of **1**, relatively high chemical shifts of the protons on the phenalene nucleus and small dipole moment [μ=2.31D (D=Debye, 1 Debye=3.3356×10^{-30} C m)][5b] of 5-ethoxy-1,3-di-*t*-butylpentaleno[1,2,3-*cd*]phenalene indicate, however, that the molecule **1** can be best represented by the perturbed [16] annulene **1(c)** rather than the dipolar form **1(b)**.

Although molecule **2** has not been synthesized, its derivatives are known. The derivative 2-ethoxy-9,10,11,12-tetrachloropentaphenafulvalene is a stable one.[6] The resonance energy, E_R/C–C and RE/PE suggest that the molecule would be a stable one in agreement with experiment. The high dipole moment of **2** (6.33 D)[6] together with the relatively low chemical shifts and the identical vicinal coupling constants[39] in its ^{1}H NMR spectrum indicates a significant participation of a dipolar resonance structure in its ground state **2(b)**.

The molecule **3** has not yet been synthesized. Its resonance energy, E_R/C–C and RE/PE which are at the lower side of the range of aromaticity and stability suggest that the molecule might not be an aromatic one.

The molecules **5** and **7** are interesting and may be considered to be composed of azulene and phenalene. Resonance energy, E_R/C–C and RE/PE suggest that they might be a stable aromatic compound. The ease of dehydrogenation during the preparation of **5** is noteworthy suggesting thermodynamic stability[10] of this compound. The diamagnetic susceptibility is 2.7.[10] The above observations furnish convincing evidence for a definite degree of aromaticity of **5**.[10]

Table 5. Heat of Atomization ΔH_a (eV), π-Bond Energy $E_{\pi b}$ (eV), Resonance Energy E_R ((eV) or in β), and Resonance Energy per Carbon–Carbon Bond E_R/C–C or Resonance Energy per π-Electron RE/PE

Molecule	Method[a)]	ΔH_a	$E_{\pi b}$	E_R	E_R/C–C or RE/PE
1	a	151.65	26.677	5.993	0.272
	b	151.85	26.253	6.035	0.279
	c	151.98	25.324	1.402	0.064
	d			0.884	0.040
	e[b)]			0.466	0.026
2	a	156.19	26.003	6.570	0.313
	b	156.36	25.590	5.534	0.264
	c	156.66	25.561	3.599	0.171
	d			0.899	0.043
	e[b)]			0.621	0.034
3	a	156.12	25.936	5.502	0.262
	b	156.30	25.522	5.466	0.260
	c	156.60	25.513	1.534	0.073
	d			0.860	0.041
	e[b)]			0.509	0.028
4	a	137.47	23.489	5.244	0.276
	b	137.63	23.118	5.237	0.276
	c	137.91	22.958	1.574	0.083
	d			0.946	0.050
	e[b)]			0.510	0.032
5	a	170.73	29.558	6.685	0.279
	b	170.94	29.086	6.793	0.284
	c	171.08	28.339	1.783	0.074
	d			1.203	0.050
	e[b)]			0.695	0.035
6	a	171.25	30.070	7.202	0.300
	b	171.45	29.601	7.208	0.300
	c	171.71	29.198	2.406	0.100
	d			1.719	0.072
	e[b)]			0.785	0.039
7	a	170.68	29.508	6.640	0.277
	b	170.89	29.040	6.647	0.277
	c	171.06	28.317	1.755	0.073
	d			1.157	0.048
	e[b)]			0.694	0.035

a) a, b, c, d, e under column method represent SCF(a), SCF(b), SCF(c), Dewar–de Llano, and Hess and Schaad methods, respectively. b) in β unit.

Table 6. Criteria of Aromaticity or Stability of Hydrocarbons

Method	Range of E_R/C–C or RE/PE for the hydrocarbons to be aromatic[35–37)]
SCF a	0.26—0.31
SCF b	0.25—0.30
SCF c	0.075—0.112
D dL[a)]	0.041—0.095
HS[b)]	0.03—0.04

a) Dewar–de Llano. b) Hess and Schaad.

Though the molecule **4** has not yet been synthesized, yet its resonance energy, E_R/C–C bond and RE/PE suggest that it might be a stable aromatic compound. It is expected that it might be synthesized in near future.

The molecule **6** has been synthesized and its chemical properties have been studied by Reid.[11)] Its high basicity, the Hammett acidity function H_0 for which K' (where K' is the apparent partition coefficient) value which is unity places the molecule **6** alongside the azulenes in order of basicity.[40)] It undergoes electrophilic substitution reaction easily. The dihydroindeno-[2,1-*a*]phenalene undergoes with striking readiness to aromatization reactions.[11)] The above reactions reflect the aromatic character of molecule **6**. This is also predicted from its calculated resonance energy, E_R/C–C and RE/PE.

Conclusion

The methods SCF a, b, and c were parameterized to predict the ground state properties and stability of molecules. SCF(d) method was parameterized to predict the spectral transitions of conjugated systems. It has been observed that the methods SCF a, b, and c are also equally good, if not better than the SCF(d) method, in predicting spectral transitions as seen earlier.

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