February, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (2), 345—348 (1977) 345

Electronic Structures and Spectra of Azulenophenalenes

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(Received July 3, 1976)

The ground-state electronic properties and electronic spectra of azuleno [5, 6, 7-*cd*] phenalene (I) and azuleno-[1, 2, 3-*cd*]phenalene(II), which are isomers of the potent carcinogen benzo[*a*]pyrene (III), have been investigated by using the SCF screened potential MO CI method in combination with the variable bond-length technique. From the calculated C–C bond lengths and the position dependence of the SCF screened potential, it may be concluded that molecules I, II, and III are all both aromatic and polyolefinic. The electronic spectra of I, II, and III predicted using the screened potential are in better agreement with the experimental values than those calculated using the bare potential.

Since the molecular geometries of azuleno[5,6,7-*cd*]phenalene (I) and azuleno[1,2,3-*cd*]phenalene (II) resemble that of the potent carcinogen benzo[*a*]pyrene (III), the electronic structures and spectra of I, II, and III have been of interest. Molecule I, which was recently synthesized by Jutz and Kirchlechner,[1] was found to be carcinogenic.[2] Very recently, Murata *et al.*[3] have synthesized molecule II.

Fischer and Ege[4] have applied the SCF MO method based on the Pariser-Parr-Pople approximation to I and have calculated its electronic structures and spectra. Using the LCI-SCF MO method, Zahradnik[5] has investigated the electronic spectra of I and II. Germer and Becker[6] and Pancir and Zahradnik[7] have studied theoretically the electronic spectra of III, but they did not mention the aromaticities and carcinogenicities of I, II, or III. Recently, Thulstrup *et al.*[8] have measured the magnetic circular dichroism (MCD) spectrum of I and assigned its absorption spectrum. Very recently, Tajiri *et al.*[9] have measured the MCD spectrum of II and interpreted its complicated absorption bands.

The purpose of this paper is to investigate theoretically the ground-state electronic properties and electronic spectra of I, II, and III by using the SCF screened potential MO CI method in combination with the variable bond-length technique,[10,11] which is known to reproduce well the electronic structures of large conjugated molecules. It is possible to use the results of such calculations to deepen our understanding of the aromatic characteristics and carcinogenicities of I, II, and III.

Method of Calculation

A procedure that combines the SCF screened potential with the variable bond-length technique[11] is used in the Pariser-Parr-Pople SCF MO CI method.[12,13] At each step of the SCF calculation, the new bond lengths are obtained from the corresponding bond orders.[14] The screened potential is evaluated by using the bare potential obtained from the new bond lengths. The bare potential is calculated using the Mataga-Nishimoto formula.[15] This screened potential is used in the calculation of the next step. The calculation is repeated until self-consistency is reached. The screened potential for the CI calculation of the five low-lying singlet excitations is calculated by omitting the low-lying subset of configurations in Eq. 8 of Ref. 10. The SCF calculation of the ground state is made by using the full effective interaction.

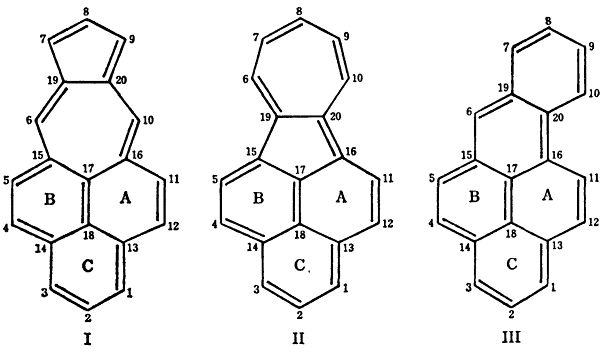

Fig. 1. Numbering of atoms.

Results and Discussion

Ground-state π-Electronic Properties. The calculated charge densities, free valence, and bond lengths are summarized in Table 1. The greatest nucleophilic reactivity is predicted at the 6 and 10 atoms in I and the 6 and 10 atoms in II. The greatest electrophilic reactivity is expected at the 7 and 9 positions in I and the 15 and 16 positions in II. The results for I agree with those of Fischer and Ege[4] and Thulstrup *et al.*[8] The calculated charge densities for III indicate that the Coulson-Rushbrooke theorem,[16] which states that, in alternant hydrocarbons, the π-electron densities for all the carbon atoms are unity, does not hold for III, when the screened potential is used. The technique of ^{13}C-NMR and ESCA[17] is capable of resolving the small charge differences in III.

From the viewpoint of carcinogenic activity, let us discuss the reactivity for the addition reactions of I, II, and III. The sum of the free valences for the two positions of the K-region,[18] $F_4+F_5=F_{11}+F_{12}=0.942$ in II, is smaller than $F_4+F_5=0.983$ in III, which is the strong carcinogen, but is comparable to the sum $F_4+F_5=F_{11}+F_{12}=0.948$ in I, which has carcinogenicity.

As for the bond lengths, it is of interest to note that the bond lengths of the azulene nucleus of I and II are almost the same as those of the free azulene molecule and that the bond lengths of the naphthalene nucleus of III are almost the same as those of the free naphthalene molecule. Two isolated C–C double

TABLE 1. CHARGE DENSITIES, FREE VALENCE NUMBERS, AND BOND LENGTHS

Molecule	Atom	Charge density	Free valence	Bond	Bond length (Å)	Molecule	Atom	Charge density	Free valence	Bond	Bond length (Å)
I	1	1.017	0.440	1—2	1.396	III	1	1.016	0.441	1—2	1.388
	2	0.977	0.395	1—13	1.404		2	0.988	0.396	1—13	1.411
	4	0.993	0.480	13—18	1.415		3	1.021	0.439	2—3	1.404
	5	0.986	0.470	4—14	1.447		4	0.993	0.491	3—14	1.396
	6	0.927	0.493	4—5	1.361		5	0.994	0.492	4—14	1.454
	7	1.135	0.478	5—15	1.445		6	1.034	0.491	4—5	1.355
	8	1.010	0.421	15—17	1.419		7	1.001	0.448	5—15	1.454
	14	0.980	0.152	17—18	1.433		8	0.993	0.418	15—17	1.432
	15	0.994	0.171	6—15	1.406		9	1.001	0.422	6—15	1.383
	17	0.951	0.177	6—19	1.403		10	0.994	0.442	6—19	1.426
	18	1.004	0.140	19—20	1.461		11	0.992	0.455	7—19	1.428
	19	0.997	0.188	7—19	1.409		12	0.998	0.468	7—8	1.373
				7—8	1.398		13	0.992	0.139	8—9	1.423
II	1	1.042	0.443	1—2	1.396		14	0.988	0.166	9—10	1.374
	2	0.984	0.394	1—13	1.405		15	0.983	0.171	19—20	1.407
	4	1.038	0.480	13—18	1.415		16	1.001	0.178	10—20	1.426
	5	0.977	0.462	4—14	1.445		17	1.005	0.158	11—12	1.364
	6	0.894	0.461	4—5	1.362		18	1.002	0.145	11—16	1.439
	7	1.010	0.440	5—15	1.442		19	0.994	0.158	12—13	1.441
	8	0.909	0.148	15—17	1.417		20	1.008	0.145	16—17	1.399
	14	0.983	0.148	17—18	1.434					16—20	1.433
	15	1.103	0.198	6—19	1.404					14—18	1.419
	17	1.008	0.160	6—7	1.399					13—18	1.410
	18	0.999	0.142	7—8	1.400					17—18	1.436
	19	1.004	0.213	19—20	1.457						
				15—19	1.416						

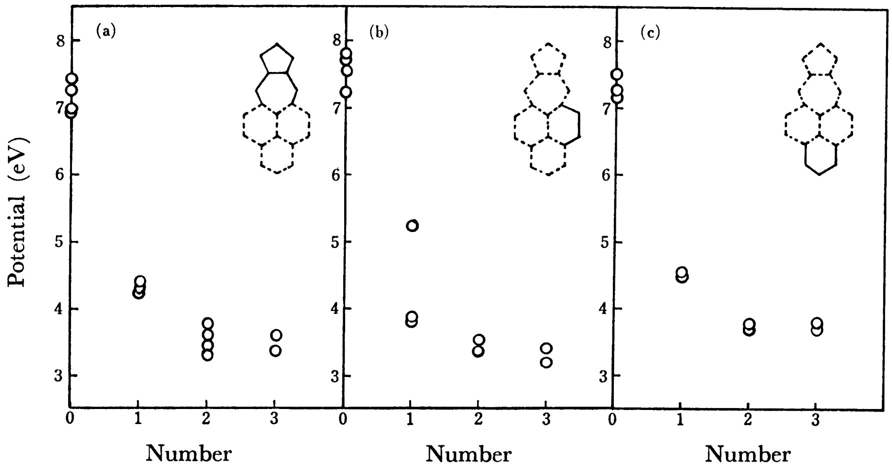

Fig. 2. The SCF screened potentials in azuleno[5,6,7-*cd*]phenalene plotted *versus* the number; (a) the azulene nucleus, (b) the benzene ring (A or B), and (c) the benzene ring (C).

bonds exist in the benzene rings (A and B) of the phenalenyl moiety for I, II, and III. The bond lengths of the benzene ring (C) in I, II, and III are composed of two vinyl molecules and 6-phenylazulene, 2-phenylazulene, and 2-phenylnaphthalene, respectively.

Position Dependence of SCF Screened Potential. Terasaka *et al.*[11] divided the SCF screened potentials V into the following groups: V_{11}, V_{12}, V_{13},$\cdots$; V_{22}, V_{23}, V_{24},$\cdots$;$\cdots$. In Fig. 2, the SCF screened potentials in each group of I are plotted *versus* a number that indicates the kinds of screened potential, that is, 0: one-center potentials V_{11}, V_{22}, V_{33},$\cdots$; 1: the nearest two-center potentials V_{12}, V_{23}, V_{34},$\cdots$; *etc.* The results in II and III are shown in Figs. 3 and 4, respectively. In the azulene nucleus of I and II, at each of the numbers the various screened potentials are almost the same as those of the free azulene molecule (see Fig. 9 of Ref. 11). In the naphthalene nucleus of III, a tendency similar to that in the free naphthalene molecule appears (see Fig. 8 of Ref. 11). In the free naphthalene molecule, there is a fairly clear double-

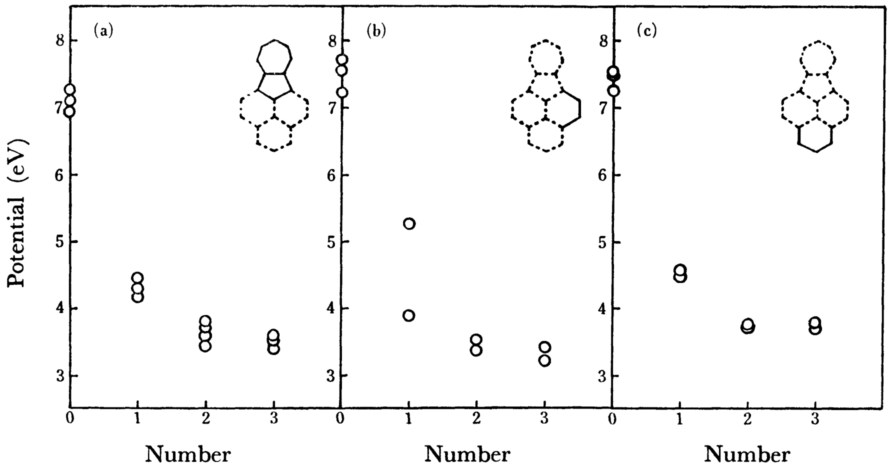

Fig. 3. The SCF screened potentials in azuleno[1,2,3-*cd*]phenalene plotted *versus* the number; (a) the azulene nucleus, (b) the benzene ring (A or B), and (c) the benzene ring (C).

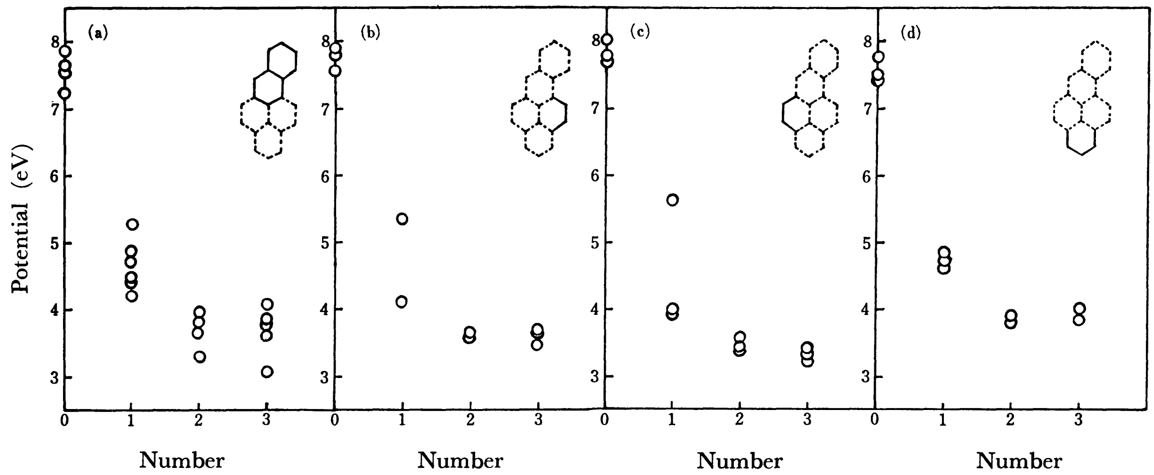

Fig. 4. The SCF screened potentials in benzo[*a*]pyrene plotted *versus* the number; (a) the naphthalene nucleus, (b) the benzene ring (A), (c) the benzene ring (B), and the benzene ring (C).

bond fixation, so that the characteristics of the screened potential are the same as those of the polyene ($n=10$) (see Fig. 8 of Ref. 11). The SCF screened potential is very sensitive to a bond alternation. There are two kinds of screening (screening and anti-screening) at the odd numbers in molecules such as polyene, in which there exists a strong bond alternation.11) The characteristics of the screened potential of the benzene rings (A and B) in the phenalenyl moiety of I, II, and III presented in Figs. 2(b), 3(b), 4(b), and 4(c) shows trends similar to those of the polyene. The screened potential of the benzene ring (C) of I, II, and III shows a tendency similar to that of the free azulene molecule. From the above results, it may be concluded that the azulene nucleus of I and II and the benzene ring (C) in the phenalenyl moiety of I, II, and III are aromatic, but the naphthalene nucleus of III and the benzene rings (A and B) in the phenalenyl moiety of I, II, and III are polyolefinic. Molecules I, II, and III may have both aromatic and polyolefinic characters.

Electronic Spectra. Table 2 shows the transition energies and oscillator strengths calculated by using the SCF screened potential (SP) in combination with the variable bond-length SCF technique, along with those calculated assuming the bare potential (BP). It may be noted that the calculated excitation energies and oscillator strengths using the screened potential are in better agreement with the experimental values than those calculated using the bare potential. The spectral results calculated for I by Fischer and Ege4) and by Thulstrup *et al.*,8) for I and II by Zahradnik,5) for II by Tajiri *et al.*,9) and for III by Germer and Becker6) and by Pancir and Zahradnik7) are in fairly good agreement with the present results obtained using the SCF screened potential.

One of the present authors (H. Y.) especially wishes to thank Professor I. Murata of Osaka University for providing him with copies of the ultraviolet absorption spectra of azuleno[1,2,3-*cd*]phenalene and to thank Dr. Y. Fujimura of Tohoku University for his fruitful discussions.

Table 2. Transition energies (ΔE(eV)) and intensities (f)

Molecule	Theoretical				Experimental
	BP		SP		
	ΔE	f	ΔE	f	ΔE
I	1.98	0.035	1.83	0.031	1.65 (f=0.01)[a]
	2.82	0.52	2.72	0.37	2.75 (f=0.4)[a]
	3.66	0.044	3.49	0.021	3.35[a]
	4.15	0.26	3.78	0.25	3.66 (f=0.3)[a]
	4.16	2.16	3.88	1.89	3.84 (f=1.6)[a]
II	1.91	0.022	1.74	0.033	1.63 (log ε=2.52)[b]
	2.81	0.57	2.54	0.68	2.60 (log ε=4.69)[b]
	3.76	0.075			
	3.89	1.99	3.60	1.58	3.53 (log ε=4.85)[b]
III	3.46	0.89	3.18	0.000	3.07 (log ε=3.61)[c]
	3.49	0.000	3.39	0.68	3.22 (log ε=4.44)[c]
	4.42	0.000	4.30	0.006	
	4.52	0.088	4.39	0.030	4.18 (log ε=4.76)[c]
	4.68	1.26	4.62	1.16	4.67 (log ε=4.64)[c]

a) Taken from Ref. 8. b) Taken from Ref. 3. c) Taken from Ref. 6.

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