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Electronic Structures, Electronic Spectra, and Aromatic Characteristics of Peri-Condensed Tetracyclic Nonbenzenoid Aromatic Hydrocarbons Containing a Naphthalene Nucleus

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The ground-state electronic properties and electronic spectra of pyracylene (I), acepleiadylene (II), and dipleiadiene (III) have been studied by using the semi-empirical SCF LCAO-π-MO method, which allows for bond order-bond length correlation at each iteration. It is shown that the I and III molecules do not belong to, respectively, the pentalenoid and heptalenoid systems, as was expected from the HMO energy diagram. The predicted chemical reactivities, diamagnetic anisotropies, and electronic spectra for I and II are in good agreement with the available experimental data. The calculated C–C bond lengths indicate that the I, II, and III molecules are all both aromatic and polyolefinic. The upfield shift of the NMR spectrum and the unusually low value of the first half-wave potential for I can be well explained in terms of, respectively, the diamagnetic anisotropy and the energy of the lowest vacant SCF MO, calculated by using the predicted equilibrium configuration that corresponds to the aromatic model (Ia).

The electronic structures and aromatic characteristics of tetracyclic nonbenzenoid aromatic hydrocarbons containing a naphthalene nucleus have been of theoretical interest since Boekelheide and Vick[1] synthesized acepleiadylene (II) in 1956.

Trost and Bright[2] have recently reported the successful synthesis of pyracylene (I). Theoretical interest in whether I or not is a pentalenoid system was then stimulated. These authors proposed two possible structures, a naphthalene core with two vinyl bridges (Ia) and a cyclododecahexene with a vinyl cross-link (Ib). They concluded, from the upfield shift of the NMR spectrum and the unusually low value of the first half-wave potential, that the peripheral model (Ib) is a better representation for I. Lo and Whitehead[3] have calculated the ground-state electronic properties of I using the LCAO MO SCF PPP ($\pi+\sigma$) method and have concluded that the most stable configuration corresponds to the aromatic model (Ia).

Pullman *et al.*[4] have studied the electronic structures and spectra of II using the Hückel MO method. From the calculated delocalization energy, they have found that II should be aromatic. Koutecký *et al.*[5] have applied the SCF MO method based on the Pariser-Parr-Pople approximation to II and have calculated its transition energies and intensities, but they have not mentioned its aromaticity.

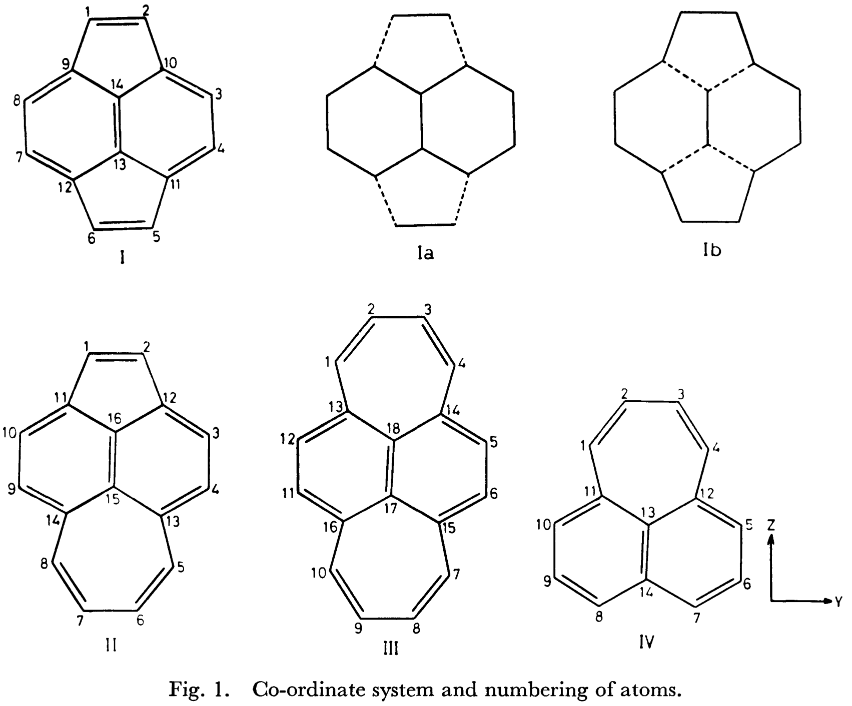

Fig. 1. Co-ordinate system and numbering of atoms.

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[1] V. Boekelheide and G. K. Vick, *J. Amer. Chem. Soc.*, **78**, 653 (1956).

[2] B. M. Trost and G. M. Bright, *ibid.*, **89**, 4244 (1967).

[3] D. H. Lo and M. A. Whitehead, *Chem. Commun.*, **1968**, 771.

[4] B. Pullman, A. Pullman, G. Berthier, and J. Pontis, *J. Chim. Phys.*, **49**, 20 (1952).

[5] J. Koutecký, P. Hochman, and J. Michl, *J. Chem. Phys.*, **40**, 2439 (1964).

Using the HMO method, Zahradnik *et al.*[6] have investigated the electronic structures, electronic spectra, and stability of I, II, and dipleiadiene (III), the last of which is yet unknown. On the basis of a new definition of stability, they have concluded that I and III are unstable, while II is stable. Recently, using the Molecules in Molecules method, Favini *et al.*[7] have calculated the transition energies and intensities for I, II, and III, but they have not considered anything with regard to the stable configurations and aromaticity of these molecules.

It is the purpose of this paper to determine the equilibrium configurations of I, II, and III by using the variable bond-length SCF LCAO-π-MO CI technique and to examine theoretically their ground-state electronic properties and electronic spectra. It should be possible to use the results of such calculations to deepen our understanding of the aromatic characteristics of I, II, and III.

Method of Calculation

The electronic structures and spectra are calculated by using the variable bond-length SCF LCAO-π-MO method, in which the C–C bond lengths and, consequently, the resonance and two-center repulsion integrals are allowed to vary with the bond order at each iteration until self-consistency is reached. The C–C bond lengths, r, are correlated with the bond orders, p, by the following relationship:

$$r(\text{Å}) = 1.520 - 0.186p \qquad (1)$$

The two-center repulsion integrals are calculated using the Mataga-Nishimoto formula.[8] The resonance integrals are evaluated using Method 2 of Ref. 9, in which the dependence of the resonance integral on the bond length is assumed to be exponential; the value of the exponent was determined by trying to reproduce as many properties of the ground and excited states as possible in a series of reference molecules. In order to discuss the properties of excited states, a configuration mixing of all the singly-excited states is included.

The diamagnetic susceptibilities are calculated by using the London[10]-Hoarau[11] method in the framework of the Wheland-Mann-type SCF MO approximation.[12] The resonance integral is assumed to be again of the exponential form, the value of the exponent in this case being 4.4 Å^{-1}. This value was determined so as to reproduce the bond lengths, electron densities, and dipole moments, which were obtained from the variable bond-length SCF LCAO-π-MO technique, for butadiene, pentafulvene, heptafulvene, and naphthalene. This method has been applied to a number of benzenoid and nonbenzenoid aromatic hydrocarbons and has been found to produce theoretical values which are in good agreement with the experimental results.[13]

Results and Discussion

Ground-state Symmetries. The HMO energy levels show that, in the I molecule, the lowest unoccupied MO is non-bonding as in pentalene, while in the III molecule the highest occupied MO is non-bonding as in heptalene. In this sense, it has been said that the I molecule belongs to the pentalenoid system, and the III molecule, to the heptalenoid system.[6,14] The energy differences between the highest occupied MO and the lowest unoccupied MO for I and III are almost the same as those of, respectively, the pentalene and heptalene molecules, both of which are pseudo-Jahn-

Table 1. Charge densities, free balence numbers and bond lengths

Molecule	Atom	Charge density	Free valence	Bond	Bond length(Å)
I	1	1.018	0.520	1—2	1.353
	3	0.970	0.439	1—9	1.462
	9	0.991	0.204	3—4	1.412
	13	1.043	0.155	8—9	1.387
				12—13	1.426
				13—14	1.414
II	1	1.033	0.484	1—2	1.362
	3	0.952	0.432	1—11	1.446
	4	1.041	0.434	3—4	1.402
	5	0.978	0.495	4—13	1.397
	6	0.983	0.464	5—6	1.364
	11	1.031	0.175	5—13	1.446
	13	0.973	0.176	6—7	1.440
	15	0.972	0.160	10—11	1.397
	16	1.045	0.159	11—16	1.428
				13—15	1.428
				15—16	1.412
III	1	0.986	0.517	1—2	1.357
	2	0.997	0.488	1—13	1.457
	5	1.019	0.438	2—3	1.452
	13	1.011	0.193	5—6	1.410
	17	0.975	0.155	12—13	1.390
				16—17	1.427
				17—18	1.413
IV	1	0.985	0.514	1—2	1.358
	2	0.993	0.480	2—3	1.449
	5	1.026	0.446	1—11	1.456
	6	0.995	0.402	5—6	1.412
	7	1.016	0.459	6—7	1.380
	11	0.997	0.179	5—12	1.388
	13	0.976	0.159	7—14	1.423
	14	0.998	0.115	11—13	1.427
				13—14	1.413

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[6] R. Zahradnik, J. Michl, and J. Pancir, *Tetrahedron*, **22**, 1355 (1966).

[7] G. Favini, A. Gamba, and M. Simonetta, *Theor. Chim. Acta*, **13**, 175 (1969).

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[9] H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta*, **12**, 349 (1968).

[10] F. London, *J. Chem. Phys.*, **5**, 837 (1937); *J. Phys. Radium*, **8**, 397 (1937).

[11] J. Hoarau, *Ann. Chim.* (Paris), **1**, 544 (1956).

[12] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

[13] H. Yamaguchi and T. Nakajima, This Bulletin, to be published.

[14] G. V. Boyd, *Tetrahedron*, **22**, 3409 (1966).

Teller molecules.[15] Therefore, it may be expected that the I and III molecules will suffer a pseudo-Jahn-Teller effect, which may result in a symmetry reduction from the fully symmetrical configuration.

We thus examined the ground-state symmetries of the I and III molecules, using a method of predicting the energetically most favourable equilibrium configuration of a conjugated hydrocarbon.[16] It turned out that, in both the molecules, the starting bond distortions belonging to irreducible representations, a_g, b_{3g}, b_{1u}, and b_{2u}, of the full symmetry group, D_{2h}, all converge into the unique self-consistent set of bond lengths corresponding to that symmetry group.

Thus, we may conclude that I and III molecules are not pentalenoid and heptalenoid respectively and that neither molecule is a so-called pseudo-Jahn-Teller molecule.

Ground-state π-Electronic Properties. The calculated charge densities, free valence numbers, and bond lengths are summarized in Table 1. The greatest nucleophilic reactivity is predicted to be exhibited by the 3, 4, 7, and 8 atoms in I, by the 3 and 10 atoms in II, and by the 17 and 18 atoms in III. The greatest electrophilic reactivity is expected at the 13 and 14 positions in I, the 16 position in II, and the 5, 6, 11, and 12 positions in III. The results for II do not agree with those of the simple HMO method,[4] which indicate that the highest reactivity for nucleophilic and electrophilic reactions is to be expected at the 5 and 8 positions and at the 1 and 2 positions, respectively. It is hoped that eventually this point can be established experimentally. From the viewpoint of chemical reactivity, it is noteworthy that the free valence values of atoms belonging to the 5- and 7-membered rings of all the molecules examined are significantly larger than those in classical aromatic hydrocarbons. This perhaps provides evidence for the fact that the attempts to isolate the I molecule produce only amorphous yellow polymers.[2]

Next, let us discuss the reactivity for the addition reactions of I, II, and III. It has been known that, in the presence of cyclopentadiene, the 1, 2-dibromo derivative of I gives an addition product[17] at the 5 and 6 positions and that II does not react with maleic anhydride under the same conditions under which maleic anhydride gives Diels-Alder adducts with pleiadiene IV.[1] These facts can be explained by comparing the sum of the free valences for the two positions concerned; $F_5+F_6=1.040$ in I and $F_1+F_4=1.028$ in IV are larger than $F_1+F_2=0.968$ and $F_5+F_8=0.990$ in II. Furthermore, it is expected that III will suffer addition reactions at the 1 and 4 positions, because the sum of the free valences at these positions ($F_1+F_4=1.034$) is comparable to F_1+F_2 for I and F_1+F_4 for IV

As for the bond lengths, it is of interest to note that the bond lengths of the naphthalene core of I, II, and III are almost the same as those of the free naphthalene molecule. There is a marked double-bond fixation in the remainder of the periphery. The I and III molecules show a double-bond fixation in their peripheries to a greater extent than II. In fact, the presence of two isolated vinyl bridges in the periphery of I is confirmed by the experimental fact that hydrogenation occurs only at the 1, 2- and 5, 6-positions to give pyracene.[2] The reason why the equilibrium configurations of I and III show such a double-bond fixation in the periphery may be explained by using a simple perturbational treatment. The I and III molecules have a 4n perimeter which has degenerate nonbonding orbitals, Φ_A and Φ_S, which are antisymmetric and symmetric respectively with respect to the y axis, as is shown in Fig. 2. The antibonding orbital of the vinyl segment located at the center of I interacts with the Φ_A state of the 12-monocyclic system and stabilizes it, as is also shown in Fig. 2. On the other hand, the bonding orbital of the vinyl segment

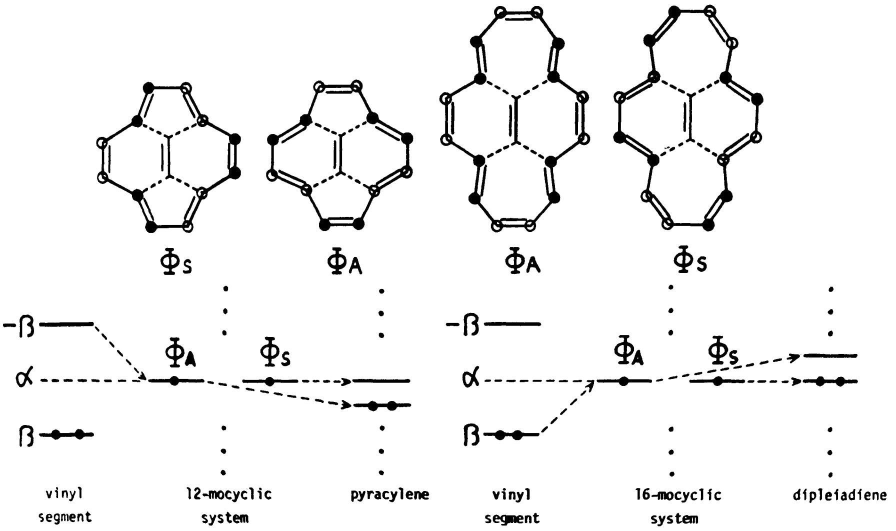

Fig. 2. Wave functions of nonbonding orbitals, Φ_A and Φ_S of 4n monocyclic systems and interaction scheme between vinyl segments and 4n monocyclic systems. The open and dark circles represent plus and minus signs of the LCAO coefficients, respectively.

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[15] H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser.* **A161**, 220 (1937).

[16] T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, **3**, 272 (1969).

[17] B. M. Trost and D. R. Brittelli, *Tetrahedron Lett.*, **1967**, 119.

located at the center of III interacts with the Φ_A state of the 16-monocyclic system and makes it unstable.

Magnetic Properties. The diamagnetic susceptibility of a ring π-electron system is one of the important indications of π-electron delocalization. The calculated molar magnetic anisotropies, ΔK, for I, II, and III are −0.40, 3.92 and −0.34 respectively, in units of $\Delta K_{\text{benzene}}$. The predicted value for II is in good agreement with the experimental exaltation ($\Delta/\Delta_{\text{benzene}}=3.87$).[18] It turned out that the magnetically-induced ring currents in I and III are very much impeded. A part of the evidence for this fact is given by the NMR spectrum of I, which consists of two singlets of equal intensity at 3.48 and 3.99τ,[2] which are close to that observed for the olefinic protons of linear conjugated polyenes. The periphery of I and III may give a paramagnetic ring current characteristic of the 4n perimeter.[19] On the other hand, the naphthalene core in I and III may exhibit a diamagnetic ring current to the same extent as that of a free naphthalene molecule. Therefore, it may be expected that the paramagnetic ring current and the diamagnetic ring current cancel out each other to give a small magnetic susceptibility in I and III.

Half-wave Reduction Potentials. It has been shown that there is an excellent correlation between the energy of the first unoccupied molecular orbital and the half-wave reduction potential. Polarographic half-wave reduction potentials for a number of hydrocarbons in aqueous dioxane are summarized in Ref. 20. A plot of these aqueous-dioxane data against m, the energy (in units of eV) of the lowest vacant SCF MO, gives a good linear correlation (see Fig. 3). The least-square correlation line is:

$$-\varepsilon_{1/2}(\text{aq. diox.}) = -0.919(-m) + 4.240 \qquad (2)$$

The half-wave potentials, $\varepsilon_{1/2}$, predicted using Eq. (2) for I, II, and III are −1.083, −1.716, and −1.935 V *vs.* SCE respectively. The predicted $\varepsilon_{1/2}$ value for I is in good agreement with the experimental value, −1.056 V *vs.* SCE.[2]

Electronic Spectra. The calculated singlet transi-

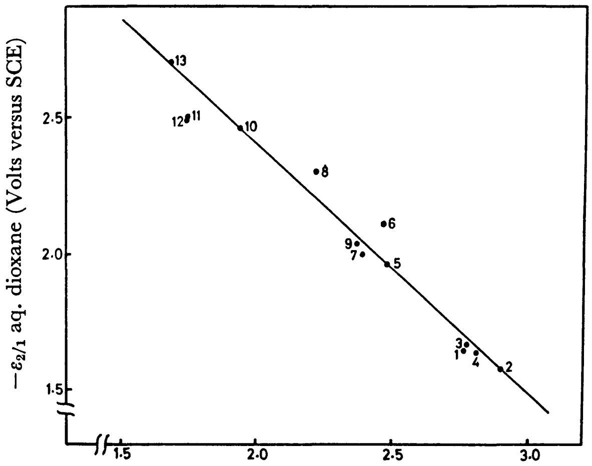

Fig. 3. Plot of half-wave potentials ($-\varepsilon_{1/2}$) in aqueous dioxane against energies ($-m$) of lowest vacant SCF orbitals. (1) Acenaphtylene, (2) Tetracene, (3) Perylene, (4) Azulene, (5) Anthracene, (6) Pyrene, (7) 1,2-Benzanthracene, (8) Chrysene, (9) Coronene, (10) Phenanthrene, (11) Naphthalene, (12) Triphenylene, (13) Biphenyl.

TABLE 2. TRANSITION TYPES, ENERGIES (ΔE) AND INTENSITIES (f)

Molecule	Transition type	Theoretical ΔE(eV)	f(cgs)	Experimental ΔE(eV)
I	$B_{3g} \longleftarrow A_g$	2.24	forb.	tailing to 2.09[a]
	$B_{2u} \longleftarrow A_g$	3.23	0.048	2.91
	$B_{1u} \longleftarrow A_g$	3.75	0.33	3.65
	$B_{2u} \longleftarrow A_g$	4.09	0.18	3.81
	$A_g \longleftarrow A_g$	4.62	forb.	5.23
	$B_{2u} \longleftarrow A_g$	5.41	0.008	
	$A_g \longleftarrow A_g$	5.97	forb.	5.71
	$B_{2u} \longleftarrow A_g$	5.99	2.18	
II	$A_1 \longleftarrow A_1$	2.98	0.28	2.20[b]
	$B_2 \longleftarrow A_1$	3.15	0.026	≀
	$B_2 \longleftarrow A_1$	3.32	0.066	3.54
	$B_2 \longleftarrow A_1$	3.87	0.025	4.14
	$A_1 \longleftarrow A_1$	4.50	0.96	
	$A_1 \longleftarrow A_1$	4.67	0.16	
	$B_2 \longleftarrow A_1$	5.09	0.87	4.98
	$A_1 \longleftarrow A_1$	5.13	0.010	
	$A_1 \longleftarrow A_1$	5.26	0.021	
	$A_1 \longleftarrow A_1$	5.64	0.021	5.90
	$B_2 \longleftarrow A_1$	5.68	0.40	
III	$B_{3g} \longleftarrow A_g$	2.15	forb.	
	$B_{2u} \longleftarrow A_g$	3.13	0.014	
	$B_{1u} \longleftarrow A_g$	3.30	0.60	
	$B_{2u} \longleftarrow A_g$	3.69	0.15	
	$A_g \longleftarrow A_g$	4.51	forb.	
	$B_{2u} \longleftarrow A_g$	4.70	0.091	
	$A_g \longleftarrow A_g$	4.94	forb.	
	$B_{1u} \longleftarrow A_g$	5.30	1.17	
	$A_g \longleftarrow A_g$	5.46	forb.	
	$B_{2u} \longleftarrow A_g$	5.49	1.71	

a) B. M. Trost, personal communication

b) V. Boekelheide and G. K. Vick, *J. Amer. Chem. Soc.*, **78**, 653 (1956).

TAVLE 3. BOND LENGTHS OF FIRST SINGLET EXCITED STATES OF I AND III

Molecule	Bond	Bond length(Å)
I	1—2	1.390
	1—9	1.430
	3—4	1.394
	8—9	1.411
	12—13	1.439
	13—14	1.399
III	1—2	1.383
	1—13	1.435
	2—3	1.428
	5—6	1.396
	12—13	1.407
	16—17	1.435
	17—18	1.403

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[18] H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Amer. Chem. Soc.*, **91**, 1991 (1969).

[19] J. A. Pople and K. G. Untch, *ibid.*, **88**, 4811 (1966).

[20] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons. Inc., New York (1961), p. 178.

tion energies and intensities are summarized and compared with the experimental data in Table 2. The predicted transition energies for I and II are in good agreement with the observed absorption peaks. The spectral results calculated for I, II, and III by Favini *et al.*,⁷⁾ who used the aromatic model, are in fairly good agreement with the present results.

The calculated bond lengths of the first singlet excited states for I and III are listed in Table 3. It can be seen that, in both the molecules, the double-bond fixation in the first singlet excited state is considerably more relaxed than that in the ground states. This may be one of the reasons for the appearence of a long tail, extending to 600mμ, on the long-wavelength side of the first absorption band in I.²⁾

Aromatic Characteristics. The predicted C–C bond lengths for I, II, and III indicate that, in these molecules, the C–C skeleton is composed of two distinguishable parts: one in which bond lengths are smoothed out and another in which a strong double bond fixation exists. Thus, there are two regions, one aromatic in the sense that π-electrons are highly delocalized and the other polyolefinic, in the peripheries of the I, II, and III molecules. Nevertheless, the II molecule is more aromatic than the I and III molecules.

No definition of aromaticity which is correlated with the global π-electronic properties of a conjugated molecule, such as the delocalization energy and the diamagnetic susceptibility, is sufficient for these molecules, which are essentially both aromatic and polyolefinic.

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