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CNDO Calculations of Electronic Structures and Spectra of Nonalternant Conjugated Hydrocarbons

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The energetically most favorable geometrical structures with respect to C–C bond-length variation of fundamental nonalternant conjugated hydrocarbons have been examined using CNDO/2 approximation with its original parameterization. It was found that all the molecules examined should exhibit a marked bond alternation, accompanied with a molecular-symmetry reduction in the case of pentalene and heptalene. The predicted molecular dipole moments are in good agreement with the available experimental values. The electronic spectra have been calculated using a modified version of the CNDO/2 method proposed by Del Bene and Jaffe, with a new parameterization. The results are found to be in good agreement with experiment.

Bond distortions in the ground states of certain nonalternant conjugated hydrocarbons have drawn considerable theoretical attention in late years. It was noticed[1–3] that heptalene (IX, Fig. 1) shows no energy minimum for the D_{2h} symmetry suggested by the superposition of the two Kekule-type resonance structures, but has a lower energy if it takes an unsymmetrically-distorted nuclear arrangement that corresponds to either of the resonance structures and exhibits a strong bond alternation of a C_{2h} type in its periphery. The experimental information[4] agrees with this in indicating that π-electrons in this molecule are strongly localized in "double" bonds, rather than uniformly delocalized over the entire molecule.

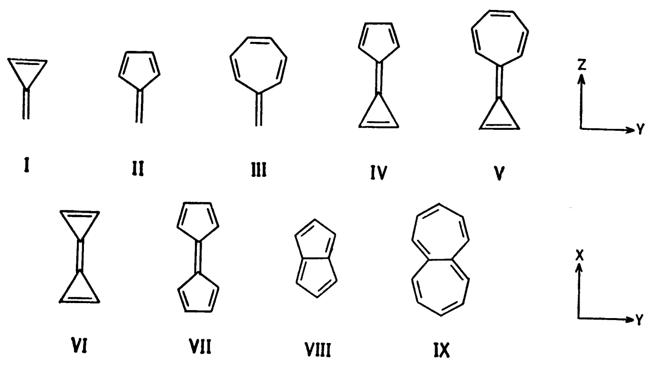

Fig. 1. Carbon skeletons and choice of axes for nonalternant hydrocarbons.

Theoretical justifications for such anomalous phenomena have been attempted by several authors.[1–3,5,6] Making allowance for the effects of σ-bond compression, they have succeeded in predicting that an unsymmetrical configuration resembling either of the two Kekule-type structures is actually energetically favored as compared with the fully symmetrical one. Binsch *et al.*[7–11] and Nakajima *et al.*[12,13] have recently developed a general theory of double-bond fixation in conjugated molecules and shown that bond alternations in certain nonalternant hydrocarbons are obtained theoretically as the energetically most favorable distortion rather than a presumed type of bond distortion.

In all the treatments so far made of the bond distortions in nonalternant hydrocarbons, however, complete σ-π separation has been assumed. That is, the total energy of a conjugated molecule is assumed to be the sum of the π-electron energy and the σ-core energy which may be regarded as the sum of the independent contributions from the C–C σ-bonds. The individual contributions of the σ-bonds have been approximated by a quadratic function of the bond-distance variation. The approximation used in computing the σ-core energy is not consistent with the molecular-orbital approximation used in calculating the π-electron energy.

It is the purpose of this paper to examine the ground-state geometries and electronic properties and the electronic spectra of certain fundamental nonalternant hydrocarbons by means of an all valence-electron molecular-orbital method, in which π-electrons and σ-electrons are treated with the same approximation.

Method of Calculation

The method used for predicting the energetically most favorable geometrical structures with respect to C–C bond-length variation is the semiempirical self-consistent all valence-electron molecular-orbital theory in the framework of the CNDO/2 approximation pro-

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posed by Pople and his coworkers.[14–16]

Although it is known[16,17] that the CNDO/2 approximation successfully predicts geometrical structures, *viz.*, equilibrium bond angles and bond lengths of a variety of molecules, it is inadequate for the calculation of the energy quantities such as dissociation energy and excitation energy. For small molecules, the bonding energies calculated by use of the Pople-Segal bonding parameters are higher than the experimental by factors 3—8.[18]

A modification along this line of the Pople-Segal CNDO/2 theory has recently been made by Sichel and Whitehead.[18,19] Using the CNDO approximation, they have developed a semiempirical SCF MO method with atomic parameters derived from atomic valence-state energies, interatomic electron-repulsion integrals calculated by use of the semiempirical formulas and bonding parameters calibrated by use of the bonding energies of binary hydrides. Bonding energies calculated using these parameters for various small molecules were found to be in much better agreement with experiment than those calculated from the Pople-Segal CNDO/2 theory.

When used for the prediction of the energetically most favorable geometrical structures of conjugated molecules, however, the parameterization proposed by Sichel and Whitehead turns out to be less satisfactory and, in certain cases, completely inadequate. As an example, the equilibrium C–C bond length for ethylene predicted with their parameterization is smaller than 1.20 Å, and is considerably shorter than that (1.320 Å) predicted with the Pople-Segal CNDO/2 method and the experimental value (1.339 Å). For benzene, the SCF iterative procedure with the Sichel-Whitehead parameterization leads to the loss of the initially assumed D_{6h} symmetry for its ground state. This unexpected result arises mainly from the fact that because of the too small values of bonding parameters proposed by Sichel and Whitehead, the orbital-intermingling occurs between the initially chosen bonding and antibonding molecular orbitals in the course of the iterative procedure.

Recently, some modifications of the CNDO/2 procedure have been attempted by several authors[20–26] aiming at making it useful for predicting and interpreting spectroscopic data. Of these, the approximation proposed by Del Bene and Jaffé[21–24] is most noteworthy, the essential modification involving the use of reduced electron-repulsion integrals instead of theoretical ones and introduction of a new empirical parameter κ to differentiate resonance integrals between σ-type orbitals from those between π-type orbitals. The value of κ and bonding parameters have been adjusted so as to give the most consistent spectroscopic data for benzene, pyridine, and diazines.

However, Del Bene-Jaffé's approximation with the original parameterization does not work well for the prediction of electronic spectra of saturated molecules. For methane and ethane, it gives the lowest excitation energies higher by 3—4 eV than the experimental values. Of course, it is desirable to be able to treat conjugated molecules and saturated molecules at the same time using a single parameterization.

For the discussion of electronic spectra, we use the Del Bene-Jaffé-type modified CNDO/2 method with the values of κ and bonding parameters, β_C^0, β_H^0, readjusted, so that they may give the most consistent spectroscopic data in methane, ethylene and benzene.[27] The values chosen for β_C^0, β_H^0, and κ are -15.0 eV, -8.0 eV, and 0.75, respectively. One-center and two-center electron-repulsion integrals were evaluated with Sichel-Whitehead's formula and Mataga-Nishimoto's formula,[28] respectively, and the local core matrix elements with Sichel-Whitehead's formula.

It should be added that the Del Bene-Jaffé-type method with the present parameterization is inadequate for the prediction of the ground-state geometrical structures. If the internuclear potential energy, V_{AB}, is written as[18]

$$V_{AB} = Z_A Z_B \gamma_{AB}$$

where Z and γ are the atomic core charge and the atomic electron-repulsion integral, the equilibrium C–C bond length r_e for ethylene is predicted to be zero. On the other hand, the use of the point-charge approximation for V_{AB} gives to an infinitely large r_e for ethylene. Another formula available for V_{AB} is that recommended by Dewar and Klopmann:[29]

$$V_{AB} = \frac{Z_A Z_B}{r_{AB} + a}$$

However, the use of this formula with the value of a adjusted so as to reproduce the experimental r_e for ethylene unexpectedly results in the ground state of benzene being of D_{3h} symmetry.

We therefore used the CNDO/2 method with its original parameterization to predict the geometrical structures of nonalternant hydrocarbons, and the Del Bene-Jaffé-type modified CNDO/2 method with the new parameterization to discuss electronic spectra.

We made the following assumptions for prediction of the energetically most favorable ground-state geometry of each molecule.

(a) Only C–C bond distances were varied and the C–H bond distances were kept constant (1.00 Å), assuming the molecule to be planar.

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(b) The internuclear distances between nonneighboring atoms were all kept constant and estimated assuming all the rings to be regular polygons.

(c) Starting from the nuclear arrangement in which all the C–C bond lengths are assumed to be equal, the C–C bonds corresponding to the double bonds in the Kekule-type structure were shortened and, at the same time, all the remaining C–C bonds lengthened in the same amount.

In calculating electronic spectra, configuration mixing of the singly excited states is partially included; the number of the configuration interactions considered is 28 for I, II, and VI (Fig. 1) and 55 for other molecules.

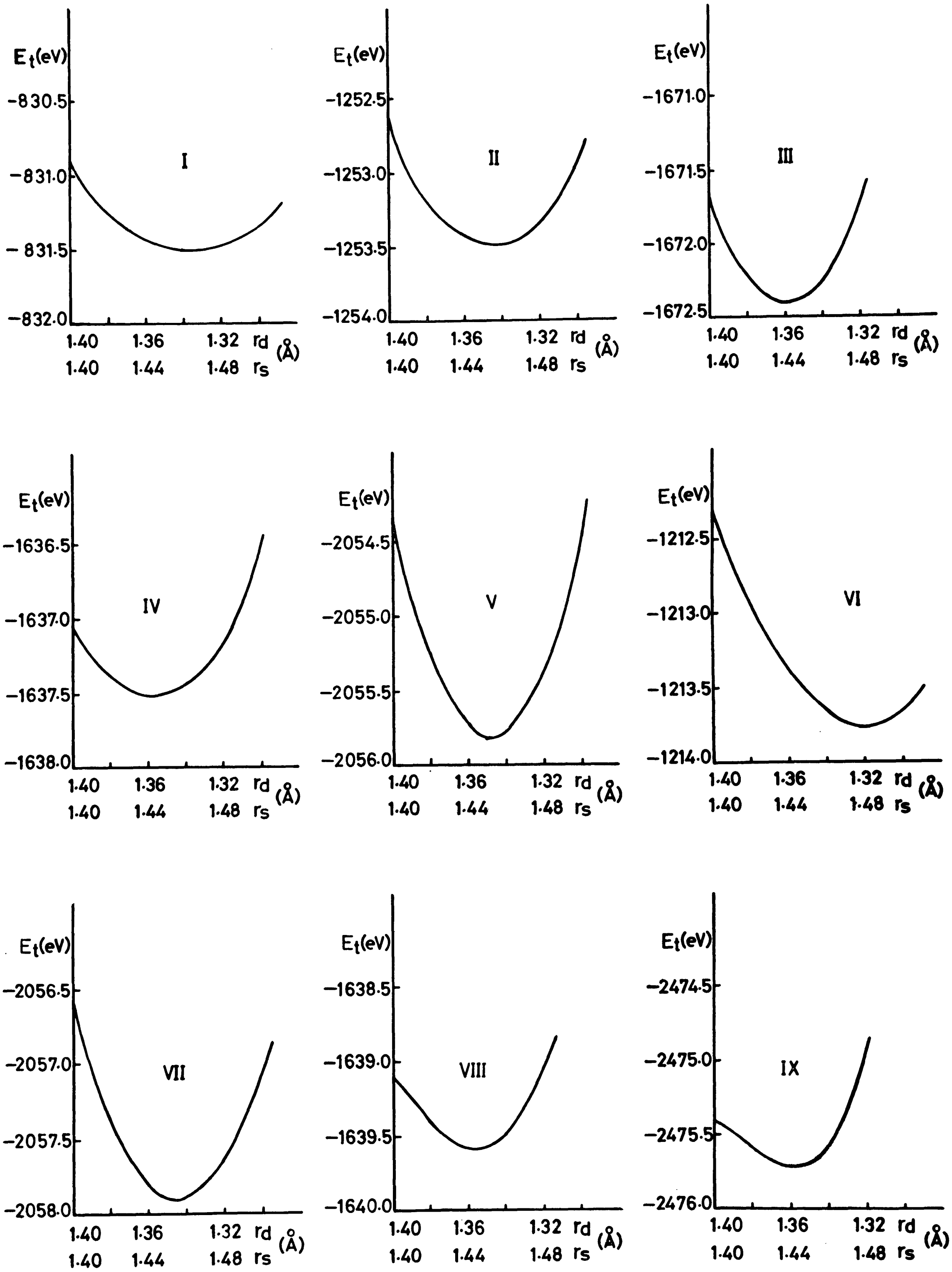

Fig. 2. Variations of total energies with C–C bond lengths. r_d and r_s mean the C–C bond lengths corresponding to the double bonds and single bonds, respectively, in the Kekulé-type structure.

Results and Discussion

Ground-State Properties. The nonalternant hydrocarbons examined are triafulvene (I), fulvene (II), heptafulvene (III), calicene (IV), triaheptafulvalene (V), triafulvalene (VI), fulvalene (VII), pentalene (VIII) and heptalene (IX) (Fig. 1). In Fig. 2, the total energies calculated for these molecules are plotted against the C–C bond-distance variation. All the curves exhibit an energy minimum at about 1.32—1.36 Å for the shorter bonds and 1.44—1.48 Å for the longer bonds, showing an agreement with the results of previous investigations[1–3,5,7,9,11,30] where in these nonalternant hydrocarbons a distorted structure in which a marked double-bond fixation exists is energetically favored as compared with the fully delocalized one. It should be noted that in pentalene (VIII) and heptalene (IX), such a bond distortion is accompanied with molecular-symmetry reduction from D_{2h} to C_{2h}. The stabilization energies which favor the C_{2h} structure for VIII and IX are calculated to be 11.04 and 6.90 kcal/mole, respectively.

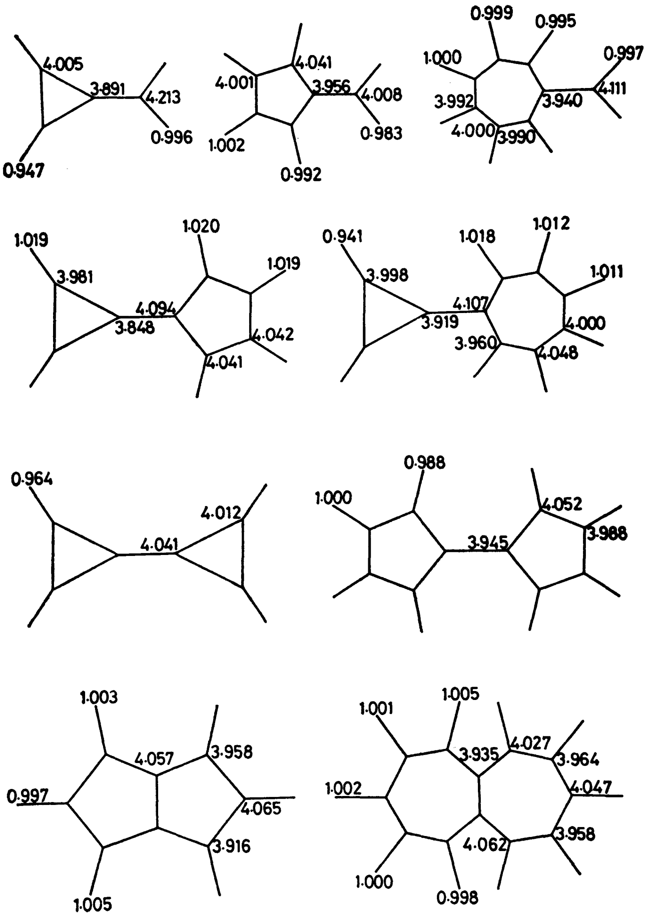

Fig. 3. Total atomic populations.

The total atomic populations calculated using the energetically most favorable set of C–C bond distances are shown in Fig. 3. The dipole moments calculated from these data for I, II, III, IV, and V are 2.12, 0.61, 0.98, 5.45, and 3.71 D, respectively. As for II, a dipole moment of 1.2 D[31] or 1.1 D[32] has, until recently, been adopted as the experimental value. Brown *et al.*[33] have measured the Stark effect of II and reported a dipole moment of 0.44±0.02 D, which is considerably smaller than the experimental estimation. They have also calculated the dipole moment of II using the CNDO/2 procedure and obtained a theoretical value 0.89 D. The discrepancy between their value and ours seems to arise from the difference in the geometrical structures adopted. Our value obtained using the set of bond distances at which the total energy is minimized should in principle be more plausible and actually is reasonably near the new experimental value.

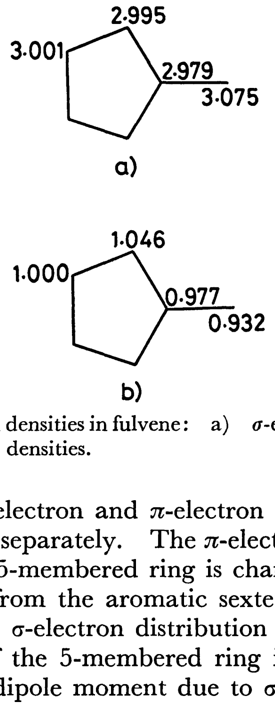

Fig. 4. Electron densities in fulvene: a) σ-electron densities; b) π-electron densities.

In Fig. 4, σ-electron and π-electron charge densities of II are shown separately. The π-electron distribution shows that the 5-membered ring is charged negatively, as is expected from the aromatic sextet rule. On the other hand, the σ-electron distribution reveals that the σ framework of the 5-membered ring is charged positively and the dipole moment due to σ charge has the direction opposite to that due to π charge. However, the dipole moment due to σ electrons (0.19 D) is completely masked by that due to π electrons (0.80 D), and the total dipole moment is such that the 5-membered ring is charged negatively. Such is the case with other polar molecules, I, III, IV, and V.

The theoretical dipole moments for III and IV are in good agreement with the experimental values 0.7 D[34] and 5.6—6.1 D,[30] respectively.

The dipole moment of I is predicted to be considerably larger than that of III, which means that the electron releasing power of the 3-membered ring is appreciably greater than that of the 7-membered ring. This fact is reflected in the appreciable dipole moment calculated for V; the dipolar structure of this molecule is such that the negative pole is directed towards the 7-

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membered ring.

Electronic Spectra. The lower singlet transition energies and intensities calculated using the geometrical structures corresponding to the energy minimum are summarized and compared with the available experimental data in Table 1. Also included are the transition symmetries and types. It will be seen that the predicted transitions are in line with the observed absorption peaks and tails.

The transition energy for the longest wavelength transition of triafulvene (I) is predicted to be considerably smaller than predicted by Julg[30] (6.27 eV), Naka-

TABLE 1. SINGLET TRANSITION ENERGIES (ΔE) AND INTENSITIES (f)

Molecule	Transition		Theoretical		Experimental ΔE(eV)
	Symmetry	Type[a]	ΔE (eV)	f (cgs)	
I	B_2	$\pi\to\pi^*$ (0.89)	4.60	0.025	
	A_2	$\pi\to\sigma^*$	4.69	Forb.	
	B_1	$\sigma\to\pi^*$	4.95	0.000	
	A_2	$\sigma\to\pi^*$	5.55	Forb.	
	A_1	$\pi\to\pi^*$ (0.89)	6.01	0.32	
II	B_2	$\pi\to\pi^*$ (0.98)	3.76	0.031	3.32(f=0.012)[b], 3.42[c]
	A_2	$\sigma\to\pi^*$	4.75	Forb.	
	A_2	$\pi\to\sigma^*$	5.14	Forb.	
	A_1	$\pi\to\pi^*$ (0.92)	5.25	0.36	5.12[b,c] (0.32)[b]
III	B_2	$\pi\to\pi^*$ (0.98)	3.06	0.034	2.91(f=0.02)[d]
	A_1	$\pi\to\pi^*$ (0.91)	4.40	0.59	4.44(0.3)
	B_1	$\sigma\to\pi^*$	4.63	0.000	
	A_2	$\pi\to\sigma^*$	4.66	Forb.	
	A_2	$\sigma\to\pi^*$	4.97	Forb.	
	B_1	$\sigma\to\pi^*$	5.24	0.000	
IV	A_1	$\pi\to\pi^*$ (0.92)	4.46	0.061	
	B_2	$\pi\to\pi^*$ (0.95)	4.50	0.052	4.13(log ε =4.64), tail[e]
	B_2	$\pi\to\pi^*$ (0.94)	4.63	0.028	
	B_1	$\sigma\to\pi^*$	4.75	0.000	
	A_2	$\sigma\to\pi^*$	4.83	Forb.	
	A_2	$\sigma\to\pi^*$	4.84	Forb.	
	A_1	$\pi\to\pi^*$ (1.00)	5.21	0.000	
V	B_2	$\pi\to\pi^*$ (0.99)	2.09	0.006	
	B_1	$\pi\to\sigma^*$	3.13	0.000	
	B_2	$\pi\to\pi^*$ (0.98)	3.45	0.023	
	A_2	$\pi\to\sigma^*$	3.79	Forb.	
	A_1	$\pi\to\pi^*$ (0.96)	3.91	0.81	
	A_2	$\pi\to\sigma^*$	4.07	Forb.	
	B_1	$\pi\to\sigma^*$	4.42	0.000	
V	B_1	$\sigma\to\pi^*$	4.67	0.000	
	B_1	$\sigma\to\pi^*$	5.09	0.000	
VI	B_{2g}	$\pi\to\sigma^*$	2.42	Forb.	
	B_{2u}	$\pi\to\pi^*$ (0.86)	3.59	0.056	
	B_{3g}	$\pi\to\pi^*$ (0.97)	3.70	Forb.	
	B_{2g}	$\sigma\to\pi^*$	4.43	Forb.	
	B_{3u}	$\sigma\to\pi^*$	4.45	0.000	
	B_{2u}	$\sigma\to\sigma^*$ (0.20)	5.33	0.080	
VII	B_{2u}	$\pi\to\pi^*$ (0.98)	3.05	0.018	
	B_{3g}	$\pi\to\pi^*$ (0.97)	3.14	Forb.	2.98(log ε =2.41), tail[f]
	B_{1u}	$\pi\to\pi^*$ (0.93)	4.25	0.93	3.95(4.67)
	B_{3u}	$\pi\to\sigma^*$	5.29	0.000	
	A_u	$\pi\to\sigma^*$	5.31	0.000	
	B_{3u}	$\sigma\to\pi^*$	5.44	0.000	
VIII	A_g	$\pi\to\pi^*$ (0.99)	1.34	Forb.	1.72(log ε =1.95), tail[g]
	A_u	$\sigma\to\pi^*$	3.41	0.000	
	B_u	$\pi\to\pi^*$ (0.91)	4.06	0.28	3.27(3.99)
	A_u	$\pi\to\sigma^*$	4.41	0.000	
	B_u	$\pi\to\pi^*$ (0.93)	5.26	0.32	4.00 (4.52)
IX	A_g	$\pi\to\pi^*$ (0.99)	1.57	Forb.	Tail[h]
	B_u	$\pi\to\pi^*$ (0.92)	2.74	0.32	3.52(f=0.15)
	A_u	$\pi\to\sigma^*$	3.50	0.000	
	B_u	$\pi\to\pi^*$ (0.90)	3.95	0.26	4.84(?)
	A_u	$\sigma\to\pi^*$	4.15	0.000	
	A_u	$\pi\to\sigma^*$	4.32	0.000	
	A_u	$\sigma\to\pi^*$	4.59	0.000	
	A_u	$\sigma\to\pi^*$	5.34	0.000	
	B_u	$\pi\to\pi^*$ (0.86)	5.36	0.77	

a) The transition type indicated refers to the configuration with the largest weight. The weight of the $\pi\to\pi^*$ configuration in the state considered are indicated in parenthesis.
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g) The spectrum of hexaphenyl pentalene; E. Le Goff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).
h) Reference 4.

jima *et al.*[35] (5.61 eV), and Meyer[36] (5.08 eV) using the π-electron approximation, but in good agreement with the value (4.3 eV) calculated by Yamaguchi *et al.*[37] using the variable bond-length SCF CI π-MO method in which the effects of the bent bonds in the 3-membered ring are taken into account. Unfortunately, there are at present no experimental spectral data available for a direct comparison of theory and experiment.

In fulvene (II) and heptafulvene (III), the lowest $\pi \rightarrow \pi^*$ transition (B_2) polarized along the short axis and the next one (A_1) polarized along the long axis are well separated in energy. On the other hand, in calicene (IV) and fulvalene (VII), these two transitions are predicted to be very close in energy. This is in agreement with the experimental data.

In heptalene (IX), the agreement between theory and experiment is less satisfactory, the predicted transition energies being found to be fairly small as compared with the observed values. This may be attributed to a nonplanar conformation, possible in this molecule owing to the steric repulsion between the ortho hydrogen atoms.

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