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Commentationes

The Electronic Structures and Spectra of Nonbenzenoid Aromatic Hydrocarbons Containing the Cyclopropenyl Ring

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The ground-state electronic properties and electronic spectra of triafulvene, I, triafulvalene, II, calicene, III, heptatriafulvalene, IV, benzocalicene, V, and dibenzocalicene, VI, have been studied by the semiempirical SCF CI LCAO-π-MO method which allows for bond order-bond length correlation at each iteration. The dependence of the resonance integral on bond length is scrutinized by trying to reproduce the properties of the ground and excited states in a series of reference compounds. For the bonds in the cyclopropenyl ring a new bond order-bond length relationship is proposed which allows for the fact that their σ components are bent. The calculated dipole moment and bond lengths of III and the predicted electronic spectra of III, V, and VI are in good agreement with the available experimental data.

Grundzustand und Elektronenspektren von Triafulven, Triafulvalen, Calicen, Heptatriafulvalen, Benzocalicen und Dibenzocalicen wurden mittels eines semiempirischen SCF-Verfahrens mit Korrelation zwischen Bindungsordnung und -länge untersucht. Die Abhängigkeit des Resonanzintegrals von der Bindungslänge wurde bestimmt, indem Grund- und angeregte Zustände einer Reihe von Bezugssubstanzen zur Justierung herangezogen wurden. Für die Bindungen im Cyclopropylenring wird eine neue Beziehung zwischen Bindungsordnung und -länge vorgeschlagen, die den verzerrten σ-Komponenten Rechnung trägt. Die berechneten Dipolmomente und Bindungslängen von Calicen und die Spektren aller drei Calicene stimmen befriedigend mit dem Experiment überein.

La méthode SCF-CI-LCAO-π-MO avec variation de la longueur de liaison en fonction de l'indice de liaison à chaque itération, a été utilisée pour l'étude des propriétés électroniques de l'état fondamental et du spectre des composés suivants: I triafulvène, II triafulvalène, III calicène, IV heptatriafulvalène, V benzocalicène, VI dibenzocalicène. La dépendance à la longueur de liaison de l'intégrale de résonance est sondée par ajustement à l'expérience de propriétés moléculaires. Pour le cyclopropylène une nouvelle relation entre longueur et indice de liaison est proposée pour tenir compte de ce que les composantes σ sont courbes. Le moment dipolaire et les longueurs de liaison de III et les spectres électroniques de III, V et VI sont prévus en bon accord avec les données expérimentales disponibles.

Recent syntheses of nonbenzenoid aromatic hydrocarbons containing the cyclopropenyl ring include derivatives of triafulvene, I [1–4], and calicene (pentatriafulvalene; III) [5–13], although the parent molecules have so far not been synthesized. Early theoretical treatments based on the simple Hückel MO method [14–16] have predicted that molecules I and III should represent stable systems because of the significant contribution, to their ground state, of dipolar structures in which the positive pole is directed toward the cyclopropenyl ring. Recently, however, Dewar and Gleicher [17] have calculated the C–C bond lengths of III and its benzo-derivatives by the use of the semiempirical SCF MO method and have suggested that they are not aromatic, showing strong bond fixation. More recently Nakajima *et al.* [18] have examined the ground-state electronic properties of I and III using the modified Hückel MO method and have concluded that these molecules have very little, if any, aromatic stability not only from the viewpoint of π-electron delocalization but also from the viewpoint of chemical reactivity (Fig. 1).

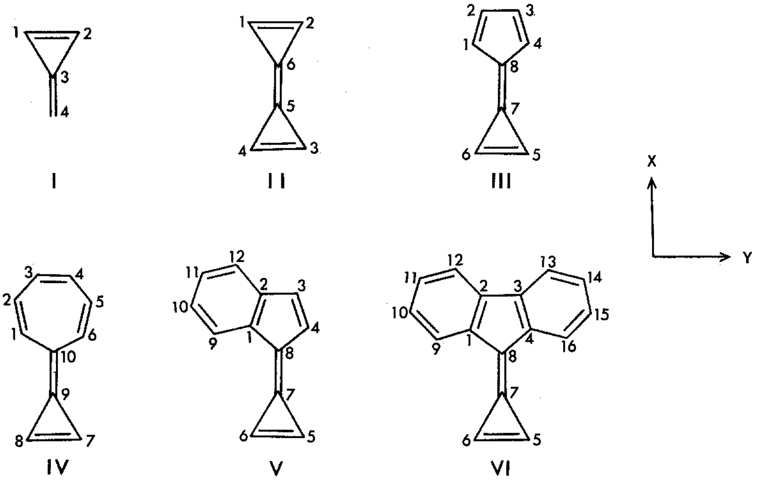

Fig. 1. Carbon skeleton, choice of axes, and numbering of nonbenzenoid hydrocarbons

The purpose of this paper is to study the ground-state electronic properties and the electronic spectra in particular of I, III, triafulvalene (bis-cyclopropenylidene, II), heptatriafulvalene (cyclopropenylidene-cycloheptatriene, IV), benzo[a]calicene, V, and dibenzo[a, c]calicene, VI, by means of a semiempirical SCF CI MO method in which allowance is made for bond order-bond length correlation. Two different sets of values are used for the repulsion integrals, one set corresponding to the values due to Pariser and Parr's formula [19], the other to the values recommended by Mataga and Nishimoto [22]. For the nonbenzenoid hydrocarbons in which strong bond fixation exists, such as those mentioned above, the calculated results for both the ground state and the excited states turn out to be sensitive to the dependence of the resonance integral on bond length. The best choice of the expressions for the dependence of the resonance integral on distance will first be made by trying to reproduce as many properties as possible in a series of reference compounds.

Method of Calculation

The method used is the self-consistent configuration-interaction formalism of the Pariser-Parr-Pople method [19, 20]. The C–C bond lengths, and consequently the resonance and the two-center repulsion integrals are allowed to vary with bond order at each iteration until self-consistency is reached. Penetration effects from carbon atoms and hydrogen atoms were all neglected. In order to discuss the properties of the excited states, configuration mixing of all the singly excited states is included.

The one-center repulsion integral for carbon given as $I_c - A_c$ was taken to be $11.16-0.03=11.13$ eV [21]. The two-center repulsion integrals were then calculated using the Pariser-Parr method or the Mataga-Nishimoto method. Only the nearest-neighbor two-center integrals were allowed to change, using a bond distance calculated by the aid of the relationship [23]

$$r_{\mu\nu}(\text{Å}) = 1.520 - 0.186\, p_{\mu\nu} \qquad (1)$$

where $p_{\mu\nu}$ is the π-bond order of the bond $\mu\nu$. Nonbonded distances were calculated assuming the rings to be regular and kept constant for simplicity.

Resonance integrals were included only between nearest neighbors. These resonance integrals were evaluated at each iteration, using the bond distances obtained from (1) and a formula

$$\beta_{\mu\nu} = \beta_0 \exp[a(r_0 - r_{\mu\nu})] \qquad (2)$$

where β_0 and r_0 are the resonance integral and the C–C distance for benzene, respectively.The value of a was determined using the two procedures.

1. Method 1: The value of a was determined from β values so adjusted as to reproduce the experimental excitation energies of ethylene and benzene; the C–C bond length and the lowest excitation energy of ethylene were taken to be 1.334 Å [24] and 7.28 eV [25], respectively. Thus we obtain $a = 1.586$ Å^{-1} and $\beta_0 = -2.38$ eV.
2. Method 2: The Mataga-Nishimoto formula for two-center repulsion integrals is used. In this case we could not use the above procedure to determine the a value, because the $|\beta|$ value for ethylene turns out to be smaller than that for benzene. In this situation it seemed to us that the best choice of the a value would be obtained by trying to reproduce as many properties of ground and excited states as possible in a series of reference compounds; the reference compounds chosen include a polyene, alternant and non-alternant polycyclic hydrocarbons. This trial-and-error procedure yielded $a = 1.7$ Å^{-1} and $\beta_0 = -2.38$ eV *(vide infra)*.

In this connection it is of interest to note that the a value should not exceed a certain limiting value, 4.0 Å^{-1} in Method 1 and 4.4 Å^{-1} in Method 2. If an a value larger than this limiting value is employed in the present SCF method, the stable equilibrium conformation of benzene is predicted to be of symmetry D_{3h}: a self-consistency of molecular orbitals is achieved for the two symmetry types, D_{6h} and D_{3h} and the skew structure (D_{3h}) turns out to be energetically favoured as compared with the symmetric one (D_{6h}) [26]. The use of Pariser-Parr's original a value, 5.007 Å^{-1}, for example, brings about the result that the stable conformation of benzene possess the D_{3h} symmetry, the length of the shorter bonds being 1.35 Å and that of the longer bonds 1.45 Å. Further, if Kon's formula for β [27] is used, in conjunction with the Pariser-Parr formula for two-center repulsion integrals, in the present SCF procedure, the stable geometry of benzene is predicted to be also of symmetry D_{3h}. Various functional formulas for β, apart from the exponential formula, proposed so far by the several authors, e.g., Kon's formula, Fischer-Hjalmars' formula [28], Ohno's formula [29], Wolfsberg-Helmholtz's overlap approximation [30], Mulliken's magic formula [31], and Nishimoto-Forster's formula [32], if these are rewritten in an approximately exponential form, give about 4.3, 3.1, 2.7, 1.7, 1.3, and 1.1 $Å^{-1}$, respectively, as an a value.

Results and Discussion

Reference Compounds

Reference compounds chosen in order to determine the a value to be used in conjunction with Mataga-Nishimoto's integrals are butadiene, pentafulvene, heptafulvene, azulene, and naphthalene. In pentafulvene and heptafulvene in particular both the excited-state and ground-state properties are very sensitive to the choice of the a value: the decrease in the a value results in the lowering of the excitation energies and in the increase in the dipole moments indicative of the ground-state π-electron delocalization. The best simultaneous agreement of the calculated excitation energies and dipole moments with the experimental values in the reference compounds considered is obtained when $a = 1.7\ Å^{-1}$. This indicates that of the various theoretical formulas proposed for β, the overlap approximation, $\beta \propto S$, works best in reproducing experimental data.

The calculated transition energies and intensities of reference compounds are compared with the experimental values in Table 1. Both the transition energies predicted using methods 1 and 2 are in good agreement with the experimental values, though the transition energies calculated using method 1 is slightly higher in general than those calculated using method 2.

Recently Bloor, Gilson, and Brearley [33] have calculated the excited-state energies of various class of conjugated hydrocarbons using the semiempirical SCF-MO method which is essentially the same as our method 2, except for the use of Mulliken's magic formula for β. For naphthalene and azulene their method gives results not significantly different from those of our method 2, whereas for butadiene, fulvene, and heptafulvene their method gives transition energies which are low by $0.2 \sim 0.3$ eV, compared with both the experimental values and those calculated using our method 2. The discrepancy between the two theoretical results is due to the fact that the dependence of β on r of the magic formula is slower than that of the exponential formula with $a = 1.7\ Å^{-1}$.

The predicted C–C bond lengths are compared with the experimental values in Table 2. Bond lengths calculated using method 1 and those calculated using method 2 differ little. The predicted values agree to about 0.01 Å with the experimental values.

In order to examine the possibility of the bond length alternation in azulene [34], a structure in which the peripheral C–C bond lengths alternate was adopted as a starting geometry in the SCF iteration. The final SCF-MO's obtained using both methods 1 and 2 turned out to possess the C_{2v} symmetry. It is noted in this connection that the condition that azulene should possess the C_{2v} symmetry reduces the highest limit of the a value.

The dipole moments for pentafulvene, heptafulvene, and azulene calculated using method 1 are 1.27, 0.79, and 2.58 D, respectively, and those calculated using

Table 1. *Transition energies* (eV) *and intensities* (f) *of reference molecules*

Molecule	Method 1		Method 2		Experimental	
	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)	f
Butadiene	5.62	1.01	5.85	1.03	5.71[a], 5.92[b]	
	7.18	0	6.91	0	7.2?[c]	
Pentafulvene	3.27	0.048 (y)[d]	3.32	0.035 (y)	3.32[e], 3.42[f]	0.012[e]
	5.05	0.67 (x)	5.06	0.63 (x)	5.12[e,f]	0.32[e]
	6.98	0.31 (x)	6.84	0.31 (x)		
Heptafulvene	2.97	0.047 (y)	2.97	0.047 (y)	2.91[g]	0.02[g]
	4.51	0.53 (x)	4.32	0.48 (x)	4.44[g]	0.3[g]
	6.09	0.036 (y)	6.05	0.096 (y)	5.83[g]	
	6.21	1.19 (x)	6.11	1.28 (x)		
Azulene	2.11	0.018 (y)	2.05	0.025 (y)	1.96[h], 2.14[i]	0.009 (y)[h,j]
	3.17	0.002 (x)	3.53	0.005 (x)	3.66[h], 3.50[j]	0.08 (x)[h,j]
	4.47	0.10 (y)	4.41	0.13 (y)	4.48[h]	?
	5.26	1.68 (x)	4.78	1.88 (x)	4.52[h,j]	1.10 (x)[h,j]
	5.80	0.37 (y)	5.68	0.41 (y)	5.24[h,j]	0.38 (y)[h,j]
	6.07	0.33 (x)	6.03	0.010 (x)	6.42[j]	0.65[j]
	6.80	0.24 (y)	6.41	0.19 (y)		
	6.87	0.048 (x)	6.72	0.39 (x)		
Naphthalene	4.27	0.000 (x)	4.18	0.000 (x)	3.97[k], 4.11[b]	0.002 (x)[k]
	4.45	0.097 (y)	4.68	0.20 (y)	4.51[k], 4.61[b]	0.18 (y)[k]
	5.56	0	5.76	0		
	5.89	0	5.77	1.96 (x)	5.63[k], 5.88[b]	1.70 (x)[k]
	6.25	2.18 (x)	5.97	0		
	6.42	0.77 (y)	6.29	0	6.51[k]	0.21[k]
	6.64	0	6.30	0.65 (y)		

[a] Jaffe, H. H., and M. Orchin: Theory and applications of ultraviolet spectroscopy. New York, N. Y.: John Wiley and Sons 1962.

[b] American Peteroleum Institute, Research Project 44, Ultraviolet Absorption Spectral Data. Carnegie Institute of Technology.

[c] Mulliken, R. S.: Rev. mod. Physics **14**, 265 (1942).

[d] Polarization. x and y are directed along the long axis and the short axis, respectively, of the molecule.

[e] Thiec, J., and J. Wiemann: Bull. Soc. chim. France **1956**, 177.

[f] Schaltegger, H., M. Neuenschwander, and D. Meuche: Helv. chim. Acta **48**, 955 (1965).

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[h] Heilbronner, E.: In: Non-benzenoid aromatic compounds, ed. D. Ginsburg. New York, N. Y.: Interscience Publishers, Inc. 1959.

[i] Plattner, Pl. A., and E. Heilbronner: Helv. chim. Acta **30**, 910 (1947); **31**, 804 (1948).

[j] Pariser, R.: J. chem. Physics **25**, 1112 (1956).

[k] Murrell, J. N.: The theory of the electronic spectra of organic molecules. London: Methuen 1963.

method 2 are 1.34, 0.94, and 2.82 D, respectively. Theoretical values are in good agreement with experimental values, 1.1 D for pentafulvene [35], 0.7 D for heptafulvene [36], and 1.0 D for azulene [37], except that the theoretical value for azulene is rather larger than the observed value.

Nonbenzenoid Aromatic Hydrocarbons Containing the Cyclopropenyl Ring

Dewar and Gleicher [17], and Nakajima *et al.* [18] have calculated the bond lengths of calicene using the bond order-bond length relation like Eq. (1) which has been established for the bonds between sp^2 carbon atoms. Their values do not of course allow for possible shortening of the bonds in the cyclopropenyl ring, due to the fact that their σ bonds are "bent". Recently the bond lengths of tetrachlorodi-*n*-propylcalicene have been determined using the X-ray technique [38]. The predicted lengths of the bonds in the 5-membered ring are in good agreement with the experimental values, while the predicted lengths of the bonds in the 3-membered ring are considerably longer (0.02 ~ 0.08 Å) than the observed values.

Table 2. *Bond lengths* (Å) *of reference compounds*

Molecule	Bond	Method 1	Method 2	Experimental
Butadiene	1–2	1.342	1.343	1.337[a]
	2–3	1.467	1.463	1.483
Naphthalene	1–2	1.376	1.378	1.364[b], 1.371[d]
	1–9	1.425	1.423	1.421[b], 1.422[d]
	2–3	1.419	1.417	1.415[b], 1.412[d]
	9–10	1.410	1.413	1.418[b], 1.420[d]
Azulene	1–2	1.397	1.398	1.391[c]
	1–9	1.406	1.405	1.413
	4–5	1.398	1.398	1.401
	4–10	1.407	1.406	1.383
	5–6	1.400	1.400	1.385
	9–10	1.468	1.469	1.483

[a] Almeningen, A., O. Bastiansen, and M. Traettberg: Acta chem. Scand. **12**, 1221 (1958).

[b] Cruickshank, D. W. J., and R. A. Sparks: Proc. Roy. Soc. (London) A **258**, 270 (1960).

[c] Robertson, J. M., M. M. Shearer, G. A. Sim, and D. G. Watson: Acta crystallogr. **15**, 1 (1962).

[d] Bastiansen, O., and P. N. Skancke: Adv. chem. Physics 3, 323 (1961).

In these circumstances we use the following various bond order-bond length relationships: for the bonds in the 3-membered ring

$$r(\text{Å}) = 1.486 - 0.186\,p\,, \tag{3}$$

for the bonds joining the 3-membered rings

$$r(\text{Å}) = 1.494 - 0.186\,p\,, \tag{4}$$

and for the bonds joining the 3-membered ring and the 5- or 7-membered ring

$$r(\text{Å}) = 1.507 - 0.186\,p\,. \tag{5}$$

For the rest of the bonds we use Eq. (1). In obtaining Eq. (3) we used 1.300 Å, the double bond length in cyclopropene [40], as the length of the double bond in the 3-membered ring, and assumed the same dependence of bond length on π-bond order as in Eq. (1). Equation (5) was obtained using 1.321 Å, the double bond length in methylenecyclopropane [41], as the length of the exocyclic double bond. The shortening of the double bond joining the 3-membered rings was assumed to be twice that of the double bond in methylenecyclopropane.

The calculated transition energies and intensities are listed and compared with available experimental data in Table 3.

Table 3. *Transition energies* (eV) *and intensities* (f) *of nonbenzenoid aromatic hydrocarbons containing the cyclopropenyl ring*

Molecule	Method 1		Method 2		Experimental
	ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)
Triafulvene, I	4.33	0.10 (y)	4.34	0.068 (y)	
	6.15	0.74 (x)	6.67	0.81 (x)	
Triafulvalene, II	3.47	0	3.34	0	
	3.55	0.13 (y)	3.37	0.081 (y)	
	5.58	0.85 (x)	5.95	0.92 (x)	
Calicene, III	3.50	0.036 (y)	3.57	0.035 (y)	*tail*
	4.03	0.074 (y)	3.93	0.043 (y)	
	4.41	0.87 (x)	4.18	0.91 (x)	4.13 (log ε 4.64)[a]
	5.30	0.001 (x)	4.39	0.003 (x)	
	6.72	0.37 (x)	6.55	0.26 (x)	$\gtrsim 6.2$[a]
Heptatriafulvalene, IV	2.38	0.012 (y)	2.21	0.007 (y)	
	3.44	0.051 (y)	3.22	0.029 (y)	
	4.28	0.90 (x)	4.03	0.83 (x)	
	5.91	0.13 (y)	5.71	0.073 (y)	
	5.98	0.78 (x)	5.82	0.90 (x)	
Benzocalicene, V	3.83	0.073	3.70	0.17	3.69 ($\varepsilon = 4400$)[b]
	3.93	0.35	3.73	0.49	
	4.10	0.30	4.1	0.13	
	4.75	0.39	4.70	0.44	4.64 (8300)[b]
	5.13	0.18	4.76	0.047	
Dibenzocalicene, VI	3.85	0.039 (y)	3.69	0.024 (y)	3.51 ($\varepsilon = 17200$)[c], 3.48 (s)[d]
	3.99	0.50 (x)	3.72	0.56 (x)	3.69 (18600)[c], 3.81 ($\varepsilon = 22000$)[d]
	4.34	0.018 (y)	4.23	0.077 (y)	3.81 (18600)[c]
	4.52	0.16 (x)	4.42	0.28 (x)	4.20 (17400)[c], 4.20 (16650)[d]
	4.64	0.010 (y)	4.53	0.035 (y)	4.37 (s)[c], 4.57 (s)[d]
	5.16	0.23 (x)	4.84	0.50 (y)	4.68 (12100)[c], 4.72 (20600)[d]
	5.35	0.50 (y)	5.19	0.25 (x)	4.80 (13600)[c], 5.02 (28100)[d]
	5.79	0.21 (x)	5.33	0.000 (x)	5.00 (s)[c], 5.23 (s)[d]
	5.83	1.18 (y)	5.46	1.00 (y)	5.28 (49000)[c], 5.32 (46000)[d]

[a] Estimated from the spectrum of tetrachlorodi-*n*-propylcalicene in methanol [12, 13].

[b] The spectrum of 5,6-dimethylbenzocalicene in ether [7].

[c] The spectrum of 5,6-dimethyldibenzocalicene in cyclohexane [8]. *s* indicates the shoulder.

[d] The spectrum of 5,6-dimethyldibenzocalicene in ethanol [8].

The gross spectral feature of triafulvene is predicted to be similar to those of pentafulvene and heptafulvene, except that absorption maxima of the former is blue-shifted as compared with those of the latter two. The first transition of triafulvene is predicted at a wavelength appreciably longer than predicted by previous authors (6.27 eV by Julg [16], 5.61 eV by Nakajima *et al.* [18], and 5.08 eV by Meyer [41]). Unfortunately, triafulvene derivatives known so far are so complicated that it is difficult to estimate, from their absorption spectra, the triafulvene spectrum available for the direct comparison between theory and experiment.

Calicene is predicted to have a strong absorption band at 4.41 eV (method 1) or 4.18 eV (method 2). Two additional transitions at longer wavelengths than the strong transition are predicted, but their oscillator strengths are less than one-tenth that of the strong transition. A second absorption band is predicted at 6.7 eV (method 1) or 6.6 eV (method 2), with an intensity lower than the first band. These theoretical predictions are in satisfactory agreement with experiment. The experimental spectrum of 1,2,3,4-tetrachloro-5,6-*n*-propylcalicene shows a strong broad band at 3.95 eV ($\log\varepsilon = 4.64$) and the second band with a lower intensity at $\gtrsim 6.2$ eV. The spectrum of the parent calicene is expected not to differ considerably from that of the calicene derivative: Kende *et al.* [13] have suggested that the first absorption maximum of calicene should lie very close to 4.13 eV (300 mμ). Two longest-wavelength weak transitions are not observed as absorption maxima. They should be hidden in the longer-wavelength region, which is relatively broad ($\log\varepsilon = 2.6$ at 390 mμ), of the strong band.

Benzocalicene is predicted to have two main absorption bands, the long-wavelength one at 3.93 eV (method 1) or 3.73 eV (method 2) and the short-wavelength one at 4.75 eV (method 1) or 4.70 eV (method 2). This is in good agreement with experiment: observed spectrum of 5,6-dimethylbenzocalicene in ether shows absorption bands at 3.69 eV ($\varepsilon \sim 4400$) and 4.64 eV (8300) [7]. The effect of the two methyl substituents on the benzocalicene spectrum is expected to be small: the second transition, which is the main contributor to the first band, is predicted to shift by about 0.06 eV toward red by the methyl groups substituted in the cyclopropenyl ring [41].

The predicted transition energies and intensities of dibenzocalicene are compared with the experimental values for the 5,6-dimethyl derivative. The predicted transitions are well assigned to the observed peaks and shoulders [8]. The transition energies calculated using method 2 in particular are in good agreement with experimental values. Again in this case, it is expected that the introduction of the methyl groups does not affect the spectrum of the parent hydrocarbon to any great extent: as for the strong second transition, for example, the red shift caused by the two methyl substituents is predicted to be about 0.07 eV [41].

The calculated bond lengths and charge densities of the nonbenzenoid hydrocarbons are listed in Table 4. The differences between the results obtained using methods 1 and 2 are minor. Table 4 indicates that the equilibrium geometry of these molecules is usually one with significant bond length alternation. However, the lateral annulation of the benzene ring on the 5-membered ring of calicene results in the considerable relaxation of the double bond fixation of the bond where the annulation takes place. The calculated bond lengths of calicene may be compared with the experimental values of its tetrachlorodi-*n*-propyl [38] or tetrachlorodiphenyl [42] derivative, because such substituents are expected not to alter considerably the geometry of the parent hydrocarbon. The calculated bond lengths are in good agreement with the experimental values; in particular predicted lengths of the bonds in the 3-membered ring are improved appreciably as compared with those due to the previous authors.

The dipole moments of I, III, IV, V, and VI are calculated to be 2.23, 5.56, 2.83, 5.12, and 4.58 D (method 1), respectively, or 2.17, 6.37, 2.94, 5.79, and 5.10 D (method 2), respectively. Experimentally the dipole moment of tetrachlorodi-*n*-propylcalicene was determined to be 7.56 ± 0.03 D [12]. If we use the value of

Table 4. *Bond lengths and charge densities of nonbenzenoid aromatic hydrocarbons containing the cyclopropenyl ring*

Molecule	Bond	Bond lengths (Å)				Atom	Charge density	
		Calculated		Experimental			Method 1	Method 2
		Method 1	Method 2					
Triafulvene, I	1–2	1.315	1.316			1	0.918	0.916
	2–3	1.432	1.432			3	0.965	0.984
	3–4	1.338	1.338			4	1.198	1.184
Triafulvalene, II	1–2	1.311	1.312			1	0.939	0.938
	2–6	1.443	1.443			5	1.123	1.124
	5–6	1.331	1.331					
Calicene, III	1–2	1.364	1.367	1.36[a]	1.33[b]	1	1.069	1.077
	1–8	1.450	1.444	1.44	1.46	2	1.048	1.065
	2–3	1.436	1.433	1.46	1.45	5	0.876	0.859
	5–6	1.323	1.326	1.31	1.34	7	0.855	0.858
	5–7	1.417	1.412	1.39	1.41	8	1.157	1.140
	7–8	1.367	1.373	1.37	1.36			
Heptatriafulvalene, IV	1–2	1.353	1.355			1	0.968	0.976
	1–10	1.464	1.460			2	1.039	1.038
	2–3	1.459	1.456			3	1.001	1.002
	3–4	1.354	1.356			7	0.910	0.905
	7–8	1.317	1.318			9	0.995	1.003
	7–9	1.403	1.429			10	1.167	1.154
	9–10	1.354	1.357					
Benzocalicene, V	1–2	1.407	1.410			1	1.008	1.021
	1–8	1.457	1.452			2	1.012	1.023
	1–9	1.408	1.408			3	1.051	1.062
	2–3	1.450	1.446			4	1.033	1.040
	2–12	1.408	1.409			5	0.885	0.870
	3–4	1.358	1.362			6	0.881	0.868
	4–8	1.453	1.447			7	0.883	0.888
	5–6	1.322	1.324			8	1.171	1.149
	5–7	1.419	1.416			9	1.035	1.030
	7–8	1.364	1.369			10	1.061	1.020
	9–10	1.389	1.389			11	1.030	1.026
	10–11	1.404	1.405			12	0.997	1.003
	11–12	1.389	1.389					
Dibenzocalicene, VI	1–2	1.407	1.409			1	0.991	1.004
	1–8	1.459	1.454			2	1.016	1.022
	1–9	1.405	1.406			5	0.888	0.877
	2–3	1.460	1.456			7	0.901	0.909
	2–12	1.404	1.405			8	1.181	1.157
	5–6	1.321	1.323			9	1.037	1.030
	5–7	1.421	1.418			10	1.004	1.011
	7–8	1.361	1.365			11	1.029	1.023
	9–10	1.392	1.391			12	0.995	0.999
	10–11	1.401	1.402					
	11–12	1.392	1.392					

[a] X-ray bond lengths of tetrachlorodi-*n*-propylcalicene [38].

[b] X-ray bond lengths of tetrachlorodiphenylcalicene [42].

1.53 D [12] or 1.1 D [11] for the effect of four chlorine atoms attached to the 5-membered ring, the estimated dipole moment of the parent hydrocarbon should be 5.6 ~ 6.1 D, since the additional moment caused by the two propyl groups can be regarded as being about 0.4 D [12]. The theoretical value is in good agreement with the value thus experimentally estimated. In this connection it is of interest to note that the dipole moment of the third excited state of calicene is calculated to be 3.14 D (method 1) or 3.55 D (method 2), which indicates that the excited state is less polar than the ground state. This offers a possible explanation of the unusual spectral solvent-shifts, observed for calicene derivatives [5, 9, 10, 12], that increasing the polarity of the solvent shifts the first band to the blue.

The dipole moment of triafulvene turns out to be larger than that of heptafulvene, which means that the electron donating 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 heptatriafulvalene; the dipolar structure of this molecule is such that the negative pole is directed toward the 7-membered ring. Further, it is expected that the dipole moment of calicene should be larger than that of sesquifulvalene. This is the case, as far as theory is concerned: the dipole moment of the latter calculated using the present procedure is 4.28 D (method 1) or 5.60 D (method 2).

Finally, it is interesting to note that the lateral fusion of the benzene ring on the 5-membered ring of calicene results in the decrease of dipole moment, a fact which seems to be unusual. An explanation for this fact is given by the following argument. The dipolar structures in III, V, and VI are considered to be due to the electron transfer from the triafulvene system to butadiene, styrene, and biphenyl, respectively. The stabilities of dipolar structures in III, V, and VI should thus be correlated with the electron affinities of butadiene, styrene, and biphenyl, respectively. On the other hand, it has been well established that the electron affinities of conjugated systems are linearly correlated with the energies of the lowest vacant MO's. For butadiene, styrene, and biphenyl the energies of the lowest vacant MO's calculated using the simple Hückel approach are -0.618, -0.662, and $-0.705\,\beta$, respectively. This indicates that the electron affinities decrease in the order mentioned. In the same way, it is expected that the vertical fusion of the benzene ring on the 5-membered ring of III (to yield benzo[b]calicene) should result in the large increase of dipole moment, because the energy of the lowest vacant MO of o-xylylene is $-0.295\,\beta$, and hence the electron affinity of o-xylylene is considerably larger than that of butadiene. A quite similar variation of dipole moment has been known for pentafulvene and its benzo-derivatives. Pullman *et al.* [43, 44] have demonstrated using the simple Hückel approach that the charge transfer from the exocyclic carbon to the 5-membered ring in pentafulvene decreases by the lateral annulation of the benzene ring. This is in good agreement with the experimental fact.

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