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THE ELECTRONIC STRUCTURES AND SPECTRA OF TRIAFULVENE, TRIAFULVALENE AND CALICENE

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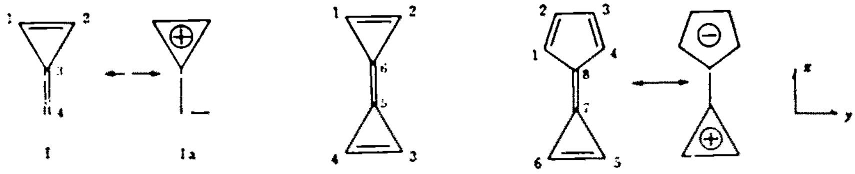
Abstract—The ground-state electronic properties of the unknown molecules, triafulvene (I), triafulvalene (bis-cyclopropenylidene; II) and calicene (III), have been studied by the modified Hückel MO method in which the effects of σ-bond compression are taken into account. It has been shown that in these molecules a very large degree of double bond fixation exists, with the result that quantities indicative of π-electron delocalization such as the delocalization energy and the diamagnetic anisotropy are reduced appreciably. The charge distributions and the free valence values in particular indicate that these molecules should be highly reactive. The calculated dipole moment of III is in good agreement with that experimentally estimated. The energies and moments for the lower electronic transitions were calculated by a Pariser-Parr type treatment. The predicted electronic spectrum of III is compared with that observed for a certain substituted calicene. The ground-state electronic properties of hexaphenylcalicene (IV) were also studied. The calculated dipole moment of this molecule agrees well with the observed value.

INTRODUCTION

Recent syntheses of nonbenzenoid aromatic hydrocarbons containing the cyclopropenyl ring include derivatives of triafulvene (I)[1-4] and calicene (III),[5-12] although



I Ia II III IIIa

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[10] E. D. Bergmann and I. Agranat, *Chem. Comm.* 512 (1965); *Tetrahedron* **22**, 1275 (1966).

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the parent hydrocarbons have so far not been synthesized. Molecules I and III should represent stable systems because of the contribution of dipolar structures Ia and IIIa, respectively, to their ground state. The ground-state electronic properties of I and III have been examined by the simple Hückel MO method.[13–15] The results accord well with the above expectation: calicene (III) in particular has been predicted to have a substantial π-electron delocalization energy and hence to be a reasonably stable system with aromatic properties. Recently, however, Dewar and Gleicher[16] have calculated the C—C bond lengths of III by the semi-empirical SCF MO procedure and have suggested that III is not aromatic, showing strong bond fixation.

The purpose of this paper is to deepen our understanding of the aromatic characteristics of I, III and triafulvalene (bis-cyclopropenylidene; II) through an attempt to calculate charge densities, bond orders, free valences, delocalization energies, diamagnetic anisotropies and electronic spectra by means of the modified Hückel MO method which has been quite successful in accounting for the bond length alternations in nonbenzenoid aromatic hydrocarbons consisting of 5- and/or 7-membered rings.[17–19]

DISCUSSION

Bond length alternations. The method employed in determining the equilibrium bond length alternation is the minimum energy method described earlier,[17] in which the effects of the σ-bond compression, now recognized to be of supreme importance in such a problem, are taken into account. The total binding energies V, taken to be the sum of π-bond energy and σ-bond energy, are calculated for a series of values ($0 \sim 1$) of the bond alternation parameter k, which is defined as

$$k = \beta_s/\beta_d \tag{1}$$

where β designates the resonance integral parameter and the subscripts s and d mean the single and double bonds in an unexcited Kekulé structure, respectively. The equilibrium bond alternation $k_{\min}$ is thus given by the minimum of the V–k curve.

The $k_{\min}$ values for molecules I, II and III are 0·52, 0·48 and 0·59, respectively. This indicates that in all these molecules there is bond length alternation, comparable in extent to that in the chain polyene, butadiene (with $k_{\min} = 0{\cdot}55$) and in homologous nonbenzenoid aromatic hydrocarbons which consist of 5- and/or 7-membered rings.[17,18]

The arrangement of molecular orbitals of triafulvalene (II) is of particular interest. This molecule, if treated by the simple Hückel MO method (with $k = 1$), is anomalous in the sense that the top two electrons enter the antibonding molecular orbital whose energy is $\alpha - 0{\cdot}4142\beta_0$.[20] The alternating bond length distortion considerably lowers the energy of this orbital: when $k = k_{\min}$ ($\simeq 0{\cdot}59$), the top two electrons occupy the bonding molecular orbital whose energy is $\alpha + 0{\cdot}3212\beta_d$. The alternating bond length

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[13] G. Berthier and B. Pullman, *Bull. Soc. Chim. Fr.* **16**, D457 (1949).

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[20] The standard β_0 is β for the case $k = 1$, namely, for benzene.

distortion thus results in the achievement of a closed electron shell. A similar rearrangement of molecular orbitals due to the bond length distortion is known to occur in heptafulvalene.[21]

Charge densities, bond orders and free valences. The charge densities, free valence values, bond orders and bond lengths calculated for the equilibrium conformations with $k = k_{\min}$ are summarized in Table 1.

TABLE 1. CHARGE DENSITIES, FREE VALENCES, BOND ORDERS AND BOND LENGTHS OF TRIAFULVENE (I), TRIAFULVALENE (II) AND CALICENE (III)

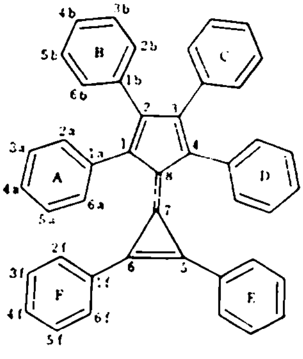
Molecule	Atom	Charge density	Free valence	Bond	Bond order	Bond length (Å)
I	1	0·937	0·538	1–2	0·937	1·346
	3	0·945	0·288	1–3	0·257	1·472
	4	1·180	0·802	3–4	0·930	1·347
II	1	0·957	0·577	1–2	0·957	1·342
	5	1·086	0·421	1–6	0·199	1·483
				5–6	0·914	1·350
III	1	1·035	0·498	1–2	0·886	1·355
	2	1·070	0·494	1–8	0·348	1·455
	5	0·887	0·488	2–3	0·352	1·454
	7	0·828	0·240	5–6	0·887	1·355
	8	1·190	0·257	5–7	0·357	1·454
				7–8	0·778	1·375

In all the molecules the charge densities are smoothed out considerably as compared with those obtained by the simple Hückel MO method.[13,14] The dipole moments of I and III were calculated to be 2·15 and 5·70D, respectively, the direction of the dipole being such that the cyclopropenyl ring is charged positively in both cases, as is to be expected from Hückel's $4n + 2$ rule. It should be noted in this connection that the dipole moments of I and III are predicted to be larger than those of their 7-membered analogues (0·7D for heptafulvene and 5·1D for sesquifulvalene[17]). This indicates that the electron-releasing power of the 3-membered ring should be appreciably greater than that of the 7-membered ring. The predicted dipole moment of III is in good agreement with the experimentally estimated value, 5·63D.[12]

Very recently Bergmann and Agranat[10] synthesized hexaphenylcalicene (IV) and reported its dipole moment. We have calculated the charge densities, free valences, bond orders and bond lengths of this molecule by using the Hückel type MO method: it was assumed that $\beta_s = 0{\cdot}59\beta_d$ for the single bonds of the calicene skeleton and for those between rings (bonds 1–1a, 2–1b, etc) and that $\beta_0 = 0{\cdot}80\beta_d$ for all the C—C bonds of the benzene rings.[22] The results are summarized in Table 2. It should be noted that the bond orders of the bonds between the calicene skeleton and the benzene rings are very small and that the substituent phenyls do not alter appreciably the charge densities and bond orders of the parent hydrocarbon. The dipole moment was calculated to be 6·04D, which is in good agreement with the observed value 6·3 ± 0·3D. It was assumed that the molecule is planar. A scale model examination, however, indicates that Ph groups A, B, C and D would be twisted from coplanarity

[21] T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Japan* 35, 910 (1962).

[22] β_0 was assumed to be the arithmetic mean of β_s and β_d.



IV

TABLE 2. CHARGE DENSITIES, FREE VALENCES, BOND ORDERS AND BOND LENGTHS OF HEXAPHENYLCALICENE (IV)

Atom	Charge density	Free valence	Bond	Bond order	Bond length (Å)
1	1·027	0·290	1–2	0·812	1·369
2	1·058	0·290	1–8	0·341	1·457
5	0·899	0·283	1–1a	0·289	1·466
7	0·846	0·257	2–3	0·340	1·457
8	1·170	0·271	2–1b	0·289	1·466
1a	0·999	0·169	5–6	0·814	1·369
2a	1·003	0·422	5–7	0·348	1·445
3a	1·000	0·397	6–1f	0·288	1·467
4a	1·002	0·407	7–8	0·780	1·375
5a	1·000	0·397	1a–2a	0·637	1·402
6a	1·002	0·422	1a–6a	0·637	1·402
1b	0·998	0·169	2a–3a	0·673	1·395
2b	1·006	0·422	3a–4a	0·662	1·397
3b	1·000	0·397	4a–5a	0·662	1·397
4b	1·005	0·407	5a–6a	0·673	1·395
5b	1·000	0·397	1b–2b	0·637	1·402
6b	1·006	0·422	1b–6b	0·637	1·402
1f	1·006	0·170	2b–3b	0·673	1·395
2f	0·993	0·422	3b–4b	0·662	1·397
3f	1·000	0·397	4b–5b	0·662	1·397
4f	0·995	0·407	5b–6b	0·673	1·395
5f	1·000	0·397	1f–2f	0·638	1·401
6f	0·993	0·422	1f–6f	0·638	1·401
			2f–3f	0·673	1·395
			3f–4f	0·663	1·397
			4f–5f	0·663	1·397
			5f–6f	0·673	1·395

with the calicene skeleton. This will slightly reduce the predicted dipole moment of IV. If we neglect the π-conjugation of Ph groups A, B, C and D with the calicene skeleton, the theoretical dipole moment of IV is given by that of 5,6-diphenylcalicene which has been calculated to be 5·73D.[11]

From the viewpoint of chemical reactivity, it should be noted that the free valence value of the methylenic carbon atom of I is very high and that the free valences of the secondary carbon atoms of I, II and III also are all significantly larger than those in classical aromatic hydrocarbons (e.g., benzene, 0·40). Furthermore, it is particularly noteworthy that the free valences of tertiary carbon atoms 5 and 6 of II are unusually large. All these molecules are thus predicted to be highly susceptible to homolytic reactions.

The bond lengths r were calculated from the bond orders p with the aid of the formula[17]

$$r(\text{Å}) = 1{\cdot}520 - 0{\cdot}186p \tag{2}$$

Delocalization energies and diamagnetic anisotropies. The delocalization energy DE is taken in the present approximation as the difference in π-electronic energy between the equilibrium configuration (with $k = k_{\min}$) and the nonresonating Kekulé structure (with $k = 0$). The calculated DE values for I, II and III (Table 3) are considerably reduced as compared with those obtained by using the simple Hückel MO method (0·962, 1·464 and 2·939β_0 for I, II and III, respectively[13,14]). The magnitude of DE per π-electron has occasionally been used as a criterion for aromaticity, as this quantity should approximate that in benzene or naphthalene (~0·3) for reasonable aromatic character. It was found that the DE/electron values for I, II and III are small as compared with those for the benzenoid aromatic hydrocarbons.

TABLE 3. DELOCALIZATION ENERGIES AND DIAMAGNETIC ANISOTROPIES OF TRIAFULVENE (I), TRIAFULVALENE (II) AND CALICENE (III)

Molecule	DE ($\lvert\beta_0\rvert$)	DE/electron ($\lvert\beta_0\rvert$)	DE* (kcal/mole)	$\Delta K/\Delta K_{\text{benzene}}$
I	0·374	0·093	6·2	0·052
II	0·602	0·100	9·9	0·067
III	1·243	0·155	20·5	0·288

* Using $\lvert\beta_0\rvert$ − 16·5 kcal/mole.[18]

The diamagnetic anisotropy ΔK of an aromatic molecule, attributable to induced ring currents in its π-electron network, is one of the important indications of π-electron delocalization. The ΔK values (in unit of $\Delta K_{\text{benzene}}$) for I, II and III calculated by means of the London-Hoarau technique[23] are also presented in Table 3. The $\Delta K/\Delta K_{\text{benzene}}$ values are all very smaller than those anticipated from the molecular area, which indicates that magnetically induced ring currents are very much impeded in these molecules.

Electronic spectra. The electronic transition energies were calculated, electron interaction terms being taken into account explicitly by using the semi-empirical method of Pariser and Parr.[24] The one-center electronic repulsion integral given as $I_C - A_C$ in the Pariser-Parr formulation was taken to be 11·54 − 0·46 = 11·08 eV.[25] The two-center repulsion integrals were obtained by using the normal extrapolation procedure of Pariser and Parr. Orbital energies are computed in units of β_d in the

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[23] J. Hoarau, *Ann. Chim. Paris* [13] 1, 544 (1956).

[24] R. Pariser and R. G. Parr, *J. Chem. Phys.* 21, 466, 767 (1953).

[25] H. D. Pritchard, *Chem. Rev.* 52, 529 (1955).

present approximation. We adopted −7·21, −7·35 and −6·96 eV as the β_d values for I, II and III, respectively.[26]

The calculated energies and oscillator strengths *f* for the lowest two singlet transitions are presented in Table 4. The spectral features of I, II and III should be similar to those of their 7-membered analogues, heptafulvene, heptafulvalene and sesquifulvalene,[17,18] respectively, except that the absorption maxima for the former are predicted to shift to short wavelengths as compared with those for the latter.

TABLE 4. PREDICTED SINGLET TRANSITIONS FOR TRIAFULVENE (I), TRIAFULVALENE (II) AND CALICENE (III)

Molecule	Transition type	Transition energy (eV)	*f* (cgs)
I	$B_2 \leftarrow A_1$	5·61	0·18
	$A_1 \leftarrow A_1$	6·85	0·75
II	$B_{1g} \leftarrow A_{1g}$	4·31	Forb.
	$B_{3u} \leftarrow A_{1g}$	4·40	0·17
III	$A_1 \leftarrow A_1$	3·81	0·92
	$B_2 \leftarrow A_1$	4·34	0·09

Unfortunately, it is difficult to verify the above theoretical results since there are at present no suitable experimental spectral data available for direct comparison. It does seem possible, however, to compare the predicted longest wavelength absorption of III, 326 mμ, with the longest wavelength λ_{max} of 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene, 316·5 mμ (log ε 4·42, cyclohexane):[12] the effect of the propyl groups on the spectrum may safely be neglected, and the chlorinations in the 5-membered ring of III would cause only a small blue shift of the spectrum, as may be expected from the comparison of the longest wavelength λ_{max} of 1,2,3,4-tetrachloro-6-phenylfulvene (336 mμ, log ε 4·38, cyclohexane) with that of 6-phenylfulvene (347·5 mμ).[27]

CONCLUSION

The above results confirm that in I, II and III the strong alternation in C—C bond lengths is comparable in extent to that in butadiene. In conclusion, we can say that all the hydrocarbons have very little, if any, aromatic stability not only from the viewpoint of π-electron delocalization but also from the viewpoint of chemical reactivity. They cannot be regarded as aromatic in a traditional sense. They should have the characteristics of a polyolefin.

Acknowledgements—The authors are grateful to Professors Y. Kitahara and I. Murata for many valuable discussions.

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[26] The β_d values for $k = 1$ and $k = 0·55$ were adjusted so as to reproduce the experimental transition energies of benzene and butadiene, and were found equal to −5·51 and −7·10 eV, respectively. A linear relationship was then assumed to obtain β_d values for various k values.

[27] Private communication from Profs. Y. Kitahara and I. Murata.