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Electronic Structures and Spectra of Quinarene Molecules

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Synopsis. The electronic structures and spectra of fundamental quinarene molecules, **1**—**9** (Fig. 1) and some of their diphenyl derivatives (Fig. 2) have been studied by using the variable bond-length SCF LCAO-π-MO CI method.

Although syntheses of the quinarene molecules have been attempted by many investigators, and although some derivatives have been synthesized,[1-6] the parent hydrocarbons, **1**—**9** (Fig. 1), have so far not been synthesized. Very recently, Takahashi *et al.* attempted to synthesize the 9,9-diphenyl derivative of **3**, (**3'**),[7] and the 10, 11-diphenyl derivative of **8**, (**8'**)[8] (Fig. 2).

The present note will report the results of calculations of the electronic structures and spectra of the quinarene molecules by the semiempirical LCAO MO method. Further, by comparing the calculated electronic spectra with the experimental ones, we will examine whether or not the unknown compound obtained recently by Takahashi *et al.* in an attempt to synthesize **8'** is really the **8'** molecule.

The method of calculation used is the variable bond-length SCF LCAO-π-MO CI method,[9] in which the bond lengths and, consequently, the resonance and Coulomb repulsion integrals are allowed to vary with the bond order at each iteration until self-consistency is reached. In order to discuss the electronic spectra, a configuration mixing of all the singly excited states is included.

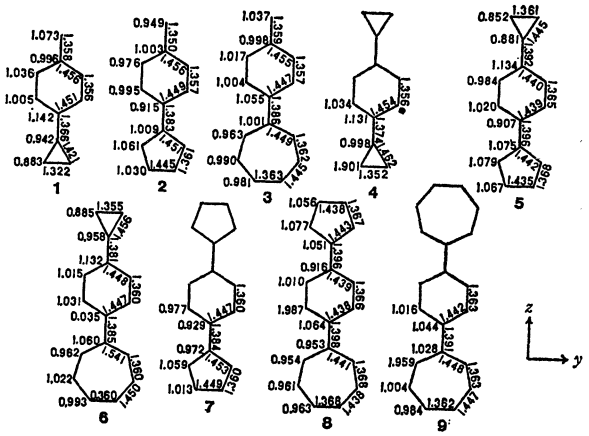

Fig. 1. Electron densities (in units of one electron) and bond lengths (in units of Å) of quinarenes.

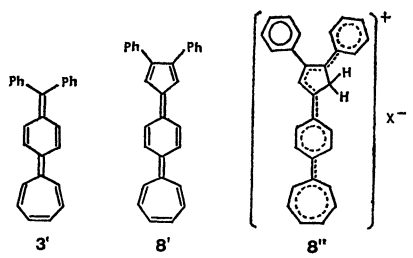

Fig. 2.

The calculated charge densities and bond lengths are shown in Fig. 1. The dipole moments of **1**, **2**, **3**, **5**, **6**, and **8** were predicted to be 5.44, 3.87, 2.94, 12.85, 4.56, and 11.08 D respectively. The dipole moments of **1** and **5** turn out to be larger than those of **3** and **8**. This means that the electron-releasing power of the 3-membered ring should be appreciably greater than that of the 7-membered ring. This fact is reflected in the appreciable dipole moment calculated for **6**, the dipolar structure of this molecule being such that the negative pole is directed toward the 7-membered ring.

The calculated transition energies and oscillator

TABLE 1. TRANSITION ENERGIES (ΔE) AND INTENSITIES (f) OF QUINARENES

Molecule	ΔE (eV)	f (cgs)
1	3.22	0.026 (y)
	3.56	1.56 (z)
	4.05	0.015 (y)
2	2.43	0.008 (y)
	3.13	1.84 (z)
	4.06	0.012 (y)
3	2.21	0.010 (y)
	2.86	1.90 (z)
	4.06	0.010 (y)
4	2.87	0
	2.88	0.044 (y)
	3.35	1.77 (z)
5	2.54	0.013 (y)
	2.70	1.93 (z)
	3.16	0.030 (y)
6	1.90	0.004 (y)
	2.69	2.18 (z)
	2.90	0.030 (y)
7	2.13	0
	2.14	0.013 (y)
	2.64	2.45 (z)
8	2.12	0.011 (y)
	2.25	0.008 (y)
	2.26	2.45 (z)
9	1.88	0.011 (y)
	1.89	0
	2.24	2.76 (z)

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Table 2. Transition energies (ΔE) and intensities (f) of **8′**, **8″**, and the unknown compound

Calc.				Exp.[a]
Molecnle **8′**		Molecule **8″**		Unknown compound
ΔE(eV)	f	ΔE(eV)	f	ΔE(eV)
2.00	0.004(y)	2.02	0.79	2.02 ($\log \varepsilon$=4.2)
2.08	0.008(y)	2.52	0.008	
2.09	2.96 (z)	3.10	0.57	3.40 ($\log \varepsilon$=4.0)
3.33	0.06 (z)	3.45	0.27	
3.81	0.000(y)	3.60	0.003	

a) Ref. 8, in chloroform.

strengths, f, for the lowest three singlet transitions are presented in Table 1. The gross spectral features of **1**—**9** should be similar to those of triafulvene, pentafulvene, heptafulvene, triafulvalene, calicene, heptatriafulvalene,[9] pentafulvalene, sesquifulvalene, and heptafulvalene[10] respectively, except for the fact that the absorption maxima for the former are predicted to shift to wavelengths longer than those for the latter.

We have also calculated the electronic spectra of **3′**. The observed electronic spectra of the pigment formed on the attempted preparation of **3′** show absorption maxima at 2.05 ($\log \varepsilon$=4.28) and 2.92 eV ($\log \varepsilon$= 4.27).[7] The calculated transition energies for **3′** are 2.05 (f=0.012), 2.25 (f=2.46), 3.69 (f=0.004), and 3.84 eV (f=0.001). The pigment obtained is not expected to be **3′**, since the observed second absorption maximum is not found in the predicted spectra.

The unknown compound obtained recently by Takahashi *et al.*[8] in an attempt to synthesize **8′** seems to be either the aimed-molecule (**8′**) or the quinarenium ion of **8′** (the **8″** molecule Fig. 2). The calculated results for **8′** and **8″** are summarized in Table 2*, and compared with the observed results for the unknown compound. The experimental values for the unknown compound are in better agreement with the calculated values for **8″** than with those calculated for **8′**. From this fact, it may be concluded that the unknown compound is likely to be **8″**, not **8′**.

References

1) A. S. Kende, *J. Amer. Chem. Soc.*, **85**, 1882 (1963).
2) R. von Helden, A. P. ter Borg, and A. F. Bickel, *Rev. Trav. Chim. Pays-Bas*, **81**, 599 (1962).
3) C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).
4) T. Nozoe, Japan 17674 (1964), *Chem. Abst.*, **62**, 5234 (1965).
5) P. Bladon, P. L. Pauson, G. P. Proctor, and W. J. Rodger, *J. Chem. Soc. C*, **1966**, 926.
6) K. Takahashi, N. Hirata, and K. Takase, *Tetrahedron Lett.*, **1970**, 1285.
7) K. Takahashi, S. Takenaka, and T. Nozoe, *Tetrahedron*, **30**, 2191 (1974).
8) K. Takahashi, S. Takenaka, J. Kikuchi, K. Takase, and T. Nozoe, This Bulletin, **47**, 2272 (1974).
9) H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta*, **12**, 349 (1968).
10) T. Nakajima, *Topics in Current Chem.*, **32**, 1 (1972).

* In calculating the electronic spectra of **8″**, we have neglected the hyperconjugation effect due to the methylenic group.