Electronic Structures and Spectra of Non-benzenoid Hydrocarbons: Fulvene, Heptafulvene, Fulvalene, Heptafulvalene and Sesquifulvalene

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Fulvene, the most fundamental non-benzenoid hydrocarbon, has received considerable attention from both theoretical and experimental points of view. Among previous theoretical treatments[1-4], François and Julg's recent calculations of the dipole moment and spectrum have been in quite satisfactory quantitative agreement with the experimental information. Compared with fulvene, however, its seven-membered analogue, heptafulvene, has been relatively little studied either theoretically or experimentally. Only recently has the attempted synthesis of heptafulvene succeeded[5]. Earlier theoretical treatments of heptafulvene[1,2] have achieved notable success in pointing out the basic causes for its dipole moment and color, but quantitative agreement with the experimental values has not been very satisfactory.

On the other hand, Doering[6] has recently reported the synthesis of the interesting non-benzenoid hydrocarbons, fulvalene and heptafulvalene, together with their ultraviolet-visible spectra. Furthermore, their even more interesting relative, sesquifulvalene, which consists, so to speak, of joined five- and seven-membered rings, has been long exposed to repeated attempts to synthesize it. Earlier theoretical predictions of the spectra of fulvalene[7-9] and heptafulvalene[9] have proved to be far from satisfactory when compared with the now available experimental data.

The aim of this paper is to add, in view of these circumstances, to the understanding of the structures and spectra of heptafulvene and fulvalenes through an attempt to calculate these by a theoretical method within the framework

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[1] E. D. Bergmann, "Progress in Organic Chemistry", Vol. III, Academic Press, Inc., New York (1955), p. 81.

[2] A. Julg and B. Pullman, *J. chim. phys.*, **52**, 481 (1955).

[3] H. Kon, *J. Chem. Phys.*, **23**, 1176 (1955).

[4] P. François and A. Julg, *J. chim. phys.*, **57**, 490 (1960).

[5] W. von Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

[6] W. von Doering, "Theoretical Organic Chemistry (Kekulé Symposium)", Butterworths Sci. Publ., Ltd., London (1959), p. 35.

[7] R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).

[8] B. Pullman and G. Berthier, *Compt. rend.*, **229**, 717 (1949).

[9] E. D. Bergmann et al., *Bull. soc. chim. France*, **18**, 697 (1951).

of the LCAO MO approximation. The method starts from the Fock self-consistent orbital equations. These are simplified by approximation of the Fock matrix elements; at the same time, special attention will be paid to the marked bond alternation inherent in these molecules. To test the validity of this method, it will be applied first to fulvene.

Method and Procedure

It will be noted at the outset that the fulvenes and fulvalenes that concern us belong to the class of molecules called "classical",[10] a typical example of which is a linear polyene such as butadiene, and therefore that all these molecules are expected to exhibit a bond alternation to almost the same considerable degree as butadiene does. The carbon skeleton structure of fulvene, heptafulvene, fulvalene, heptafulvalene and sesquifulvalene are taken as in Fig. 1, with the lengths of the single and double bonds set equal to 1.48 and 1.34 Å respectively, as in butadiene[11], the rings being assumed to be regular in all cases.

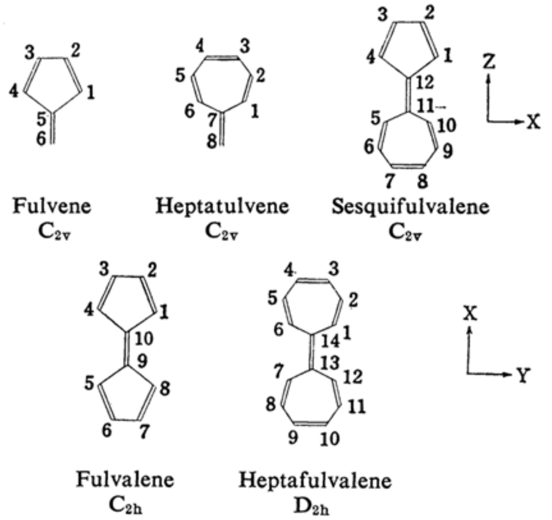

Fig. 1. Carbon skeleton, choice of axes, and numbering of non-benzenoid hydrocarbons.

According to the self-consistent orbital theory[12], the orbital energies of a conjugated hydrocarbon are obtained by solving the Fock secular equation,

$$| F_{pq} - S_{pq}\varepsilon | = 0 \tag{1}$$

where F_{pq} is the Fock matrix element and S_{pq} the overlap integral between atoms p and q. The simplifying approximations that we make in order to build and solve the Fock equations for conjugated hydrocarbons are as follows: (a) The overlap integral, S_{pq} is neglected unless $p=q$, in which case it is unity. (b) The diagonal Fock elements, F_{pp}, are taken as empirical parameters, α_p^F and the off-diagonal ones, F_{pq}, as parameters, β_{pq}^F for nearest neighbors, and zero otherwise[13]. The Fock secular equations thus reduce to expressions involving empirical parameters analogous to those in the Hückel theory. (c) All the carbon atoms are presumed to have the same α^F. The energy zero is therefore assumed to be such that $\alpha^F=0$, and energies are computed in units of one of the β_{pq}^F in the same manner as in the Hückel theory.

In setting up the Fock equations for the non-benzenoid hydrocarbons that concern us, we introduce, in addition to the above simplifying parameters, the bond alternation parameter defined by

$$\gamma = \beta^F_{\text{single}} / \beta^F_{\text{double}}, \tag{2}$$

where the subscripts single and double mean the single and double bonds in the Kekulé structures respectively. The value for γ used throughout this paper is so chosen as to reproduce, with the above simplifications of the secular equation, the self-consistent orbitals of butadiene (trans) calculated by using the standard self-consistent field technique. This makes practically unnecessary successive solutions of the Fock equations to find the self-consistent orbitals and so they are not allowed for in this paper. Of the self-consistent orbitals of butadiene so far reported[14-16], we take Lefebvre and Moser's as the reference orbitals to determine the value of γ. The reason for this choice is that in Lefebvre and Moser's procedure, the overlap is neglected, as in the present procedure, and the Coulomb repulsion integrals necessary for the spectral calculations were estimated using the same approximation (Pariser and Parr's) as will be used in this paper (vide infra). The value for γ with which Lefebvre and Moser's orbitals can be reproduced was found to be equal to 0.55[17].

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[10] A classical molecule is defined as one for which only a single (unexcited) resonance structure can be written.

[11] A. Almenningen, O. Bastiansen and M. Troettbery, *Acta Chem. Scand.*, **12**, 1221 (1958).

[12] R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry", Interscience Publishers, New York (1959), Part II.

[13] L. Goodman and H. Shull, *J. Chem. Phys.*, **22**, 1138 (1954).

[14] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

[15] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[16] R. Lefebvre and C. M. Moser, *J. chim. phys.*, **53**, 393 (1956).

[17] In butadiene, the ratio of the Fock element for the single bond (−3.3 eV.) to that for the double bond (−6.5 eV.) actually proves to be about 0.5, while the ratio of the core resonance integral for the single bond (−2.40 eV.) to that for the double bond (−2.95 eV.) is about 0.8; for the numerical values, see A. Julg, *J. chim. phys.*, **57**, 19 (1960).

The electron transition energies are calculated by the following formula, no configuration interaction being allowed for:

$$\left.\begin{matrix}{}^1E_{ij}\\{}^3E_{ij}\end{matrix}\right\}-E_N=(\varepsilon_j-\varepsilon_i)-(J_{ij}-K_{ij})\pm K_{ij} \qquad (3)$$

where E_N, ${}^1E_{ij}$, and ${}^3E_{ij}$ designate the energy of the ground, excited singlet, and excited triplet states respectively, the electronic excitation being from i to j. J_{ij} and K_{ij} are the Coulomb repulsion and exchange repulsion integrals in terms of molecular orbitals. Neglecting differential overlap, these may be rewritten in terms of Coulomb repulsion integrals over atomic orbitals. The integrals of the latter type are evaluated using Pariser and Parr's procedure[18]. Orbital energies are computed in units of β^F_{double}. The value for β^F_{double} was determined so as to reproduce, by application of Eq. 3, the observed energy of the lowest singlet transition ($B_{1u}\leftarrow A_{1g}$), i. e., 5.9 eV. of *trans*-butadiene, and was found equal to -7.0 eV. The oscillator strengths are calculated on the basis of the well-known formula:

$$f=1.085\times 10^{11}\nu Q^2 \qquad (4)$$

where Q designates the transition moment.

Results and Discussion

The calculated transition energies and oscillator strengths are summarized and compared with experimental data in Tables I. Tables II, III, IV, V and VI present the molecular orbitals and energies of fulvene, heptafulvene, fulvalene, heptafulvalene and sesquifulvalene respectively. The bond orders and charge densities are also included in these Tables.

Fulvene. — Comparison of the calculated orbitals with those so far obtained by using the SCF technique, among others, Francois and Julg's orbitals, which have been calculated with the same skeleton structure as assumed in this paper, shows that these two sets of orbitals agree well with each other. Further, application of Coulson's formula for bond order vs. bond distance[19] predicts 1.35 Å for the double bonds and 1.47 to 1.48 Å for the single bonds, while the assumed lengths are 1.34 and 1.48 Å respectively, the situation being satisfactorily self-consistent. The calculated dipole moment proves to be 1.14 D, which is in remarkable agreement with the experimental value, 1.1 D.[20] The direction of

TABLE I. TRANSITION ENERGIES AND OSCILLATOR STRENGTHS OF NON-BENZENOID HYDROCARBONS

Molecule	Assignment	Calculated		Experimental	
		Energy (eV.)	f	Energy (eV.)	f
Fulvene	${}^3B_1\leftarrow{}^1A_1$	2.48			
	${}^1B_1\leftarrow{}^1A_1$	3.31	0.049	3.32	0.012
	${}^1A_1\leftarrow{}^1A_1$	5.16	0.92	5.13	0.32
Heptafulvene	${}^3B_1\leftarrow{}^1A_1$	2.30			
	${}^1B_1\leftarrow{}^1A_1$	2.96	0.057	2.91	0.02
	${}^1A_1\leftarrow{}^1A_1$	4.55	0.89	4.43	0.4
Fulvalene	${}^3B_{3u}\leftarrow{}^1A_{1g}$	1.96			
	${}^3B_{1g}$, ${}^3B_{2u}\leftarrow{}^1A_{1g}$	2.03			
	${}^1B_{1g}\leftarrow{}^1A_{1g}$	2.38	forb.		
	${}^1B_{2u}\leftarrow{}^1A_{1g}$	2.47	0.03	2.98	?
	${}^1B_{3u}\leftarrow{}^1A_{1g}$	3.81	1.2	3.95	0.3
Heptafulvalene	${}^3B_{3u}\leftarrow{}^1A_{1g}$	1.64		1.7—2.8	?
	${}^3B_{1g}$, ${}^3B_{2u}\leftarrow{}^1A_{1g}$	2.30			
	${}^1B_{1g}\leftarrow{}^1A_{1g}$	2.54	forb.		
	${}^1B_{2u}\leftarrow{}^1A_{1g}$	2.62	0.02		
	${}^1B_{3u}\leftarrow{}^1A_{1g}$	3.11	1.1	3.42	0.38
Sesquifulvalene	${}^3A_1\leftarrow{}^1A_1$	1.59			
	${}^3B_1\leftarrow{}^1A_1$	2.75			
	${}^3B_1\leftarrow{}^1A_1$	2.94			
	${}^1A_1\leftarrow{}^1A_1$	3.20	1.0		
	${}^1B_1\leftarrow{}^1A_1$	3.33	0.05		
	${}^1B_1\leftarrow{}^1A_1$	3.50	0.02		

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

[19] C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939).

[20] J. Thiec and J. Wiemann, *Bull. soc. chim. France*. **1956**, 177.

TABLE II. FULVENE MOLECULAR ORBITALS, ENERGIES, CHARGE DENSITIES AND BOND ORDERS

MO	Sym	Orbital[a]				Energy[c]	Charge density	Bond order
		$(\chi_1\pm\chi_4)$[b]	$(\chi_2\pm\chi_3)$[b]	(χ_5)	(χ_6)			
1	b_2	0.4198	0.4035	0.4802	0.3020	1.5904	$q_1=1.019$	$p_{1,2}=0.926$
2	b_2	0.1303	0.4033	−0.5265	−0.6030	0.8731	$q_2=1.018$	$p_{1,5}=0.266$
3	a_2	0.5624	0.4286	0.0000	0.0000	0.7621	$q_5=1.016$	$p_{2,3}=0.284$
4	b_2	0.3894	−0.3655	0.3001	−0.5828	−0.5150	$q_6=0.910$	$p_{5,6}=0.925$

a) By definition for the ith MO, $\phi_i=\sum_p C_{pi}\chi_p$. The C_{pi} are listed under the corresponding χ_p.

b) + and − refer to MO's of symmetry b_2 and a_2, respectively.

c) The energies are in units of β^F_{double} (=−7.0 eV.).

TABLE III. HEPTAFULVENE MOLECULAR ORBITALS, ENERGIES, CHARGE DENSITIES AND BOND ORDERS[a]

MO	Sym	Orbital					Energy	Charge density	Bond order
		$(\chi_1\pm\chi_6)$	$(\chi_2\pm\chi_5)$	$(\chi_3\pm\chi_4)$	(χ_7)	(χ_8)			
1	b_2	0.3712	0.3501	0.3314	0.4305	0.2723	1.5801	$q_1=0.994$	$p_{1,2}=0.926$
2	b_2	0.1233	−0.1323	−0.4996	0.4972	0.4340	1.1456	$q_2=0.994$	$p_{1,7}=0.266$
3	a_2	0.4727	0.5084	0.1347	0.0000	0.0000	1.0755	$q_3=0.994$	$p_{2,3}=0.285$
4	b_2	0.3469	0.3137	−0.3453	−0.2547	−0.5091	0.5004	$q_7=0.995$	$p_{3,4}=0.921$
5	a_2	0.4463	−0.2920	−0.4643	0.0000	0.0000	−0.6541	$q_8=1.043$	$p_{7,8}=0.925$
6	b_2	0.2343	−0.4109	0.1296	0.4299	−0.5778	−0.7441		

a) See notes to Table II.

TABLE IV. FULVALENE MOLECULAR ORBITALS, ENERGIES, CHARGE DENSITIES AND BOND ORDERS

MO	Sym	Orbital[a]			Energy	Charge density	Bond order
		$(\chi_1\pm\chi_4)$[b]	$(\chi_2\pm\chi_3)$[b]	$(\chi_9\pm\chi_{10})$[c]			
1	b_{1u}	0.2918	0.2512	0.4511	1.7114	$q_1=1.022$	$p_{1,2}=0.926$
2	b_{2g}	0.3194	0.3707	−0.1457	1.4116	$q_2=1.006$	$p_{1,10}=0.269$
3	b_{1u}	0.0880	0.3444	−0.4973	0.8054	$q_9=0.944$	$p_{2,3}=0.271$
4	a_{1u}	0.3977	0.3031	0.0000	0.7621		$p_{9,10}=0.859$
5	b_{3g}	0.3977	0.3031	0.0000	0.7621		
6	b_{2g}	0.2628	−0.3080	−0.4150	−0.3034		
7	b_{1u}	0.3964	−0.2613	−0.2217	−0.9669		

a) See footnote a to Table II.

b) + refers to MO's of symmetry b_{1u} or b_{2g}, and − refers to those of symmetry a_{1u} or b_{3g}. The C_{pi} corresponding to $(\chi_5\pm\chi_8)$ and $(\chi_6\pm\chi_7)$ are the same as those corresponding to $(\chi_1\pm\chi_4)$ and $(\chi_2\pm\chi_3)$, respectively, for MO's of symmetry b_{1u} and a_{1u} and different in sign from these for MO's of symmetry b_{2g} and b_{3g}.

c) + and − refer to MO's of symmetry b_{1u} and b_{2g}, respectively.

the moment is such that the ring is negative with respect to the methylenic group.

The lowest singlet transition corresponds to a ${}^1B_1\leftarrow{}^1A_1$ electronic transition, with its moment directed along the short axis, whereas the next singlet corresponds to an ${}^1A_1\leftarrow{}^1A_1$ transition with its moment directed along the long axis. The predicted energies of these singlet transitions are in remarkably good agreement with the experimental values[20]. The calculated f value for the lowest singlet transition is lower than that for the next one, which is in agreement with the order of magnitude of the experimental f values. However, as is often the case[21], the absolute values of the calculated f values are too high. A correction factor of 0.30 is introduced, which is the ratio of f_{obs} to f_{calcd} for the lowest allowed singlet transition in benzene. It will be seen that the corrected values accord well with the observed ones.

The validity of the present theoretical approach is thus demonstrated by the results for the spectrum as well as for the dipole moment of fulvene.

Heptafulvene.—The bond lengths predicted from the bond orders, 1.48 Å for the single bonds and 1.34 to 1.35 Å for the double bonds, are in satisfactory agreement with the assumed lengths. The dipole moment was calculated to be 0.63 D, reduced considerably from the value, 4.6 D, predicted by the conventional Hückel

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[21] R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

TABLE V. HEPTAFULVALENE MOLECULAR ORBITALS, ENERGIES, CHARGE DENSITIES AND BOND ORDERS

MO	Sym	Orbital[a]				Energy	Charge density	Bond order
		$(\chi_1\pm\chi_6)$[b]	$(\chi_2\pm\chi_5)$[b]	$(\chi_3\pm\chi_4)$[b]	$(\chi_{13}\pm\chi_{14})$[c]			
1	b_{1u}	0.2733	0.2196	0.1716	0.4384	1.6857	$q_1=0.991$	$p_{1,2}=0.921$
2	b_{2g}	0.2315	0.2828	0.3333	−0.1033	1.4668	$q_2=1.001$	$p_{2,3}=0.283$
3	b_{1u}	−0.0623	0.1324	0.3980	−0.3747	1.1829	$q_3=0.994$	$p_{3,4}=0.921$
4	b_{3g}	0.3342	0.3595	0.0953	0.0000	1.0755	$q_{13}=1.029$	$p_{1,14}=0.281$
5	a_{1u}	0.3342	0.3595	0.0953	0.0000	1.0755		$p_{13,14}=0.850$
6	b_{2g}	0.3006	0.1354	−0.3524	−0.1849	0.7887		
7	b_{1u}	0.2225	0.2792	−0.2324	−0.3704	0.3392		
8	b_{2g}	−0.1503	0.3394	−0.1146	0.4452	−0.6286		
9	b_{3g}	0.3156	−0.2065	−0.3283	0.0000	−0.6541		
10	a_{1u}	0.3156	−0.2065	−0.3283	0.0000	−0.6541		

a) See footnote a to Table II.

b) + refers to MO's of symmetry b_{1u} or b_{2g}, and − refers to those of symmetry a_{1u} or b_{3g}. The C_{pi} corresponding to $(\chi_7\pm\chi_{12})$, $(\chi_8\pm\chi_{11})$, and $(\chi_9\pm\chi_{10})$ are the same as those corresponding to $(\chi_1\pm\chi_6)$, $(\chi_2\pm\chi_5)$ and $(\chi_3\pm\chi_4)$, respectively, for MO's of symmetry b_{1u} and a_{1u} but different in sign from these for MO's of symmetry b_{2g} and b_{3g}.

c) + and − refer to MO's f symmetry b_{1u} and b_{2g}, respectively.

TABLE VI. SESQUIFULVALENE MOLECULAR ORBITALS, ENERGIES, CHARGE DENSITIES AND BOND ORDERS[a]

MO	Sym	Orbital							Energy	Charge density	Bond order
		$(\chi_1\pm\chi_4)$	$(\chi_2\pm\chi_3)$	$(\chi_5\pm\chi_{10})$	$(\chi_6\pm\chi_9)$	$(\chi_7\pm\chi_8)$	(χ_{11})	(χ_{12})			
1	b_2	0.3010	0.2620	0.2656	0.2098	0.1652	0.4388	0.4532	1.6987	$q_1=1.026$	$p_{1,2}=0.914$
2	b_2	0.2836	0.3162	−0.2403	−0.3122	−0.3843	−0.0645	0.1710	1.4468	$q_2=1.033$	$p_{1,12}=0.295$
3	a_2	0.0000	0.0000	0.4727	0.5084	0.1347	0.0000	0.0000	1.0755	$q_5=0.993$	$p_{2,3}=0.299$
4	b_2	0.1592	0.3149	−0.1958	0.0446	0.4417	−0.4570	−0.2670	1.0556	$q_6=0.973$	$p_{5,6}=0.914$
5	a_2	0.5624	0.4286	0.0000	0.0000	0.0000	0.0000	0.0000	0.7621	$q_7=0.987$	$p_{5,11}=0.294$
6	b_2	−0.0110	0.2553	0.3259	0.2920	−0.3245	−0.2284	−0.4743	0.5070	$q_{11}=0.915$	$p_{6,7}=0.297$
7	b_2	0.3241	−0.3216	−0.0779	0.3110	−0.1174	−0.5007	0.3149	−0.4759	$q_{12}=1.062$	$p_{7,8}=0.914$
8	a_2	0.0000	0.0000	0.4463	−0.2920	−0.4643	0.0000	0.0000	−0.6541		$p_{11,12}=0.866$

a) See footnotes to Table II.

theory[1]. No experimental dipole moment data for heptafulvene are available. However, a comparison may be made with an experimentally estimated moment, e. g., the value of about 0.7 D estimated from the observed moment of tropone[22]. The direction of the moment is such that the ring is positive, contrary to the case of fulvene, with respect to the exocyclic carbon atom. This contradicts the prediction based on the non-empirical SCF theory[1] but accords with the conclusions put forward on the basis of the conventional Hückel[1] and semi-empirical SCF theories[2].

No unambiguous spectral assignment in heptafulvene has been made so far. According to the results of the present calculations, the first long wavelength absorption band, with its maximum at 427 mμ, is assigned to a $^1B_1\leftarrow{}^1A_1$ transition (transverse polarization), and the next band, at 280 mμ, to an $^1A_1\leftarrow{}^1A_1$ transition (symmetry-axis polarization). The expected energies for these two transitions are in good agreement with the experimental values. In addition, the relative order of magnitude of the calculated oscillator strengths for the two transitions is consistent with these assignments. If, further, a correction factor of 0.30 is introduced, the calculated and experimental f values are brought into good agreement in their numerical values.

Fulvalene.—The calculated bond lengths are 1.35 to 1.36 Å for the double bonds and 1.47 to 1.48 Å for the single bonds. These are in fairly good agreement with the assumed lengths.

Brown[7] and Pullman and Berthier[8] have discussed the orbitals and spectrum of fulvalene on the basis of the conventional Hückel theory.

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[22] Y. Kurita et al., This Bulletin, **26**, 272 (1953). See also M. Yamakawa et al., *J. Am. Chem. Soc.*, **82**, 5665 (1960). The latter authors have estimated a value of 3.07 D from the observed moment of heptafulvene dinitrile. This unreasonably high value for the moment of heptafulvene is not compatible with the results of the present calculation. On the other hand, one of the present authors and his associates have independently measured the moment in heptafulvene dinitrile and estimated from it the moment of heptafulvene to be from 0.7 D to 1.0 D; S. Katagiri et al., (to be published).

The predicted orbitals and spectrum possess the following curious features: (a) The lowest vacant orbital is bonding in the sense that its energy value is positive in β units. (b) If electron interactions are taken into account using Eq. 3, the first and second excited states of symmetries B_{1g} and B_{2u} respectively prove to be lower in energy than the ground state (A_{1g}), which implies that the lowest energy state is not totally symmetric. (c) If the value $\gamma=23$ k.cm^{-1}*, which was found to be moderately successful in accounting for the spectra of the ring conjugated hydrocarbons[23], the lowest allowed singlet transition, with excitation energy 0.296 γ is predicted to appear in the infrared. These are somewhat unexpected, since in no known hydrocarbons have such circumstances been known to occur. The orbitals of fulvalene calculated by using the present procedure show no such unusual features. The lowest vacant orbital is very sensitive to bond alternation and becomes anti-bonding in the sense that its energy value is now negative.

The fulvalene absorption spectrum shows an intense band characterized by a series of comparatively sharp maxima, which is no doubt due to the vibrational fine structures and culminates in a maximum at 314 mμ, and a weak maximum at 416 mμ, followed by long tailing into the visible[6,24]. The calculated transition energies and oscillator strengths are compared with the experimental values in Table I. The longer wavelength weak maximum is assigned to the electronic transition ($^1B_{2u}\leftarrow{}^1A_{1g}$), with its moment directed along the short axis, whereas the shorter wavelength strong maximum is assigned to the transition ($^1B_{3u}\leftarrow{}^1A_{1g}$), with its moment directed along the long axis.

Heptafulvalene.—The predicted bond lengths, 1.35 to 1.36 Å for the double bonds and 1.47 to 1.48 Å for the single bonds, are in fairly good agreement with the assumed lengths.

Heptafulvalene molecular orbitals calculated on the basis of the conventional Hückel theory[9] are similar in their unusual features to the fulvalene Hückel orbitals; that is, the top occupied orbital is anti-bonding in the sense that its energy value is negative in β units, and if electron interactions are taken into account, the lowest energy state loses its total symmetry. Further, the lowest allowed transition is predicted to appear in the infrared, which is not supported by the experimental facts now available.

The top occupied orbital of heptafulvalene is calculated to be bonding in the present procedure. Bond alternation stabilizes it considerably. The absorption spectrum of heptafulvalene shows an intense maximum at 362 mμ (log $\varepsilon=4.32$), followed by an almost linearly decreasing absorption throughout the visible region[6,24]. According to the results of the present calculations of transition energies and oscillator strengths, it appears that the intense maximum at 362 mμ is to be assigned to an electronic transition ($^1B_{3u}\leftarrow{}^1A_{1g}$), with its moment directed along the long axis, and that the long tail is composed of one singlet-allowed transition ($^1B_{2u}\leftarrow{}^1A_{1g}$), with its moment directed along the short axis, one singlet-forbidden transition ($^1B_{1g}\leftarrow{}^1A_{1g}$), and three triplet transitions.

Sesquifulvalene.—The calculated distribution of bond orders reproduces fairly well the assumed bond lengths. In this connection, it is interesting to note the order of the central bond calculated on the basis of the conventional Hückel theory. The Hückel bond order of this bond is 0.446[9], which is particularly small as an order of double bonds[25]. This is not consistent with the high double bond character of the central bond expected from the fact that only a single Kekulé structure can be written for sesquifulvalene.

The predicted dipole moment is 3.0 D, reduced considerably from the value of about 12 D predicted using the conventional Hückel theory. The direction of the moment is such that the negative pole is directed toward the pentagonal ring. This accords with the expectation based upon the aromatic sextet rule.

Sesquifulvalene Hückel orbitals show no peculiar characteristics such as those seen in fulvalene and heptafulvalene Hückel orbitals. The top occupied orbital is positive, and the lowest vacant orbital is negative in β units. Neither of the orbitals is so sensitive to bond alternation as in fulvalene and heptafulvalene.

As for the predicted spectrum of sesquifulvalene, it should be noted that the lowest singlet transition is expected to correspond to an $^1A_1\leftarrow{}^1A_1$ electronic transition polarized along the long axis*. The electronic transitions ($^1B_1\leftarrow{}^1A_1$) polarized along the short axis are expected to be considerably higher in energy than the corresponding transitions in fulvalene and heptafulvalene.

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* For the spectral calculations in the conventional Hückel approximation, orbital energies are corrected for the overlap and written in units of γ instead of β.

[23] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[24] W. von Doering, private communication.

[25] It is noted that the Hückel bond order of the central single bond of butadiene is 0.447.

* *Note added in proof*: Very recently Prinzbach and his associates have reported the synthesis of sesquifulvalene; see Prinzbach et al., *Angew. Chem.*, 73, 169, 543 (1961). The absorption spectrum of sesquifulvalene shows an intense maximum at 404 mμ (log $\varepsilon=4.4$) which may be assigned to the lowest singlet transition ($^1A_1\leftarrow{}^1A_1$).

Summary and Conclusion

It appears now well established that in fulvene, heptafulvene, and the fulvalenes that we have dealt with in this paper, there is a remarkable difference in length between the single bonds and the double bonds, the bond alternation being substantially in a degree comparable to that in open chain polyenes. The foregoing calculations show that the assignment of a value of 0.55 to the bond alternation parameter is essential for the theoretical elucidation of the electronic structures and spectra of these molecules. In conclusion, it may be said that although all the above molecules can be shown to be endowed a priori with an aromatic character on the basis of Craig's criterion26), none of them can, from the viewpoint of bond alternation, be regarded, as a matter of fact, as belonging to the " aromatic " category in a traditional sense. They have, rather, characteristics of the cyclic polyolefins. Indeed, neither fulvene, heptafulvene, fulvalene, nor heptafulvalene has been shown to exhibit the chemical integrity characteristic of the so-called aromatic hydrocarbons5,6).

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26) D. P. Craig, " Theoretical Organic Chemistry (Kekulé Symposium) ", Butterworths Scientific Publications Ltd., London (1959), p. 20.