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ELECTRONIC STRUCTURE AND SPECTRUM OF BENZO[g]SESQUIFULVALENE

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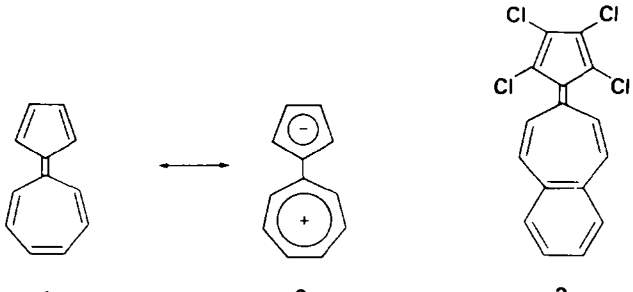
Abstract—Calculations have been made for benzo[g]sesquifulvalene using the Hückel MO method with the bond alternation technique. The bond lengths, charge densities, dipole moment and electronic spectrum of this molecule as given by the MO calculations have been compared with the experimental values.

1. INTRODUCTION

CYCLOPENTADIENYLIDENECYCLOHEPTATRIENE (sesquifulvalene; 1) is one of the most interesting class of cross-conjugated non-benzenoid aromatic systems.[1] Hückel molecular orbital calculation suggests that polar resonance structure **2** would make an unusually large contribution to the ground state of this molecule, since the charge transfer in such a contributor might be stabilized with the pair of six *pi*-electron systems.[2,3] From these theoretical predictions, sesauifulvalene (**1**) should have a high dipole moment and have low bond order at the bond between each pair of rings. Furthermore, Hückel theory has predicted substantial *pi*-electron delocalization energy (0·33 β/*pi*-electron) and closed-shell electronic configuration for the ground state of **1**, suggesting that it would have a pronounced aromatic character.



1 2 3

FIG. 1.

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[1] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, p. 299, Wiley, New York (1961).

[2] B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, D. Fischer, Y. Hirschberg, D. Lavie and M. Mayot, *Bull. soc. chim. Fr.*, 73 (1952).

[3] J. F. Tinker, *J. Chem. Phys.* **19**, 981 (1951).

Recently, Prinzbach *et al.* have synthesized **1**[4] and some of its derivatives.[5-7] The parent hydrocarbon, however, does not possess the chemical integrity of aromatic molecules such as predicted by Hückel theory. On the other hand, we have reported in preliminary form[8] a synthesis of a stable derivative of **1**, 1,2,3,4-tetrachlorobenzo[g]sesquifulvalene **3**, by the condensation of tetrachlorocyclopentadiene with 4,5-benzotropone.

This paper presents a theoretical treatment of the *pi*-electron system by the modified Hückel theory and a correlation of the calculations with the observed dipole moment and electronic spectrum of **3**.

2. METHOD OF CALCULATIONS

In order to apply the Hückel method to molecules for which only a single unexcited Kekulé structure can be written, the appreciable bond length fixation must be taken into consideration. Nakajima and Katagiri[9-11] introduced the bond alternation technique for such problems and succeeded in interpreting the experimental dipole moments and the electronic transition energies of various non-benzenoid aromatic hydrocarbons.

The carbon skeleton structure and numbering of benzo[g]sesquifulvalene (**4**) are taken as in Fig. 2, the ring being assumed to be regular in all calculations.

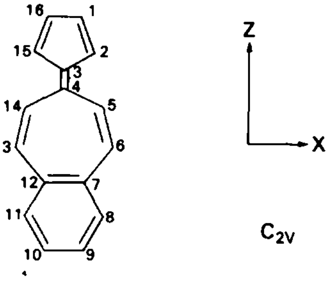

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FIG. 2 Carbon skeleton, choice of axes and numbering of **4**.

The bond alternation parameter,

$$k = \beta_s/\beta_d$$

was introduced where β designates the resonance integral and the subscripts *s* and *d* mean the single and double bonds in an unexcited Kekulé structure, respectively.

[4] H. Prinzbach und W. Rosswog, *Angew. Chem.* 73, 543 (1961).

[5] H. Prinzbach, *Angew. Chem.* 73, 169 (1961).

[6] H. Prinzbach, *Angew. Chem.* 73, 169 (1961).

[7] H. Prinzbach und W. Rosswog, *Tetrahedron Letters* No. 19, 1217 (1963).

[8] Y. Kitahara, I. Murata und S. Katagiri, *Angew. Chem.* 77, 345 (1965).

[9] T. Nakajima and S. Katagiri, *Mol. Phys.* 7, 149 (1963).

[10] T. Nakajima, *Molecular Orbitals in Chemistry, Physics and Biology* (Edited by B. Pullman and P. O. Löwdin) p. 451, Academic Press, New York (1964).

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

The values of the parameter k are taken to be 0·55, 0·60, 0·63* and 0·65, while the same value of 0·78 β_d is retained for the resonance integral in the condensed benzene ring.†

The usual Hückel type secular equations with overlap neglected are written down and solved. The solution leads to bond order, p_{ij}, and hence to bond lengths, r_{ij}, with the aid of the formula[9, 10]

$$r_{ij}(\text{Å}) = 1{\cdot}520 - 0{\cdot}186\, p_{ij}.$$

In calculating the electronic transition energies, electron interactions are taken into account using the following formula without allowance being made for configuration interaction:

$${}^1E_{ij} - E_N = (\varepsilon_j - \varepsilon_i) - (J_{ij} - K_{ij}) + K_{ij}$$

where E_N and ${}^1E_{ij}$ designate the energy of the ground and excited singlet 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. The Coulomb penetration and non-neighbor resonance integrals are neglected. In computing electronic interaction terms for adjacent atoms, bond orders were used to predict the internuclear distances. Non-neighbor internuclear distances were calculated assuming the rings to be regular. Orbital energies were computed in units of β_d in the present procedure. Following earlier work,[9, 10] the value of β_d when $k = 0{\cdot}63$ was found equal to $-6{\cdot}86$ eV by the assumption of a linear relationship between

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* $k = 0{\cdot}63$ was suggested by Nakajima and Katagiri for k_{min} of sesquifulvalene (1).[9, 10]

† The bond alternation parameter k may be understood as a ratio of Pariser–Parr–Pople matrix elements (in the approximation of neglect of all the non-neighbor matrix elements)

$$k(= \beta_{\text{single}}/\beta_{\text{double}}) \simeq \bar{\beta}_{\text{single}}/\bar{\beta}_{\text{double}}$$

where

$$\bar{\beta}_{ij} = \beta_{ij} - \tfrac{1}{2}\mathrm{p}_{ij}(ii|jj).$$

Here β_{ij}, p_{ij} and $(ii|jj)$ mean the resonance integral, bond order and Coulomb repulsion integrals, respectively. Using the numerical values of Julg‡, one obtains

$$\bar{\beta}_{\text{double}}(1{\cdot}34\ \text{Å}) = -6{\cdot}53\ \text{eV};\ \bar{\beta}_{\text{benzene}}(1{\cdot}39\ \text{Å}) = -5{\cdot}05\ \text{eV}$$

Hence

$$\bar{\beta}_{\text{benzene}} = 0{\cdot}77\, \bar{\beta}_{\text{double}}$$

Although the ratio resulting above is depending on the choice of parameters, the deviation from 0·77 may be taken as small. For simplicity in this paper the following relation was used.

$$\begin{aligned} \beta_{\text{benzene}} &= \tfrac{1}{2}(\beta_{\text{single}} + \beta_{\text{double}}) \\ &= \tfrac{1}{2}(0{\cdot}55 + 1)\,\beta_{\text{double}} \\ &= 0{\cdot}78\,\beta_{\text{double}} \end{aligned}$$

which was taken as constant in the range, $k = 0{\cdot}55 \sim 0{\cdot}65$.

‡ A. Julg, *J. Chim. Phys.* **57**, 19 (1960).

In his paper the value of $-4{\cdot}6$ eV for β_{benzene} seems incorrect; it should be corrected by $-5{\cdot}05$ eV.

TALBE 1. MOLECULAR ORBITALS AND THEIR ENERGIES OF BENZO[g]SESQUIFULVALENE[a]

MO	Sym.	Orbital[b,c]									Energy[d]
		$(\chi_1 \pm \chi_{16})$	$(\chi_2 \pm \chi_{15})$	(χ_3)	(χ_4)	$(\chi_5 \pm \chi_{14})$	$(\chi_6 \pm \chi_{13})$	$(\chi_7 \pm \chi_{12})$	$(\chi_8 \pm \chi_{11})$	$(\chi_9 \pm \chi_{10})$	
1	b_2	0·20439	0·24463	0·38498	0·39509	0·26732	0·23946	0·27009	0·16911	0·12599	1·82692
2	b_2	−0·26961	−0·27951	−0·31152	−0·16704	0·02628	0·14903	0·35257	0·28044	0·24669	1·66673
3	b_2	−0·32135	−0·22360	0·03950	0·33411	0·32022	0·21407	−0·05777	−0·21333	−0·30485	1·32584
4	a_2	0·00000	0·00000	0·00000	0·00000	−0·40417	−0·47371	−0·23973	−0·21734	−0·08684	1·17204
5	b_2	0·24090	0·07254	−0·27516	−0·34762	−0·03850	0·18315	0·33180	−0·08364	−0·43164	0·93113
6	a_2	−0·41820	−0·57019	0·00000	0·00000	0·00000	0·00000	0·00000	0·00000	0·00000	0·73344
7	a_2	0·00000	0·00000	0·00000	0·00000	0·25518	0·18030	−0·20284	−0·53221	−0·27925	0·70655
8	b_2	0·27192	−0·04131	−0·46297	−0·16928	0·30320	0·25160	−0·29034	−0·09083	0·23467	0·47808
9	b_2	0·28902	−0·28809	−0·29103	0·46973	0·09424	−0·33050	0·04282	0·20398	−0·13874	−0·36678
10	a_2	0·00000	0·00000	0·00000	0·00000	−0·39267	0·23053	0·40846	−0·08517	−0·34435	−0·58708
11	b_2	−0·13145	0·18617	−0·02368	−0·21596	0·15355	0·01533	−0·26286	0·51543	−0·25669	−0·78623
12	a_2	0·00000	0·00000	0·00000	0·00000	−0·30744	0·35108	−0·14837	−0·21472	0·46272	−1·14194
13	b_2	0·19538	−0·35499	0·35869	0·02155	−0·30497	0·34841	−0·17233	0·15316	−0·06073	−1·18694
14	a_2	−0·57019	0·41820	0·00000	0·00000	0·00000	0·00000	0·00000	0·00000	0·00000	−1·36344
15	b_2	−0·10640	0·24777	−0·49921	0·53584	−0·32623	0·21661	−0·06624	0·03555	−0·01119	−1·69875
16	a_2	0·00000	0·00000	0·00000	0·00000	0·15106	−0·25826	0·46101	−0·34082	0·28599	−1·70957

[a] $k = 0{\cdot}63$, $\beta_{\text{benzene}} = 0{\cdot}78\, \beta_d$.

[b] By definition for the i-th MO, $\phi_i = \sum_p C_{pi}\chi_p$. The C_{pi} are listed under the corresponding χ_p

[c] + and − refer to MO's of symmetry b_2 and a_2, respectively.

[d] The energies are given in units of β_d (= −7·0 eV).

β_d and k. The one-center electronic repulsion integral, (pp/pp), given in the Pariser–Parr theory[12] was taken to be 10·53 eV, while the two-center electronic repulsion integrals, (pp/qq), were determined by the extrapolation procedure of Pariser–Parr. The oscillator strengths f were evaluated from the well-known formula

$$f = 1{\cdot}085 \times 10^{11}\, \nu Q^2$$

where Q is the dipole strength and ν is the observed transition energy in cm^{-1}. The MO calculations were made on a NEAC 2230 electronic computer at the Computing Centre of Tohoku University.

The calculated molecular orbitals and energies with $k = 0{\cdot}63$ are summarized in Table 1.

3. RESULTS AND DISCUSSION

Charge densities, bond orders and free valences

The calculated charge densities, bond orders and free valences ($k_{sesquifulvalene} = 0{\cdot}63$, $\beta_{benzene} = 0{\cdot}78\,\beta_d$) are listed in Table 2. The charge transfer from the electron-donating seven-membered ring towards the electron-accepting five-membered ring is clearly demonstrated by these calculations. The lowest charge density was found at C_4 and the highest at C_3. At the carbon atoms of the condensed benzene ring, the charge densities are almost equal to unity. In connection with the charge separation in this molecule, it is interesting to note that the bond order of the "pinch bond" (0·783) is considerably smaller than that in fulvalene (0·846 with $k = 0{\cdot}58$)[9,10] and in heptafulvalene (0·823 with $k = 0{\cdot}60$)[9,10] where there is no contribution of the dipolar resonance structure to their ground states as determined by the same method of calculations. This means that the pinch bond in benzo[g]sesquifulvalene has more single bond character than in the fulvalenes. Recently Kakudo and Sasada *et al.*[13] reported the crystal structure of **3** and they obtained experimental bond lengths.

TABLE 2. CHARGE DENSITIES, FREE VALENCES, BOND ORDERS AND BOND LENGTHS

Atom	Charge density	Free valence	Bond	Bond order	Bond length (Å) Calc.	Bond length (Å) Obs.[13]
1	1·049	0·505	1–2	0·884	1·36	1·355
2	1·040	0·499	2–3	0·343	1·46	1·475
3	1·075	0·263	3–4	0·783	1·37	1·400
4	0·890	0·268	4–5	0·341	1·46	1·455
5	0·993	0·505	5–6	0·886	1·36	1·330
6	0·958	0·507	6–7	0·339	1·46	1·475
7	0·987	0·169	7–8	0·631	1·40	1·450
8	0·997	0·425	8–9	0·676	1·39	1·380
9	0·993	0·405	9–10	0·651	1·40	1·390
			1–16	0·350	1·46	1·420
			7–12	0·593	1·41	1·430

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

[13] Y. Nishi, Y. Sasada, T. Ashida and M. Kakudo, *Bull. Chem. Soc. Japan*, **39**, 818 (1966).

These values are also summarized in Table 2. The calculated bond lengths are in fairly good agreement with the experimental values. The average of the double bond lengths is 1·365 Å and that of the single bond lengths is 1·46 Å in the sesquifulvalene moiety, the extent of bond length alternation being comparable to those in heptafulvene and fulvalenes. In contrast to this, the distribution of bond lengths for the condensed benzene ring is fairly constant at 1·40 Å which is comparable to that of a normal benzenoid ring.

Dipole moment

The experimental value of the dipole moment for **3** is 5·20 D in benzene solution at 25°.[8] This indicates that the dipolar structure is a major contributor to its ground state.[8] On the other hand, our theoretical calculation for the dipole moment of benzo[g]sesquifulvalene (**4**) gives 2·76, 3·85, 4·66 and 5·21 D for the series of the k values 0·55, 0·60, 0·63 and 0·65 respectively. It is clear that the calculated dipole moments are very sensitive to the bond alternation parameter, k.

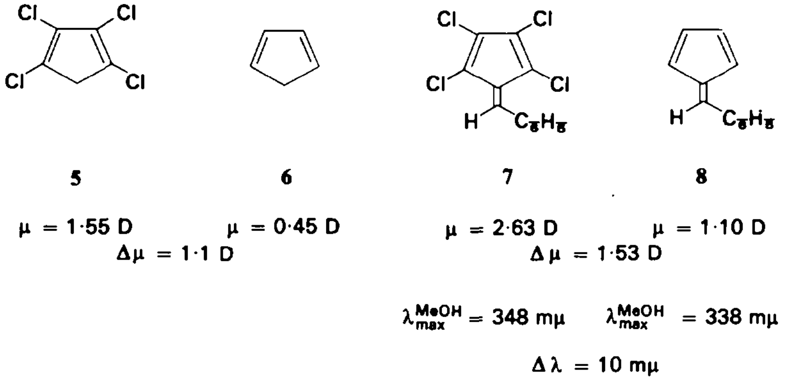

Fig. 3 Estimation of the effects of four chlorine atoms for dipole moment and electronic spectrum.

It is difficult to estimate the effect of the four chlorine atoms on the dipole moment of this system, but there are two possibilities for this problem [see Fig. 3].

Table 3. Dipole moment of benzo[g]sesquifulvalene (4)

k*	μ_{theor} (D)	μ_{exp} (D)
0·55	2·76	3·7–4·1
0·60	3·85	
0·63	4·66	
0·65	5·21	

* $\beta_{benzene} = 0{\cdot}78\ \beta_d$ was assumed.

Experimentally the resultant moment of four C—Cl bonds is taken as 1·1 D [difference between the observed dipole moment of tetrachlorocyclopentadiene (5), 1·55 D[8, 14] and that of cyclopentadiene (6), 0·45 D[15]], or 1·53 D [difference between the observed dipole moment of 1,2,3,4-tetrachloro-6-phenylfulvene, (7) 2·63 D[14] and that of 6-phenylfulvene (8), 1·10 D[16]]. This would give a value of 3·7 ~ 4·1 D for the dipole moment of **4**. Table 3 shows that the estimated dipole moment for **4** is reproduced within the range of $k = 0{\cdot}6 \sim 0{\cdot}61$. The usual results from the simple Hückel theory are over-estimated for the dipole moment. The predicted dipole moments summarized in the second column of Table 3 are considerably less than the value of 16·7 D[19] predicted using the simple Hückel theory.

Electronic spectrum

The observed electronic spectrum of **3** is shown in Fig. 4.[8]

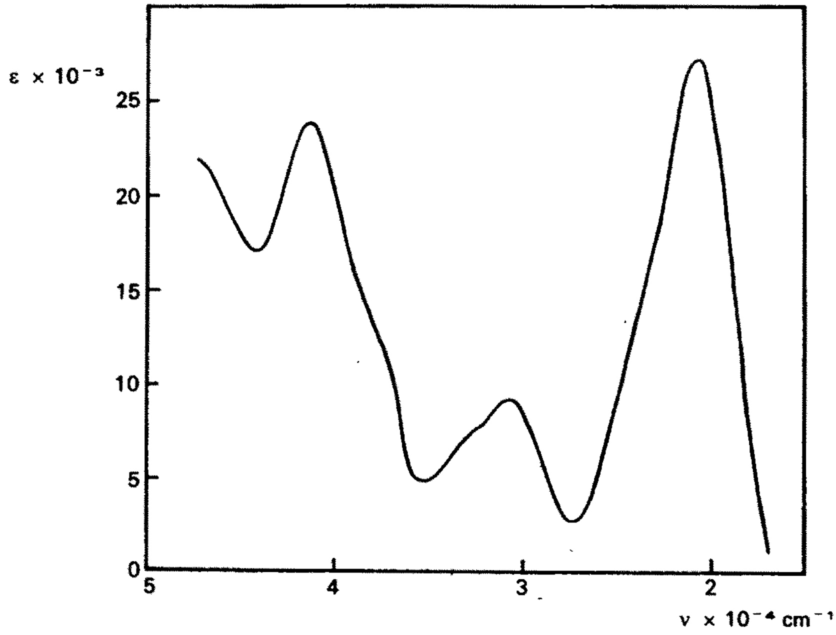

FIG. 4 The observed electronic spectrum of **3** in methanol.

The calculated singlet–singlet transition energies and oscillator strengths for (4) using $k = 0{\cdot}63$ are listed in Table 4, together with the observed values of **3**. It is well known that in the *pi*-system substituents such as C—Cl give rise to only small red shifts[20] in the spectrum so that we may expect that the spectrum of **4** would be

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[14] Unpublished data, measured in benzene at 25°.

[15] Ya. K. Syrkin and E. A. Shott-L'vova, *Acta Physicochem. URSS*, **19**, 379 (1944).

[16] Estimated from the value of 1·1 D[17] for fulvene and 1·09, 1·12 D for 6,6-diphenylfulvene.[18]

[17] J. Thiec and J. Wiemann, *Bull. soc. chim. Fr.* 177 (1956).

[18] G. Kresze, S. Rau, G. Sabelus and H. Goetz. *Liebigs Ann.* **648**, 51 (1961).

[19] This value was derived with the assumption of all the C—C distances equal to 1·4 Å.

[20] H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, p. 175, 248, Wiley, New York (1964).

similar to that of 3. It is obvious that the lowest singlet transition should be polarized along the symmetry axis ($^1A_1 \leftarrow {}^1A_1$), and hence to be very intense. This transition is mainly responsible for the observed longest-wavelength band in 3, which is very strong with log ε equal to 4·44, the next two transitions of low intensity polarized perpendicular to the symmetry axis ($^1B_1 \leftarrow {}^1A_1$) being hidden under the stronger band. This situation is very similar to that found in the electronic transitions of sesquifulvalene (**1**).[4,5,6,11] Chlorine subsituents usually cause a red shift compared to the parent hydrocarbon, and in the present molecule **3** the shift caused by the four chlorine atoms substituted in the pentagonal ring would be ca. 0·11 eV [estimated from the difference between the observed longest wavelength band of 1,2,3,4-tetrachloro-6-phenylfulvene (**7**; 3·56 eV) and that of 6-phenylfulvene (**8**; 3·67 eV)] [see Fig. 3]. The first transition energy of **4** would therefore be expected to be 2·69 eV and is in fairly good agreement with the calculated lowest singlet transition energy.

TABLE 4. CALCULATED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS OF BENZO[g]SESQUIFULVALENE (4)

Assignment	Energy (eV)		Oscillator strength (cgs)	
	Calc.	Obs. for (3)	Calc.	Obs. for (3)
$^1A_1 \leftarrow {}^1A_1$	2·46		1·397	
$^1B_1 \leftarrow {}^1A_1$	3·03	2·58	0·023	1·2
$^1B_1 \leftarrow {}^1A_1$	3·07		0·084	
$^1B_1 \leftarrow {}^1A_1$	3·73	3·87	0·107	0·26
$^1A_1 \leftarrow {}^1A_1$	4·42	5·12	0·002	0·78
$^1A_1 \leftarrow {}^1A_1$	4·77		0·388	

Acknowledgement—We thank Professor T. Nakajima for his continued interest and stimulating discussions.