

# ELECTRONIC PROPERTIES OF $[n]$ -RADIALENES AND THEIR METHYL DERIVATIVES

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The structural and electronic properties of  $[n]$ -radialenes are considered with the following five methods: the Hückel method, the SC LCAO MO method with variation of resonance integrals, the SC- $\omega$  LCAO MO method with variation of resonance integrals and Coulomb integrals, the SCF LCAO MO method within the PPP approximation scheme and the SCF LCAO MO CI method in the PPP approximation. Additionally the substituent effect of methyl groups on the spectrum of hexamethyl-[3]-radialene is discussed.

## 1. Introduction

$[n]$ -radialenes are highly symmetric hydrocarbons of the general formula  $C_{2n}H_{2n}$ , with  $n$  cross-conjugated double bonds (Fig. 1). The longest known representative is the hexamethyl derivative of [6]-radialene (denoted henceforth by I). It was synthesized by Hopff and Wick in 1961. Since then [4]-radialene (denoted by II) and its octaphenyl derivative have been obtained by Griffin and Peterson (1962) and the hexamethyl derivative of [3]-radialene (denoted by III) by Köbrich and Heinemann (1965).

The electronic spectra of  $[n]$ -radialenes have been the subject of three theoretical works. Weltin, *et al.* (1961) have considered the spectrum of [6]-radialene using the limited CI method, and Gołębiwski (1962) using the Hückel, the SC LCAO MO, the SCF LCAO MO and the zeroth order CI methods. The spectral predictions of the second work were in better agreement with experiment than those of the first one; the two approaches differed primarily in the choice of resonance integrals and electron repulsion integrals. A general discussion of all  $[n]$ -radialenes was published by Heilbronner

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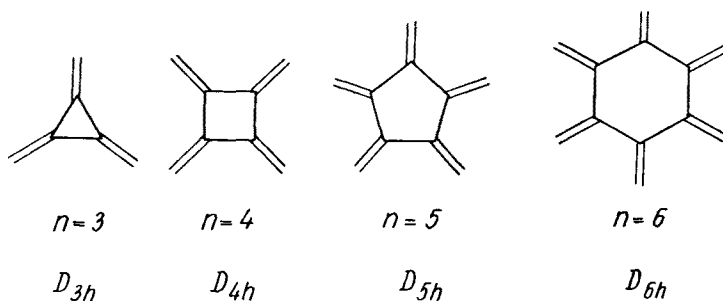


Fig. 1.  $\pi$ -electronic framework in  $[n]$ -radialenes

in 1966. However, his treatment was perturbational and the results were semiquantitative. This is why a more general analysis of the electronic properties of  $[n]$ -radialenes was thought to be necessary and useful.

Let us recall for completeness that also other properties of  $[n]$ -radialenes have been the subject of a theoretical analysis: thermochemistry has been discussed by Dewar and Gleicher (1965) and the EPR spectrum by Gerson (1964) and by Gerson *et al.* (1965).

## 2. Methods used for planar free $[n]$ -radialenes

The main part of this work deals with planar free  $[n]$ -radialenes of  $D_{nh}$  symmetry. Analyzing the  $\pi$ -electronic structure of these molecules we have applied the following five methods: 1) the Hückel method (Hückel 1932; Coulson, Longuet-Higgins 1947), 2) the SC LCAO MO method with variation of resonance integrals  $\beta_{rs}$  with the appropriate bond length  $R_{rs}$ ,  $\beta_{rs} = \beta_0 \exp(-4.2 \Delta R_{rs})$  (Gołębiewski, Nowakowski 1964), 3) the SC- $\omega$  LCAO MO method with the same variation of resonance and additionally of the Coulomb integrals  $\alpha_r$ , with the appropriate average number of  $2p\pi$  electrons at center  $r$ ,  $\alpha_r = \alpha_0 + 0.5\beta_0(1-q_r)$  (Wheland, Mann 1949; Streitwieser, Nair 1959), 4) the SCF LCAO MO method in the Pariser-Parr-Pople (PPP) approximation, with neglect of all penetration integrals and all resonance integrals other than those for neighbouring atoms, with an exponential form of resonance integrals for next neighbours,  $\beta_{rs} = -2.3697 \exp(-2.1888 \Delta R_{rs})$  eV, where  $\Delta R_{rs} = R_{rs} - 1.397$  Å, and with a Mataga-Nishimoto approximation for interelectronic repulsion integrals,  $g_{ij} = 14.402(1.328 + R_{ij})^{-1}$  eV (Mataga, Nishimoto 1957), 5) the SCF LCAO MO CI method within the same approximation scheme for integrals, but with a configuration interaction (CI) of the ground state and all singly excited singlet states.

Let us consider the general case of a  $[n]$ -radialene (Fig. 2). Throughout this paper we use small Latin symbols for quantities which refer to the internal ring atoms or pairs of them, capital Latin symbols for quantities which refer to external atoms or pairs of them, and small Greek symbols for quantities which depend both on internal and external atoms. Thus, the atomic distances will be described as  $r_{ij}$ ,  $R_{ij}$ ,  $\rho_{ij}$  accordingly (Fig. 2),  $p_{ij}$ ,  $P_{ij}$ ,  $\pi_{ij}$  will be the appropriate elements of the mobile bond order matrix,  $g_{ij}$ ,  $G_{ij}$ ,  $\gamma_{ij}$  will be the appropriate electron repulsion integrals, and  $f_i$  and  $F_i$  will denote the appropriate  $2p\pi$  orbitals of carbon atoms.

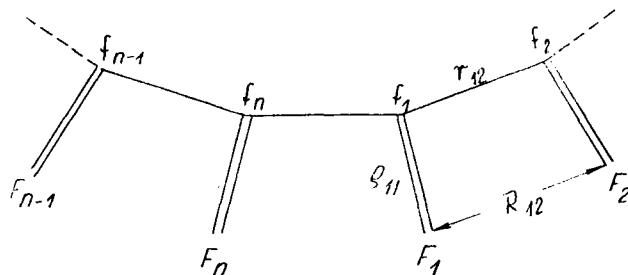


Fig. 2. Notation in the general case of an  $[n]$ -radialene

Let us describe the molecular orbitals of  $[n]$ -radialenes within the  $C_n$  subgroup scheme. Then

$$\Psi(K) = \frac{1}{\sqrt{n}} \sum_{j=1}^n \exp(2\pi iKj/n) (af_j + AF_j) = a\varphi_K + A\Phi_K \quad (1)$$

where  $K = 0, \pm 1, \pm 2, \text{etc.}$ , until  $+\frac{1}{2}n$  for even values of  $n$  and  $\pm\frac{1}{2}(n-1)$  for odd values of  $n$ . For  $K = 0$  the orbitals span an  $A$  representation, for  $K = \pm 1$  an  $E_1$  representation, for  $K = \pm 2$  an  $E_2$  representation, *etc.*, except for  $K = \frac{n}{2}$ . For  $K = \frac{n}{2}$  the orbitals belong to  $B$ . Thus for any allowed value of  $K$  two molecular orbitals exist. Their energy eigenvalues  $E_K$  and the linear coefficients  $a$  and  $A$  of Eq. (1) follow from the secular equations,

$$\begin{aligned} [H_{aa}(K) - E_K] a(K) + H_{aA}(K) A(K) &= 0 \\ H_{aA}(K) a(K) + [H_{AA}(K) - E_K] A(K) &= 0 \end{aligned}$$

where

$$H_{aa}(K) = \langle \varphi_K | \hat{H} | \varphi_K \rangle, H_{aA}(K) = \langle \varphi_K | \hat{H} | \Phi_K \rangle, H_{AA}(K) = \langle \Phi_K | \hat{H} | \Phi_K \rangle \quad (2)$$

and  $a^2 + A^2 = 1$ . In the case of the first three methods under consideration

$$\begin{aligned} H_{aa}(K) &= 2 \cos \nu \beta(\varepsilon, p_{12}) + \omega (1 - q_1) \beta_0 \\ H_{aA}(K) &= \beta(\varepsilon, \pi_{11}) \\ H_{AA}(K) &= \omega (1 - Q_1) \beta_0 \end{aligned} \quad (3)$$

where

$$\beta(\varepsilon, x) = \beta_0 \exp[\varepsilon(-0.504 + 0.756 x)], \quad q_1 = p_{11}, \quad Q_1 = P_{11};$$

$\varepsilon = 0$  for the Hückel method and 1 for the SC and SC- $\omega$  methods, whereas  $\omega = 0$  for the Hückel and the SC methods, but 0.5 for the SC- $\omega$  method, and  $\nu = \frac{2\pi K}{n}$ .

In the case of the SCF LCAO MO method, on the other hand, one finds that (in eV):

$$H_{aa}(K) = W_{2p} + 2 \cos \nu \beta^{\text{SCF}}(p_{12}) + (q_1 - 1) \sum_{m=1}^n (g_{1m} - \gamma_{1m}) - \frac{1}{2} \sum_{m=1}^n p_{1m} g_{1m} \cos [(m-1)\nu]$$

$$H_{aA}(K) = \beta^{\text{SCF}}(\pi_{11}) - \frac{1}{2} \sum_{m=1}^n \pi_{1m} \gamma_{1m} \cos [(m-1)\nu]$$

$$H_{AA}(K) = W_{2p} + (Q_1 - 1) \sum_{m=1}^n (G_{1m} - \gamma_{1m}) - \frac{1}{2} \sum_{m=1}^n P_{1m} G_{1m} \cos [(m-1)\nu] \quad (4)$$

where  $\nu = 2\pi K/n$ ,  $W_{2p}$  is the  $2p$  orbital energy in a free carbon atom and  $\beta^{\text{SCF}}(x) = -2.3697 \exp[-2.1888(0.120-0.180x)]$ .

All the SC and SCF calculations have been repeated until selfconsistency between the assumed and calculated values of  $p_{1m}$ ,  $\pi_{1m}$ ,  $P_{1m}$ ,  $g_{1m}$ ,  $\gamma_{1m}$  and  $G_{1m}$  has been achieved. The new interatomic distances at each step have been recalculated according to a formula derived by Coulson and Gołębiewski (1961). Thus  $r_{12} = 1.517-0.180 p_{12}$  (Å) and  $\varrho_{11} = 1.517-0.180 \pi_{11}$  (Å).

Passing on to configuration interaction of the ground state single determinantal wave function  $V_0$  and all singly excited singlet wave functions  $V_{KK'}$  (which correspond to an excitation from  $\Psi(K)$  to  $\Psi(K')$ ), it is convenient to group these functions into irreducible representations of the  $C_n$  group. With this purpose in mind let us notice that

$$\hat{C}_n^k \Psi(K) = \varepsilon^{kK} \Psi(K) \quad (5)$$

where  $\hat{C}_n^k$  is the  $k$ -fold rotation operator of the coordinate system by  $\frac{2\pi}{n}$  and  $\varepsilon = \exp \frac{2\pi i}{n}$ .

Hence it is easy to check that

$$\hat{C}_n^k V_{KK'} = \varepsilon^{k(K'-K)} V_{KK'}. \quad (6)$$

It follows that all functions  $V_{KK'}$  for which  $K'-K=0$  belong to representation  $A$ , all functions  $V_{KK'}$  for which  $|K'-K|=1$  or  $n-1$  belong to  $E_1, \dots$ , all function  $V_{KK'}$  for which  $|K'-K|=j$  or  $n-j$  belong to  $E_j$ , and all functions  $V_{KK'}$  for which  $|K'-K| = \frac{n}{2}$  belong to representation  $B$ . Two wave functions, such that  $(K'-K)$  differs in sign, never mix together. Thus  $n+1$  configurations at most can mix together.

### 3. Theoretical properties of planar free $[n]$ -radialenes

In Table I we compare the  $\pi$ -electronic charges, the bond lengths and the delocalization energies obtained for the various  $[n]$ -radialenes with the methods 1 to 4. We notice that the bond lengths in the internal ring are closer to those of single bonds and the external lengths are closer to those of double bonds. They vary almost negligibly with  $n$ . We also

TABLE I  
 Charge densities, bond lengths (Å) and delocalization energies per bond ( $|\beta_0|$ )

Method	$n$	$q_1 = p_{11}$	$Q_1 = P_{11}$	$r_{12}$	$Q_{11}$	Delocalization energy per bond
HMO	3	0.938	1.062	1.448	1.367	0.217
	4	1	1	1.453	1.364	0.207
	5	1.008	0.992	1.448	1.367	0.216
	6	1	1	1.448	1.367	0.219
	7	0.999	1.001	1.448	1.367	0.216
SC LCAO MO	3	0.979	1.021	1.468	1.351	0.084
	4	1	1	1.471	1.350	0.082
	5	1.001	0.999	1.468	1.351	0.084
	6	1	1	1.468	1.351	0.084
	7	0.999	1.000	1.468	1.351	0.084
SC- $\omega$ LCAO MO	3	0.984	1.016	1.468	1.351	
	4	1	1	1.471	1.350	
	5	1.001	0.999	1.468	1.351	
	6	1	1	1.468	1.351	
	7	0.999	1.000	1.468	1.351	
SCF LCAO MO	3	0.986	1.014	1.468	1.351	
	4	1	1	1.470	1.350	
	5	1.001	0.999	1.466	1.352	
	6	1	1	1.466	1.353	
	7	0.999	1.000	1.465	1.353	

see that there is almost no difference in bond lengths predicted by the SC LCAO MO, SC- $\omega$  LCAO MO and SCF LCAO MO methods indicating once again that the SC LCAO results are very close to those obtained by the SCF LCAO MO method. On the other hand, the bond lengths predicted by the Hückel method differ from the other ones appreciably. Similarly the atomic charges  $q_1 = p_{11}$  and  $Q_1 = P_{11}$ , predicted by the SC, SC- $\omega$  and SCF methods, are close one to each other and approximately equal 1.0 except for  $n = 3$ . In this case there is a shift of  $\pi$ -electrons towards the external atoms.

It is easy to see from Table I that the delocalization energy per bond is almost constant in all radicalenes. It might seem to be much smaller in the case of the SC method than in the case of the Hückel method (Table I). The difference is apparent, for the  $\beta_0$  unit has a different value in both methods.

In Table II we give the calculated singlet-singlet transition energies obtained with the SCF LCAO MO CI scheme for  $n = 3$  to 8. In this table we use the full notation of the  $D_{nh}$  group. The oscillator strengths have been calculated in a standard way (Daudel *et al.* 1959). Transitions of the type  $A \rightarrow E_1$  having the polarization components  $x$  and  $y$  are always allowed. To abridge the table we list only all excited singlet states below 7 eV and those which lie above 7 eV to which the transition is allowed. In Fig. 3 we compare the calculated transition energies and oscillator strengths (in a relative scale) with the experi-

TABLE II

Excitation energies (eV), oscillator strengths and symmetry properties of excited singlet states for (*n*)-radialenes according to the SCF LCAO MO CI method

<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	<i>n</i> = 7	<i>n</i> = 8
5.09(0.627) $E'_1$	4.57 $B_{1g}$	4.69 $E'_2$	4.59 $B_{1u}$	4.67 $E'_3$	4.57 $B_{1g}$
7.02 $A'_2$	5.47(0.0) $E_{1u}$	5.30 $E'_2$	5.04 $E_{2g}$	4.96 $E'_3$	4.76 $E_{3u}$
7.23(0.443) $E'_1$	6.01(1.295) $E_{1u}$	5.48(0.695) $E'_1$	5.05 $E_{2g}$	5.09 $E'_2$	4.92 $B_{2g}$
:	6.56 $B_{2g}$	6.35(0.545) $E'_1$	5.13 $B_{2u}$	5.46 $E'_2$	5.04 $E_{3u}$
10.92(0.004) $E'_1$	6.56 $A_{2g}$	6.72 $A'_2$	5.63(0.962) $E_{1u}$	5.89 $E'_3$	5.23 $E_{2g}$
:	:	:	5.76 $B_{1u}$	5.90(1.129) $E'_1$	5.56 $B_{1g}$
:	9.85(0.095) $E_{1u}$	7.94(0.337) $E'_1$	6.62(0.0) $E_{1u}$	6.39(0.236) $E'_1$	5.72 $E_{2g}$
:	:	:	6.76 $A_{2g}$	6.50 $E'_2$	6.09(1.549) $E_{1u}$
:	:	9.33(0.150) $E'_1$	:	6.60 $A'_2$	6.15 $E_{3u}$
:	:	:	7.31(0.799) $E_{1u}$	:	6.35 $E_{2g}$
:	:	10.07(0.012) $E'_1$	:	7.47(0.355) $E'_1$	6.36(0.0) $E_{1u}$
:	:	:	9.36(0.328) $E_{1u}$	:	6.47 $E_{3u}$
:	:	:	:	8.43(0.252) $E'_1$	6.54 $A_{2g}$
:	:	:	9.88(0.001) $E_{1u}$	:	:
:	:	:	:	9.21(0.296) $E'_1$	8.10(0.540) $E_{1u}$
:	:	:	:	:	:
:	:	:	:	9.42(0.176) $E'_1$	9.27(0.681) $E_{1u}$
:	:	:	:	:	:

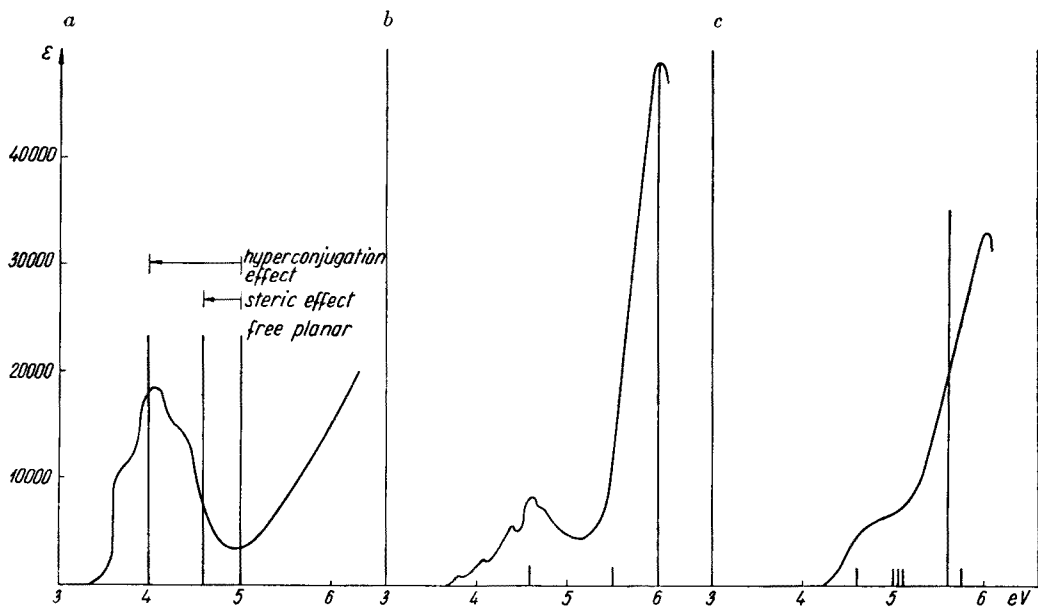


Fig. 3. Absorption spectra of solutions of a) hexamethyl-[3]-radialene, b) [4]-radialene, c) symmetric hexamethyl-[6]-radialene and a comparison with the theoretical spectra

mental spectra of I, II and III. We see that the agreement with experiment is excellent for the free radialene II, fair for the methyl derivative I and bad for the hexamethyl derivative III. The reason for the disagreement in the last case is presumably connected with the presence of six methyl groups in a relatively small hydrocarbon. The effect of these groups on the spectrum of III will be discussed in the next section.

Let us also note that the CI effect on the position of the lowest singlet-singlet transition is relatively small, the shift being obviously always bathochromic. For  $n = 3$  it is equal to 0.05 eV, for  $n = 4$  to 0.01 eV, for  $n = 5$  to 0.02 eV and for  $n = 6$  to 0.03 eV.

According to Heilbronner's perturbational "independent system approach" (1966) in all  $[n]$ -radialenes except for  $n = 3$  weak (forbidden) transitions should precede the first intense one (allowed). This statement is confirmed by our calculations. However, we predict 4 forbidden transitions to precede the first allowed one for  $n = 6$ , in contrast to Heilbronner, who predicts two. Another general property predicted by Heilbronner is the shift of the first allowed band towards shorter waves with larger  $n$ . This general behaviour is confirmed in our work, although we do note a slight irregularity for  $n = 4$ .

#### 4. Substituent effect in hexamethyl-[3]-radialene

As is seen, the lowest calculated transition energy in III is about 1 eV too high in comparison with experiment. One could hardly expect such a difference in view of the limitations of the PPP theory. Thus we expect this difference to be caused by the presence of six methyl groups. In principle three types of effects can be caused by these groups:

- a) a steric effect due to overcrowding of methyl groups;
- b) an inductive effect due to the difference in electronegativity of methyl groups and hydrogen atoms;
- c) a hyperconjugation effect.

It would be difficult to consider all these effects simultaneously and precisely. To see the possible influence of these effects on the spectrum we decided, therefore, to analyze the effects separately. As the configuration interaction was shown to change the energy of the first transition negligibly we decided to neglect the additional effect of CI in this discussion.

##### a) Steric effect

Let us assume that the  $\sphericalangle$  ( $\text{CH}_3\text{-C-CH}_3$ ) angle is equal to  $120^\circ$ , the  $\text{C-C(H}_3)$  bond length equal to 1.54 Å, the  $\text{C-H}$  bond length equal to 1.11 Å, the van der Waals radius of hydrogen atoms equal to 1.20 Å and that the structure of the radialene part is that what follows from the SCF LCAO MO method (Table I). Then there is a molecular conformation in which no steric effects can appear. However, methyl groups may be expected to rotate around the single bond. Then, taking  $R(\text{H}\dots\text{H}) = 2.40$  Å for hydrogen atoms of two geminal methyl groups and  $R(\text{CH}_3\text{-CH}_3) = 4.0$  Å for the distance between the whole "vicinal" methyl groups we obtain a twisting of the external bonds by  $25^\circ 52'$ . Assuming this twisting angle (let us denote it by  $\varphi$ ) and the general relation  $\beta = \beta_0 \exp(-4.2 \Delta r) \cos \varphi$ , we could easily find the new SC LCAO molecular orbitals expectedly close enough to the SCF LCAO molecular orbitals.

In Table III we list some of the results which have been obtained with the use of the SC LCAO method for the planar and twisted system. We turn attention to the small differences in bond lengths and  $\pi$ -electron populations and to a large decrease of the transition energy.

TABLE III  
The steric effect in hexamethyl-(3)-radialene according to the SC LCAO MO method

Structure	Lowest excitation energy (in $ \beta_0 $ )	$q_1 = p_{11}$	$Q_1 = P_{11}$	$r_{12}(\text{\AA})$	$q_{11}(\text{\AA})$
planar	1.577	0.979	1.021	1.468	1.351
twisted	1.315	0.970	1.030	1.462	1.355

To analyze the influence of the steric hindrance on the spectrum more realistically, we have recalculated the first transition energy within the PPP scheme without CI and with the new SCLCAO molecular orbitals as the basis. Resonance integrals and electronic repulsion integrals have been corrected for twisting in a manner proposed by Gołębiewski and Parczewski (1966). The calculated value of the first transition energy was 4.67 eV. It was better by about 0.5 eV than that found for the planar molecule. The improvement is significant, although the disagreement with experiment is still higher than could be expected.

#### b) Inductive effect

Let us assume that a methyl group is substituted in position  $r$  of a conjugated system and that  $c_{nr}$  and  $c_{(n+1)r}$  are the LCAO coefficients of the  $r$ -th  $2p\pi$  orbital in the highest occupied ( $n$ -th) and the lowest unoccupied [( $n+1$ )-th] molecular orbitals, respectively. According to Coulson (1952) a first-order correction of the transition energy is expected such that

$$\Delta E = [c_{(n+1)r}^2 - c_{nr}^2] \Delta\alpha \quad (7)$$

where  $\Delta\alpha$  is a change of the Coulomb integral for the center  $r$  to which a methyl group is attached. Assuming additivity for all the methyl groups we get  $\Delta E = 0.2273 \Delta\alpha$ . Making a similar analysis for the methyl derivatives of azulene we find from the known values of  $\Delta E$  that  $\Delta\alpha \sim 0.5$  eV. Hence  $\Delta E = +0.1$  eV in our case. Thus the inductive effect does not improve the agreement with experiment (wrong sign), the correction being almost negligible.

#### c) Hyperconjugation effect

Discussing the hyperconjugation of methyl groups with a conjugated system it is customary to hybridize the  $-\text{C} \equiv \text{H}_3$   $\sigma$ -orbitals. Let us denote the hydrogen atoms of a methyl group by  $a$ ,  $b$ ,  $c$  and let us assume that atom  $c$  is in the plane of the conjugated system,  $a$  is above it and  $b$  is symmetrically below. Then one of the hybridized  $1s$  hydrogenic orbitals has the properties of a pseudo  $p\pi$  orbital,  $\chi = (h_a - h_b) (2 - 2S)^{-1/2}$ , where  $h$  denotes a  $1s$  orbital and  $S$  is the overlap integral  $\langle h_a | h_b \rangle$ . Obviously we have to hybridize the atomic



orbitals of C of the methyl group accordingly (to insure bonding with appropriate  $H_3$  hybridizes). Thus a  $2p\pi$  orbital of C of the methyl group has to be isolated for our purpose. Assuming planarity of the set of all carbon atoms we arrive at the situation shown in Fig. 4.

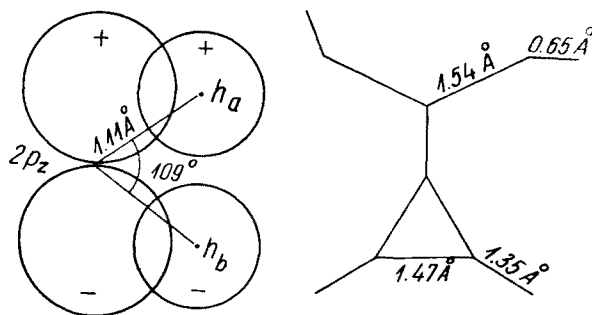


Fig. 4

New integrals now appear for which approximations are necessary. Following suggestions in the literature (Morita 1957) we have assumed what follows:

a)  $I_C = 11.526$  eV for the ionization potential of C of the methyl group and  $I_{H_2} = 10.3725$  eV for the ionization potential of the pseudo  $p\pi$  orbital (Morita 1957);

b)  $(h_a h_a | h_a h_a) = I_H - A_H = 12.848$  eV. Thus, applying the Mataga-Nishimoto formula,  $(h_a h_a | h_b h_b) = 14.402 (a_H + R_{ab})^{-1} = 4.918$  eV, where  $a_H = \frac{14.402}{12.848} = 1.121$  Å;

c) Applying the Mulliken approximation for three-center integrals we find that  $(\chi_i \chi_i | \chi_j \chi_j) = 1/2 [(h_a h_a | h_a h_a) + (h_a h_a | h_b h_b)] = 8.883$  eV and  $(\chi_i \chi_i | \chi_j \chi_j) = 14.402 (a_{H_i} + R_{ij})^{-1}$  eV, where  $a_{H_i} = \frac{14.402}{8.883} = 1.621$  Å.

d) Electronic repulsion integrals between  $2p\pi$  electrons of carbon atoms and pseudo  $p\pi$  electrons of  $H_2$  groups have been calculated according to a Mataga-Nishimoto type formula,  $14.402 (A + R_{ij})^{-1}$ , where  $A = 1.460$  Å and  $R_{ij}$  is the distance between the carbon atom and the center of gravity of the  $H_2$  group. The value of  $A$  is chosen such that for  $R_{ij} = 0$  the integral is equal to an arithmetic mean of appropriate integrals for two  $2p\pi$  electrons of a carbon atom and two pseudo  $p\pi$  electrons of the  $H_2$  group.

e) The resonance integral for the pseudo  $p\pi$  orbital and the closest  $2p\pi$  orbital of the carbon atom was reduced to a  $\beta(1s_H, 2p\sigma_C)$  integral

$$\beta_{C_x} = \sqrt{2} \sin \alpha (1-S)^{-1/2} \beta(1s_H, 2p\sigma_C) \quad (8)$$

where, according to the Mulliken formula (Bloor, Gilson 1967)

$$\beta(1s_H, 2p\sigma_C) = -\frac{1}{2} (I_H + I_C) \frac{S(1s_H, 2p\sigma_C)}{1 + S(1s_H, 2p\sigma_C)} \quad (9)$$

The overlap integral  $S(1s_H, 2p\sigma_C)$  was calculated for  $R_{CH} = 1.11$  Å and for Slater atomic orbitals. It was found that  $\beta_{C_x} = -4.155$  eV.

In order to analyze the hyperconjugation new SCF LCAO molecular orbitals have been found perturbationally. The zeroth-order total wave function was taken as antisymmetrized product of the [3]-radialene  $\pi$ -electronic wave function and the six bonding and antibonding  $\pi$ -type molecular orbitals of the methyl groups. With the corrected SCF molecular orbitals a correction to the first transition energy was then estimated. We found  $\Delta E \approx -1$  eV. The hyperconjugation seems then to be able to explain the strong bathochromic shift in the hexamethyl-[3]-radialene due to the methyl groups.

### 5. Final remarks

It was shown that the SCF LCAO MO CI method does properly account for the spectral properties of free  $[n]$ -radialenes. In methyl derivatives the agreement between the calculated and observed transitions is not so satisfactory, particularly in the case of hexamethyl-[3]-radialene. In this case two different effects may cause a strong shift of the first allowed band towards longer waves: the steric effect due to rotating  $\text{CH}_3$  groups and the hyperconjugation effect of these groups. These two effects might seem to exclude each other. However, rotating the  $\text{CH}_3$  group we pass from one pseudo  $p$  orbital (e. g.  $[h_a-h_b]$ ) to another (e. g.  $[h_a-h_c]$  or  $[h_b-h_c]$ ). We expect therefore that the strong decrease of the transition energy of the first band is due to the simultaneous action of both the steric effect and hyperconjugation.

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