

SC LCAO MO TREATMENT OF NONALTERNANT HYDROCARBONS AND IONS

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A possible extension of the validity of the SC LCAO MO method (with empirical parameters due to Gołębiewski and Nowakowski (1964)) to nonalternant hydrocarbons has been discussed. It is shown that this modification of the Hückel method allows for a more reliable prediction of bond lengths and probably of $N \rightarrow V_1$ transitions, and in some well defined cases of dipole moments and $N \rightarrow T_1$ transitions also. The correlation lines of experimental and calculated $N \rightarrow V_1$ transitions are different for alternants and nonalternants. It is shown that a possible explanation of this fact lies in a different singlet-triplet splitting of the lowest orbital excitation.

1. Introduction

Many calculations have been already performed on the π -electronic properties of non-alternant conjugated hydrocarbons which are based on the standard Hückel method (Daudel, Lefebvre and Moser 1959; Pullman and Pullman 1952; Streitwieser 1961). However, in contrary to alternant hydrocarbons, the agreement with experiment obtained with this method is known to be rather poor (Streitwieser 1961).

At least two important explanations could be given for this disagreement:

- 1) the relation between the π -electronic charge at the atom r , q_r , and the Coulomb integral, α_r , which is disregarded in this method,
- 2) the dependence of the resonance integral β_{rs} on the bond length R_{rs} , which is disregarded also.

The first of these two effects is taken into account in what is called ω -technique (Wheland and Mann 1949; Streitwieser and Nair 1959). In this modification of Hückel's method it is assumed, that the solution of the eigenvalue problem is consistent with the assumption that

$$\alpha_r = \alpha_0 + \omega(1 - q_r)\beta_0, \quad (1)$$

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where ω is an adjustable parameter and β_0 is the resonance integral for benzene. It was shown that in many respects this improvement is significant, although certainly not sufficient (Ehrenson 1962; Zalewski 1961).

The second effect was also considered occasionally. It was shown to be significant also. It seems that in some kind of problems this effect is even more important than the first one.

The problem of variation of resonance integrals with bond lengths was considered in details by Coulson and Gołębiewski (1961) and by Gołębiewski and Nowakowski (1964). Gołębiewski and Nowakowski required the solution of the eigenvalue problem to be self-consistent with the assumptions that

$$\beta_{rs} = \beta_0 \exp \{-x(R_{rs} - 1.397 \text{ \AA})\}, \quad (2)$$

$$R_{rs} = 1.517 \text{ \AA} - 0.180 p_{rs}, \quad (3)$$

where p_{rs} is the mobile bond order and Eq. (2) is valid for nearest neighbours only, β_{rs} being zero for not-neighbours. The authors called this method selfconsistent LCAO MO method (SC LCAO MO) due to the fact that the iterative procedure is employed and that calculations are carried out up to obtain results which are consistent with the assumptions. Gołębiewski and Nowakowski have been able to prove that taking $x = 4.0/\text{\AA}$ a good correlation between calculated and observed values of many physical and chemical properties can be obtained for alternant hydrocarbons, the correlation being the same for benzenoid hydrocarbons, polyenes and vinyl compounds.

The aim of this work was to investigate the $N \rightarrow V_1$ transitions, the dipole moments and bond lengths in nonalternant hydrocarbons in order to see to what extent the approach due to Gołębiewski and Nowakowski can be transferred to this class of conjugated hydrocarbons.

However, according to a suggestions of these authors, a slightly higher value of the parameter x should be preferable to obtain a still better agreement with experiment. The value about $x = 4.2/\text{\AA}$ was considered as optimal and therefore this value of x is assumed in the present calculations. It was found that for nonalternant hydrocarbons $x = 4.2/\text{\AA}$ leads to a better agreement with experiment than $x = 4.0/\text{\AA}$.

2. Electronic $N \rightarrow V_1$ and $N \rightarrow T_1$ transitions

The lowest excitation energy of some nonalternant hydrocarbons and cations, has been calculated with both, the simple Hückel method and the SC LCAO MO method. The results are listed in Table I. We can compare them with the experimental $N \rightarrow V_1$ transition energies, which are listed in column 4 of this Table. A graphical comparison is made in Fig. 1 where the solid line is the best overall correlation line for alternant hydrocarbons as quoted by Gołębiewski and Nowakowski. In this figure crosses correspond to the Hückel method and circles to the SC LCAO MO method. Full circles correspond to nonalternant hydrocarbons which seem to give a satisfactory correlation between the observed and calculated transition energies. Black-white circles correspond to nonalternant neutral hydrocarbons which evidently do not fit to this correlation. White circles correspond to cations.

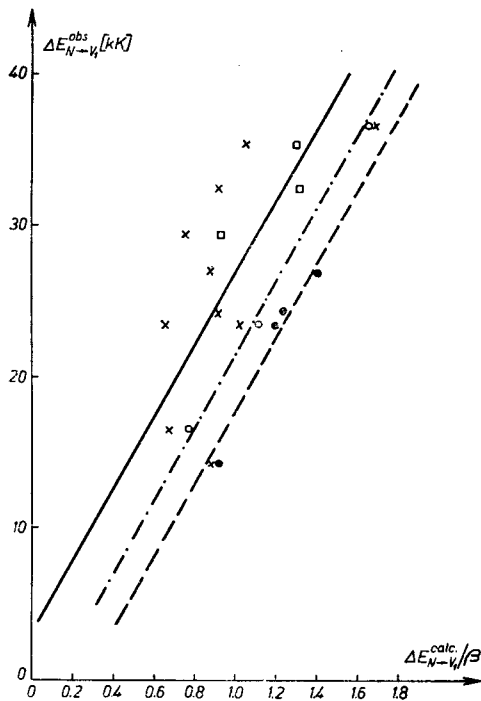


Fig. 1

TABLE I
 $N \rightarrow V_1$ transitions in nonalternant hydrocarbons and cations

Molecule	ΔE		
	calculated (in β_0 units)		observed (in kK)
	Huckel method	SC LCAO MO method	
Azulene	0.878	0.900	14.4 ¹
Heptafulvene	0.661	1.201	23.4 ²
Acenaphthylene	0.922	1.235	24.3 ³
Fulvene	0.872	1.389	27.0 ⁴
Dibenzofulvene	1.069	1.307	35.5 ¹
4,4-Benzofulvene	0.423	0.845	not known
3,4-Benzofulvene	0.925	1.315	32.5 ¹
Diphenylfulvene	0.757	0.938	29.4 ⁵
Tropylium cation	1.692	1.661	36.8 ⁶
Benzotropylium cation	1.028	1.105	23.5 ⁶
Naphthotropylium cation	0.672	0.774	16.5 ⁶

¹ Zimmermann and Joop (1960a, 1960b, 1961)
 ⁴ Pullman and Pullman (1952).

² Doering and Wiley (1960)
 ⁵ Bergmann and Hirschberg (1952)

³ Herrington and Jones (1949)
 ⁶ Götz and Heilbronner (1961)

It follows that for azulene, heptafulvene, acenaphthylene and fulvene a single correlation of calculated and observed $N \rightarrow V_1$ transitions exists which is displaced by about 1 eV to that found for alternant hydrocarbons. In diphenylfulvene a strong steric effect is active and hence it is not wondering that the appropriate results do fit to either of these two correlations. However, some explanation is necessary in the case of dibenzofulvene and 3,4-benzofulvene, which do not satisfy the correlation found for the other nonalternant hydrocarbons; the appropriate points in Fig. 1 lie, however, rather closer to the correlation line typical for alternants.

A possible explanation of this happening may be following one. The benzenoid parts of dibenzofulvene and 3,4-benzofulvene seem to preserve its alternant character to a high degree; the variation of charge densities q_r around the value $q_r = 1$ is in these parts usually distinctly smaller than 0.017. On the other hand in acenaphthylene, which fits to the correlation found for azulene, heptafulvene and fulvene, the variation of charge densities in the benzenoid part of the molecule is rather strong, being even as large as 0.054. This may be the reason why acenaphthylene fits to the correlation found for "pure" nonalternant hydrocarbons and why dibenzofulvene and 3,4-benzofulvene correlate rather with alternants.

We have a feeling that nonalternants which contain benzenoid rings could be divided into two classes, peri- and cata-condensed hydrocarbons, where peri-condensed hydrocarbons like acenaphthylene should fit to the correlation found for "pure" nonalternants and where for cata-condensed hydrocarbons the correlation points should lie closer to the correlation found for alternants,

We are going to consider this point closer in next future.

As regards cations of nonalternant hydrocarbons (tropylium cation and derivatives) they lie on still a different correlation line which is approximately parallel to the precedings ones.

One can see from Fig. 1 that the results obtained by the standard Hückel method allow for no correlation at all, and hence that the allowance for the variation of resonance integrals is of high importance.

The question arises why the correlation line for $N \rightarrow V_1$ transition of nonalternant hydrocarbons (neutral and ions) is displaced relative to that of neutral alternant hydrocarbons.

The main cause of this displacement seems not to be the unequal charge distribution in nonalternant hydrocarbons; the excitation energies calculated by the SC LCAO MO method including the ω -technique differ not much from those in which the last effect is neglected. A detailed comparison of this happening is made in Table II. Excitation energy changes due to variation of the Coulomb integrals are calculated using first order perturbation approximation

$$\Delta(\Delta E) = \sum_r (q_r^* - q_r^0)(1 - q_r^0)\omega\beta_0, \quad (4)$$

where q_r^* and q_r^0 are the π -electron charge densities in position r in excited and ground state respectively and ω is a parameter for which the value 1.0 is taken.

TABLE II

Changes of the energy of the $N \rightarrow V_1$ transition due to ω -technique

Molecule	$\Delta(\Delta E)$ (in β_0 units)
Azulene	-0.15
Heptafulvene	-0.03
Acenaphthylene	-0.05
Fulvene	-0.07
Dibenzofulvene	-0.04

It seems, on the contrary, that the main cause of this displacement is due to a different behaviour of the singlet-triplet splitting in alternant and nonalternant hydrocarbons; it is well-known that the one-electronic Hamiltonian leads to a center of gravity of the singlet and triplet excitation energies, and hence a correlation of calculated and observed excitation energies is expected to happen only if this splitting is roughly proportional to the excitation (Moffitt 1954).

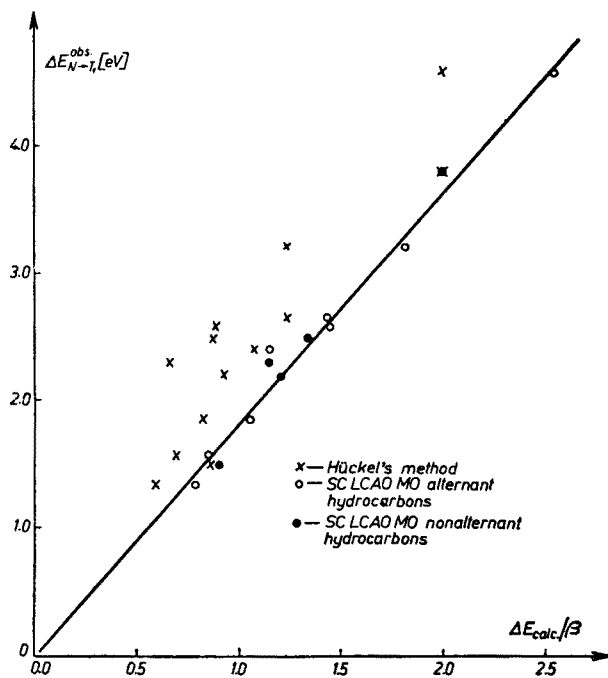


Fig. 2

That this might be the explanation is best seen from Table III and Fig. 2 in which a similar comparison of calculated and observed $N-T_1$ transition energies for alternant and nonalternant hydrocarbons is made.

TABLE III

Comparison of $N \rightarrow T_1$ transitions for all types of conjugated and aromatic hydrocarbons with the calculated values of ΔE

Molecule	observed (in eV)	ΔE calculated (in β_0 units)		
		Hückel method	SC LCAO MO method	
			$x = 4.0/\text{\AA}^1$	$x = 4.2/\text{\AA}$
Ethylene	4.60 ²	2.000	2.542	
t-Butadiene	3.22 ³	1.236	1.814	
t-Hexatriene	2.58 ³	0.890	1.447	
Benzene	3.80	2.000	2.000	
Naphthalene	2.66 ⁴	1.236	1.436	
Coronene	2.400 ⁵	1.078	1.147	
Anthracene	1.85 ⁵	0.828	1.051	
Perylene	1.57 (calc.) ⁵	0.695	0.854	
Tetracene	1.34 ⁵	0.590	0.780	
Fulvene	2.48 ⁶	0.872	1.346	1.389
Acenaphthylene	2.19 ⁷	0.922	1.201	1.235
Azulene	1.48 (calc.) ⁸	0.878	0.898	0.900
Heptafulvene	2.30 (calc.) ⁸	0.661	1.146	1.201

¹ Gołębiewski and Nowakowski (1964) (alternant hydrocarbons)

² Evans (1960)

³ Allinger and Miller (1964)

⁴ Mataga, Nishimoto and Mataga (1959)

⁵ Muel and Hubert-Habart (1962)

⁶ Nakajima and Katagiri (1962)

⁷ Grabowska, private communication

⁸ Pariser (1956)

The correlation is strikingly good, being the same for benzenoid hydrocarbons and polyenes and most probably for nonalternant hydrocarbons also. However, we know only the experimental value of $N \rightarrow T_1$ transition for one nonalternant hydrocarbon (acenaphthylene); the other three values are the calculated ones with more sophisticated methods. Hence the inclusion of nonalternant hydrocarbons in this correlation is likely to be grounded, although not necessarily so.

3. Bond lengths

The bond lengths of neutral nonalternant hydrocarbons which are calculated with the Hückel method and the SC LCAO MO method are listed in columns 6 and 7 of Table IV, respectively. Unfortunately, the experimental data are very scarce in this respect. The only bond lengths known are those for azulene (column 8, Table IV), the agreement with experiment is good for the Hückel method and very good for the SC LCAO MO method in this case. The bond lengths calculated for fulvene are in agreement with those assumed by Julg (1960), Berthier (1953) in more advanced calculated in which the interelectronic interactions are taken into account explicitly.

TABLE IV

Calculated π -electron densities and bond lengths in nonalternant hydrocarbons

Molecule	Position ¹	Charge density		Bond ¹	Bond length (in Å)		
		Hückel	SC LCAO MO $x = 4.2/\text{Å}$		Hückel	SC LCAO MO $x = 4.2/\text{Å}$	Experimental
1	2	3	4	5	6	7	8
Fulvene (I)	1	0.622	0.860	1—2	1.381	1.356	—
	2	1.047	1.023	2—3	1.436	1.461	—
	3	1.092	1.030	3—4	1.377	1.356	—
	4	1.073	1.023	4—5	1.423	1.455	—
4,4'-Benzofulvene(II)	1	0.670	0.806	1—2	1.375	1.361	—
	2	1.030	1.023	2—3	1.441	1.455	—
	3	1.033	1.044	3—4	1.385	1.369	—
	4	1.040	1.023	4—5	1.435	1.451	—
	5	1.039	1.004	5—6	1.372	1.360	—
	7	1.018	1.009	4—4'	1.447	1.455	—
				6—6'	1.430	1.448	—
Dibenzofulvene(III)	1	0.876	0.943	1—2	1.368	1.353	—
	2	1.022	1.009	2—7	1.447	1.465	—
	3	0.997	0.993	3—4	1.395	1.395	—
	4	1.005	1.002	4—5	1.400	1.400	—
	5	1.005	1.002	5—6	1.395	1.395	—
	6	0.997	0.993	6—3	1.415	1.403	—
	7	1.023	1.010	8—8'	1.446	1.461	—
	8	1.022	1.010	7—8	1.415	1.407	—
				3—7	1.402	1.402	—
Heptafulvene (IV)	1	1.311	1.081	1—2		1.356	—
	2	0.976	0.991	2—3		1.462	—
	3	0.942	0.937	3—4		1.356	—
	4	0.952	0.936	4—5		1.454	—
	5	0.953	0.938	5—5'		1.358	—
Acenaphthylene (V)	1	1.066	1.028	1—1'	1.420	1.437	—
	2	1.044	1.027	1—2	1.434	1.456	—
	3	0.939	0.945	2—3	1.403	1.388	—
	4	1.003	1.004	3—4	1.403	1.415	—
	5	0.927	0.957	4—5	1.390	1.380	—
	6	0.993	0.999	5—7	1.418	1.424	—
	7	1.095	1.054	6—7	1.421	1.413	—
				2—7	1.424	1.427	—
Azulene (VI)	1	1.155	1.147	1—2	1.399	1.399	~1.40 ²
	2	1.042	1.041	2—3	1.411	1.408	~1.40
	3	1.027	1.027	3—4	1.412	1.411	~1.40
	4	0.869	0.875	4—5	1.398	1.397	~1.40
	5	0.985	0.939	5—6	1.402	1.402	~1.40
	6	0.879	0.883	3—3'	1.445	1.456	1.458

Table IV (continued)

1	2	3	4	5	6	7	8
3,4-Benzofulvene(VII)	1	0.780	0.914	1—2	1.373	1.354	—
	2	1.032	1.014	2—6	1.439	1.462	—
	3	1.038	1.017	5—6	1.372	1.355	—
	4	1.033	1.016	4—5	1.436	1.458	—
	5	1.050	1.017	4—7	1.408	1.404	—
	6	1.051	1.018	7—8	1.394	1.394	—
	7	0.998	0.997	8—9	1.401	1.401	—
	8	1.010	1.004	9—10	1.398	1.398	—
	9	1.012	1.004	3—10	1.405	1.402	—
	10	0.995	0.997	3—4	1.417	1.408	—
Diphenylfulvene(VIII)	1	1.006	1.004	1—2	1.410	1.405	—
	2	0.945	0.979	2—3	1.394	1.394	—
	3	1.001	1.000	3—4	1.399	1.399	—
	4	0.947	0.979	1—7	1.438	1.455	—
	7	0.761	0.850	7—8	1.413	1.382	—
	8	1.084	1.054	8—9	1.426	1.449	—
	9	1.127	1.053	9—10	1.385	1.362	—
	10	1.108	1.053	10—10'	1.417	1.448	—

¹ Numbering of atoms as in Fig. 3
² Robertson, Sherer, Sim and Watson (1958)

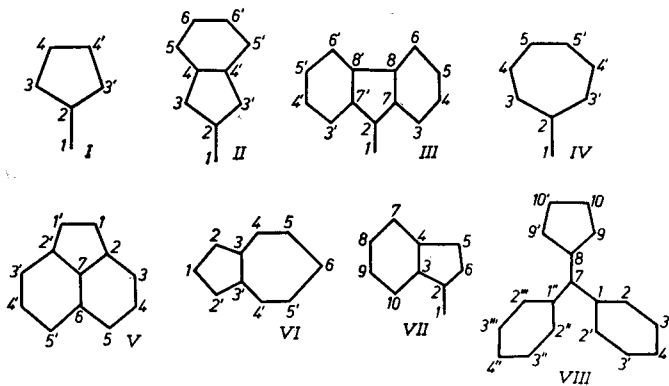


Fig. 3

4. Charge densities and dipole moments

The π -electron charges q_r of some nonalternant hydrocarbons are given in Table IV. One can see by glance that the variation of resonance integrals leads to a more uniform charge distribution, the effect being particularly strong for fulvene and fulvene-type molecules. For azulene there is almost no difference. It is tempting to analyse this effect of smoothing

the charge distribution by a comparison of dipole moments, calculated with the Hückel method and the SC LCO MO method, and the dipole moments found experimentally. This is done in Table V.

One can see that for heptafulvene acenaphthylene and fulvene the SC technique reduces the dipole moment almost to those found in the experiment. In the diphenylfulvene the reduction is very large, but still not sufficient (perhaps the effect of twisting due to the steric effect would still reduce the value (Sadlej 1963)). In azulene the reduction is small and the calculated dipole moment still much too high.

Clearly the dipole moment depends strongly on the charge distribution and then discussing this property the ω -technique (or a technique equivalent to it) plays an important role. This should be particularly true for azulene and azulene-type molecules. But also for fulvenes it is of some importance. It is best seen from Table VI, in which the effect of a combined variation of resonance integrals and Coulomb integrals (for various values of ω) is shown for fulvene.

TABLE V
Comparison of the experimental and calculated dipole moments

Molecule	Dipole moment (in D)		
	calculated		experimental
	Hückel method	SC LCAO MO ($x = 4.2/\text{\AA}$)	
Azulene	6.9	5.05	1.05 ¹
Heptafulvene	4.8	1.24	0.8 ^{2,3}
Acenaphthylene	2.89	1.34	0.9 ²
Fulvene	4.8	1.48	1.2 ¹
Diphenylfulvene	9.4	4.21	1.34 ²
4,4'-Benzofulvene	4.48	2.59	—
Dibenzofulvene	1.46	0.57	—
3,4-Benzofulvene	2.7	1.05	—

¹ Ginsburg (1959)

² Pullman and Pullman (1952)

³ Kurita, Seto, Nozoe and Kubo (1953)

TABLE VI
Calculations of the dipole moment of fulvene by SC LCAO MO method including ω -technique

ω	0.0	0.2	0.5	1.0	1.4
μ (in D)	1.48	1.34	1.26	1.14	no convergency

One finds that for $\omega = 1.0$ the calculated dipole moment agrees practically exactly with that found experimentally.

5. Final remarks

It was shown that the variation of resonance integrals with bond lengths as suggested by Gołębiewski and Nowakowski for alternant hydrocarbons, yields also some useful results in the case of nonalternant hydrocarbons. It was however shown that in some respects (for example for dipole moment calculations) a combination of this approach and ω -technique with $\omega = 1$ would lead to still better results.

Finally we like to point out that similar problems concerned with spectra of alternant and nonalternant hydrocarbons and its ions were discussed also by Götz and Heilbronner (1961). The full discussion of the differences between the SC LCAO MO treatment and that of Götz and Heilbronner was given by Gołębiewski and Nowakowski.

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