

Application of the MIM Method to the Study of Electronic Absorption Bands Involving Triplet States in Hydrocarbons

ALDO GAMBA, GIANFRANCO TANTARDINI, and MASSIMO SIMONETTA
Department of Chemistry, University of Milano, Milano, Italy

Received June 2, 1971

Singlet-triplet and triplet-triplet electronic spectra of numerous hydrocarbons have been interpreted by the MIM method. For flexible molecules the calculations have been carried out considering the minimum conformational energy geometry. Calculated transition energies, oscillator strengths, and polarizations are discussed and compared with experiment.

On a interprété par la méthode MIM les spectres électroniques singulet-triplet et triplet-triplet des différents polyènes et hydrocarbures. On a effectué les calculs pour les molécules flexibles en considérant la géométrie des états à minimum énergie conformationnelle. On a discuté et comparé les énergies de transition, les forces des oscillateurs et les polarisations calculés avec données expérimentales.

Singlet-Triplet und Triplet-Triplet-Elektronenspektren von verschiedenen Polyenen und anderen Kohlenwasserstoffen wurden mit der MIM Methode interpretiert. Die Berechnungen für flexible Moleküle wurden unter Beachtung der Geometrie des Zustandes mit der minimalen Konformationsenergie durchgeführt. Die berechneten Übergangsenergien, Oszillatorstärken und Polarisierungen werden diskutiert und mit dem Experiment verglichen.

1. Introduction

The "Molecules in Molecules" (MIM) method has been previously applied to the study of singlet-singlet transition energies in a large number of hydrocarbons [1] and azines [2]. The method is also qualified to characterize electronic bands of spiroconjugated molecules in terms of locally excited and charge-transfer configurations [3].

In the present work the method is applied to the study of singlet-triplet and triplet-triplet absorption spectra of a variety of polyenes and aromatic hydrocarbons, planar and non-planar, alternant and non-alternant.

Only molecules for which reliable experimental data for comparison were available, have been considered.

2. Calculations

Calculations were carried out for the hydrocarbons shown in Fig. 1, where the reference axes, chosen as suggested by the Joint Commission for Spectroscopy [4] are also reported. The details and the conditions of applicability of MIM computations have been discussed elsewhere [1].

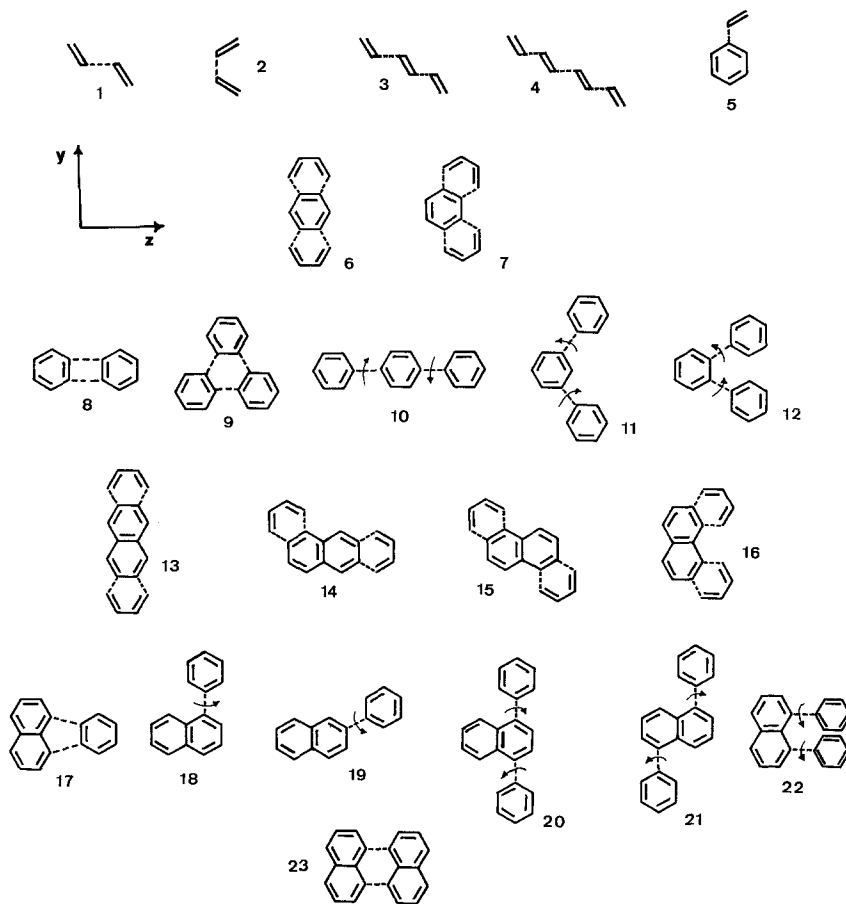


Fig. 1. Numbering of molecules and reference axes

Only single electron excitations have been included and the non-zero Hamiltonian matrix elements between triplet configurations are summarized in Appendix A. Ethylene, *cis*-butadiene, benzene, and naphthalene are the component fragments necessary in the building up process of the molecules shown in Fig. 1.

Molecular orbitals, ionization potentials, electron affinities and geometries for these fragments are the same as used in [1]. The rigid hydrocarbons and linear polyenes have been assumed to be planar; for phenyl-naphthalenes [5] and terphenyls the twist angle has been evaluated by a semiempirical Westheimer calculation [6].

The assumed (or calculated) inter-fragment bond-lengths are collected in Table 1; the corresponding resonance integrals β have been evaluated through the relationship [11]

$$\beta = \beta_0 \cdot \frac{1 + S_0}{S_0} \cdot \frac{S}{1 + S},$$

Table 1. Interfragment bondlengths (in Å) assumed for the different hydrocarbons^a

1.40	1.45	1.48	1.49	1.50	1.52
6-7-13-14 15-16-17 b	5-9 c	2-3-4 ^d 10-11-12 ^e	18-19-20 21-22 f	23 g	8 h



^a The numbering of molecules is that of Fig. 1.

^b Ref. [1]. - ^c Ref. [7]. - ^d Ref. [8].

^e Values evaluated by the conformational procedure described in Ref. [5].

^f Ref. [5]. - ^g Ref. [9]. - ^h Ref. [10].

Table 2. Energies and wavefunctions for triplet locally excited configurations of benzene and naphthalene

Molecule	Energy (eV)	Wavefunction ^a
	3.66	${}^3\lambda_1 = 1/\sqrt{2}(\lambda_1^{-1} + \lambda_2^{-2})$
	4.69	${}^3\lambda_2 = 1/\sqrt{2}(\lambda_1^{-2} + \lambda_2^{-1})$
	4.69	${}^3\lambda_3 = 1/\sqrt{2}(\lambda_1^{-1} - \lambda_2^{-2})$
	5.72	${}^3\lambda_4 = 1/\sqrt{2}(\lambda_1^{-2} - \lambda_2^{-1})$
 ^b	2.64	${}^3\lambda_1 = 0.937 \lambda_3^{-3} + 0.209 \lambda_2^{-2} + 0.279 \lambda_1^{-1}$
	3.71	${}^3\lambda_2 = 1/\sqrt{2}(\lambda_2^{-3} + \lambda_3^{-2})$
	5.65	${}^3\lambda_3 = 1/\sqrt{2}(\lambda_3^{-1} - \lambda_1^{-3})$

^a Only orbitals involved in the transitions have been numbered: bonding orbitals of increasing energy are numbered from 1 to k ; antibonding orbitals from $-k$ to -1 .

^b Naphthalene's wavefunctions, taken from Ref. [15] and purified from less contributing configurations have been renormalized.

where: $\beta_0 = -2.50$ eV (see Ref. [1]); $S_0 = 0.24428$. S and S_0 are overlap integrals evaluated using Slater orbitals.

The dependence of the resonance integral β on the twist angle θ is given by the relation:

$$\beta(\theta) = \beta(0) \cos \theta.$$

Electron repulsion integrals have been evaluated according to formulas given by Hoffmann *et al.* [12].

The highest occupied and the lowest nonoccupied molecular orbitals have been considered for ethylene and butadiene; the corresponding energies of the excited states taken from triplet excitation experimental data [13], are 4.60 eV (ethylene) and 3.20 eV (butadiene).

For benzene and naphthalene the two and three highest occupied and the two and three lowest nonoccupied molecular orbitals, respectively, have been taken into consideration. The "experimental" energies, taken from literature [14a] and the corresponding wavefunctions are collected in Table 2.

3. Results

The theoretical results for $T_1 \leftarrow S_0$ transition energies are collected in Table 3 and compared with the experimental data available in literature. The numbering of molecules is indicated in Fig. 1 and the state symmetry of T_1 is also reported in Table 3. For molecules [18–21], calculations have been performed for two values of the twist angle; the former corresponding to minimum energy values and the latter to a planar conformation.

In Tables 4 and 5 triplet-triplet calculated transition energies are compared with available experimental data. The calculated oscillator strengths and polarization directions are also reported; experimental transition energies with $f < 10^{-3}$ are not presented except for biphenylene for which the results for the detailed study of weak transitions were available.

Table 3. Theoretical and experimental singlet-triplet energy transitions

Molecule	ΔE (eV) theor.	State symmetry	ΔE (eV) exp.	Refs.
1 <i>trans</i> -butadiene	3.084	B_u	3.20	[13]
2 <i>cis</i> -butadiene	2.996	B_2	(2.90) ^a	[13]
3 <i>trans</i> -1,3,5-hexatriene	2.453	B_u	2.60	[13]
4 <i>trans</i> -1,3,5,8-octatetraene	2.202	B_u	2.20	[16]
5 styrene	2.992	—	2.68	[17]
6 anthracene	2.233	B_{1u}	1.82	[18]
7 phenanthrene	2.383	A_1	2.68	[18]
8 biphenylene	2.618	B_{3g}	2.36	[19]
9 triphenylene	2.858	A_2	2.95	[32]
10 <i>para</i> -terphenyl ^b	3.129	B_2	2.56	[20]
11 <i>meta</i> -terphenyl ^b	3.259	B	2.81	[21]
12 <i>ortho</i> -terphenyl ^b	3.411	A	2.67	[22]
13 naphthacene	1.631	B_{1u}	1.27	[18]
14 1,2-benzanthracene	1.927	—	2.05	[18]
15 chrysene	2.404	B_u	2.45	[18]
16 3,4-benzphenanthrene	2.467	B_2	(2.55) ^c	[19]
17 fluoranthene	2.107	B_2	2.29	[14b]
18 1-phenyl-naphthalene	2.626 ^c 2.406 ^d	—	2.49	[23]
19 2-phenyl-naphthalene	2.572 ^c 2.547 ^d	—	2.52	[24]
20 1,4-diphenyl-naphthalene	2.612 ^c 2.196 ^d	B B_2	2.35	[23]
21 1,5-diphenyl-naphthalene	2.612 ^c 2.210 ^d	B B_u	2.43	[23]
22 1,8-diphenyl-naphthalene	2.199 ^c	A	2.38	[23]
23 perylene	1.719	B_{1u}	(1.56) ^e	[25]

^a This value refers to singlet-triplet absorption maximum for cyclohexa-1,3-diene.

^b ΔE evaluated in the minimum energy geometry; the interfragment twist angle θ is 35°, 40° and 53° for 10, 11, and 12 respectively.

^c ΔE evaluated in the minimum energy geometry; 18: $\theta = 75^\circ$; 19: $\theta = 30^\circ$; 20: $\theta = 75^\circ$; 21: $\theta = 75^\circ$; 22: $\theta = 75^\circ$.

^d ΔE evaluated in the planar geometry.

^e This value is calculated (not observed).

Table 4. Energy, oscillator strength, and polarization of triplet-triplet absorption bands

Molecule	Theory			Experiment		
	$\Delta E(\text{eV})$	f	Pol.	$\Delta E(\text{eV})$	f	$\Delta E(\text{eV})$
6 (D_{2h})			[18]		[31]
	2.393	0.000	z	2.65	0.01	2.65
	2.398	0.622	y	2.93(y) ^a	0.40	2.92
	2.977	0.000	z	3.07		3.08
	3.547	0.016	y			3.92
	5.267	0.000	y	4.52		
7 (C_{2v})			[18]		[31]
	1.383	0.024	y			1.495
	1.653	0.016	y			1.710
	2.500	0.001	z			1.910
	2.629	0.272	y	2.58(y) ^a		2.495
	2.784	0.079	y			2.690
	2.800	0.125	z			2.880
	3.039	0.000	z			3.020
	8 (D_{2h})	1.042	—	—	[26]	
1.219		0.000	y	1.41	w^d	
1.460		—	—	1.50	w	
1.798		—	—	1.67	w	
1.925		0.000	y	1.88	w	
2.072		0.000	y	1.92	w	
.....						
3.259		1.210	z	3.06	s	
3.788		0.004	z			
9 (D_{3h})		2.038	0.003	yz	[18]	
	2.973	0.232	yz	2.89	0.025	1.70
	3.508	0.239	yz	3.54	0.060	2.88
10 (D_2)			[29]		
	2.646	0.873	z	2.69	0.88	
11 (C_2)			[30]		
	1.848	0.008	y			
					
	2.745	0.454	y	3.09		
2.846	0.154	z				

Table 4 (continued)

Molecule	Theory			Experiment		
	$\Delta E(\text{eV})$	f	Pol.	$\Delta E(\text{eV})$	f	$\Delta E(\text{eV})$
12 (C_2)			[30]		
	1.833	0.003	y			
	2.474	0.067	y			
	2.691	0.005	y			
	2.694	0.082	z			
	2.708	0.216	z	2.54		
13 (D_{2h})				[18]		
				2.60	0.10	
	2.503	0.960	y	2.69	0.40	
	3.471	0.050	y			
	3.680	0.000	z	3.95	0.05	
	3.704	0.010	y			
	4.324	0.000	z	4.34	0.90	
14 —				[18]		
					
	2.143	0.101	—	2.29	0.02	
	2.492	0.592	—	2.56	0.34	
	3.425	0.094	—	3.93		
15 (C_{2h})				[18]		[31]
					
	1.664	0.143	yz ^b	2.17 ^c	0.15	2.14
	2.283	0.099	yz			2.32
	2.901	0.144	yz	3.09	0.025	3.10
	3.211	0.159	yz	3.28		
16 (C_{2v})				[18]		
					
	2.435	0.020	y	2.40	0.05	
	2.756	0.060	y			
	3.140	0.230	y	3.10	0.03	
23 (D_{2h})				[18]		
	2.468	1.075	z	2.54	s	
	2.876	0.409	y			
					
	3.731	0.003	y	4.43		

^a Ref. [27].^b By inspection of the calculated transition moment components, the first three transitions are polarized along the long axis of the molecule and the fourth along the short axis.^c Polarized parallel to the long axis of the molecule [27].^d w: weak; s: strong.

Table 5. Energy, oscillator strength, and polarization of triplet-triplet absorption bands for phenyl-naphthalenes

Molecule	$\Delta E(\text{eV})^a$	f	pol.	Experiment [29]			
				$\Delta E(\text{eV})^b$	f	pol.	$\Delta E(\text{eV})$ f
18 —			
	2.525	0.049	—	2.599	0.227	—	2.50 0.16
	2.564	0.146		2.711	0.005		(2.69) ^c
	3.331	0.003					
	3.381	0.361		3.033	0.333		(2.81)
19 —			
	2.692	0.001		2.721	0.001		2.61
	2.890	0.503		2.874	0.405		2.86 0.31
	3.151	0.051		3.104	0.092		3.02
20 (C_{2v})			
	2.523	0.204	z	2.586	0.052	z	2.45 0.02
	2.678	0.008	y	2.624	0.040	y	
				2.715	0.005	y	
	2.682	0.003	z	2.719	0.004	z	
	2.826	0.710	y	3.062	0.307	z	2.79 0.52
21 (C_2)			
				2.577	0.088	yz	2.17
	2.387	0.477	yz	2.710	0.005	yz	2.31 0.25
	2.714	0.002	yz	3.062	0.315	yz	(2.43)
	3.539	0.017	yz				

^a ΔE evaluated in the planar geometry.

^b ΔE evaluated in the minimum energy geometry.

^c The values in brackets correspond to maxima interpreted as due to vibrational progression [29].

Discussion

The molecules were classified according to the fragments in which they have been split to perform the calculations. In the first group we consider molecules in which the ethylene fragment is present. This group consists of *cis* and *trans* butadiene, 1,3,5-hexatriene and 1,3,5,8-octatetraene, which are built from two or from three ethylene fragments and styrene which is made of one ethylene and one benzene fragment.

As can be seen from Table 3 the calculated and observed positions of the first singlet-triplet absorption band are in good agreement for all these molecules.

The experimental transition energies for the second band, where available, compare with our results as follows

trans butadiene 4.60 eV (calc.) – 3.90 eV (obs.) [13]

trans 1,3,5-hexatriene 3.66 eV (calc.) – 3.20 eV (obs.) [13]

trans 1,3,5,8-octatetraene 3.00 eV (calc.) – 2.85 eV (obs.) [16].

Anthracene and phenanthrene belong to the second group of our classification, where one benzene and two butadiene fragments are present. The $T_1 \leftarrow S_0$ transition energies for anthracene and phenanthrene are predicted too high and too low, respectively, by about 0.3 eV. The singlet-triplet intervals ($S_1 - T_1$) as obtained

from these and previous calculations [1] are 1.08 eV for anthracene and 1.09 eV for phenanthrene, to be compared with the experimental values [14c] 1.42 and 1.40 eV, respectively.

We find five triplet-triplet absorption bands for anthracene, and the first three correspond reasonably well for energy, intensity, and polarization with experiment. For phenanthrene we find a series of triplet-triplet transitions, consisting of three lower-energy low intensity transitions, followed by four higher intensity transitions. The general features of the experimental results are well reproduced by our calculation and the polarization of the most intense band agrees with experiment [27].

The third group, where only the benzene fragment is present, can be split in two subgroups: the rigid biphenylene and triphenylene and the flexible *o*-, *m*-, and *p*-terphenyls. For biphenylene our calculations predict very satisfactorily both the energy for the first singlet-triplet band [19] and the structure for the triplet-triplet absorption spectrum [26]¹. For triphenylene our singlet-triplet separation compares favourably with an experimental value for the 0–0 band in a phosphorescence spectrum in rigid glass hydrocarbon solvent [32]. It can be seen from the spectrum, however, that the triplet and the ground state have significantly different geometry, since the maximum energy band shows the minimum intensity. The two strong, triplet-triplet transitions found experimentally are reproduced by the MIM calculations within 0.1 eV.

The observed singlet-triplet transition energies for polyphenyls, reported in Table 3 are taken from phosphorescence data [20–22], consequently a comparison with theoretical calculations performed assuming the same geometry for the singlet ground and triplet excited states must be viewed as purely indicative.

The most intense triplet-triplet transitions for *o*-, *m*-, and *p*-terphenyls are reported in Table 4. The agreement with experiment is very satisfactory for *p*-terphenyl, both for the energy and the intensity; the polarization for this band is calculated to be along the long-axis of the molecule in agreement with the prediction of PPP calculations [29].

The fourth group is characterized by the presence of one naphthalene and two butadiene fragments. A considerable amount of experimental data is available for the four molecules that have been considered in this group. As a whole the agreement between calculated and observed spectra is satisfactory.

By using a naphthalene and one or two benzene fragments we built the molecules included in the fifth group. Fluoranthene is rigid while mono and diphenyl-naphthalenes are flexible.

For these last molecules the calculations were performed for the geometry predicted as the most stable for the ground-state since from previous calculations on biphenyl by the MIM method [33] it turns out that the twist angle changes little from the ground to the first excited triplet-state. Except for 1,8-diphenyl-naphthalene, the calculations were performed also for an assumed planar geometry in order to compare with calculations found in the literature [24] carried out under the same assumption. For the $T_1 \leftarrow S_0$ transitions the agreement between calculated and experimental transition energy is always very good and significantly

¹ The purity of the sample of biphenylene from which this spectrum has been taken, has been questioned [19].

better than when the PPP technique is used, both for the minimum energy and the planar geometry. The experimental value lies between our two theoretical results, except for 2-phenyl-naphthalene where the equilibrium twist angle value is rather low. The comparison between calculated and experimental values does not allow a choice for the geometry of triplet state, but the general pattern of the transition energy calculations seems to indicate that the equilibrium twist angle is overestimated. When the results for the $T_j \leftarrow T_1$ absorption spectra are considered the agreement between experiment and theory is satisfactory; in the case of 1,5-diphenyl-naphthalene the results for planar geometry are significantly better.

For the last molecule, perylene, which is built from two naphthalene fragments, no experimental results are available for $T_1 \leftarrow S_0$ transition; we can only compare with a previous theoretical calculation given by Hall [25]; the first triplet-triplet absorption band found experimentally is well predicted.

From the body of the MIM results for twenty-three hydrocarbons it can be concluded that the MIM method can be confidently applied to the interpretation of emission and absorption spectra involving triplet-states. The agreement with experiment is at least as good as when the PPP method is used (see for example Refs. [24, 29, 31, 34–36]) and the necessary computational time is one order of magnitude less.

Appendix A

Non-zero Hamiltonian matrix elements between triplet singly-excited configurations

*Locally excited – charge transfer interactions*²

$$(k m | H | k m') = F_{m m'}$$

$$(k m | H | k' m) = -F_{k k'}$$

Charge transfer – charge transfer interactions

$$(k m' | H | k n') = -(k k | m' n')$$

$$(k m' | H | l m') = -(m' m' | k l)$$

$$(k m' | H | l n') = -(k l | m' n')$$

$$(k m' | H | k m'') = F_{m' m''}$$

$$(k m' | H | k'' m') = -F_{k k''},$$

where

$$F_{m m'} = (m | F | m') = \sum_{b=1}^L c_{b m} c_{b m'} \beta_b \quad (L = \text{interfragment bonds number})$$

$$(k m | l n) = \iint \phi_k(1) \phi_l(2) \frac{1}{r_{12}} \phi_m(1) \phi_n(2) d\tau_1 d\tau_2.$$

Acknowledgement. We thank the Italian Consiglio Nazionale delle Ricerche for financial support.

² Different apices indicate different fragments.

References

1. Favini, G., Gamba, A., Simonetta, M.: *Theoret. chim. Acta (Berl.)* **13**, 175 (1969).
2. Simonetta, M., Gamba, A., Rusconi, E.: *The Israel Acad. Sciences and Humanities (Jerusalem)* **1970**, 213.
3. Gamba, A., Tantardini, G. F., Simonetta, M.: *Theoret. chim. Acta (Berl.)* **20**, 12 (1971).
4. Joint Commission for Spectroscopy: *J. chem. Physics* **23**, 1997 (1955).
5. Gamba, A., Rusconi, E., Simonetta, M.: *Tetrahedron* **26**, 871 (1970).
6. Westheimer, F. H.: *Steric effects in organic chemistry*. Ed. by M. S. Newman, Chap. 12. New York: Wiley and Sons 1966.
7. Ahmed, F. R., Trotter, J.: *Acta crystallogr.* **16**, 503 (1963).
8. Marais, B. D., Sheppard, N., Stoicheff, B. P.: *Tetrahedron* **17**, 163 (1962).
9. Tables of interatomic distances and configurations in molecules and ions Special publ. N° 11, Scient, ed. by Sutton, London: The Chemical Society 1958.
10. Donaldson, D. M., Robertson, J. M., White, J. G.: *Proc. Roy. Soc. (London) A* **220**, 311 (1953).
11. Allinger, N. L., Chow Tai, J.: *J. Amer. chem. Soc.* **87**, 2081 (1965).
12. Hoffmann, R., Imamura, A., Zeiss, G. D.: *J. Amer. chem. Soc.* **89**, 5215 (1967).
13. Evans, D. F.: *J. chem. Soc. (London)* **1960**, 1735.
14. McGlynn, S. P., Azumi, T., Kinoshita, M.: *Molecular spectroscopy of the triplet state*, a) Chap. 4, b) p. 316, c) p. 78–79, New Jersey: Prantice-Hall Inc. 1969.
15. Pariser, R.: *J. chem. Physics* **24**, 250 (1956).
16. Evans, D. F.: *J. chem. Soc. (London)* **1961**, 2566.
17. — *J. chem. Soc. (London)* **1959**, 2753.
18. Porter, G., Windsor, M. W.: *Proc. Roy. Soc. (London) A* **245**, 238 (1958).
19. Hamilton, T. D. S., Ray, J. P., Moore, G. F.: *Phys. Lett.* **20**, 368 (1966).
20. Clar, E., Zander, M.: *Chem. Ber.* **89**, 749 (1956).
21. Brinen, J. S., Koren, J. G., Hodgson, W. G.: *J. chem. Physics* **44**, 3095 (1966).
22. Layton, E. M.: *J. molecular Spectroscopy* **5**, 181 (1960).
23. Zweig, A., Gallivan, J. B.: *J. Amer. chem. Soc.* **91**, 260 (1969).
24. Orloff, M. K., Brinen, J. S.: *Int. J. quant. Chemistry* **3**, 225 (1969).
25. Hall, G. G.: *Proc. Roy. Soc. (London) A* **213**, 113 (1952).
26. Hilpern, J. W.: *Trans. Faraday Soc.* **61**, 605 (1965).
27. El-Sayed, Pavlopoulos, T.: *J. chem. Physics* **39**, 834 (1963).
28. Astier, R., Meyer, Y.: *J. Chim. physique* **64**, 919 (1967).
29. Brinen, J. S., Orloff, M. K.: *J. chem. Physics* **51**, 527 (1969).
30. Ramsay, I. A., Munro, I. H.: *The triplet state*, Proceedings of an int. symposium held at the department of physics, p. 415, American University of Beirut 1967.
31. Nouchi, G.: *J. Chim. physique* **66**, 554 (1969).
32. Herkstroeter, W. G., Lamola, A. A., Hammond, G. S.: *J. Amer. chem. Soc.* **86**, 4537 (1964).
33. Unpublished work.
34. Allinger, N. L., Tai, J. C., Stuart, T. W.: *Theoret. chim. Acta (Berl.)* **8**, 101 (1967).
35. Orloff, M. K.: *J. chem. Physics* **47**, 235 (1967).
36. Benard, M.: *Thèse-Faculté des Sciences de l'Université d'Aix-Marseille* (1969).

Prof. Massimo Simonetta
Istituto di Chimica Fisica
dell'Università di Milano
V. Saldini 50
Milano, Italia