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Ultraviolet Spectra of benzene and pyridine derivatives interpreted by generalized Molecules in Molecules method

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<http://www.bdim.eu/item?id=RLINA_1974_8_56_6_957_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1974.

Chimica fisica. — *Ultraviolet Spectra of benzene and pyridine derivatives interpreted by generalized Molecules in Molecules method* (*). Nota di ALDO GAMBA e GIAN FRANCO TANTARDINI, presentate (**) dal Corrisp. L. MALATESTA.

RIASSUNTO. — Il metodo «Molecole nelle Molecole» generalizzato è stato applicato allo studio degli spettri ultravioletti dei nitrobenzeni, aniline, nitroaniline, nitropiridine, amminopiridine, fenilpiridine e dipiridili. I risultati sono discussi e confrontati con quelli ottenuti con formulazioni diverse del metodo stesso, impiegando la medesima parametrizzazione.

Viene anche discusso l'impiego degli operatori dipolo e gradiente nel calcolo della forza dell'oscillatore associata alle transizioni.

1. INTRODUCTION

In the field of quantum mechanical methods proposed to interpret the electronic spectra of organic molecules, two semiempirical approaches turned out to be the most useful and versatile, that is the LCAO–SCF method developed by Pariser and Parr [1] and the "Molecules in Molecules" (MIM) method proposed by Longuet-Higgins and Murrell [2].

Both methods, widely used to interpret the electronic spectra of large molecules, are based on σ/π approximation and, when heteroatoms are present in the molecules, their success is strongly dependent on a fortunate choice of energy and geometry parameters.

MIM method is particularly qualified for molecules which can be formally built up by chromophoric fragments, UV spectra of which are known in details. Starting from the original proposal of Longuet-Higgins and Murrell [2], strictly valid only for alternate hydrocarbons, other formulations were given to interpret the electronic spectra of molecules which exhibit inhomogeneous charge distributions. In particular, Godfrey and Murrell [3] suggested to introduce into the expressions of locally-excited and charge transfer configurations energies (diagonal elements of CI matrix) a perturbation parameter which describes the inductive effect of each fragment. However, the inductive effect in the off-diagonal matrix elements was considered negligible.

Recently, Giovanelli *et al.* [4] derived diagonal and off-diagonal matrix elements which take into account the mutual influence of the charge distributions of the fragments. These supplementary terms make the treatment invariant with respect to local symmetry transformations of MO's of each fragment. However, these Authors found it necessary to introduce a further

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(**) Nella seduta del 29 giugno 1974.

parametrization, substantially different from those generally accepted in the literature.

Purpose of this work is the revision of the possibilities and the limits of the different versions of MIM method [2–4], examined on the basis of an unique set of parameters. Several organic molecules were studied, such as nitro- and amino-derivatives of benzene and pyridine, phenyl-pyridines, and bipyridines. The figures of molecules with the corresponding symmetry axes are shown in the first column of Table III–VII, collecting MIM results and experimental data.

2. CALCULATIONS

Transition Energies.

Transition energies were calculated according to MIM method, in the version of Giovanelli *et al.* [4]. Owing to some misprints found in the paper [4], a general revision of reported formulas seemed necessary. Revised formulas for non-zero diagonal and off-diagonal matrix elements of the inductive perturbation hamiltonian are reported in Table I. To check the correctness of these formulas, specific tests of energy invariance with respect to local symmetry transformations of MO's were performed for molecules such as nitrobenzene and nitrosobenzene.

TABLE I

Non-zero inductive contributions to CI *matrix elements in* MIM *method*(*).

$$\langle I_R^{-1} J_R \,|\, H' \,|\, I_R^{-1} J_R \rangle = -\sum_{\substack{\mu,\rho \\ \mu \in R \\ \rho \notin R}} Q_\rho \left(c_{J\mu}^2 - c_{I\mu}^2 \right) \gamma_{\mu\rho}$$

$$\langle I_R^{-1} J_R \,|\, H' \,|\, K_R^{-1} L_R \rangle = -\sum_{\substack{\mu,\rho \\ \mu \in R \\ \rho \notin R}} Q_\rho \left(\delta_{IK}\, c_{J\mu}\, c_{L\mu} - \delta_{JL}\, c_{I\mu}\, c_{K\mu} \right) \gamma_{\mu\rho}$$

$$\langle I_R^{-1} J_R \,|\, H' \,|\, \Gamma_0 \rangle = -\sqrt{2} \sum_{\substack{\mu,\rho \\ \mu \in R \\ \rho \notin R}} Q_\rho\, c_{I\mu}\, c_{J\mu}\, \gamma_{\mu\rho}$$

$$\langle I_R^{-1} J_S \,|\, H' \,|\, I_R^{-1} J_S \rangle = \sum_{\substack{\mu,\rho \\ \mu \in R \\ \rho \notin R}} Q_\rho\, c_{I\mu}^2\, \gamma_{\mu\rho} - \sum_{\substack{\mu,\rho \\ \mu \in S \\ \rho \notin S}} Q_\rho\, c_{J\mu}^2\, \gamma_{\mu\rho}$$

$$\langle I_R^{-1} J_S \,|\, H' \,|\, K_T^{-1} L_V \rangle = \delta_{RT}\, \delta_{SV} \left\{ \delta_{JL} \sum_{\substack{\mu,\rho \\ \mu \in R \\ \rho \notin R}} c_{I\mu}\, c_{K\mu}\, Q_\rho\, \gamma_{\mu\rho} - \delta_{IK} \sum_{\substack{\mu,\rho \\ \mu \in S \\ \rho \notin S}} c_{J\mu}\, c_{L\mu}\, Q_\rho\, \gamma_{\mu\rho} \right\}$$

(*) H' = perturbation hamiltonian; $Q_\rho = Z_\rho^{core} - q_\rho^\pi$, where Z_ρ^{core} is the " core " charge of ρ atom and q_ρ^π is the π–electron charge; I, J, K, L = M.O.'s indices; R, S, T, V = fragments indices; $c_{I\mu}$ = L.C.A.O. coefficients; $\gamma_{\mu\rho}$ = coulombic integrals. Γ_0 = ground configuration; δ = Kronecker's delta.

Oscillator Strengths.

Oscillator strengths (f) were evaluated both through the dipole-length operator (f_1) and the dipole-gradient operator (f_2). Primitive integrals necessary in the calculation of transition gradients are available in Refs. [5] and [6]. The following exponents were used for the different $2p_\pi$ Slater orbitals:

$$\delta_C = 1.625; \quad \delta_{N(NO_2)} = 2.125; \quad \delta_{N(-N<)} = 1.95; \quad \delta_O = 2.275.$$

As an empirical test, it seemed interesting to verify the results obtained by using a " mixed " expression of the oscillator strength, so that the calculated value is independent from the excitation energy [7]. In this case, the f value is the geometric mean of the values calculated through dipole-length and dipole-gradient operators ($\sqrt{f_1 \cdot f_2}$).

TABLE II

Ionization Potentials (I) and Electron Affinities (A) for the considered molecular fragments.

	I (eV)	A (eV)
Benzene	9.25 (*a*)	—0.54 (*a*)
Pyridine	10.086 (*b*) 10.942	—1.06 (*b*) —1.347
NO_2	—	—0.56 (*c*)
NH_2	10.15 (*d*)	—

(*a*) Ref. [11]; (*b*) Ref. [8]; (*c*) Ref. [12]; (*d*) Ref. [13].

Energy and Geometry Parameters.

Geometries and MO's of the molecular fragments (benzene, pyridine, nitrogroup (NO_2), and aminogroup (NH_2)), were the same used in preceding papers [8–10], where energies and wavefunctions of locally-excited states of benzene and pyridine are also reported. Following previous works [3, 8], only the lowest unoccuppied MO of NO_2 and the highest occupied MO of NH_2 were considered, owing to the specific character of acceptor (NO_2) and donor (NH_2).

Ionization Potentials (I), and Electron Affinities (A) of the fragments are collected in Table II.

Resonance integrals (β) relative to the interfragment bond between pyridine and benzene (or pyridine) were assumed to be: $\beta = -2.00$ eV (R = 1.49 Å). For the bond between NO_2 and pyridine or benzene, a value of $\beta = -2.40$ eV (R = 1.46 Å) was assumed, while for NH_2 the value $\beta = -1.80$ eV was preferred, as suggested by previous MIM calculations [3, 8].

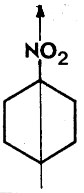
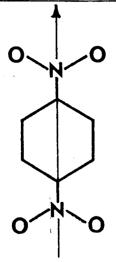
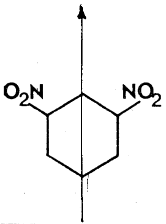
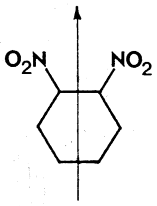
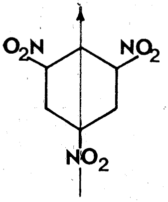
All molecules were considered planar.

3. RESULTS AND DISCUSSION

In the formulation of MIM method which includes the mutual inductive effect of the fragments, supplementary matrix elements are present, which depend on the term $Q_\rho = Z_\rho^{\text{core}} - q_\rho^\pi$. This term represents, in the frame-

TABLE III

Electronic Transitions, oscillator strengths, and polarizations for nitrobenzenes.

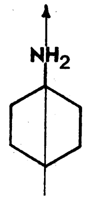
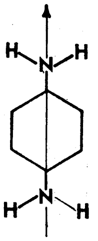
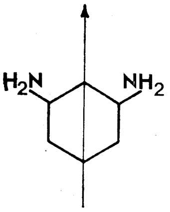
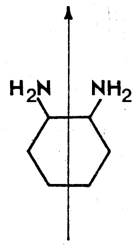
	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.335	⊥	0.032	0.034	0.033	4.42	0.03
	5.398	∥	0.247	0.051	0.113	5.18	0.25
	6.098	⊥	0.271	0.148	0.200		
	6.383	∥	0.689	0.214	0.384	6.43	
	7.204	⊥	0.769	0.277	0.461		
	7.240	⊥	0.246	0.168	0.203	7.56	
	4.012	⊥	0.066	0.084	0.074	(4.00)	(*b*)
	5.083	∥	0.437	0.143	0.250	4.85	0.40
	6.380	∥	0.801	0.296	0.487		
	6.409	⊥	0.418	0.207	0.294		
	6.605		0.000	0.000	0.000		
	7.156		0.000	0.000	0.000		
	7.654	∥	0.584	0.180	0.325		
	4.248	⊥	0.043	0.035	0.039	4.38	0.02
	5.339	∥	0.034	0.004	0.012	5.43	0.40
	5.759	⊥	0.918	0.296	0.521		
	5.986	∥	0.467	0.252	0.343		
	7.127	⊥	0.000	0.010	0.000		
	7.235	∥	0.321	0.064	0.143		
	7.571	⊥	0.254	0.138	0.187		
	4.280	⊥	0.023	0.018	0.020	(4.40)	
	5.178	∥	0.134	0.048	0.081	(5.30)	
	5.992	∥	0.446	0.260	0.340	5.80	0.40
	6.400	⊥	0.879	0.243	0.462		
	7.066	∥	0.197	0.036	0.084		
	7.265	⊥	0.027	0.000	0.003		
	7.608	⊥	0.183	0.118	0.147		
	7.845	∥	0.315	0.114	0.190		
	4.284		0.000	0.000	0.000	(4.40)	
	5.638		0.000	0.000	0.000		
	5.773	⊥,∥	0.932	0.386	0.600	5.58	
	7.166	⊥,∥	0.029	0.001	0.006		
	8.194	⊥,∥	0.208	0.086	0.133		

(*a*) Ref. [3]; (*b*) Numbers in brackets refer to shoulders.

work of MIM approximations, the net charge on the ρ atom, and describes the contribution of ρ centre to the electrostatic field which acts on the other fragments of the molecule. However, Q_ρ takes into account only the effect of π electrons and even if in many cases such contribute is essential, examples are known for which the π electron charge distribution fails to predict the correct sign of the dipole moment (pyrrole is an example).

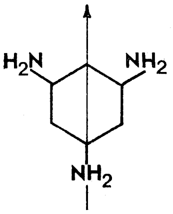
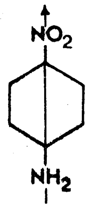
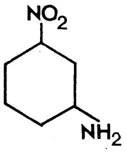
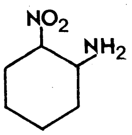
TABLE IV

Electronic Transitions, Oscillator Strengths, and Polarizations for Anilines and Nitro-anilines.

	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.396 5.217 6.109 6.348 7.330 7.429	⊥ ∥ ⊥ ∥ ∥ ⊥	0.015 0.313 0.444 0.650 0.218 0.614	0.012 0.132 0.218 0.233 0.165 0.226	0.013 0.204 0.311 0.388 0.190 0.372	4.35 5.27 6.28	0.03 0.17
	4.137 4.705 6.121 6.337 7.766 7.893	⊥ ∥ ⊥ ∥ ∥ ⊥	0.032 0.482 0.503 0.655 0.080 0.509	0.029 0.321 0.247 0.263 0.091 0.173	0.031 0.394 0.353 0.415 0.086 0.297	4.05 5.08 6.14	0.038 0.17
	4.227 5.238 5.387 5.841 6.912 7.204	⊥ ∥ ⊥ ∥ ⊥ ∥	0.020 0.123 0.845 0.378 0.028 0.253	0.018 0.060 0.386 0.196 0.039 0.060	0.019 0.086 0.571 0.272 0.033 0.123	4.21 5.20 5.63	0.024 0.19
	4.197 4.742 5.736 5.830 6.846 6.862 7.599 7.679	⊥ ∥ ∥ ⊥ ∥ ⊥ ⊥ ∥	0.014 0.168 0.299 0.873 0.141 0.001 0.245 0.464	0.010 0.098 0.172 0.330 0.029 0.004 0.166 0.195	0.012 0.129 0.227 0.537 0.064 0.002 0.202 0.301	4.21 5.19 5.69	0.039 0.11

(*a*) Ref. [3].

Segue: TABLE IV.

	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.132		0.000	0.000	0.000	(4.40)	
	5.271		0.000	0.000	0.000	(5.30)	
	5.329	⊥,∥	0.800	0.420	0.580	5.61	
	6.583	⊥,∥	0.006	0.001	0.003		
	7.985	⊥,∥	0.315	0.154	0.220		
	4.156	⊥	0.004	0.006	0.005		
	4.761	∥	0.383	0.065	0.158	4.31	0.38
	5.316	⊥	0.241	0.162	0.198	5.44	
	5.409	∥	0.022	0.003	0.009		
	6.332	∥	0.531	0.124	0.256		
	3.865		0.069	0.071	0.070	3.81	
	4.553		0.104	0.048	0.071	4.86	
	5.578		0.486	0.167	0.285	5.44	0.60
	5.824		0.161	0.084	0.116		
	6.006		0.209	0.027	0.076		
	6.713		0.106	0.018	0.044		
	3.864		0.054	0.040	0.047	3.44	
	4.876		0.386	0.183	0.265	4.59	
	5.203		0.455	0.153	0.264	5.00	0.60
	5.662		0.053	0.017	0.030	5.41	
	5.954		0.003	0.005	0.004		
	6.759		0.531	0.277	0.384		

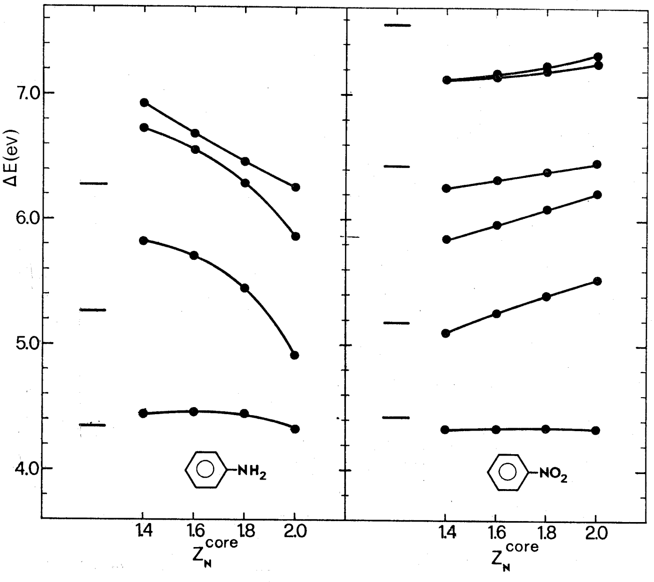


Fig. 1. – Calculated transition energies for aniline and nitrobenzene on σ core charge of nitrogen atom. Solid lines on the left represent experimental transition energies.

To verify the importance of the σ core charge of heteroatoms present in the molecule, we studied the effect on electronic transition energies and oscillator strengths of different Z_p^{core} values for heteroatoms in the case of nitrobenzene and aniline. The trends are shown in fig. 1.

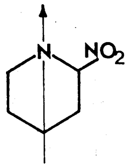
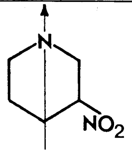
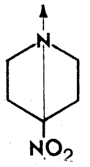
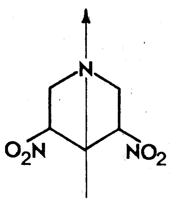
In general, it can be observed that the assignment of a calculated transition to an observed absorption band does not depend on Z_p^{core}, and the best agreement with experimental data is obtained for the following values of Z_p^{core}:

$$\text{nitrobenzene: } \begin{cases} Z_N^{core} = 1.8 \\ Z_O^{core} = 1.1 \end{cases} \qquad \text{aniline: } Z_N^{core} = 1.9 .$$

These Z_p^{core} values were used in the calculations of transition energies for all benzene and pyridine derivatives, while for the N atom of pyridine a value $Z_N^{core} = 1.0$ was assumed.

TABLE V

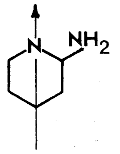
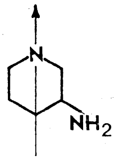
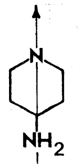
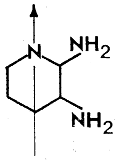
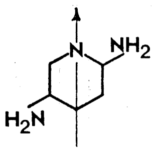
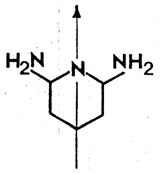
Electronic Transitions, Oscillator Strengths, and Polarizations for Nitropyridines.

	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.666 5.913 6.474 6.840		0.040 0.200 0.730 0.800	0.010 0.040 0.320 0.270	0.020 0.090 0.480 0.460	4.70 5.43 6.53	0.08 0.24 0.56
	4.768 5.896 6.525		0.040 0.210 0.800	0.020 0.050 0.280	0.030 0.100 0.480	4.66 5.25 6.05 (*b*)	0.11 0.34
	4.460 6.075 6.686 6.775	⊥ ∥ ∥ ⊥	0.110 0.110 0.980 0.280	0.050 0.020 0.330 0.130	0.080 0.050 0.570 0.190	4.44 5.509 6.480	0.03 0.22 0.24
	4.763 6.012 6.172 6.752 7.714 7.978	⊥ ∥ ⊥ ∥ ⊥ ∥	0.002 0.196 1.008 0.577 0.040 0.094	0.004 0.061 0.328 0.284 0.047 0.010	0.002 0.109 0.575 0.405 0.043 0.031	4.58 5.45	0.05 (*b*) 0.67

(*a*) Ref. [8]; (*b*) In acetonitrile.

TABLE VI

Electronic Transitions, Oscillator Strengths, and Polarizations for Amino Pyridines.

	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.593 5.665 6.399 6.897		0.081 0.344 0.286 0.620	0.020 0.140 0.130 0.230	0.040 0.220 0.200 0.380	4.32 5.37 6.59	0.06 0.23 0.53
	4.565 5.695 6.528 6.871		0.060 0.360 0.560 0.720	0.020 0.150 0.270 0.250	0.030 0.230 0.390 0.430	4.25 5.34 (6.39) 6.61	0.06 0.22 0.67
	4.731 5.765 6.457 6.590	⊥ ∥ ⊥ ∥	0.000 0.300 0.680 0.800	0.000 0.140 0.270 0.310	0.000 0.200 0.430 0.500	(4.77) 5.33 6.22	0.20 0.66
	4.376 5.280 6.175 6.373		0.080 0.270 0.280 0.720	0.020 0.160 0.140 0.270	0.040 0.210 0.200 0.440	4.16 5.27 6.26	0.11 0.17 0.52
	4.331 5.190 6.482 6.720		0.100 0.490 0.460 0.380	0.030 0.290 0.220 0.140	0.060 0.380 0.320 0.230	3.80 5.09 6.57	0.05 0.26 0.48
	4.342 5.623 5.899 6.330	⊥ ∥ ⊥ ∥	0.130 0.290 0.450 0.120	0.040 0.150 0.150 0.090	0.070 0.210 0.260 0.100	4.13 5.10 6.24	0.11 0.21 0.66

(*a*) Ref. [6].

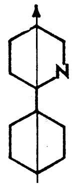
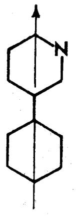
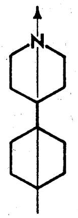
The theoretical transition energies, oscillator strengths and polarizations are collected in Tables III–VII, where experimental data are also reported.

From the data reported in Tables III–VII, it appears that, for all molcules, each theoretical transition can be assigned unequivocally to the corresponding experimental absorption band on the basis of the energy and oscillator strength values. It is noteworthy that MIM method succeeds to predict the correct order of electronic transitions in UV spectra of so a large number of molecules.

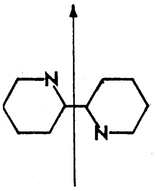
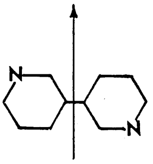
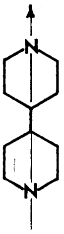
The overall agreement between calculated and experimental values of transition energies is satisfactory for the first absorption bands of each molecule. Nitropyridines are an exception: the energy of the second transition is overestimated, in present calculations, by at least 0.5 eV. A measure of the agreement between calculated and experimental energy values is given by the regression lines reported in figs. 2–4, with the corresponding correlation coefficients *r*. In each figure, the dashed line represents the perfect agreement.

TABLE VII

Electronic Transitions, Oscillator Strengths, and Polarizations for Phenylpyridines and Bipyridines.

	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.541		0.003	0.002	0.003		
	4.633		0.284	0.134	0.195	4.52	0.27
	5.224		0.634	0.329	0.457	5.00	0.37
	6.047		0.193	0.092	0.133		
	6.121		0.438	0.198	0.295		
	4.531		0.000	0.000	0.000		
	4.693		0.128	0.045	0.076	(4.66)	
	5.069		0.840	0.456	0.619	5.08	0.38
	6.050		0.278	0.131	0.191		
	6.104		0.277	0.123	0.184		
	6.451		0.786	0.352	0.526		
	6.556		0.724	0.338	0.496		
	4.526	⊥	0.000	0.000	0.000		
	4.705	⊥	0.030	0.005	0.013		
	5.081	∥	0.949	0.535	0.713	4.98	0.47
	6.081	⊥	0.084	0.044	0.061		
	6.106	∥	0.738	0.355	0.512		
	6.322	∥	0.423	0.199	0.290		
	6.544	⊥	0.876	0.374	0.570		

Segue: TABLE: VII.

	CALCULATED					EXP. (*a*)	
	ΔE (eV)	Pol.	f_1	f_2	$\sqrt{f_1 \cdot f_2}$	ΔE (eV)	f
	4.627		0.280	0.111	0.176	4.43	0.22
	(4.664) (*b*)		(0.248)	(0.094)	(0.153)		
	4.799		0.000	0.000	0.000		
	(4.817)		(0.014)	(0.001)	(0.003)		
	5.651		0.749	0.349	0.511	5.32	0.24
	(5.605)		(0.707)	(0.328)	(0.482)		
	6.263		0.000	0.000	0.000		
	(6.411)		(0.356)	(0.113)	(0.200)		
	6.578		1.137	0.492	0.748		
	(6.641)		(0.802)	(0.403)	(0.568)		
	7.000		1.571	0.513	0.898		
	(6.974)		(1.448)	(0.461)	(0.817)		
	4.724		0.157	0.034	0.073	4.61	0.26
	(4.705)		(0.130)	(0.030)	(0.060)		
	4.744		0.000	0.000	0.000		
	(4.709)		(0.000)	(0.000)	(0.000)		
	5.398		0.915	0.430	0.627	5.19	0.38
	(5.388)		(0.910)	(0.430)	(0.620)		
	6.284		0.000	0.002	0.000		
	(6.378)		(0.050)	(0.010)	(0.020)		
	6.537		0.000	0.003	0.000		
	(6.378)		(0.110)	(0.040)	(0.070)		
	6.566		1.080	0.293	0.563		
	(6.532)		(1.000)	(0.270)	(0.520)		
	6.917		1.430	0.595	0.923		
	(6.924)		(1.300)	(0.540)	(0.840)		
	4.725	⊥	0.000	0.000	0.000		
	4.742	⊥	0.069	0.014	0.031	(4.59)	
	5.513	∥	1.117	0.650	0.852	5.19	0.50
	6.313	∥	1.050	0.494	0.720		
	6.949	∥	1.400	0.533	0.864		

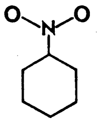
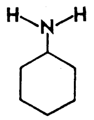
(*a*) Ref. [9].
(*b*) Numbers in brackets refer to *cis* isomer.

To compare the results obtained by MIM method, applied in different versions, two molecules, the UV spectra of which are well known, have been examined: nitrobenzene and aniline. The different columns of Table VIII give the results obtained by: (*a*) MIM method in the original formulation [2]; (*b*) MIM method with the inclusion of inductive parameters [3]; (*c*) generalized MIM method (present work). Experimental data are collected in column (*d*).

It is evident that the original version of MIM method does not lead to adequate quantitative descriptions of UV spectra of molecules of this type. The inclusion of inductive perturbation proposed by Godfrey and

TABLE VIII

A comparison among MIM *results for nitrobenzene and aniline obtained by the different versions of the method.*

	(*a*)		(*b*)		(*c*)		(*d*)	
	ΔE	f_1	ΔE	f_1	ΔE	f_1	ΔE	f
	4.28 4.77 5.62 6.10 7.07 7.08	0.14 0.42 0.16 0.34 0.45 0.89	4.46 4.92 5.62	0.002 0.22 0.04	4.34 5.40 6.10 6.38 7.20 7.24	0.03 0.25 0.27 0.70 0.77 0.25	4.42 5.18 6.43 7.56	0.03 0.25 strong
	4.33 4.89 5.86 6.26 7.20 7.26	0.01 0.39 0.29 0.45 0.33 0.75	4.34 5.39 6.24 6.39	0.004 0.16 0.19 0.32	4.40 5.22 6.11 6.35 7.33 7.43	0.02 0.31 0.44 0.65 0.22 0.61	4.35 5.27 6.28	0.026 0.17

(*a*) MIM method in the original formulation (Ref. [2]);
(*b*) MIM method with inclusion of inductive parameter (Ref. [3]);
(*c*) Present work;
(*d*) Experimental values (Ref. [3]).

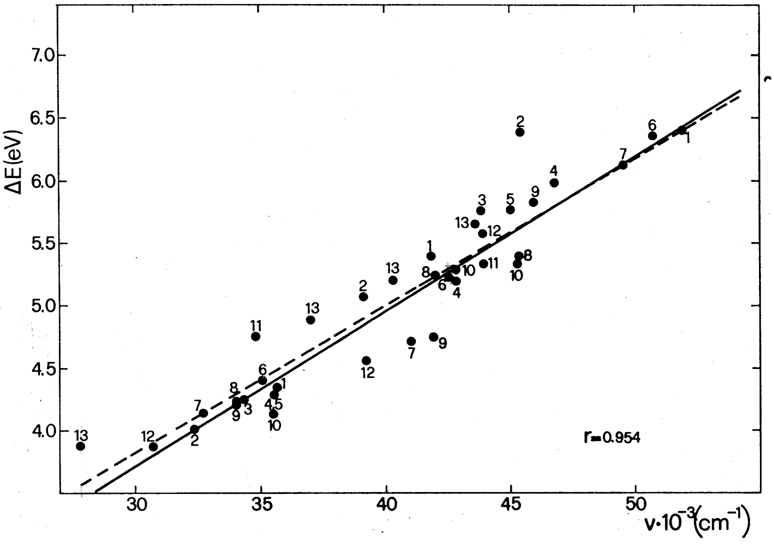


Fig. 2. – Regression of theoretical excitation energies on observed frequencies (solid line) for nitro and aminobenzenes; correlation coefficient $r = 0.954$; number of points $n = 37$. Numbers in the figure correspond to molecules in the order of Tables III–IV.

Murrell [3] significantly improves the results obtained by using the original version of the method. However, the best overall fit is obtained by means of the generalized formulas (column *c*). Particularly significant is the improvement obtained for the oscillator strengths of the first bands, which are underestimated by Godfrey and Murrell calculations [3].

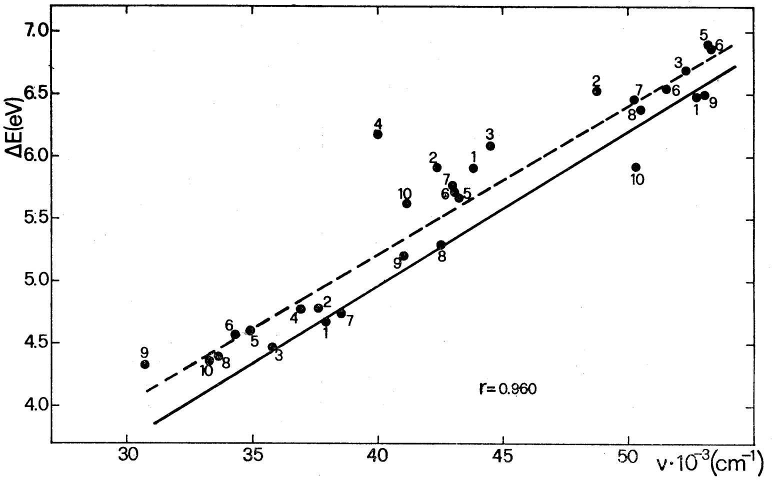


Fig. 3. – Regression of theoretical excitation energies on observed frequencies (solid line) for nitro and aminopyridines; correlation coefficient $r = 0.960$; number of points $n = 30$. Numbers in the figure correspond to the molecules in the order of Tables V, VI.

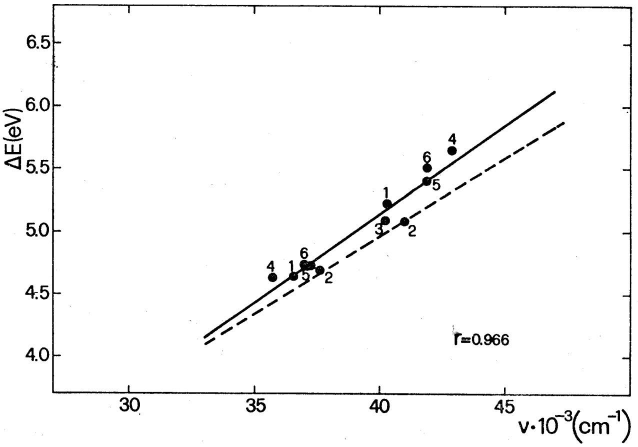


Fig. 4. – Regression of theoretical excitation energies on observed frequencies (solid line) for phenylpyridines and bipyridines; correlation coefficient $r = 0.966$; number of points $n = 11$. Numbers in the figure correspond to molecules in the order of Table VII.

On the basis of present results few points emerge. For poly-substituted benzenes and pyridines, where the substituents exhibit a strong character of donor or acceptor, the original version of the method is not recommended. In this case, the generalized version of the method must be preferred for the following reasons. The set up of CI matrix in the version given by Godfrey and Murrell, needs, besides the usual parameters (that is: Ionization Potentials of donor group; Electron Affinities of acceptor group; resonance integrals related to substituent-carbon bonds; energies of lowest excited states of aromatic fragments and substituents), the inductive parameter of the substituents. This parameter is not always readily available from UV spectra of reference compounds. On the other hand, generalized formulas take into account the effect of inductive perturbation by including this effect also in off-diagonal CI matrix elements. Finally, the energy invariance in local symmetry transformation is another point in favour of MIM version proposed in Ref. [4].

Oscillator strengths were calculated both through dipole-length operator (f_1) and dipole-gradient operator (f_2). The comparison with f values obtained by UV spectra is difficult. This is due to the overlapping of bands of most of the UV spectra of the considered molecules. An example is the absorption spectrum of *ortho*-dinitrobenzene reported in Ref. [14]. In this view, f values of weak bands must be considered as upper limits of the true values.

From the body of previous [5, 6] and present results, it seems that f values of strong bands are overestimated, when calculated through dipole-length operator. Significant examples are the second bands of phenylpyridines, and much more of bipyridines (see Table VII). However, for molecules containing strong acceptor or donor groups, for which both the intensity of bands is strongly dependent on solvent, and, owing to low solubility, apolar solvents can be scarcely employed, a " mixed " expression which *averages* the merits of the two operators is recommended for oscillator strength calculations.

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