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Calculation of Electronic Spectra of Aza-Benzenes and Aza-Naphthalenes by the Pariser-Parr-Pople Method

By

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The semiempirical treatment due to **Pariser** and **Parr** and to **Pople** has been used to calculate transition energies and intensities of the $\pi - \pi^*$ bands in the electronic spectra of 31 azines (aza-benzenes and aza-naphthalenes). A comparison with experimental data and a discussion of the wave functions for the ground and excited states are presented.

Nach der halbempirischen Pariser-Parr-Pople-Methode berechneten wir Übergangsenergien und -intensitäten für die $\pi - \pi^*$-Banden von 31 Azinen (Azabenzole und Azanaphthaline) und verglichen mit experimentellen Daten. Die Eigenfunktionen für Grund- und angeregte Zustände werden diskutiert.

Nous avons calculé les énergies et intensités des bandes $\pi - \pi^*$ dans les spectres de 31 azines (azabenzènes et azanaphthalènes) au cadre de la méthode sémiempirique de **Pariser-Parr-Pople**. Les résultats sont comparés à de données expérimentales, et les fonctions d'onde des états fondamentaux et excités sont discutées.

Introduction

The semiempirical treatment due to **Pariser** and **Parr** [*15*] and to **Pople** [*18*], recently referred to as the P method [*13*], has been extensively and successfully used for the calculation of the energies of electronically excited states of conjugated hydrocarbons. A complete list of references can be found in the most recent contributions to the field [*7*, *13*, *16*, *20*]. Applications of the P method to the corresponding aza-substituted molecules have been less numerous [*16*, *19*] and not systematic enough.

The present paper reports the results of calculations of $\pi - \pi^*$ electronic singlet transitions by the P method for several one- and two- ring azines.

Calculations

Calculations were performed for all possible mono-, di-, tri- and tetra- aza-benzenes, for all possible mono- and di- aza-naphthalenes and for all tri- and tetra-aza-naphthalenes for which spectral data were known.

The molecules were numbered as in Fig. 1, where the numbering of the atoms and the reference axes are also shown (for pyridine and quinoline). A conventional geometry has been assumed for all molecules except symmetric triazine and tetrazine, for which the geometry, as determined by experiment [*2*, *21*], has been used: for aza-benzenes the geometry was the same previously used by **Pariser** and **Parr** [*15*]. For aza-naphthalenes the geometry was obtained "welding" the geometries of the two component rings along the shared carbon-carbon bond.

To provide a suitable basis, HMO's for each azine were calculated according to the following prescriptions: 1. all exchange integrals equal to β, the exchange integral in benzene; 2. $\alpha_N = \alpha_C + 0.5\,\beta$. For pyridine, pyrazine and *s*-triazine, the molecular orbitals calculated with these prescriptions were shown to be fairly close to SCF MO's [*11*].

The HMO's were expressed in the form

$$\varphi_i = \Sigma_\mu\, c_{i\mu}\, \chi_\mu$$

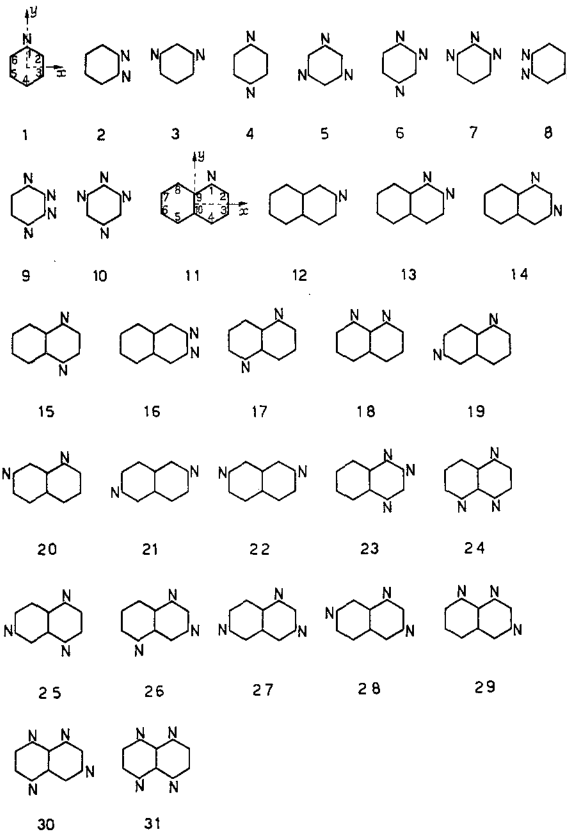


Fig. 1. Topology and notation

where χ_μ is the $2p_\pi$ atomic orbital for atom μ (i, $\mu = 1\ldots6$ for aza-benzenes; i, $\mu = 1\ldots10$ for aza-naphthalenes). Tables for all the eigenvalues ε_i and the matrices $C_{i\mu}$ are not included in the paper but are available upon request; HMO's were labelled in order of increasing energy.

The lowest closed-shell configuration Φ_0 for a π-electron system with $2\,n$ electrons is then written as

$$\Phi_0 = \|\psi_1\bar{\psi}_1\cdots\psi_k\bar{\psi}_k\cdots\psi_n\bar{\psi}_n\|$$

where ψ_k and $\bar{\psi}_k$ (spin orbitals) have the following meaning:

$$\psi_k = \varphi_k\,\alpha \quad \text{and} \quad \bar{\psi}_k = \varphi_k\,\beta$$

α and β are the usual spin functions.

The symbol $\|\ldots\|$ implies a normalized Slater determinant. Singlet singly excited configurations are defined as:

$$\Phi_k^l = \frac{1}{\sqrt{2}}\{\|\psi_1\bar{\psi}_1\cdot\psi_k\bar{\psi}_l\cdot\psi_n\bar{\psi}_n\| - \|\psi_1\bar{\psi}_1\cdots\bar{\psi}_k\psi_l\cdots\psi_n\bar{\psi}_n\|\}$$

$k = 1\ldots n$; $l = n + 1\ldots 2\,n$.

The matrix of the hamiltonian was then diagonalized by means of well-known formulas [*15, 18*] and the wave functions for the ground state and the lowest excited states of the π-electron systems were obtained in the form

$$\Psi_j = d_{j;0}\Phi_0 + \Sigma_{k,l}\, d_{j;k,l}\Phi_k^l \qquad j = 0, 1, 2\ldots$$

We included, for the benzene-type molecules, the interactions between the ground configuration and all singly excited configurations and for the naphthalenetype molecules the same interactions except those involving the lowest occupied and/or the highest unoccupied molecular orbital. The following choice of values (in eV. units) was made for the parameters included in the calculation:

$$\beta_{C-C} = -2.29 \qquad \beta_{C-N} = -2.62 \qquad \beta_{N-N} = -2.25 \;\star$$

$$\alpha_\mu = -I_\mu - \sum_{\nu \neq \mu} (\mu\mu/\nu\nu)$$

$(\mu\mu/\nu\nu)$ are two center electron repulsion integrals, and were evaluated theoretically for interatomic distances > 2.80 Å (using Slater orbitals with $Z_C = 3.25$ and $Z_N = 3.90$).

For $R < 2.80$ Å the following formulas were used:

$$(\mu\mu/\nu\nu)_{CC} = 11.130 - 2.912\, R + 0.253\, R^2$$
$$(\mu\mu/\nu\nu)_{CN} = 11.735 - 3.255\, R + 0.302\, R^2$$
$$(\mu\mu/\nu\nu)_{NN} = 12.340 - 1.779\, R + 0.414\, R^2$$

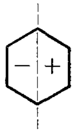
Ionisation potentials (I_μ) and electron affinities (A_μ) taken from Hinze and Jaffe [5] were used to evaluate one center electron repulsion integrals: $(\mu\mu/\mu\mu) = I_\mu - A_\mu$.

Calculations were performed on an IBM 1620 computer (storage 20000 digits); due to limitation in storage the program was organized in different steps: diagonalization of the Hückel and Configuration Interaction Matrices was performed by the Jacobi method (programmed in SPS language). The calculation of the CI matrix and of transition moments was programmed in Fortran language.

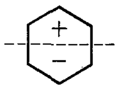
Results and Discussion

The energies of the ground state and the lowest excited states relative to the energy of the ground configuration are reported in Tab. 1, together with the oscillator strengths of the most interesting transitions and the weight of the most important configurations in the different states (in %).

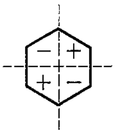
In discussing the first bands in electronic spectra of azines, reference is usually made to the corresponding bands in the spectra of the parent hydrocarbons: α, p, β bands in Clar's classification [10, 13]. For the spectra of monocyclic azines the following benzene-type molecular orbitals are relevant:



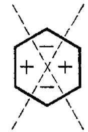
A



B



C



D

In benzene A and B are degenerate, and so are C and D. In s-triazine the orbitals A, B and C, D are still degenerate: the upper states for the first and second band have symmetry A_2' and A_1', respectively, and correspond to the upper states of the benzene α and p bands (symmetry B_{2u} and B_{1u} respectively): both transitions are symmetry forbidden. In molecules 1, 4, 6, 9, 10 the orbital B is more stable than A, and D is more stable than C as expected from the one electron charge distributions in these orbitals. In molecules 2, 3, 8, A and C are more stable than B and D, respectively. In v-triazine A is more stable than B, but D is more stable than C. In terms of the symmetry of the configurations, the first two

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* Consistent values in the literature are $\beta_{C-C} = -2.39$ [15], $\beta_{C-N} = -2.74$ [6], $\beta_{N-N} = -2.35$ [14]. β_{C-C} was changed to obtain agreement with experimental energy for the first singlet excited state in benzene, β_{C-N} and β_{N-N} were then reduced by the same ratio.

Table 1. *Results of computations*

Compound	Energy relative to ground configuration (eV.)	$f^{(a)}$	$m_x^{(b)}$	$m_y^{(c)}$	weight (in %) of most important configurations	
1 (C_{2v})	-0.019 (A_1)				Φ_0	99.7
	4.872 (B_1)	0.050	0.343	0	Φ_3^4; Φ_2^5	67.3; 31.7
	5.246 (A_1)	0.018	0	0.199	Φ_3^5; Φ_2^4	61.1; 35.8
	7.166 (B_1)				Φ_2^5; Φ_3^4	66.0; 28.2
	7.204 (A_1)				Φ_2^4; Φ_3^5	55.7; 36.6
2 (C_{2v})	-0.063 (A_1)				Φ_0	98.8
	4.913 (A_1)	0.060	-0.370	0	Φ_3^4; Φ_2^5	68.0; 30.4
	5.240 (B_1)	0.025	0	0.233	Φ_2^4; Φ_3^5	62.6; 34.2
	7.154 (B_1)				Φ_3^5; Φ_2^4	62.7; 33.3
	7.351 (A_1)				Φ_2^5; Φ_3^4	68.3; 29.3
3 (C_{2v})	-0.104 (A_1)				Φ_0	98.4
	5.137 (B_1)	0.100	-0.467	0	Φ_3^4; Φ_2^5	76.2; 23.5
	5.668 (A_1)	0.049	0	0.312	Φ_3^5; Φ_2^4	66.5; 28.2
	7.608 (A_1)				Φ_2^4; Φ_3^5	69.8; 27.0
	7.775 (B_1)				Φ_2^5; Φ_3^4	70.0; 21.2
4 (D_{2h})	-0.062 (A_{1g})				Φ_0	98.1
	4.718 (B_{3u})	0.261	0.789	0	Φ_3^4; Φ_2^5	87.6; 12.4
	5.422 (B_{2u})	0.095	0	0.444	Φ_3^5; Φ_2^4	76.9; 21.5
	7.889 (B_{2u})				Φ_2^4; Φ_3^5	77.4; 22.3
	8.047 (B_{3u})				Φ_2^5; Φ_3^4	87.6; 12.4
5 (D_{3h})	-0.214 (A_1')				Φ_0	96.9
	5.784 (A_2')	0	0	0	Φ_3^4; Φ_2^5	50.0; 50.0
	6.311 (A_1')	0	0	0	Φ_3^5; Φ_2^4	47.7; 47.7
	8.021 (E')				Φ_2^5; Φ_3^4	49.2; 49.2
	8.021 (E')				Φ_2^4; Φ_3^5	49.2; 49.2
6	-0.115				Φ_0	98.1
	4.935	0.203	0.600	0.315	Φ_3^4; Φ_2^5	83.4; 15.2
	5.648	0.006	0.040	0.106	Φ_3^5; Φ_2^4	53.0; 43.0
	7.601				Φ_2^4; Φ_3^5	50.3; 43.4
	8.069				Φ_2^5; Φ_3^4	71.8; 14.0
7 (C_{2v})	-0.034 (A_1)				Φ_0	99.5
	4.948 (B_1)	~ 0	-0.028	0	Φ_3^5; Φ_2^4	51.5; 48.2
	5.142 (A_1)	0.100	0	0.468	Φ_3^4; Φ_2^5	75.0; 22.3
	7.273 (B_1)				Φ_2^4; Φ_3^5	50.8; 48.5
	7.446 (A_1)				Φ_2^5; Φ_3^4	74.8; 23.9
8 (D_{2h})	-0.055 (A_{1g})				Φ_0	99.4
	4.779 (B_{3u})	0.227	-0.733	0	Φ_3^4; Φ_2^5	84.6; 15.4
	5.534 (B_{2u})	0.038	0	0.277	Φ_2^4; Φ_3^5	69.2; 29.0
	7.492 (B_{2u})				Φ_3^5; Φ_2^4	69.8; 30.0
	8.232 (B_{1g})	0	0	0	Φ_1^4	95.0
	8.358 (B_{3u})				Φ_2^5; Φ_3^4	84.6; 15.4

Table 1 (Continuation)

Compound	Energy relative to ground configuration (eV.)	$f^{(a)}$	$m_x{}^{(b)}$	$m_y{}^{(c)}$	weight (in %) of most important configurations	
9 (C_{2v})	−0.069 (A_1)				Φ_0	98.7
	4.882 (A_1)	0.070	0.402	0	Φ_3^4; Φ_2^5	69.7; 28.8
	5.231 (B_1)	0.033	0	0.265	Φ_3^5; Φ_2^4	65.4; 31.6
	7.403 (A_1)				Φ_2^5; Φ_3^4	70.6; 29.2
	7.467 (B_1)				Φ_2^4; Φ_3^5	66.0; 32.7
10 (C_{2v})	−0.109 (A_1)				Φ_0	98.3
	5.141 (B_1)	0.093	0.450	0	Φ_3^4; Φ_2^5	75.3; 24.3
	5.739 (A_1)	0.023	0	0.212	Φ_2^4; Φ_3^5	60.4; 34.3
	7.753 (A_1)				Φ_3^5; Φ_2^4	61.9; 30.3
	7.860 (B_1)				Φ_2^5; Φ_3^4	74.4; 24.1
11	−0.056				Φ_0	99.0
	4.085	0.048	0.341	−0.132	Φ_4^6; Φ_5^7	57.6; 34.3
	4.224	0.107	0.063	0.532	Φ_5^6; Φ_4^7	74.6; 19.0
	5.554	0.080	0.177	−0.363	Φ_3^6; Φ_5^8	47.4; 35.3
	5.816	0.461	−0.937	−0.136	Φ_4^8; Φ_3^7; Φ_5^7	29.3; 19.2; 14.0
					Φ_4^6; Φ_2^6; Φ_5^9	12.4; 10.3; 10.1
12	−0.062				Φ_0	99.0
	4.066	0.124	−0.048	0.584	Φ_5^6; Φ_4^6; Φ_5^7	48.9; 20.0; 19.0
	4.285	0.079	−0.201	−0.410	Φ_5^7; Φ_5^6; Φ_4^6	34.1; 32.7; 21.3
	5.401	0.017	0.133	0.133	Φ_3^6; Φ_5^8	47.1; 45.3
	5.885	0.285	0.678	−0.296	Φ_3^7; Φ_4^8; Φ_5^9	34.0; 23.2; 10.5
13	−0.062				Φ_0	98.8
	3.909	0.193	−0.081	0.741	Φ_5^6; Φ_4^7	79.2; 11.0
	4.126	0.033	0.255	−0.161	Φ_4^6; Φ_5^7	51.4; 34.9
	5.360	0.013	−0.131	0.100	Φ_3^6; Φ_5^8	62.1; 31.5
	5.843				Φ_4^8; Φ_3^7; Φ_5^9	22.9; 19.8; 16.3
					Φ_2^6; Φ_5^7	10.7; 10.0
14	−0.104				Φ_0	98.4
	4.120	0.122	0.190	−0.542	Φ_5^6; Φ_4^6; Φ_5^7	49.2; 22.2; 15.4
	4.402	0.044	0.042	0.329	Φ_5^6; Φ_4^6; Φ_5^7	29.5; 29.5; 24.2
	5.806	0.126	−0.482	0.110	Φ_5^8; Φ_3^6	43.8; 27.6
	6.141				Φ_4^7; Φ_4^8; Φ_3^6	22.3; 20.4; 18.4
					Φ_3^7	15.1
15 (C_{2v})	−0.042 (A_1)				Φ_0	99.4
	4.001 (A_1)	0.151	0.654	0	Φ_4^6; Φ_5^7	69.6; 25.7
	4.113 (B_1)	0.090	0	0.497	Φ_5^6; Φ_4^7	78.7; 15.5
	5.681 (A_1)	0.660	−1.147	0	Φ_5^7; Φ_4^8; Φ_4^6	29.1; 27.2; 14.7
					Φ_3^7; Φ_2^6	10.6; 10.1
	5.909 (B_1)	0.209	0	−0.633	Φ_4^7; Φ_3^6	58.1; 23.4
	5.966 (B_1)	0.010	0	−0.135	Φ_5^8; Φ_3^6	66.9; 18.5

Table 1 (Continuation)

Compound	Energy relative to ground configuration (eV.)	$f^{(a)}$	$m_x^{(b)}$	$m_y^{(c)}$	weight (in %) of most important configurations
16 (C_{2v})	−0.126 (A_1)				Φ_0 98.0
	4.200 (A_1)	0.017	−0.210	0	Φ_5^7; Φ_4^6 50.6; 39.5
	4.389 (B_1)	0.097	0	0.495	Φ_5^6; Φ_4^7 70.2; 22.7
	5.709 (B_1)	∼0	0	−0.004	Φ_3^6; Φ_5^8 51.6; 40.0
	5.917 (A_1)	0.300	0.753	0	Φ_3^7; Φ_4^8; Φ_5^7 43.7; 26.8; 10.3
17 (C_{2h})	−0.071 (A_g)				Φ_0 98.9
	4.077 (B_u)	0.174	0.682	−0.118	Φ_4^6; Φ_5^7 70.8; 23.4
	4.488 (B_u)	0.077	0.022	0.439	Φ_5^6; Φ_4^7 68.9; 27.6
	5.795 (A_g)	0	0	0	Φ_3^6; Φ_5^8 66.2; 17.0
	6.041 (A_g)	0	0	0	Φ_4^8; Φ_3^7; Φ_5^8 49.9; 18.9; 11.1
18 (C_{2v})	−0.092 (A_1)				Φ_0 98.5
	4.086 (B_1)	0.195	0.730	0	Φ_4^6; Φ_5^7 73.5; 22.2
	4.480 (A_1)	0.090	0	0.474	Φ_5^6; Φ_4^7 72.3; 23.2
	5.915 (B_1)	0.021	0.201	0	Φ_3^6; Φ_5^8 67.2; 21.6
	6.059 (A_1)				Φ_4^8; Φ_3^7; Φ_2^6 52.8; 15.4; 12.4
19	−0.086				Φ_0 98.7
	4.160	0.124	0.260	0.516	Φ_5^6; Φ_4^6; Φ_5^7 46.7; 26.3; 15.2
	4.408	0.055	−0.050	−0.372	Φ_5^6; Φ_4^6; Φ_5^7 34.9; 27.0; 26.7
	5.582	0.133	0.469	−0.218	Φ_3^6; Φ_5^8 47.7; 25.0
	5.926	0.574	−1.034	0.141	Φ_3^7; Φ_4^8; Φ_4^6 19.3; 17.0; 15.5
					Φ_5^7; Φ_5^8 14.7; 10.9
20	−0.082				Φ_0 98.7
	4.058	0.136	0.248	−0.561	Φ_5^6; Φ_4^6; Φ_5^7 48.6; 27.7; 14.6
	4.387	0.047	−0.044	0.342	Φ_5^6; Φ_5^7; Φ_4^6 32.6; 28.0; 25.1
	5.702	0.056	−0.226	−0.243	Φ_3^6; Φ_5^8 39.4; 39.4
	5.809	0.732	−1.165	−0.248	Φ_5^7; Φ_4^6; Φ_4^8 22.2; 18.4; 16.0
					Φ_3^7 14.3
21 (C_{2h})	−0.087 (A_g)				Φ_0 98.8
	4.070 (B_u)	0.278	0.110	0.867	Φ_5^6; Φ_4^7 85.6; 9.9
	5.098 (B_u)	0.573	−1.123	0.022	Φ_5^7; Φ_4^6 88.9; 4.2
	5.390 (A_g)	0	0	0	Φ_3^6; Φ_5^8 49.3; 44.5
	6.041 (B_u)				Φ_4^6 89.1
22 (C_{2v})	−0.094 (A_1)				Φ_0 98.5
	4.306 (B_1)	0.035	−0.301	0	Φ_5^7; Φ_4^6 57.8; 37.3
	4.315 (A_1)	0.214	0	0.745	Φ_5^6; Φ_4^7 85.1; 11.9
	5.494 (B_1)	0.113	0.481	0	Φ_5^8; Φ_3^6 44.7; 38.9
	5.939 (A_1)	0.149	0	−0.532	Φ_4^7; Φ_3^7; Φ_5^9 35.2; 24.4; 14.0
					Φ_4^8 12.3

Table 1 (Continuation)

Compound	Energy relative to ground configuration (eV.)	$f^{(a)}$	$m_x{}^{(b)}$	$m_y{}^{(c)}$	weight (in %) of most important configurations
23	−0.088				Φ_0 98.3
	3.817	0.154	0.129	0.659	Φ_5^6; Φ_4^7 78.3; 7.3
	4.105	0.116	0.548	−0.124	Φ_4^6; Φ_5^7 60.0; 22.0
	5.741	0.183	0.581	0.142	Φ_5^8; Φ_3^6; Φ_4^8 30.7; 23.8; 11.1
	5.811	0.456	−0.922	−0.180	Φ_5^8; Φ_6^7; Φ_3^6 20.6; 15.8; 14.8
					Φ_2^6; Φ_4^8 11.3; 11.0
	5.992	0.080	0.298	−0.250	Φ_4^7; Φ_3^6; Φ_5^8 40.0; 28.0; 17.2
24	−0.072				Φ_0 98.9
	3.973	0.359	1.005	−0.056	Φ_4^6; Φ_5^7 80.6; 15.4
	4.540	0.057	−0.005	0.376	Φ_5^6; Φ_4^7 68.7; 26.5
	5.973	0.133	0.396	0.308	Φ_4^8; Φ_3^6; Φ_4^7 48.2; 12.6; 9.9
	6.130				Φ_3^6; Φ_4^7; Φ_4^8 38.6; 17.6; 11.8
25	−0.074				Φ_0 98.9
	3.988	0.190	0.524	0.509	Φ_5^6; Φ_4^6 56.8; 25.6
	4.346	0.040	0.182	−0.267	Φ_4^6; Φ_5^6; Φ_5^7 38.9; 27.1; 23.3
	5.626	0.729	−1.153	0.363	Φ_5^7; Φ_4^6; Φ_4^8 35.7; 16.0; 12.1
	6.042				Φ_5^8; Φ_4^7 57.3; 26.1
26	−0.132				Φ_0 98.0
	4.145	0.191	0.559	−0.445	Φ_4^6; Φ_5^6; Φ_5^7 44.3; 32.3; 16.1
	4.654	0.053	−0.001	0.356	Φ_5^6; Φ_4^6; Φ_4^7; 44.3; 18.1; 17.7
					Φ_5^7 14.7
	6.057	0.040	−0.216	0.166	Φ_5^8; Φ_3^6 41.1; 34.6
	6.138				Φ_4^8; Φ_3^6; Φ_5^7; 26.4; 17.4; 14.0
					Φ_4^7 10.6
27	−0.148				Φ_0 97.8
	4.441	0.170	0.123	0.640	Φ_5^6; Φ_4^7 82.2; 12.0
	4.453	∼0	0.032	−0.042	Φ_4^6; Φ_5^7 49.1; 45.3
	5.906	0.166	−0.555	0.068	Φ_5^8; Φ_3^6 40.1; 33.5
	6.079				Φ_4^7; Φ_3^7; Φ_4^8; 23.3; 16.0; 12.4
					Φ_4^6 10.4
28	−0.140				Φ_0 97.9
	4.047	0.232	0.139	−0.783	Φ_5^6; Φ_4^6 72.1; 11.7
	4.607	0.048	−0.280	0.196	Φ_5^7; Φ_4^6; Φ_5^6 45.9; 28.0; 13.9
	5.748	0.089	−0.414	−0.029	Φ_5^8; Φ_3^6 49.5; 28.8
	6.313				Φ_3^7; Φ_5^9; Φ_4^6; 21.7; 17.2; 15.1
					Φ_4^8 15.0
29	−0.177				Φ_0 97.6
	4.163	0.221	0.762	0.041	Φ_4^6; Φ_5^7 66.3; 15.6
	4.510	0.109	−0.073	0.511	Φ_5^6; Φ_4^7 65.6; 17.8
	5.984	0.022	0.048	0.197	Φ_3^6; Φ_5^8 54.4; 18.4
	6.123				Φ_4^8; Φ_5^8; Φ_3^7 44.3; 13.6; 11.1

Table 1 (Continuation)

Compound	Energy relative to ground configuration (eV.)	$f^{(a)}$	$m_x{}^{(b)}$	$m_y{}^{(c)}$	weight (in %) of most important configurations	
30	-0.140				Φ_0	98.0
	4.074	0.350	0.904	-0.361	Φ_4^6; Φ_5^6	43.0; 41.3
	4.830	0.032	0.002	0.272	Φ_5^6; Φ_4^6; Φ_5^7; Φ_4^7	36.1; 25.7; 18.5 15.2
	6.101	0.312	0.584	0.481	Φ_5^8; Φ_5^7; Φ_4^8; Φ_3^6	20.8; 18.4; 17.7; 13.8
	6.388				Φ_3^6; Φ_4^8	45.5; 22.4
31 (D_{2h})	-0.065 (A_{1g})				Φ_0	99.1
	3.844 (B_{3u})	0.544	1.261	0	Φ_4^6; Φ_5^7	87.1; 10.2
	4.787 (B_{2u})	0.019	0	0.214	Φ_5^6; Φ_4^7	57.9; 39.4
	6.015 (A_{1g})	0	0	0	Φ_4^8	81.3
	6.493 (B_{1g})	0	0	0	Φ_3^6; Φ_5^8; Φ_4^9	64.0; 16.9; 14.4

(a) oscillator strength
(b) x component of the transition moment
(c) y component of the transition moment

bands are of α and p type, respectively, for all monocyclic azines, while β and β' are usually very close in energy and do not follow a regular order. In the last three groups of molecules α, p, β, β' bands are symmetry allowed.

In the molecular orbital approach [*3*] for polyacenes other than benzene the following considerations apply: the transitions $\varphi_n \rightarrow \varphi_{n+2}$ and $\varphi_{n-1} \rightarrow \varphi_{n+1}$ for an alternant system [*16*] with $2n$ π-electrons are degenerate, and electronic interactions mix the resulting configurations: the antisymmetric and the symmetric combination give a forbidden low energy and an allowed high energy state, that are the upper states of the electronic transitions corresponding to the α and β band respectively. The p band is due to the $\varphi_n \rightarrow \varphi_{n+1}$ transition. Aza substitution destroys the degeneracy of Φ_n^{n+2} and Φ_{n-1}^{n+1} configurations, and the lower energy configuration contributes more to the upper state of the α band; while the higher energy configuration predominates in the upper state of the β band; the result is an increased intensity of the α band and a decreased intensity of the β band. In this context it is interesting to see how the contribution of the different configurations to the ground and lowest excited states comes out from our calculation. In the ground state the ground configuration is absolutely predominant, its contribution being always $> 96\%$. The results for the lowest excited states are less clear cut. For quinoline, quinoxaline, phthalazine, 1,5-, 1,8- and 2,7-naphthyridine, 1,4,5- and 1,3,8-triazanaphthalene and 1,4,5,8-tetrazanaphthalene, the first excited state wave function is built almost exclusively from Φ_4^6 and Φ_5^7 with coefficients $d_{1;4,6}$ and $d_{1;5,7}$ having different sign (the sum of the weights of the two configurations is $> 90\%$, with the only exception of 1,3,8-triazanaphthalene for which it is $\Sigma = 81.9\%$) and in the second excited state the configuration Φ_5^6 predominates (weight $> 65\%$ except in 1,4,5,8-tetrazanaphthalene for which it is only 57.9%). For cinnoline, 2,6-naphthyridine, 1,2,4-, 1,3,6- and 1,3,7-triazanaphthalene the situation is reversed, while for the remaining dicyclic compounds at least four configurations give a substantial contribution to both the first and the second excited state. It is evident that the present method does not allow a discussion of the spectra of dicyclic azines following the lines traced by DEWAR and LONGUET-HIGGINS [3] for the alternant hydrocarbons. The molecular orbitals we used as basis, are probably too different from the orbitals of the parent hydrocarbons, so that the consequences of the pairing property are lost and the interaction between Φ_n^{n+2} and Φ_{n-1}^{n+1} configurations may be not sufficient to push the energy of the more stable combination below the energy of the state arising mainly from the configuration Φ_n^{n+1}.

Table 2. *Experimental data*

Compound No.	first π-π* ΔE (eV.)	ε	second π-π* ΔE (eV.)	ε	third π-π* ΔE (eV.)	ε
1	4.938	2000	(6.26)[1]	(6300)[1]	(7.07)[1]	(63000)[1]
2	5.039	1300				
3	5.101	2030				
4	4.767	5600				
5	5.583	150				
8	4.918	2150				
11	3.960	2360	4.591	3880	5.509	30000
12	3.910	3100	4.660	4030	5.712	37000
13	3.849	2170	4.491	2810	5.609	36400
14	3.986	2100	4.642	2810	5.634	41000
15	3.922	5840	(4.427)	2600	5.343	26700
16	4.090	788	4.823	3800	5.765	36500
17	4.025	6860	4.823	4900	6.017	54000
18	4.025	5780	4.880	4100		
19	3.935	2400	4.899	4100	5.609	30000
20	3.947	1400	4.767	3300	5.634	24000
22	4.064	2600	4.524	4100		
23	4.187	2750	5.413	32000		
24	4.025	10200	4.842	2840		
25	4.025	3760	4.557	2260	5.413	20000
26	4.064	6300	4.938	3470		
27	4.608	2890	5.186	2690	5.738	31700
28	3.922	3020	5.039	3090	5.792	22900
29	4.077	4370	5.080	3020		
30	4.118	7490	5.275	2910	5.902	11000
31	3.861	16000	5.534	5500		

[1] in vacuum [17]

Comparison with experiment has been made for the first three absorption bands, on the basis of absorption spectral data in cyclohexane solution, except for 2,7-naphthyridine for which spectral data in methanol were used; no correction for solvent shifts was introduced. Experimental data for 1,3,5-, 1,3,6-, 1,3,7- and 1,3,8-triazanaphthalene were taken from reference [1], all the others from reference [10]: they are collected in Tab. 2.

The position of the absorption bands can be predicted by use of the formula $\Delta E_i = E_i - E_0$. However it may be suggested that when only singly excited configurations are included in a calculation of this kind, the stabilization of the ground state due to interaction with singly excited configurations should not be considered, as this is approximately equal to the stabilization of the singly excited states due to interaction with doubly excited configurations, which cannot appear, so that $\Delta E_i \approx E_i$. In Fig. 2, 3, 4 excitation energies for the first, second and third

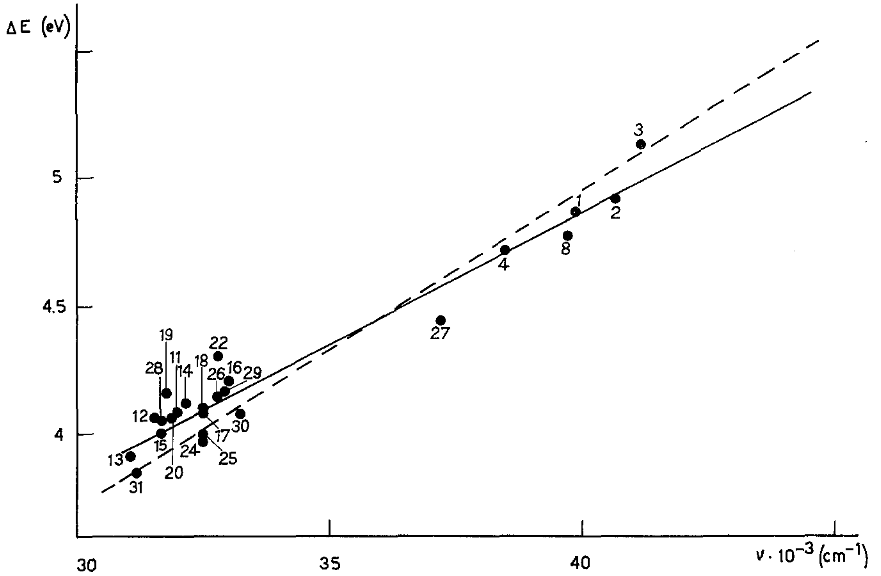

Fig. 2. Regression of theoretical excitation energies of the first π—π^* band on observed frequencies (solid line); standard deviation $\Delta = 0.0825$, correlation coefficient $r = 0.971$

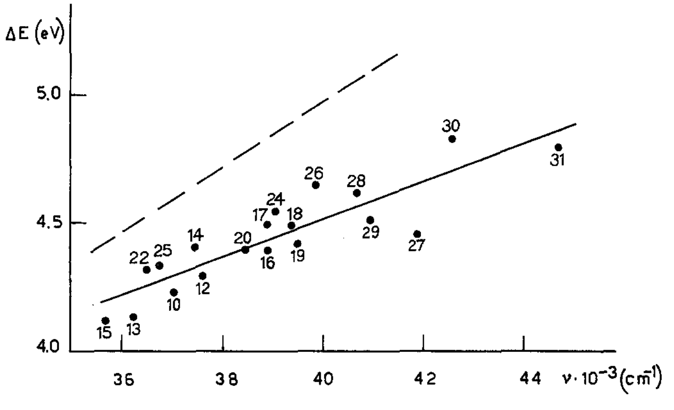

Fig. 3. Regression of theoretical excitation energies of the second π—π^* band on observed frequencies (solid line); standard deviation $\Delta = 0.0891$, correlation coefficient $r = 0.881$

band obtained in this approximation are plotted against experimental values for the position of the maximum of the bands.

The dotted lines in these figures correspond to perfect agreement between theory and experiment; the solid lines are linear regression lines obtained by the least squares method. In calculating the regression lines in Fig. 2 and 3, *s*-triazine and 1,2,4-triazanaphthalene have been omitted: *s*-triazine represents a special case owing to its high symmetry; 1,2,4-triazanaphthalene has the spectrum shown in Fig. 5 [*19*], together with the calculated position of the bands (the first band on the long wave length side corresponds to a $n - \pi^*$ transition); the agreement between theory and experiment is good if we assume that the first $\pi - \pi^*$ band is due to the first and the second electron transition, which is likely to be true as the difference in excitation energies is low. The equations for the regression lines of Fig. 2, 3 and 4 are the following:

$$\Delta E_1 = 0.7468 + 1.032 \times 10^{-4}\,\nu, \qquad \Delta E_2 = 1.595 + 0.728 \times 10^{-4}\,\nu$$

(on 24 points) (on 19 points)

$$\Delta E_3 = 2.857 + 0.620 \times 10^{-4}\,\nu$$

(on 13 points)

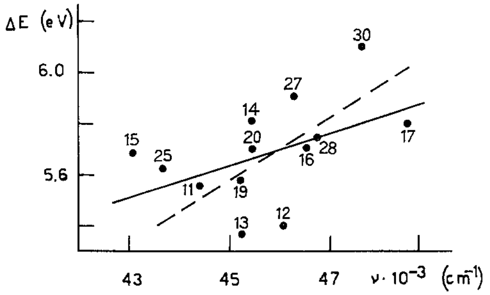

Fig. 4

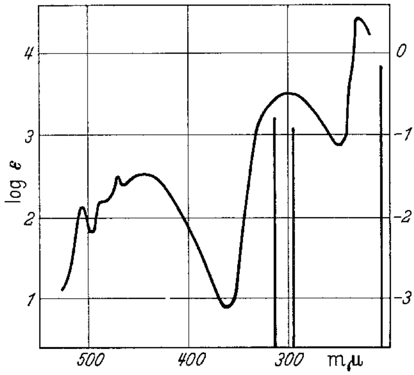

Fig. 5

Fig. 4. Regression of theoretical excitation energies of the third π— π^* band on observed frequencies (solid line); standard deviation $\Delta = 0.168$, correlation coefficient $r = 0.469$

Fig. 5. 1,2,4-benzotriazine spectrum in cyclohexane

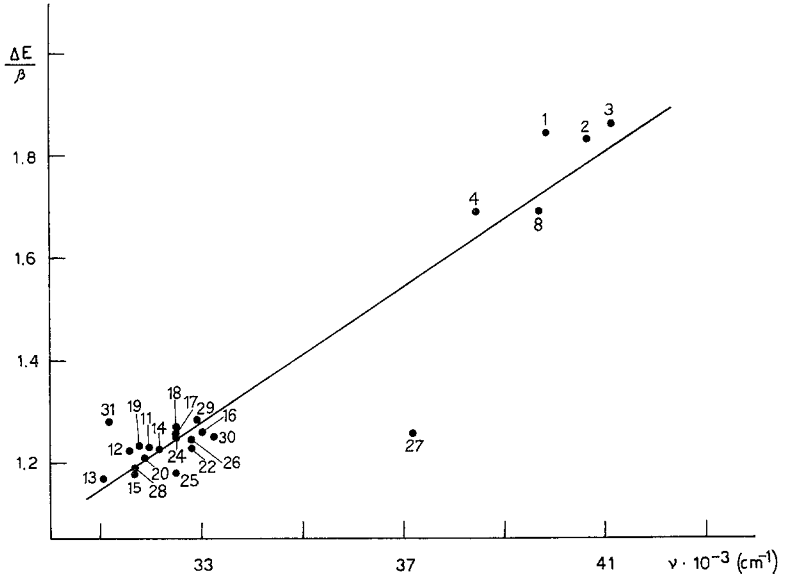

Fig. 6. Regression of the Hückel's excitation energies of the first π— π^* band on observed freqnencies; standard deviation $\Delta = 0.0757$, correlation coefficient $r = 0.943$

The variance about the regressions increases and the correlation coefficient decreases on going to the highest energy transitions.

When using Hückel energies, the correlation between theory and experiment is as good as for the P method for the first transition, but it becomes very poor for

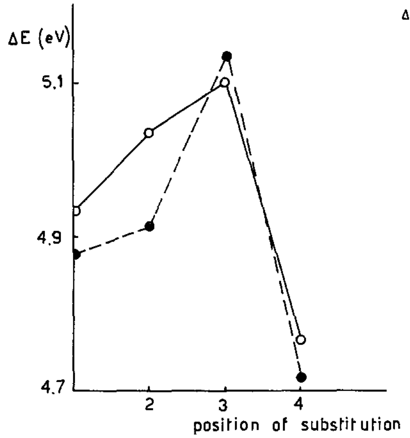

Fig. 7

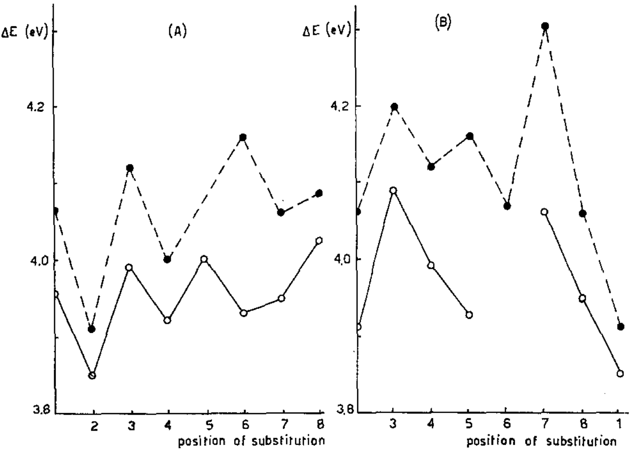

Fig. 8

Fig. 7. Energy shift of the first $\pi-\pi^*$ band of pyridine due to aza-substitution (● calculated; ○ observed)

Fig. 8. Energy shift of the first $\pi-\pi^*$ band of quinoline (A) and isoquinoline (B) due to aza-substitution (● calculated; ○ observed)

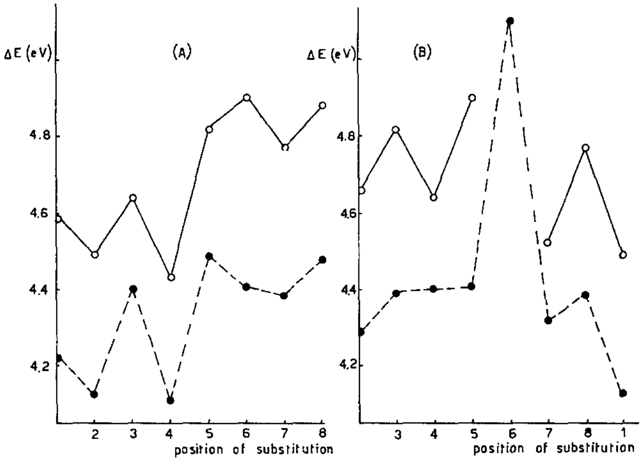

Fig. 9. Energy shift of the second $\pi-\pi^*$ band of quinoline (A) and isoquinoline (B) due to aza-substitution (● calculated; ○ observed)

the second and third band. Fig. 6 shows for the first transition the regression line for the Hückel $\Delta E/\beta$ on the observed frequencies. The equation for the line is

$$\Delta E/\beta = -0.872 + 6.523 \times 10^{-5} \nu$$

(on 24 points)

We also considered the effect of aza substitution on the spectra of monoazines. This is shown in Fig. 7 for aza substitution in pyridine; the blue-shift for substitution in positions 2 and 3 and the red-shift for substitution in position 4 are correctly predicted. Fig. 8 and 9 show the shifts of the first and the second band in quinoline and isoquinoline.

With quinoline as a reference compound, the sign of the shifts for the first band in 1,6-naphthyridine is wrong, all other shifts being in the right direction and also with good agreement in magnitude; with isoquinoline as reference, all the signs for the first band's shifts are correct except for 1,7-naphthyridine, for which the theory predicts no shift in contrast with an experimental hypsochromic shift of about 300 cm^{-1}. For the second band, the shifts are all in the right directions when referred to quinoline and show two failures when referred to isoquinoline.

Table 3. *First π-π^* band*

Compound No.	f_{theor}	f_{obs}	Reference
1	0.05	0.04	[*4*]
2	0.06	0.02	[*4*]
3	0.10	0.04	[*4*]
4	0.26	0.08	[*4*]
5	0. –	~0	[*6*]
8	0.23	0.05	[*10*]
11	0.05	0.03	[*19*]
12	0.12	0.03	[*19*]
13	0.19	0.04	[*19*]
14	0.12	0.03	[*19*]
15	0.15	0.11	[*19*]
16	0.02	0.02	[*19*]
17	0.17	0.13	[*12*]
23	0.27	0.10	[*19*]
24	0.36	0.21	[*8*]
30	0.35	0.11	[*10*]

Table 4. Second π-π^* band

Compound No.	f_{theor}	f_{obs}	Reference
11	0.10	0.10	[*19*]
12	0.08	0.09	[*19*]
13	0.03	0.06	[*19*]
14	0.04	0.07	[*19*]
15	0.09	(*s*)	[*19*]
16	0.10	0.09	[*19*]
17	0.08	0.09	[*12*]
23	0.64	0.43	[*19*]
24	0.06	0.15	[*8*]
30	0.03	(*s*)	[*10*]

(*s*) shoulder

As to intensities, a comparison between theoretical and experimental oscillator strengths is made in Tab. 3 and 4, for the first and second absorption band, respectively.

The experimental values were approximately calculated from the absorption curves (as $f = 4.32 \times 10^{-9}\, \varepsilon_{\max}\, \Delta\, \nu$, where $\Delta\, \nu$ is the band width (in cm^{-1}) at half-maximum extinction). The order of magnitude is always correct: it is possible however to see that theory tends to predict a higher intensity than the experimental for the first band, and a lower intensity for the second band.

It may be concluded that the general features of the spectra of mono and dicyclic azines are well interpreted by the results of the P method. Better numerical agreement could be obtained by a careful search of "best values" for the parameters included in the calculation.

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