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Calculation of Electronic Spectra of Aza-Benzenes and Aza-Naphthalenes by a Simplified Version of the Pariser-Parr-Pople Method*

By

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The simplified version given by Heilbronner and others of the P-treatment was 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 results in a better agreement than for the complete treatment.

Nach dem von Heilbronner u. Mitarb. angegebenen vereinfachten P-Verfahren berechneten wir Übergangsenergien und -intensitäten der $\pi - \pi^*$-Elektronenbanden von 31 Azinen (Aza-Benzole und Aza-Naphthaline). Die Übereinstimmung mit dem Experiment ist besser als beim vollständigen Verfahren.

Nous utilisons la version simplifiée de la méthode P, d'après Heilbronner et al., pour le calcul des énergies et intensités des transitions électroniques $\pi - \pi^*$ de 31 azines (aza-benzènes et aza-naphthalènes). L'accord avec l'expérience y est mieux que pour la méthode complète.

Introduction

A calculation of the electronic spectra of aza-benzenes and aza-naphthalenes by the P method has recently been published [2] and a good agreement between theoretical and experimental data was found.

A simplified version of the P method has been given by Heilbronner and coworkers [9] and successfully applied to a number of alternant and non-alternant hydrocarbons. The mean features of Heilbronner's method are the reduction of the set of electronic interaction integrals to $(11 \mid 11)$ and $(11 \mid 22)$, where 1 and 2 refer to bonded centers, the assumption of empirical values for these two integrals, the simulation of the dependence of the resonance integral β on the interatomic distance by a quadratic function of the Hückel bond orders and the limitation of the number of configurations.

In the present paper an extension of these simplifications has been used to make the method suitable to the study of the electronic spectra of simple azines. In the following we shall call this method the "reduced" Pariser-Parr-Pople method, that is the RP method.

Calculations

The same molecules were considered as in reference [2] and the same topology and notation were used (see Fig. 1 in Ref. [2]). Also the same Hückel molecular orbitals were used as a basis. Five configurations (Φ_0, Φ_3^4, Φ_3^5, Φ_2^4, Φ_2^5) were included for the monocyclic molecules and ten (Φ_0, Φ_5^6, Φ_5^7, Φ_5^8, Φ_4^6, Φ_4^7, Φ_4^8, Φ_3^6, Φ_3^7, Φ_3^8) for the

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dicyclic molecules. The following eight parameters were included: $(\gamma_{11})_\mathrm{C}$; $(\gamma_{11})_\mathrm{N}$; $(\gamma_{12})_\mathrm{CC}$; $(\gamma_{12})_\mathrm{CN}$; $(\gamma_{12})_\mathrm{NN}$; β'_CC; β'_CN; β'_NN; γ_{ij}'s are the "reduced" values of the $(ii \mid jj)$ integrals; β' the "reduced" values for the β parameters. Owing to the lack of experimental values for interatomic distances in most of the molecules under consideration, the values of all the parameters were taken as independent from bond length, but two independent sets were used for the benzene and naphthalene series. The calibration of the parameters was based on the spectra of benzene [*8*], pyridine and pyridazine [*3*] for the monocyclic series and on the spectra of naphthalene [*6*], quinoline and isoquinoline [*3*] for the dicyclic series.

The results were (in eV):

	$(\gamma_{11})_\mathrm{C}$	$(\gamma_{11})_\mathrm{N}$	$(\gamma_{12})_\mathrm{CC}$	$(\gamma_{12})_\mathrm{CN}$	$(\gamma_{12})_\mathrm{NN}$	β'_CC	β'_CN	β'_NN
monocyclic	8.03	10.00	1.43	1.00	1.10	−2.24	−2.52	−2.25,
dicyclic	12.00	13.00	2.10	2.00	1.80	−2.20	−2.40	−2.20.

Calculations were performed on an IBM 1620 computer using the same program as in previous calculations, apart from the necessary changes in the configuration interaction matrix program.

Results and Discussion

A justification for the use of different values of the same integrals in the benzene and naphthalene series is the fact that now these quantities are empirical parameters whose values have to take care of different approximations. As an example let us consider a simplified calculation for benzene and naphthalene. For benzene, after interaction between the configurations Φ_3^4 and Φ_2^5, Φ_2^4 and Φ_3^5, the first excitation energies are given by:

$$\begin{aligned}
E\,(B_{2u}) - E_0 &= -2\,\beta_\mathrm{CC} + \tfrac{1}{6}\,[(11 \mid 22) - (11 \mid 33)] - \tfrac{2}{6}\,[(11 \mid 33) - (11 \mid 44)]\,.\\
E\,(B_{1u}) - E_0 &= -2\,\beta_\mathrm{CC} + \tfrac{2}{6}\,[(11 \mid 11) - (11 \mid 22)] - \tfrac{3}{6}\,[(11 \mid 22) - (11 \mid 33)] +\\
&\quad + \tfrac{4}{6}\,[(11 \mid 33) - (11 \mid 44)]\,.\\
E\,(E_{1u}) - E_0 &= -2\,\beta_\mathrm{CC} + \tfrac{1}{6}\,[(11 \mid 11) - (11 \mid 22)] + \tfrac{5}{6}\,[(11 \mid 22) - (11 \mid 33)] +\\
&\quad + \tfrac{1}{6}\,[(11 \mid 33) - (11 \mid 44)]\,.
\end{aligned}$$

The electron repulsion integrals and β_CC are taken from PARISER's paper [*7*]. When the assumption $(11 \mid 33) = (11 \mid 44) = 0$ is introduced, the same energies are given by:

$$\begin{aligned}
E\,(B_{2u}) - E_0 &= -2\,\beta'_\mathrm{CC} + \tfrac{1}{6}\,\gamma_{12}\,.\\
E\,(B_{1u}) - E_0 &= -2\,\beta'_\mathrm{CC} + \tfrac{1}{3}\,\gamma_{11} - 5/6\,\gamma_{12}\,.\\
E\,(E_{1u}) - E_0 &= -2\,\beta'_\mathrm{CC} + \tfrac{1}{6}\,\gamma_{11} + 2/3\,\gamma_{12}\,.
\end{aligned}$$

If we want the simplified treatment to reproduce the results of the complete treatment, we have to use the values:

$$\beta'_\mathrm{CC} = -2.254\ \mathrm{eV}; \quad \gamma_{11} = 7.389\ \mathrm{eV}; \quad \gamma_{12} = 1.213\ \mathrm{eV}.$$

When the same calculations for naphthalene including only Φ_4^6 and Φ_5^7 interaction are performed, the theoretical (P method) excitation energies for α, p and β bands are reproduced by the RP treatment with the following values of the parameters (see Tab. 1):

$$\beta'_\mathrm{CC} = -2.214\ \mathrm{eV}; \quad \gamma_{11} = 9.622\ \mathrm{eV}; \quad \gamma_{12} = 3.522\ \mathrm{eV}.$$

Table 1

Excitation energies	P method	RP method
$E(\alpha) - E_0$	$-1.618\,\beta - 0.023\,A + 0.149\,B - 0.138\,C +$ $+ 0.107\,D + 0.093\,E - 0.027\,F - 0.096\,G$	$-1.618\,\beta' - 0.023\,\gamma_{11} +$ $+ 0.172\,\gamma_{12}$
$E(p) - E_0$	$-1.236\,\beta + 0.150\,A + 0.274\,B + 0.505\,C +$ $+ 0.374\,D - 0.105\,E - 0.005\,F + 0.014\,G$	$-1.236\,\beta' + 0.150\,\gamma_{11} +$ $+ 0.124\,\gamma_{12}$
$E(\beta) - E_0$	$-1.618\,\beta + 0.069\,A + 0.517\,B + 0.230\,C +$ $+ 0.476\,D + 0.462\,E + 0.341\,F + 0.180\,G$	$-1.618\,\beta' + 0.069\,\gamma_{11} +$ $+ 0.448\,\gamma_{12}$

$A = (11 \mid 11) - (11 \mid 22)$
$B = (11 \mid 22) - (11 \mid 33)$
$C = (11 \mid 33) - (11 \mid 44)$
$D = (11 \mid 44) - (11 \mid 55)$
$E = (11 \mid 55) - (11 \mid 66)$
$F = (11 \mid 66) - (22 \mid 77)$
$G = (22 \mid 77) - (22 \mid 66)$

Table 2. *First* $\pi - \pi^*$ *band*

Compound[a]	transition energies (eV)		oscillator strengths (f)	
	theor.	obs.	theor.	obs.
1 (*)	4.909	4.928	0.023	0.032
2 (*)	5.051	5.039	0.015	0.018
3 (*)	5.080	5.069	0.039	0.024
4 (*)	4.966	4.750	0.100	0.084
5 (*)	5.236	5.583	0.—	0.004
6	5.073	—	0.080	—
7	5.106	—	~ 0	—
8	4.965	4.918	0.096	0.05
9	5.064	—	0.023	—
10	5.072	—	0.038	—
11 (*)	4.008	3.960	0.032	0.025
12 (*)	4.063	3.910	0.039	0.020
13 (*)	3.895	3.849	0.087	0.028
14 (*)	4.041	3.986	0.058	0.031
15 (*)	3.965	3.910	0.119	0.065
16 (*)	4.201	4.091	0.017	0.013
17	4.017	4.025	0.126	0.13
18	4.057	4.025	0.146	—
19	4.095	3.935	0.069	—
20	4.162	3.947	0.059	—
21	4.011	—	0.116	—
22	4.180	4.064	0.022	—
23	4.029	4.187	0.138	0.10
24	3.969	4.025	0.125	0.21
25	4.052	4.025	0.149	—
26	4.127	4.064	0.126	—
27	4.201	(4.159)	0.005	—
28	4.033	3.922	0.119	—
29	4.125	4.077	0.147	—
30	4.099	4.118	0.268	0.11
31	3.904	3.861	0.420	—

[a] For experimental results of compounds without asterisk (*) see literature in reference [*2*]; for compounds with an asterisk the spectra were taken in hexane [*3*].

Table 3. *Second $\pi - \pi^*$ band*

Compound[a]	transition energies (eV)		oscillator strengths (f)	
	theor.	obs.	theor.	obs.
1 (*)	6.232	6.276	0.124	0.122
2 (*)	6.324	(6.523)	0.099	(s)
3 (*)	6.576	(6.610)	0.306	(s)
4 (*)	6.340	6.382	0.436	0.119
5 (*)	7.140	>7.2	1.060	—
6	6.752	—	0.518	—
7	6.238	—	0.271	—
8	6.881	—	0.783	—
9	6.449	—	0.334	—
10	6.962	—	0.393	—
11 (*)	4.420	4.591	0.158	0.120
12 (*)	4.535	4.660	0.166	0.108
13 (*)	4.200	4.507	0.097	0.075
14 (*)	4.385	4.642	0.102	0.095
15 (*)	4.120	(4.245)	0.102	(s)
16 (*)	4.577	4.804	0.140	0.118
17	4.732	4.823	0.199	0.094
18	4.604	4.880	0.184	—
19	4.592	4.899	0.138	—
20	4.525	4.767	0.146	—
21	4.705	—	0.171	—
22	4.497	4.524	0.215	—
23	5.299	5.413	1.210	0.43
24	4.612	4.842	0.316	0.15
25	4.369	4.557	0.077	—
26	4.742	4.938	0.171	—
27	4.445	4.608	0.173	—
28	4.609	5.039	0.070	—
29	4.690	5.080	0.159	—
30	4.780	(5.275)	0.150	(s)
31	4.948	5.534	0.162	—

[a] For experimental results of compounds without asterisk (*) see literature in reference [*2*]; for compounds with an asterisk the spectra were taken in hexane [*3*].

(s) Shoulder.

A table with the energies relative to ground configuration and the weights of the most important configurations in the different states, similar to Tab. 1 in reference [*2*] is not included, but is available upon request.

The following considerations emerge from the data. For all monocyclic azines the first two bands are of α and p type, respectively, while β and β' bands are usually very close in energy and do not follow a regular order (the same conclusion was reached by use of the standard P method). For dicyclic azines more than two configurations give a substantial contribution to the first two excited states; besides the mixing of the configurations is often quite different from that obtained by the standard P method; this suggests that the discussion of the spectra of dicyclic azines following the lines traced by DEWAR and LONGUET-HIGGINS [*1*] for the alternant hydrocarbons is not advisable.

Table 4. *Third* $\pi - \pi^*$ *band*

Compound[a]	transition energies (eV)		oscillator strengths (f)	
	theor.	obs.	theor.	obs.
1 (*)	6.927	6.959	1.136	0.660
2 (*)	6.876	6.886	1.029	0.150
3 (*)	7.077	~7.205	1.110	—
4 (*)	7.263	>7.2	1.106	—
5	7.191	—	0.—	—
6	7.046	—	1.044	—
7	6.825	—	1.113	—
8	7.220	—	0.309	—
9	6.987	—	1.107	—
10	7.069	—	1.110	—
11 (*)	5.535	5.509	1.259	0.537
12 (*)	5.685	5.752	1.507	1.015
13 (*)	5.377	5.647	1.135	0.909
14 (*)	5.497	5.657	1.347	0.858
15 (*)	5.418	5.348	1.167	0.326
16 (*)	5.513	5.847	1.305	0.993
17	5.812	6.017	1.905	1.08
18	5.885	—	1.450	—
19	5.727	5.609	1.879	—
20	5.814	5.634	1.264	—
21	5.811	—	1.970	—
22	5.877	—	1.661	—
23	5.299	—	1.210	—
24	5.764	—	0.840	—
25	5.622	5.413	1.384	—
26	5.683	—	0.856	—
27	5.632	5.738	1.341	—
28	5.658	5.792	0.994	—
29	5.834	—	1.437	—
30	6.000	5.902	1.229	—
31	5.907	—	0.—	—

[a] For experimental results of compounds without asterisk (*) see literature in reference [*2*]; for compounds with an asterisk the spectra were taken in hexane [*3*].

Table 5. *Fourth* $\pi - \pi^*$ *band*

Compound	transition energies (eV)		oscillator strengths (f)	
	theor.	obs.	theor.	obs.
11	6.130	6.083	0.482	0.932
12	6.001	(a)	0.352	—
13	6.305	6.229	0.548	0.944
14	6.340	6.282	0.621	0.843
15	6.368	6.321	0.739	0.693
16	6.171	(a)	0.622	—

(a) The separation in energy between the calculated ΔE for the fourth and third $\pi - \pi^*$ bands is about one half that for molecules 11, 13, 14 and 15; no resolved fourth band was found, but the third band was strongly asymmetric, with bigger absorption coefficients on the higher energy side.

Calculated transition energies and oscillator strengths for the first three $\pi - \pi^*$ bands are compared with experimental data in Tab. 2, 3, 4. The stabilization of the ground state due to interaction with singly excited configurations has not been included (however it is always < 0.03 eV).

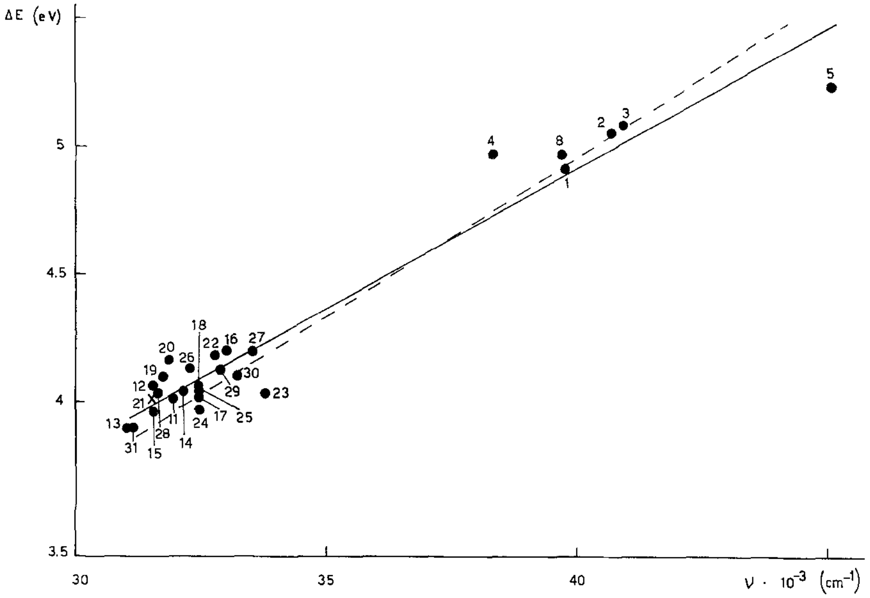

Fig. 1. Regression of theoretical excitation energies of the first π—π^* band on observed frequencies (solid line); standard deviation $\Delta = 0.098$, correlation coefficient $r = 0.973$

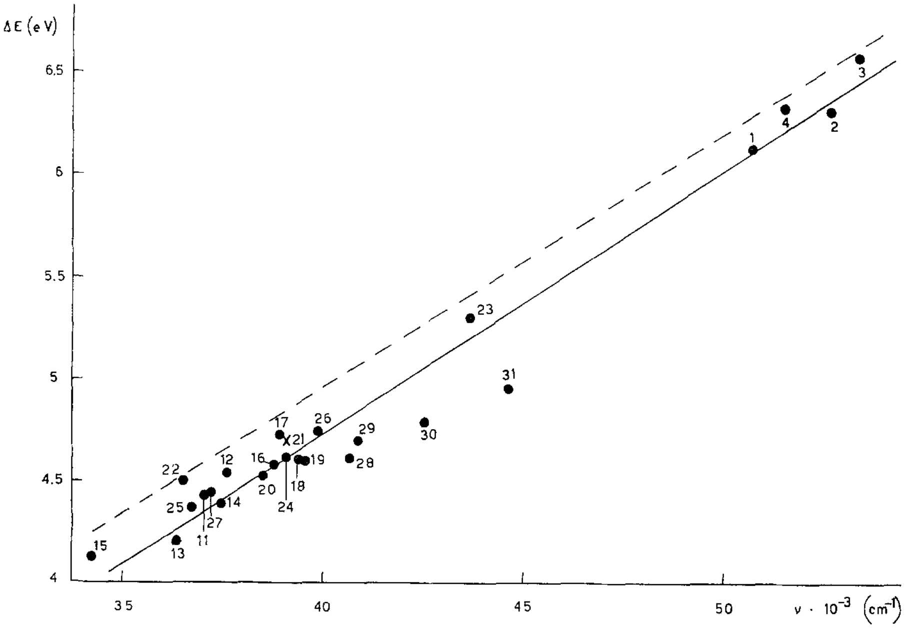

Fig. 2. Regression of theoretical excitation energies of the second π—π^* band on observed frequencies (solid line); standard deviation $\Delta = 0.144$, correlation coefficient $r = 0.980$

The assignment of the bands for the 1,3,6-triazanaphthalene is different from the one previously given by Armarego (see Ref. [2]). The spectrum for this compound has been published only in a table form; however the results of our calculations suggest that the shoulder at 298 mμ with $\varepsilon = 850$ corresponds to the first $\pi - \pi^*$ band, the series of peaks and shoulders regularly spaced between 269 and 239 mμ (ε between 2700 and 3200) to the second band and the peak at 216 mμ with $\varepsilon = 31700$ to the third band. This assignment is supported by the spectrum in water solution at pH = 7.0, also given by Armarego.

In Tab. 4 it may be noticed that the third band in the two ring molecules is probably due to two electron transitions lying very close in energy but strongly different in transition moment.

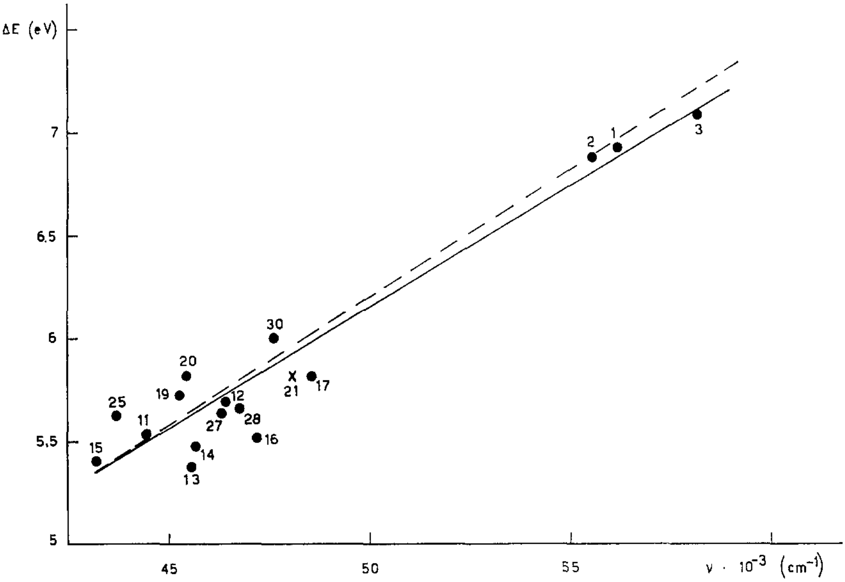

Fig. 3. Regression of theoretical excitation energies of the third π—π^* band on observed frequencies (solid line); standard deviation $\Delta = 0.156$, correlation coefficient $r = 0.957$

From our work [3] $\lambda_{\max}$ and f values for the fourth $\pi - \pi^*$ band in a few molecules became available. These results are collected in Tab. 5 with the corresponding theoretical values. Even for this band the general agreement is quite good; the calculated ΔE's are very close in value to the experimental ones and reproduce the right sequence; f values are always of the right order of magnitude.

In Fig. 1, 2, 3, calculated excitation energies for the first, second and third band 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 all the available experimental data have been used. The corresponding equations are:

$$\Delta E_1 = 0.535 + 1.095 \times 10^{-4}\,\nu \quad \text{(on 26 points)},$$
$$\Delta E_2 = -0.409 + 1.285 \times 10^{-4}\,\nu \quad \text{(on 24 points)},$$
$$\Delta E_3 = 0.281 + 1.173 \times 10^{-4}\,\nu \quad \text{(on 16 points)}.$$

From Fig. 1, 2, 3, a much better agreement between experiment and theory is evident than when the results of our previous calculations were used.

Calculated f values and band shifts due to aza-substitution reproduce the nice agreement with experiment already found.

After the present calculations were performed, the synthesis of 2,6-naphthyridine was published [4], and the UV spectrum of this new compound was taken [5]. The results were: $\Delta E_1 = 3.910$ eV; $f_1 = 0.06$; $\Delta E_2 = 4.842$ eV; $f_2 = 0.12$; $\Delta E_3 = 5.959$ eV; the crosses in our diagrams correspond to this molecule. As they lie close to our regression lines, the equations given above were not recalculated.

We also wish to point out that, beside a better agreement with experiment, the new calculations permit a considerable saving of computing time. The dimensions of the C.I. matrices are reduced (apart from reduction due to symmetry) from 10 × 10 and 17 × 17 to 5 × 5 and 10 × 10 for one and two ring compounds respectively, and the time for computing matrix elements is reduced by a 1/3 to 1/15 ratio.

Literature

[1] Dewar, M. J. S., and H. C. Longuet-Higgins: Proc. physic. Soc. **A 67**, 795 (1954).

[2] Favini, G., I. Vandoni, and M. Simonetta: Theoret. chim. Acta **3**, 45 (1965).

[3] —, M. Simonetta, and I. R. Bellobono: Unpublished work.

[4] Giacomello, G., F. Gualtieri, F. M. Riccieri, and M. L. Stein: Tetrah. Lett. **16**, 1117 (1965).

[5] —, P. Gramaccioni, F. M. Riccieri, and A. Vaciago: Chem. Communications: in press. Personal communication by A. Vaciago.

[6] Murrell, J. N.: The Theory of the Electronic Spectra of Organic Molecules, p. 120, London: Methuen. New York: J. Wiley and Sons, 1963.

[7] Pariser, R.: J. chem. Physics **24**, 250 (1956).

[8] Petruska, J.: J. chem. Physics **34**, 1120 (1961).

[9] Weltin, E., J. Weber, and E. Heilbronner: Theoret. chim. Acta **2**, 114 (1964).

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