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Commentationes

SCF MO Calculations of Ultraviolet Electronic Spectra of Azanaphtalenes with the Variable β Approximation

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The SCF MO method in the variable β approximation has been applied to some azanaphtalenes. The transition energies and bond lengths of these molecules have been calculated. The results are in satisfactory agreement with experiment.

Nous avons appliqué la méthode SCF MO dans l'approximation des β variables à quelques azanaphtalènes et calculè les énergies de transition et les longueurs de liaison de ces molécules. Les résultats sont en accord satisfaisant avec l'expérience.

Das SCF-Verfahren wurde in Form der β-Variationsmethode nach NISHIMOTO und FORSTER auf einige Azanaphthaline angewendet. Die berechneten Übergangsenergien und Bindungslängen stimmen in befriedigender Weise mit dem Experiment überein.

Introduction

The Pariser-Parr-Pople semiempirical method has been widely used for the calculation of electronic properties of π-electron systems. NISHIMOTO and FORSTER [4, 5] made a variable β modification to this method, in which each β for neighbouring atoms is determined by means of a linear relationship from the corresponding bond order after every iteration. The results obtained by this way were quite satisfactory.

Except for the case of quinoline ans isoquinoline, NISHIMOTO and FORSTER did not apply this method to azanaphtalenes. We have done this more extensively in this work. We used the original relation found by NISHIMOTO and FORSTER for the β_{CC}, but the relation for β_{CN} was slightly modified, in order to obtain a better agreement with experiment for molecules containing more than one nitrogen atom.

Method and Parameter Evaluation

The SCF formalism of the P-P-P method was employed. It is known that the variable β method is unsensitive to the assumed geometry. All molecules were assigned regular polygonal structures with equal atom-atom bond lengths (1.4 Å). The two-center repulsion integrals for non-neighbour atoms were computed from this conventional geometry.

The two-center core integrals, the distances and the two-center repulsion integrals $\gamma_{\mu\nu}$ between neighbouring atoms were adjusted at every iteration by means of the relations:

$$\beta_{\mu\nu} = A_0 + A_1 \cdot p_{\mu\nu}; \qquad r_{\mu\nu} = B_0 + B_1 \cdot p_{\mu\nu}$$

$$\gamma_{\mu\nu} = \frac{14.397}{a_{\mu\nu} + r_{\mu\nu}} .$$

The one-center repulsion integrals were computed from the valencestate ionization energies and electron affinities:

$$\gamma_{\mu\mu} = W_\mu - A_\mu$$

Table 1. *Parameter summary*

	$-W_\mu$ (eV)	$\gamma_{\mu\mu}$ (eV)	
C^+	11.16	11.13	$\beta_{CC} = -0.51\,p - 1.900$
N^+	14.15	12.82	$\beta_{CN} = -0.53\,p - 2.180$
			$r_{CC} = -0.18\,p + 1.517$
			$r_{CN} = -0.18\,p + 1.451$

The configuration interaction included the four highest occupied orbitals and the four lowest empty ones.

Results

Transition energies: The results for the calculated singlet transition energies are summarized in Tab. 2.

The experimental data were taken from a recent atlas of UV absorption spectra [1]. The experimental values of the oscillator strength f were estimated from the absorption curves by means of the relation

$$f = 4.32 \cdot 10^{-9}\, \varepsilon_{\max}\, \Delta\bar{\nu} \qquad [3]$$

where $\Delta\bar{\nu}$ is the band with (in cm^{-1}) at half-maximum extinction.

Bond lengths: The calculated bond lengths are given in Tab. 3. Accurate experimental bond lengths are lacking for most of the molecules discussed in this paper.

The atomic charge densities are given in Tab. 4 and the π-electron ionization potentials in Tab. 5. The ionization potentials have been calculated from the expression

$$\text{I.P.} = -\varepsilon_1 + [\varepsilon_1(\text{parent}) + \text{I.P. (parent)}]$$

where ε_1 refers to the highest occupied orbital energy and parent means the parent hydrocarbon. Few experimental values are available for comparison. We observe that the molecular ionization potentials increase with the number of nitrogen atoms and that the contribution of α-situated nitrogen atoms is greater than the contribution of β-situated ones.

The calculations were performed on an IBM 7044 computer. We used the SCF MO CI program of Bloor and Gilson, distributed by the QCPE organization [6]. We modified it to include the variable β modification.

It may be concluded that the general features of the spectra of naphtalene and azanaphtalenes are well interpreted by the variable β modification of the P-P-P method. The accurate geometry of the molecules need not be known. Better

Table 2. *Transition energies (eV) and intensities (f)*

Molecule	calc. ΔE	calc. f	expt. ΔE	expt. f
Naphtalene	3.943	0.001	3.97	0.002
	4.450	0.196	4.51	0.18
	5.461	0		
	5.585	1.974	5.63	1.70
	5.677	0		
	6.058	0.606	6.51	0.21
	6.883	0		
	6.997	0		
	7.535	0		
	7.587	0		
	7.628	0.943	7.44	0.8
Quinoline	4.000	0.026	3.96	
	4.527	0.163	4.49	0.09
	5.460	0.753	5.49	
	5.786	1.077		
	5.883	0.196	6.11	
	6.146	0.513		
	6.229	0.149		
Isoquinoline	4.004	0.040	3.91	
	4.497	0.194	4.66	0.09
	5.527	0.207		
	5.618	0.831	5.74	0.9
	5.772	0.836		
	6.068	0.070		
	6.258	0.519		
Quinazoline	4.071	0.051	3.99	0.02
	4.607	0.138	4.65	0.07
	5.573	0.887	5.64	0.5
	5.771	0.598		
	6.162	0.298		
	6.305	0.539		
Quinoxaline	3.999	0.099	3.92	0.06
	4.498	0.124		
	5.429	0.918	5.33	0.3
	5.884	0.252		
	6.052	0.954		
	6.313	0.399		
1,5 Naphtyridine	4.023	0.124	4.03	0.07
	4.758	0.146	4.82	0.14
	5.656	0		
	5.867	1.930	6.01	0.9
	6.093	0.750		
	6.150	0		
1,8 Naphtyridine	4.021	0.131	4.03	0.08
	4.755	0.140	4.88	0.1
	5.716	0.027		
	5.863	1.849		
	6.101	0.686		
	6.136	0.007		

Table 2 (Continued)

Molecule	calc. ΔE	calc. f	expt. ΔE	expt. f
Pyrido (2,3-b) pyrazine	3.993	0.254	3.93	0.16
	4.854	0.099	4.85	0.1
	5.723	0.283		
	6.003	0.702		
	6.149	1.396		
	6.580	0.287		
Pyrido (3,4-b) pyrazine	4.075	0.109	4.03	0.05
	4.568	0.099	4.54	
	5.479	0.993	5.42	0.3
	5.981	0.114		
	6.176	0.849		
	6.464	0.418		
Pteridine	4.089	0.245	4.10	0.1
	5.000	0.123	5.21	
	6.030	0.917	5.90	
	6.178	0.402		
	6.297	0.943		
	6.780	0.190		

Table 3. *Calculated bond lengths,* r_{ij} (Å)

i	j	Naphtalene	Quinoline	Isoquinoline	Quinazoline	Quinoxaline
1	2	1.380	1.316	1.317	1.319	1.315
1	9	1.423	1.355	1.423	1.355	1.354
2	3	1.416	1.417	1.349	1.350	1.421
3	4	1.380	1.380	1.383	1.317	1.315
4	10	1.423	1.422	1.421	1.422	1.354
5	6	1.380	1.380	1.380	1.379	1.379
5	10	1.423	1.423	1.423	1.423	1.425
6	7	1.416	1.416	1.416	1.417	1.417
7	8	1.380	1.379	1.380	1.379	1.379
8	9	1.423	1.425	1.423	1.425	1.425
9	10	1.415	1.416	1.415	1.416	1.418

i	j	1,5 Naphtyridine	1,8 Naphtyridine	Pyrido (2,3-b) pyrazine	Pyrido (3,4-b) pyrazine	Pteridine
1	2	1.316	1.316	1.314	1.314	1.313
1	9	1.356	1.357	1.354	1.355	1.366
2	3	1.418	1.418	1.422	1.422	1.357
3	4	1.379	1.379	1.314	1.314	1.312
4	10	1.424	1.422	1.356	1.354	1.431
5	6	1.316	1.379	1.315	1.316	1.322
5	10	1.356	1.422	1.358	1.427	1.345
6	7	1.418	1.418	1.419	1.350	1.410
7	8	1.379	1.316	1.378	1.381	1.327
8	9	1.424	1.357	1.425	1.423	1.339
9	10	1.416	1.418	1.419	1.417	1.426

Table 4. *Atomic charge densities*

i	Naphtalene	Quinoline	Isoquinoline	Quinazoline	Quinoxaline
1	1	1.185	0.883	1.210	1.150
2	1	0.883	1.182	0.809	0.902
3	1	1.019	0.920	1.203	0.902
4	1	0.958	1.024	0.840	1.150
5	1	0.996	1.000	0.988	1.000
6	1	1.004	0.988	1.007	0.995
7	1	0.989	1.001	0.980	0.995
8	1	1.003	0.990	1.007	1.000
9	1	0.939	1.026	0.914	0.953
10	1	1.024	0.985	1.042	0.953

i	1,5 Naphtyridine	1,8 Naphtyridine	Pyrido (2,3-b) pyrazine	Pyrido (3,4-b) pyrazine	Pteridine
1	1.183	1.192	1.148	1.154	1.218
2	0.889	0.873	0.908	0.889	0.803
3	1.010	1.025	0.890	0.905	1.198
4	0.963	0.955	1.157	1.143	0.833
5	1.183	0.955	1.189	0.883	1.140
6	0.889	1.025	0.877	1.179	0.921
7	1.010	0.873	1.016	0.918	0.890
8	0.963	1.192	0.959	1.027	1.152
9	0.955	0.873	0.969	0.932	0.871
10	0.955	1.039	0.888	0.971	0.975

Table 5. *Ionization potentials* I. P. (eV)

molecule	calc.	expt. [7]
Naphtalene		8.12
Quinoline	8.400	
Isoquinoline	8.186	
Quinazoline	8.473	
Quinoxaline	8.597	
1,5 Naphtyridine	8.754	
1,8 Naphtyridine	8.831	
Pyrido (2,3-b) pyrazine	8.790	
Pyrido (3,4-b) pyrazine	8.598	
Pteridine	8.984	

numerical agreement, especially for the second and third π-π^* bands could be obtained by further adjustment of the parameters, but the overall concordance with experiment justifies the use of the Tab. 1 parameters.

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