

# Semi-empirical SCF MO CI Calculation of the $\pi$ -Electron Structure of Hydroxy and Amino Derivatives of Anthracene Azaanalogues with Variable $\beta$ -Approximation

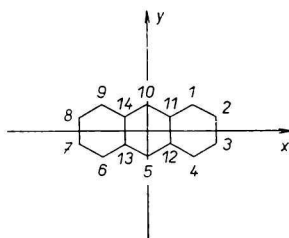
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Using the method of *Pariser, Parr* and *Pople* with variable  $\beta$ -approximation, the authors studied the  $\pi$ -electron properties of some hydroxy and amino derivatives of anthracene azaanalogues. The calculated singlet excitation energies of the UV spectra agree very well with the measured ones.

The classical approximation of Roothaan's SCF LCAO MO method [1] introduced by *Pariser* and *Parr* [2] and *Pople* [3] has been refined in recent times by introduction of the SC variability of resonance integrals [4–11]. The method of  $\beta$ -variability introduced by *Nishimoto* and *Forster* [6] is simple one and it reproduces very well the experimental data of the  $\pi$ -electron structure and the excitation energies of the UV spectra. Besides the basic works by *Nishimoto* and *Forster* [6–8] in which the method is applied to the basic types of  $\pi$ -systems and of some of their hydroxy and amino derivatives, the method was successfully applied to further series of hydrocarbon analogues and derivatives with conjugated  $\pi$ -system [12–18]. *Tinland* corrects by an iteration process even two-centre repulsion integrals, just like *Koutecký* [9]. The variability of integrals has, however, after *Nishimoto* [8] only a negligible influence upon the change of the overall energy and thereby also upon the parameters of the linear variability of  $\beta$ . Aim of this work is, besides the study of  $\pi$ -electron structure of the compounds mentioned, the verification of the method for another structural type:



## *Method of calculation and parameters*

The resonance integrals  $\beta_{ij}$  were corrected by the iterative process according to the relations [7]:

$$\begin{aligned}\beta_{ij} &= -1.84 - 0.51 p_{ij} \quad \text{for C-C bonds,} \\ \beta_{ij} &= -2.02 - 0.53 p_{ij} \quad \text{for C-N bonds,} \\ \beta_{ij} &= -2.20 - 0.56 p_{ij} \quad \text{for C-O bonds.}\end{aligned}$$

The two-centre coulomb repulsion integrals  $\gamma_{ij}$  were calculated by the method of *Mataga* and *Nishimoto* [19]:

$$\gamma_{ij} = 14.397/(a_{ij} + r_{ij}),$$

where  $r_{ij}$  are interatomic distances. The changes in the integrals  $\gamma_{ij}$  were not taken into account. The parameters  $a_{ii}$  are listed in Table 1 [7]. The values  $a_{ij}$  were calculated by means of the relation

$$1/a_{ij} = \frac{1}{2} (1/a_{ii} + 1/a_{jj}).$$

The one-centre repulsion integrals were calculated from the atomic valence state ionization potentials  $W_i$  and from the electron affinities  $A_i$ :

$$\gamma_{ii} = -W_i - A_i.$$

The interaction with hydrogen atoms was neglected and the penetration integrals were approximated by the relation of *Pople* [3]. The values of the integrals  $\alpha$  in the diagonal elements of the Hamiltonian matrix were calculated according to the relation

$$\alpha_i = W_i - \sum_{j \neq i} Z_j \gamma_{ij},$$

where  $Z_j$  is the effective charge of the particular atom after subtracting the electrons which it contributes to the  $\pi$ -system. ( $Z_j = 1$  or  $2$ .) The values  $W_i$  and  $\gamma_{ii}$  are shown in Table 1 [7].

Table 1  
Parameters

	$-W_i$ [eV]	$\gamma_{ii}$ [eV]	$a_{ii}$
C <sup>+</sup>	11.16	11.13	1.294
N <sup>+</sup>	14.12	12.34	1.167
N <sup>2+</sup>	26.70	17.44	0.826
O <sup>2+</sup>	32.90	21.53	0.669

It is known that the PPP method with the variable  $\beta$ -approximation is not sensitive to the assumed geometry. So we used an idealized geometry: for every six-member ring a regular hexagon with equal bond length of 1.395 Å. For the bond lengths C—OH and C—NH<sub>2</sub> the values 1.36 and 1.38 Å respectively, were used [7]. The iteration procedure started with Hückel's molecular orbitals.

The configuration interaction involves the five highest occupied and the five lowest unoccupied molecular orbitals.

Table 2

The  $\pi$ -electron densities

Atom	5-Azaanthracene													5,10-Diazaanthracene		
	amino					diamino				hydroxy				hydroxy		
	1	2	3	4	10	2,7	2,8	3,7	4,6	1	2	3	4	1	2	
1	0.980	1.101	0.986	1.051	1.009	1.099	1.103	0.986	1.050	0.965	1.079	0.987	1.037	0.996	0.966	1.082
2	1.107	0.991	1.049	0.991	1.023	0.997	0.993	1.058	0.993	1.086	0.997	1.043	0.993	0.988	1.074	0.961
3	0.972	1.029	0.973	1.093	0.987	1.033	1.036	0.976	1.095	0.974	1.022	0.958	1.070		0.976	1.025
4	1.055	0.992	1.107	0.987	1.006	0.996	0.992	1.109	0.989	1.041	0.993	1.085	0.971		1.038	0.987
5	1.257	1.248	1.269	1.259	1.308	1.265	1.246	1.284	1.266	1.254	1.249	1.263	1.256	1.195	1.199	1.193
6	1.001	1.001	1.005	1.005		1.106				1.001	1.001	1.004	1.004		0.996	0.996
7	0.987	0.992	0.988	0.989		0.979				0.986	0.990	0.987	0.987		0.989	0.994
8	1.009	1.007	1.012	1.006		1.052				1.007	1.006	1.010	1.005		0.991	0.990
9	1.000	0.999	0.996	0.995		0.989				0.998	0.998	0.996	0.995		0.999	0.999
10	0.948	0.955	0.936	0.943	0.919	0.954	0.974	0.936	0.950	0.943	0.949	0.935	0.940		1.200	1.209
11	1.040	1.000	1.029	1.003	1.072	1.010	0.998	1.039	1.002	1.037	1.003	1.026	1.006	0.919	0.941	0.910
12	0.901	0.925	0.899	0.936	0.903	0.925	0.936	0.899	0.947	0.903	0.922	0.901	0.934		0.912	0.929
13	0.910	0.920	0.909	0.920		0.909				0.909	0.917	0.909	0.917		0.918	0.928
14	1.021	1.011	1.022	1.012		1.027				1.019	1.011	1.020	1.012		0.928	0.918
15	1.814	1.829	1.820	1.810	1.776	1.833	1.832	1.823	1.815	1.877	1.884	1.878	1.875		1.873	1.878
16						1.824										

Table 3  
Bond lengths (Å)

Bond	5-Azaanthracene													5,10-Diazaanthracene		
	amino					diamino				hydroxy				hydroxy		
	1	2	3	4	10	2,7	2,8	3,7	4,6	1	2	3	4	1	2	
1—2	1.390	1.388	1.373	1.378	1.379	1.388	1.388	1.374	1.378	1.385	1.384	1.374	1.377	1.375	1.384	1.384
2—3	1.417	1.431	1.431	1.418	1.419	1.430	1.430	1.430	1.418	1.419	1.428	1.429	1.419	1.423	1.420	1.430
3—4	1.379	1.373	1.389	1.390	1.377	1.374	1.373	1.389	1.390	1.378	1.374	1.385	1.385		1.377	1.373
4—12	1.428	1.432	1.425	1.438	1.428	1.431	1.432	1.425	1.438	1.429	1.432	1.427	1.436		1.430	1.433
5—12	1.342	1.341	1.343	1.340	1.345	1.342	1.342	1.344	1.342	1.342	1.341	1.343	1.341	1.340	1.340	1.338
5—13	1.343	1.343	1.343	1.343		1.343				1.343	1.342	1.343	1.343		1.340	1.341
6—13	1.430	1.430	1.429	1.430		1.426				1.430	1.430	1.430	1.430		1.431	1.431
6—7	1.376	1.376	1.376	1.376		1.389				1.376	1.376	1.376	1.376		1.375	1.375
7—8	1.421	1.421	1.421	1.421		1.431				1.421	1.422	1.421	1.422		1.423	1.422
8—9	1.376	1.376	1.376	1.376		1.373				1.376	1.376	1.376	1.376		1.375	1.375
9—14	1.429	1.430	1.429	1.429		1.432				1.429	1.430	1.429	1.430		1.431	1.431
10—14	1.408	1.406	1.408	1.406		1.403				1.407	1.406	1.407	1.406		1.341	1.341
13—14	1.425	1.425	1.424	1.425		1.428				1.425	1.425	1.425	1.425		1.427	1.427
10—11	1.401	1.406	1.402	1.405	1.420	1.403	1.406	1.405	1.406	1.402	1.406	1.403	1.405		1.337	1.340
11—12	1.427	1.426	1.428	1.425	1.422	1.425	1.426	1.427	1.424	1.427	1.426	1.427	1.425	1.428	1.429	1.430
1—11	1.438	1.428	1.432	1.430	1.425	1.427	1.427	1.431	1.430	1.436	1.429	1.431	1.430	1.432	1.438	1.428
* <i>i</i> —15	1.374	1.377	1.375	1.374	1.364	1.378	1.378	1.375	1.375	1.337	1.365	1.347	1.346		1.346	1.347
* <i>j</i> —16						1.376										

\* *i*, *j* are atoms with a substituent on them.

*Table 4*  
Singlet excitation energies and intensities

Molecule	$\Delta E$ [eV]		Direction of polarization	$f$	$\log \epsilon$			
	calc.	exp.		calc.	exp.			
5-azaanthracene 1-amino	2.961	2.98	$y, x$	0.212	3.423			
	3.995		$y, x$	0.056				
	4.364		$x, y$	0.873				
	4.783		$y, x$	0.090				
	4.903		4.72	$x, y$		1.330	4.602	
	5.481			$y, x$		0.071		
	5.768		$y, x$	0.282				
	5.808		$y, x$	0.122				
	5.917		$x, y$	0.188				
	5.939		$x, y$	0.096				
	2-amino		3.066	3.06		$x, y$	0.230	3.716
			3.494			$y, x$	0.089	
			4.147	3.49		$x, y$	0.083	3.778
4.434		$x, y$	0.321					
4.698		4.77	$x, y$	2.053	4.839			
4.862			$x, y$	0.020				
5.282		$y, x$	0.012					
5.486		$x, y$	0.080					
5.567		$y, x$	0.170					
5.608		$y, x$	0.313					
5.961		$y, x$	0.032					
6.156		$y, x$	0.033					
3-amino		3.119	3.02	$x, y$	0.249	3.756		
	3.523	$y, x$		0.101				
	4.113	3.50	$x, y$	0.141	3.880			
	4.478		$x, y$	0.249				
	4.700	4.72	$x, y$	1.912	4.851			
	4.942		$x, y$	0.082				
	5.279	5.21	$x, y$	0.011	4.477			
	5.402		$x, y$	0.269				
	5.519	$y, x$	0.321					
	5.707	$x, y$	0.074					
	6.007	$y, x$	0.167					
	6.189	$x, y$	0.014					
	4-amino	2.933	3.03	$y, x$	0.189	3.491		
3.990		$y, x$		0.053				
4.320		3.80	$x, y$	0.927	3.176			
4.735			$y, x$	0.094				
4.886		4.72	$x, y$	1.159	4.638			
5.224			$x, y$	0.119				
5.390		5.18	$y, x$	0.061	4.562			
5.750			$y, x$	0.240				
5.810		$y, x$	0.110					
5.875		$x, y$	0.392					
10-amino	3.325	3.20	$y$	0.340	3.845			
	4.416		$x$	0.123				
	4.548	4.77	$x$	0.035	4.869			
	4.716		$x$	2.128				
	5.710	$x$	0.084					
	5.793	$y$	0.229					

Table 4 (Continued)

Molecule	$\Delta E$ [eV]		Direction of polarization	$f$	$\log \varepsilon$
	calc.	exp.		calc.	exp.
2,7-diamino	2.941	2.83	$x, y$	0.314	3.799
	3.531	3.54	$y, x$	0.058	3.658
	3.772	3.73	$x, y$	0.015	3.531
	4.344		$x, y$	0.033	
	4.521	4.54	$x, y$	2.498	4.839
	5.217		$x, y$	0.041	
	5.253		$x, y$	0.062	
	5.306		$x, y$	0.097	
	5.543		$y, x$	0.381	
	5.768		$y, x$	0.037	
	5.990		$x, y$	0.053	
	6.055		$x, y$	0.051	
	2,8-diamino	3.122		$x$	0.235
3.137		3.17	$y$	0.168	4.033
4.021			$x$	0.289	
4.269		4.22	$y$	0.025	4.290
4.601		4.71	$x$	1.837	4.898
4.725			$x$	0.398	
5.229			$y$	0.323	
5.420			$y$	0.050	
5.613			$x$	0.096	
5.696			$y$	0.110	
6.027		$x$	0.027		
3,7-diamino	3.119	3.13	$x$	0.341	4.158
	3.261		$y$	0.150	
	4.048		$x$	0.373	
	4.656	4.72	$x$	1.994	4.716
	4.869		$x$	0.016	
	5.051		$y$	0.280	
	5.146		$y$	0.184	
	5.489		$x$	0.186	
	5.660		$y$	0.245	
6.045		$x$	0.018		
4,6-diamino	2.950	2.91	$y$	0.279	3.591
	3.418		$x$	0.020	
	4.471	4.61	$x$	1.783	4.908
	4.726		$x$	0.209	
	5.104		$y$	0.312	
	5.780		$y$	0.063	
	5.830		$x$	0.156	
5.976		$x$	0.117		
1-hydroxy	3.176	3.10	$y, x$	0.230	3.477
	3.474	3.47	$x, y$	0.031	3.562
	4.060		$y, x$	0.041	
	4.525		$x, y$	0.859	
	4.858	4.77	$x, y$	1.008	4.716
	4.934		$x, y$	0.521	
	5.645		$x, y$	0.014	
	5.833		$y, x$	0.416	
	5.890		$y, x$	0.084	
5.962		$x, y$	0.147		

Table 4 (Continued)

Molecule	$\Delta E$ [eV]		Direction of polarization	$f$	$\log \varepsilon$
	calc.	exp.		calc.	exp.
2-hydroxy	6.112		$x, y$	0.033	
	3.244	3.26	$y, x$	0.216	3.732
	3.498	3.52	$y, x$	0.117	3.880
	4.202		$x, y$	0.026	
	4.589		$x, y$	0.183	
	4.788	4.85	$x, y$	2.274	5.029
	4.933		$x, y$	0.061	
	5.388		$y, x$	0.010	
	5.594		$y, x$	0.043	
	5.699		$y, x$	0.369	
	5.767		$y, x$	0.056	
	5.997		$y, x$	0.072	
3-hydroxy	3.279		$x, y$	0.219	
	3.518	3.44	$y, x$	0.125	4.008
	4.186		$x, y$	0.085	
	4.605		$x, y$	0.062	
	4.793	4.47	$x, y$	2.324	4.550
	4.977		$x, y$	0.022	
	5.533		$y, x$	0.184	
	5.670		$y, x$	0.265	
5.805		$x, y$	0.082		
4-hydroxy	3.168	3.22	$y, x$	0.201	3.493
	3.471	3.47	$x, y$	0.025	3.638
	4.056		$y, x$	0.033	
	4.493		$x, y$	0.904	
	4.861	4.83	$x, y$	1.162	4.893
	4.896		$x, y$	0.287	
	5.343		$x, y$	0.049	
	5.801		$y, x$	0.383	
5.891		$x, y$	0.184		
5,10-diazaanthracene	3.342		$y$	0.187	
	3.396	3.42	$x$	0.295	4.120
	4.929	4.99	$x$	2.212	5.093
	5.548		$y$	0.052	
	5.945	5.88	$y$	0.291	4.439
	6.052		$x$	0.258	
	6.109		$y$	0.385	
1-hydroxy	2.960	2.95	$y, x$	0.163	3.342
	3.410	3.33	$x, y$	0.177	4.000
	3.794		$y, x$	0.039	
	4.489		$x, y$	0.865	
	4.877	4.73	$x, y$	1.198	4.799
	5.157		$x, y$	0.103	
	5.900		$y, x$	0.667	
	6.062		$x, y$	0.192	
2-hydroxy	3.132	3.06	$x, y$	0.286	3.778
	3.413	3.39	$x, y$	0.217	3.996
	3.901		$y, x$	0.013	
	4.601		$x, y$	0.124	

Table 4 (Continued)

Molecule	$\Delta E$ [eV]		Direction of polarization	$f$	$\log \epsilon$
	calc.	exp.		calc.	exp.
	4.842	4.85	$x, y$	2.082	4.845
	5.441		$y, x$	0.062	
	5.518		$y, x$	0.055	
	5.834		$y, x$	0.519	
	5.907		$y, x$	0.098	

### Results and Discussion

The selfconsistent charge densities of the monoamino and monohydroxy derivatives and of some diamino derivatives of acridine, further those of free phenazine and its hydroxy derivatives are listed in Table 2\*. The bond lengths calculated by means of the relations

$$r_{ij} = -0.18 p_{ij} + 1.517 \quad (\text{C}-\text{C}),$$

$$r_{ij} = -0.18 p_{ij} + 1.451 \quad (\text{C}-\text{N}),$$

$$r_{ij} = -0.18 p_{ij} + 1.410 \quad (\text{C}-\text{O})$$

are listed in Table 3. The bond lengths of most the studied compounds have not been measured till now and therefore no comparison is possible; the method, however, gives good prediction for the bond lengths [7].

Table 4 brings the calculated singlet excitation energies and the oscillator strengths. There are also listed the directions of the polarization following from the interaction wave function. In the case plane polarization the direction of the more intensive component is given first. Experimental excitation energies belonging to the maxima of the intensive bonds and the values of  $\log \epsilon$  are given for comparison purposes. The comparison of the calculated and the measured intensities on the basis of *Kouteckij's* relation [20]:

$$\log \epsilon = \log f + 4$$

shows good agreement. Fig. 1 shows the measured [21] and the calculated spectra of four different derivative types of anthracene azaanalogues. The very good agreement is evident from this figure.

The structure of the UV spectra of all the studied derivatives is similar. The long wave band of the spectrum of the acridine derivatives has the character of a clear  ${}^1L_a$  band with 80–90% weight value. In the other intensive band there participate two to three configurations. The long wave band of phenazine derivatives corresponds to two related singlet excitation energies the lower one of them having

\* Before finishing our work *Seiffert et al.* [22] published the calculations of monohydroxy derivatives of acridine. The authors, however, applied another range of the configuration interaction, and therefore in the present study we are giving the results of our calculations.



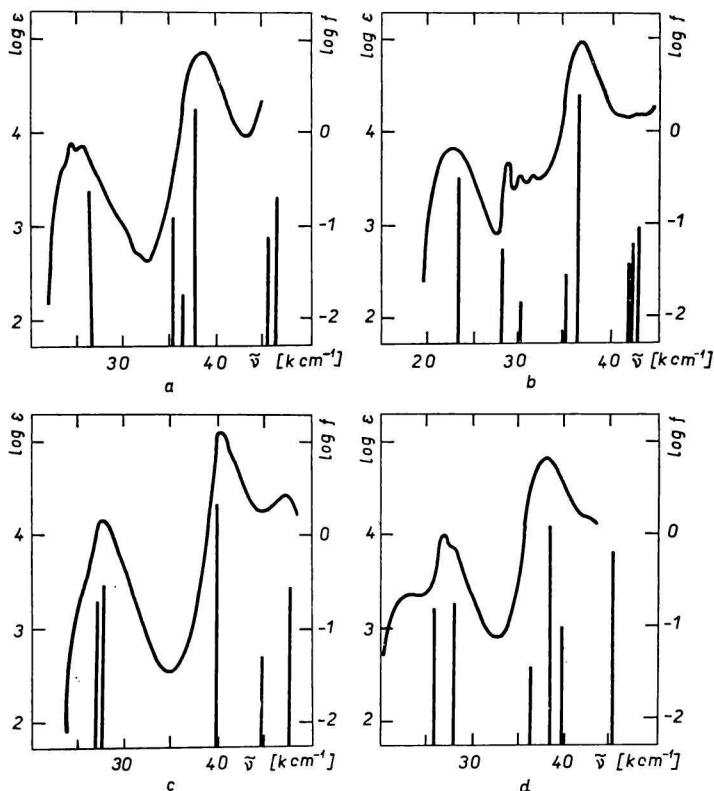


Fig. 1. Experimental and calculated UV spectra.

- a) 10-amino-5-azaanthracene; b) 2,7-diamino-5-azaanthracene; c) 5,10-diazaanthracene;  
d) 1-hydroxy-5,10-diazaanthracene.

again the character of  ${}^1L_a$  with about 90% weight. The second is connected with two configurations. Another intensive band is mostly the result of mixing two or more configurations.

The calculations have been carried out with the computer IBM 7040 in the Computing Centre of the Slovak National Council. We are grateful to Dr. P. Trgala for the programming the calculations.

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Translated by A. Farkaš