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A SEMI-EMPIRICAL SCF MO CI TREATMENT OF SOME AMINOPHENOLS AND AMINORESORCINOLS WITH A VARIABLE β APPROXIMATION

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Abstract—The semi-empirical method due to Pariser, Parr and Pople has been used to calculate π-electron properties of some conjugated molecules containing amino and hydroxy groups. Good agreement with experiment has been obtained for the UV spectra transition energies.

METHOD AND PARAMETERS

THE Pariser–Parr–Pople method[1-3] has been widely applied to the calculation of ground and excited state properties of hydrocarbons with π-electron systems and the study of molecules containing heteroatoms has received increasing attention.[4] In this paper, we extend these calculations to encompass systems containing NH_2 and OH groups.

We used a variable β modification of the P–P–P method, introduced by Nishimoto and Forster.[6] It is known that the variable β method is not sensitive to the assumed geometry. All rings were assigned regular polygonal structures with equal C—C bond lengths (1·4 Å). The C—NH_2 and C—OH bond lengths were also assumed to be 1·4 Å. The 2-centre repulsion integrals for non-neighbour atoms were computed from this conventional geometry.

The 2-centre core integrals, the bond lengths and the 2-centre repulsion integrals between neighbouring atoms were adjusted at every iteration by means of the relations:

$$\left.\begin{aligned}\beta_{\mu\nu} &= -0{\cdot}51\,p_{\mu\nu} - 2{\cdot}04\\ r_{\mu\nu} &= -0{\cdot}18\,p_{\mu\nu} + 1{\cdot}517\end{aligned}\right\}\ \text{for all C—C bonds}$$

$$\left.\begin{aligned}\beta_{\mu\nu} &= -0{\cdot}53\,p_{\mu\nu} - 2{\cdot}24\\ r_{\mu\nu} &= -0{\cdot}18\,p_{\mu\nu} + 1{\cdot}451\end{aligned}\right\}\ \text{for the C—NH}_2\text{ bonds}$$

$$\left.\begin{aligned}\beta_{\mu\nu} &= -0{\cdot}56\,p_{\mu\nu} - 2{\cdot}44\\ r_{\mu\nu} &= -0{\cdot}18\,p_{\mu\nu} + 1{\cdot}410\end{aligned}\right\}\ \text{for the C—OH bonds}$$

and the classical Nishimoto–Mataga approximation[7]:

$$\gamma_{\mu\nu} = \frac{14{\cdot}397}{a_{\mu\nu} + r_{\mu\nu}}$$

We used the empirical parameter values given in Table 1· which were found to give the best agreement with experiment.

The configuration interaction was complete.

TABLE 1. PARAMETER SUMMARY

Atom or group	I_μ (eV)	$\gamma_{\mu\mu}$ (eV)
C	11·16	11·13
NH_2	26·7	15·15
OH	32·90	21·53

TABLE 2. TRANSITION ENERGIES (eV) AND INTENSITIES (f)

Molecule	calc. ΔE	expt. ΔE	calc. f	expt. f
Phenol[8]	4·635	4·59	0·04	0·02
	5·775	5·82	0·21	0·1
	6·729	6·70	0·91	
	6·787		1·14	
2,4-Diaminophenol	4·289	4·12	0·09	0·05
	5·315	5·21	0·24	0·1
	6·251	6·01	1·21	0·6
	6·371		0·73	
2,6-Diaminophenol	4·385	4·44	0·01	0·02
	5·290	5·27	0·03	0·15
	5·989	5·84	1·08	0·7
	6·142		1·06	
Resorcinol[5]	4·507	4·48	0·03	0·02
	5·634	5·63	0·09	
	6·377		1·33	
	6·383		0·81	
2-Aminoresorcinol	4·385	4·57	0·001	0·02
	5·289	5·29	0·04	0·1
	6·050	6·05	1·16	0·66
	6·107		1·01	
4-Aminoresorcinol	4·288	4·22	0·08	0·04
	5·331	5·41	0·24	0·12
	6·289	6·27	1·10	0·65
	6·341		0·89	
2,4-Diaminoresorcinol	4·246	4·29	0·02	0·03
	5·171	5·27	0·02	0·14
	5·865	5·90	1·13	0·7
	5·957		1·06	
4,6-Diaminoresorcinol	4·148	4·03	0·12	0·1
	5·165	5·33	0·25	0·1
	6·243		0·72	
	6·247		1·42	
2,4,6-Triaminoresorcinol	4·153	4·25	0·04	0·02
	5·081	5·27	0·05	0·14
	5·826	5·83	1·04	0·6
	5·915		1·30	

TABLE 3. CALCULATED BOND LENGTHS r_{ij} (Å)

i	j	Phenol	2,4-Diamino-phenol	2,6-Diamino-phenol	Resorcinol	2-Amino-resorcinol	4-Amino-resorcinol	2,4-Diamino-resorcinol	4,6-Diamino-resorcinol	2,4,6-Tria-minoresorcinol
1	2	1·405	1·410	1·407	1·403	1·407	1·405	1·408	1·403	1·406
2	3	1·396	1·400	1·402	1·403	1·407	1·401	1·405		1·406
3	4	1·398	1·404	1·397	1·406	1·404	1·410	1·409	1·409	1·408
4	5		1·403		1·396	1·397	1·400	1·401	1·401	1·402
5	6		1·398		1·396	1·397	1·398	1·399		1·402
1	6		1·402		1·406	1·404	1·404	1·403		1·408
1	7	1·347	1·353	1·355	1·347	1·351	1·349	1·353	1·353	1·357
2	8		1·398	1·398						
4	9		1·396	1·398						
3	8				1·347	1·351	1·351	1·355		1·357
2	9					1·403		1·403		1·403
4	9						1·401		1·401	1·401
4	10							1·401		
6	11									1·401

TABLE 4. ATOMIC π CHARGE DENSITIES

Atom	Phenol	2,4-Diamino-phenol	2,6-Diamino-phenol	Resorcinol	2-Amino-resorcinol	4-Amino resorcinol	2,4-Diamino-resorcinol	4,6-Diamino-resorcinol	2,4,6-Tria-minoresorcinol
1	0·970	1·039	1·061	0·965	1·009	0·988	1·032	1·032	1·077
2	1·064	1·022	1·025	1·128	1·087	1·122	1·081	1·116	1·075
3	0·994	1·099	1·073	0·965	1·009	1·007	1·054		1·077
4	1·035	0·998	1·023	1·097	1·090	1·058	1·052	1·053	1·048
5		1·074		0·989	1·015	1·041	1·065	1·091	1·114
6		1·054		1·097	1·090	1·090	1·084		1·047
7	1·880	1·896	1·900	1·880	1·890	1·887	1·896	1·896	1·905
8		1·910	1·911	1·880	1·890	1·889	1·899		1·905
9		1·907	1·911		1·921	1·917	1·921	1·917	1·921
10							1·917		1·917
11									1·917

RESULTS

The singlet transition energies and oscillator strengths are summarized in Table 2. The experimental electronic absorption spectra were taken from a recently published atlas.[9] The experimental values uf the oscillator strengths were estimated from the absorption curves by means of the relation:[10]

$$f = 4{\cdot}32 \cdot 10^{-9}\, \varepsilon_{max}\, \Delta\bar{\nu}$$

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

The discrepancies between computed and observed singlet transitions are probably due to important steric effects between OH and NH_2 groups which cause a deviation from coplanarity.

The computed bond lengths are given in Table 3. Accurate experimental interatomic distances are lacking for most of the molecules discussed in this paper.

The atomic π charge densities are listed in Table 4. As usual, the substitution reactions are assumed to occur most readily at C atoms having:

(a) the maximum value uf π-electron density for electrophilic reactions.
(b) the minimum value of π-electron density for nucleophilic.

The computed π dipole moments are summarized in Table 5. For compounds containing π bond networks, it is usually convenient to dissect the total dipole moment into σ moment and a π moment. The σ moment is estimated from analogous systems without π bonds, and the π moment is given as the difference between the experimental total dipole moment and the estimated σ moment.

TABLE 5. THE ETICAL π DIPOLE MOMENTS

Molecule	Computed π dipole moments (Debye units)
Phenol	1·60
2,4-Diaminophen	1·35
2,6-Diaminophen	2·62
Resorcinol	1·56
2-Aminoresorcino	2·60
4-Aminoresorcino	1·37
2,4-Diaminoresor nol	2·19
4,6-Diaminoresor nol	0·26
2,4,6-Triaminores cinol	1·26

It may be seen that the computed values are of a reasonable order of magnitude, though probably somewhat too high.

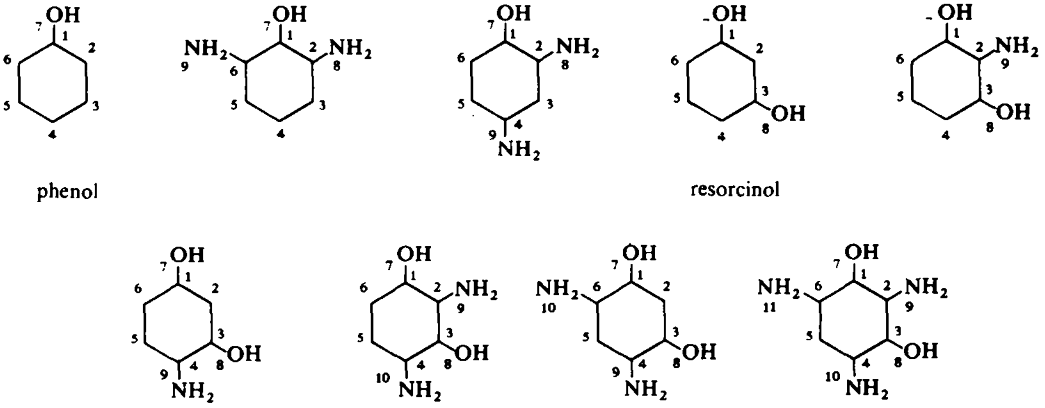

FIG. 1 Numbering scheme.

The calculations were performed on an IBM 7044 computer. We used the program No. 71 distributed by the QCPE organization,[11] which was modified to include the variable β procedure.

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