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LCAO-MO-SCF-CI Semi-Empirical π-Electron Calculations on Heteroaromatic Systems

II. Amino Aromatic Compounds*

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The electronic spectra and structures of aromatic monoamino and diamino compounds have been calculated using a modification of the Pariser-Parr-Pople method. Electronic transitions investigated involve singlet-singlet and triplet-triplet π–π^* excitations. A limited configuration interaction has been included involving single electron excitations and both single and double electron excitations between the two highest occupied and two lowest unoccupied molecular orbitals. Improvement of oscillator strengths was observed with increasing number of configurations considered. Good agreement was obtained between calculated and experimental molecular ionization potentials.

Mono- und Diaminoaromaten wurden mit der modifizierten PPP-Methode von ADAMS und MILLER untersucht, speziell ihre π–π^*-Übergänge und Ionisationspotentiale. CI- Rechnungen mit einfachangeregten Konfigurationen wie mit einfach- und doppeltangeregten Konfigurationen zeigten eine mit der Zahl der Konfigurationen steigende Verbesserung der Oszillatorenstärken.

Les spectres électroniques et les structures de composés aromatiques mono et di-aminés ont été calculés en utilisant une variante de la méthode de Pariser-Parr-Pople. Les transitions électroniques étudiées sont les transitions $\pi \rightarrow \pi^*$ singulet-singulet et triplet-triplet. Une interaction de configurations limitée est introduite en considérant des mono et des di excitations entre les deux plus hautes orbitales moléculaires occupées et les deux plus basses libres. Les forces oscillatrices sont améliorées lorsque le nombre de configurations considérées augmente. Un bon accord est obtenu entre les poteientls d'ionisation moléculaire calculés et expérimentaux.

Introduction

Recent investigations by ADAMS and MILLER [2] on aromatic hydrocarbons elucidated a method to circumvent one major limitation of semi-empirical calculations, that of the degree of applicability to various molecular properties. Most semi-empirical methods of calculation can be calibrated to satisfactorily describe one property of a molecule, for example the electronic spectrum; however, general applicability to several molecular properties such as electronic spectra, electronic structure, and molecular ionization potential has been lacking.

Using the method described in the first paper of this series [24] to evaluate the core integrals of heteroatoms, the electronic structure and spectra of aniline, *o*-phenylenediamine, *m*-phenylenediamine, *p*-phenylenediamine, α-naphthylamine,

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and β-naphthylamine have been calculated. Löwdin orthogonalized atomic orbitals and a limited configuration interaction were used. Calculated results are in good agreement with experimental values; calculated oscillator strengths show improvement with more extensive configuration interaction treatment.

Method

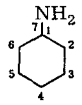
The method of calculation used in this investigation including core integral evaluation and calculation of electronic and molecular properties is described in Part I of this series of papers [24].

Table 1. *Valence State Data and Effective Nuclear Charges Used for Carbon and Nitrogen Atoms*

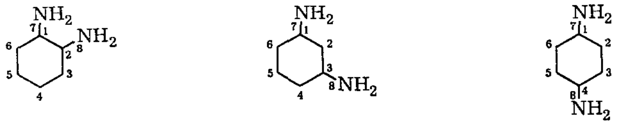
Property	Carbon	Nitrogen
First Ionization Potential	11.16[a,b]	14.12[c,d]
Second Ionization Potential	—	27.73[c]
First Electron Affinity	0.03[a,b]	1.78[c,d]
Second Electron Affinity	—	14.12[c]
Effective Nuclear Charge	3.25[e,f,g]	3.90[e,f,g]

[a] See Ref. [13].
[b] For the sp^3 valence state.
[c] See Ref. [15].
[d] For the sp^4 valence state.
[e] See Ref. [19].
[f] See Ref. [20].
[g] See Ref. [21].

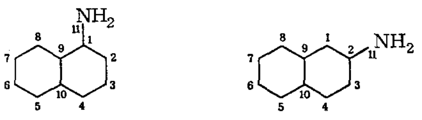
The benzene and naphthalene derivatives were assumed to be planar and to have regular hexagonal and bihexagonal structures with the following bond lengths [1, 7]: $R_{\mathrm{C-C}} = 1.396$ Å and $R_{\mathrm{C-N}} = 1.360$ Å.



Aniline



o-phenylenediamine m-phenylenediamine p-phenylenediamine



α-naphthylamine β-naphthylamine

Fig. 1. Numbering scheme for aromatic amino compounds

The procedure for evaluating the empirical parameters H^0_{ij} given in the previous paper (Part I) was used in this investigation with the exception that aniline was employed as the calibration molecule for the amino compounds. The time required to carry out the calculations ranged from 12 min for aniline (Method I) to 90 min for α-naphthylamine (Method II) using a G-20 Control Data Corporation digital computer.

Valence state data and the effective nuclear charge for carbon and nitrogen are given in Table 1.

The numbering system for the six amino derivatives is given in Fig. 1.

Results and Discussion

Results for the six amino compounds are shown in Tables 2 through 7 and include singlet and triplet transition energies and oscillator strengths, calculated molecular ionization potentials, π-electron charge densities and π-dipole moments, together with known experimental values. Table 2 lists the values of the H^0 parameters used in the calculations.

Calculation of the electronic spectra of aniline by several investigators [3, 5, 9, 10] using both SCF and Hückel techniques demonstrated that calculated transition energies were generally in good agreement with experimental values and the cal-

Table 2. *Values for the Empirical Parameter* H^0_{ij}*

Molecule	Element	Value	
		Method I	Method II
Aniline	H^0_{11}	−11.597	−11.388
	H^0_{12}	− 4.322	− 3.882
	H^0_{13}	− 0.856	− 0.745
	H^0_{14}	− 0.264	− 0.235
	H^0_{17}	− 4.772	− 4.908
	H^0_{27}	− 0.810	− 0.772
	H^0_{37}	− 0.078	− 0.070
	H^0_{47}	− 0.024	− 0.023
	H^0_{77}	−20.893	−22.302
o-phenylenediamine	H^0_{78}	− 0.107	− 0.200
m-phenylenediamine	H^0_{78}	− 0.001	− 0.001
p-phenylenediamine	H^0_{78}	0.000	0.000
α-naphthylamine	H^0_{15}	− 0.050	− 0.045
	H^0_{16}	− 0.010	− 0.009
	H^0_{26}	− 0.001	− 0.001
	H^0_{36}	− 0.002	− 0.002
	$H^0_{5,11}$	− 0.003	− 0.003
	$H^0_{6,11}$	− 0.003	− 0.003
	$H^0_{7,11}$	− 0.015	− 0.014
	$H^0_{8,11}$	− 0.153	− 0.140
β-naphthylamine	$H^0_{5,11}$	0.000	0.000
	$H^0_{6,11}$	0.000	0.000
	$H^0_{7,11}$	0.000	0.000
	$H^0_{8,11}$	− 0.024	− 0,023

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* See Fig. 1 for numbering scheme.

Table 3. *Transition Energies (in* eV*) and Oscillator Strengths**

Molecule	Singlet States			Triplet States	
	Method I	Method II	Experimental	Method I	Method II
Aniline	4.31 (0.083)	4.31 (0.043)	4.31[a] (0.03)[b]	3.11 (0.035)	3.00 (0.023)
	5.30 (0.485)	5.28 (0.154)	5.27[c] (0.17)[b]	3.26 (0.058)	3.33 (0.021)
	6.68 (0.787)	6.39 (0.575)	6.30[c] —	3.74 (0.045)	3.65 (0.008)
	6.74 (1.028)	7.97 (0.117)	> 7.06[c] —	5.14 —	4.84 (0.000)
o-phenylenediamine	4.11 (0.178)	3.99 (0.075)	4.21[d] (0.039)	2.93 (0.037)	2.84 (0.027)
	4.73 (0.355)	4.72 (0.125)	5.19 (0.11)	3.05 (0.129)	3.00 (0.041)
	6.03 (0.436)	5.83 (0.648)	5.69 —	3.76 (0.003)	3.45 (0.035)
	6.25 (1.362)	6.06 (0.515)	— —	4.67 —	4.45 (0.005)
m-phenylenediamine	4.38 (0.094)	4.11 (0.008)	4.21[d] (0.024)	3.19 (0.075)	2.97 (0.027)
	5.22 (0.101)	4.90 (0.002)	5.20 (0.19)	3.23 (0.145)	3.12 (0.076)
	5.69 (0.565)	5.49 (0.541)	5.63 —	3.94 (0.161)	3.57 (0.007)
	5.75 (1.383)	5.81 (0.871)	— —	4.46 —	4.38 (0.001)
p-phenylenediamine	3.98 (0.332)	4.16 (0.092)	4.05[d] (0.038)	2.52 (0.000)	2.80 (0.000)
	5.02 (1.022)	5.34 (0.316)	5.08 (0.17)	3.05 (1.393)	2.95 (0.000)
	5.95 (0.000)	6.56 (0.655)	6.14 —	5.09 (0.000)	3.75 (0.000)
	6.87 (0.000)	6.83 (0.512)	— —	5.74 —	5.43 (0.601)
α-naphthylamine	3.78 (0.400)	3.76 (0.186)	3.73[e] (0.13)	2.35 (0.019)	2.28 (0.011)
	4.09 (0.072)	3.84 (0.047)	3.90 (0.13)	3.39 (0.057)	3.22 (0.001)
	5.51 (1.565)	5.19 (1.155)	5.11 (0.34)	4.26 (0.008)	3.86 (0.013)
	6.52 (0.807)	6.00 (0.517)	5.88 (0.82)	4.39 —	3.92 (0.067)
β-naphthylamine	3.70 (0.201)	3.54 (0.108)	3.56[e] (0.033)	2.17 (0.265)	2.29 (0.077)
	4.49 (0.102)	4.14 (0.056)	4.44 (0.10)	3.27 (0.006)	3.11 (0.000)
	5.38 (1.946)	5.11 (1.242)	5.25 (0.86)	3.84 (0.013)	3.56 (0.004)
	6.03 (0.755)	5.62 (0.534)	— —	4.72 —	4.23 (0.209)

* Values for oscillator strengths are in parenthesis.

[a] See Ref. [12].

[b] See Ref. [5].

[c] See Ref. [14].

[d] All experimental values for *o*-, *m*-, and *p*-phenylenediamine have been taken from Ref. [11].

[e] All experimental values for α- and β-naphthylamine have been taken from Ref. [4].

culated oscillator strengths were generally too high. Similar results were observed for the calculated electronic spectra of the isomeric forms of phenylenediamine [16] and for α- and β-naphthylamine [4].

A comparison of the calculated transition energies given in Table 3 with experimental values shows that good agreement is obtained for all of the molecules investigated. The largest deviation from an experimental value is 0.6 eV for the fourth singlet transition energy of α-naphthylamine using one-electron excitation (Method I) in the CI calculations; the average deviation from experimental transition energies for this method is approximately ±0.15 eV.

The largest deviation from experimental transition energies for the one- and two-electron excitation calculations (Method II) is 0.5 eV for the second singlet transition energy of *o*-phenylenediamine with an average deviation of approximately ±0.1 eV. The calculated oscillator strengths using one-electron excitations

Table 4. *Molecular Ionization Potentials*

Compound	Ionization Potential, eV		
	Method I	Method II	Observed
Aniline	7.67	7.89	7.69[a]
o-phenylenediamine	6.77	7.15	7.45[b]
m-phenylenediamine	7.18	7.42	7.35[c]
p-phenylenediamine	6.56	6.96	7.15[b]
α-naphthylamine	7.28	7.39	7.30[a]
β-naphthylamine	7.43	7.55	7.25[a]

[a] See Ref. [23].
[b] See Ref. [6].
[c] See Ref. [22].

(Method I) generally gave poor agreement with experimental values; however, incorporation of more configurations (Method II) improved agreement with experimental values.

The carbon-nitrogen interatomic distance was varied from 1.36 Å to 1.46 Å; the change in the electronic spectra was about 0.01 eV which agrees with the results reported by PEACOCK [18].

Table 4 lists the molecular ionization potentials of the compounds investigated. The calculated ionization potentials agree quite well with the experimental values. This method of calculation appears to provide satisfactory values for the molecular ionization potential while simultaneously predicting the electronic spectra with reasonable accuracy.

Table 5 gives calculated localized atom charge distributions. The calculated atom π-charge density of aniline shows a higher π-electron charge density on the ortho position than on the para position; this result is in agreement with calculated values reported by FISCHER-HJALMARS [9].

The calculated ground state π-dipole moments given in Table 6 for all of the molecules are higher than those reported by other investigators [8, 17]. The choice of H^0 parameters necessary to achieve agreement with observed electronic spectra resulted in reduction of the value of the one-center nitrogen H^0 term which is related to the nitrogen valence state ionization potential. This reduction allowed the electrons to move more freely into the ring system and increased the calculated ground state π-dipole moment. Non-localized atom and bond charge distributions are shown in Table 7. Each atomic center is approximately 0.2 electrons deficient with each bond between adjacent carbon atoms having an excess of about 0.2 electron; the carbon-nitrogen bond has an excess of about 0.1 electron.

Table 6. *Calculated π-Electron Dipole Moments (in Debyes)*

Molecule	π-Electron Dipole Moment	
	Method I	Method II
aniline	2.78	2.58
o-phenylenediamine	4.43	4.04
m-phenylenediamine	2.66	2.49
p-phenylenediamine	0.00	0.00
α-naphthylamine	3.12	2.67
β-naphthylamine	3.20	3.01

Table 5. *Localized Atom Charges* (q_i)*

Molecule	Method	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	q_{10}	q_{11}
Aniline	I	0.956	1.019	0.990	1.063	0.990	1.019	1.784				
	II	0.938	1.103	0.994	1.060	0.994	1.103	1.813				
o-phenylenediamine	I	1.034	1.034	1.105	1.048	1.048	1.105	1.814	1.814			
	II	1.014	1.014	1.101	1.046	1.046	1.101	1.840	1.840			
m-phenylenediamine	I	0.947	1.221	0.947	1.164	0.982	1.164	1.788	1.788			
	II	0.926	1.209	0.926	1.156	0.991	1.156	1.818	1.818			
p-phenylenediamine	I	1.001	1.095	1.095	1.001	1.095	1.095	1.810	1.810			
	II	0.978	1.094	1.094	0.978	1.094	1.094	1.834	1.834			
α-naphthylamine	I	0.963	1.142	0.987	1.088	1.016	1.005	1.021	1.031	1.028	0.960	1.759
	II	0.928	1.129	0.987	1.071	1.017	1.008	1.018	1.034	1.036	0.964	1.808
β-naphthylamine	I	1.150	0.959	1.083	0.996	1.009	1.026	1.004	1.031	0.957	1.005	1.779
	II	1.139	0.928	1.084	0.999	1.011	1.026	1.004	1.029	0.963	1.004	1.813

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* See Fig. 1 for numbering scheme.

Table 7. *Nonlocalized Atom and Bond Charges* (q_{ij})*

Molecule	Method	q_{11}	q_{22}	q_{33}	q_{44}	q_{77}	q_{12}	q_{23}	q_{34}	q_{17}		
Aniline	I	0.695	0.900	0.757	0.841	1.738	0.208	0.246	0.237	0.122		
	II	0.683	0.902	0.774	0.844	1.776	0.206	0.227	0.230	0.104		
		q_{11}	q_{33}	q_{44}	q_{77}	q_{12}	q_{23}	q_{34}	q_{45}	q_{17}		
o-phenylenediamine	I	0.793	0.894	0.825	1.782	0.189	0.229	0.226	0.247	0.092		
	II	0.781	0.896	0.829	1.815	0.195	0.224	0.217	0.244	0.077		
		q_{11}	q_{22}	q_{44}	q_{55}	q_{77}	q_{12}	q_{34}	q_{45}	q_{17}		
m-phenylenediamine	I	0.684	1.033	0.962	0.747	1.743	0.213	0.205	0.243	0.124		
	II	0.675	1.022	0.957	0.764	1.781	0.211	0.203	0.235	0.103		
		q_{11}	q_{22}	q_{77}	q_{12}	q_{23}	q_{17}					
p-phenylenediamine	I	0.748	0.884	1.774	0.215	0.238	0.102					
	II	0.736	0.894	1.805	0.212	0.218	0.087					
		q_{11}	q_{22}	q_{33}	q_{44}	q_{55}	q_{66}	q_{77}	q_{88}	q_{99}	$q_{10,10}$	$q_{11,11}$
α-naphthylamine	I	0.713	0.938	0.753	0.881	0.800	0.774	0.794	0.812	0.784	0.700	1.710
	II	0.683	0.925	0.758	0.864	0.803	0.781	0.795	0.818	0.794	0.709	1.768
		q_{12}	q_{23}	q_{34}	$q_{4,10}$	$q_{5,10}$	q_{56}	q_{67}	q_{78}	q_{89}	q_{19}	$q_{1,11}$
α-naphthylamine	I	0.239	0.207	0.274	0.178	0.181	0.277	0.204	0.274	0.190	0.153	0.129
	II	0.246	0.199	0.274	0.178	0.179	0.275	0.197	0.273	0.184	0.157	0.108
		q_{11}	q_{22}	q_{33}	q_{44}	q_{55}	q_{66}	q_{77}	q_{88}	q_{99}	$q_{10,10}$	$q_{11,11}$
β-naphthylamine	I	0.959	0.698	0.869	0.777	0.791	0.798	0.774	0.817	0.696	0.753	1.733
	II	0.947	0.673	0.873	0.783	0.797	0.801	0.778	0.817	0.705	0.753	1.774
		q_{12}	q_{23}	q_{34}	$q_{4,10}$	$q_{5,10}$	q_{56}	q_{67}	q_{78}	q_{89}	q_{19}	$q_{2,11}$
β-naphthylamine	I	0.242	0.171	0.285	0.176	0.184	0.277	0.201	0.278	0.179	0.185	0.124
	II	0.246	0.173	0.277	0.177	0.179	0.274	0.198	0.274	0.178	0.181	0.106

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* See Fig. 1 for numbering scheme.

Conclusions

The present calculations of the electronic structure and spectra of aromatic amines have demonstrated the capability of a semi-empirical scheme of calculation to predict electronic structures and spectra of related compounds using one basic set of parameters. It extends the method of ADAMS and MILLER from aromatic hydrocarbons to any general aromatic system containing heteroatoms. Using calibration H^0 values from benzene, naphthalene, and aniline, calculated transition energies, oscillator strengths, and molecular ionization potentials of other aromatic amines give good agreement with observed values. The present method of calculation is an improvement of existing methods in two respects: 1. The calculations for the various amines use one basic parameter set. In other work, no single set of parameters has accurately predicted experimental transition energies, oscillator strengths, and molecular ionization potentials simultaneously. 2. The present calculated values for transition energies and oscillator strengths, generally, give better agreement with observed values than those of previous investigations. The present method gives transition energies with an average deviation of approximately $\pm 4\%$ and oscillator strenghts to the correct order of magnitude.

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