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Electronic Spectra and Dipole Moments of *p*-Phenylendiamine-*N*-*N'*-dibenzylidene and Its Aza-derivatives

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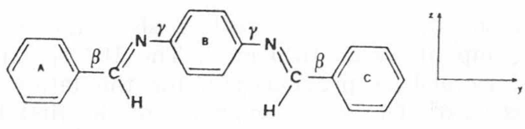
The synthesis of three unreported aza-derivatives of *p*-phenylendiamine-*N*-*N'*-benzylidene is described. Their electronic spectra are discussed on the basis of solvent shift measurements and an INDO/S-CI calculation on the parent compound. The dipole moments of the ground and the first two excited states are also reported. The analysis of the results obtained seems to confirm for every molecule the same molecular conformation as that obtained for benzylidenaniline by crystallographic studies.

INTRODUCTION

The benzylideneaniline (BA) derivatives are of remarkable interest owing to their ability to give mesophases. Here we report the electronic spectra and the ground and excited dipole moments of *p*-phenylenediamine-*N*-*N'*dibenzylidene (PPDD, referred as compound *I*) and three new aza-derivatives (compounds *II, III* and *IV*). The UV spectrum features of the parent compound *I* have been theoretically investigated at INDO/S level by assuming a molecular geometry in which the benzylidenic fragments are twisted by 55^0 around the C-N bond whilst the terminal benzene rings are rotated by 45^0.



These angle values were found by a crystallographic study on benzylideneaniline[1] and agree fairly well with the theoretically predicted values[2,3]. The absence of *ortho*-substitution suggests that the transfer of geometrical data from BA to PPDD is reasonable.

EXPERIMENTAL AND CALCULATIONS

The amine and pyridin-aldehyde isomers required for the synthesis of the title compounds were available commercially. Compound *I* was prepared by dissolving equivalent quantities of *p*-phenylenediamine and benzaldehyde in absolute ethyl alcohol. For the aza-substituted ones (compounds *II, III, IV*) equivalents of pyridin-aldehyde and amine were refluxed in benzene for about five hours and the H_2O of reaction removed azeotropically. The product yield was 70—80%. In each case the crude products were purified by several crystallizations at low temperature from anhydrous ethanol to constant melting point (reported in Table 1) and positively verified by elementary analysis.

TABLE I

Electronic Spectra (Cyclohexane Solution), Ground and Excited State Dipole Moments of the Studied Compounds

Compound[a]	λ_{max}/nm	ε_{max}	f[b]	a[c]/Å	μ_g[c]/D	μ_e[c]/D
I (139—140)	237	18200	—	4.42	1.90	—
	274	20470	0.63	—	—	3.10
	354	22050	0.51	—	—	0.29
II (150)	237	16700	—	4.36	2.24	—
	285	17100	0.54	—	—	3.49
	360	21040	0.48	—	—	2.30
III (155)	238	18100	—	4.36	2.31	—
	276	16660	0.55	—	—	6.32
	359	19400	0.46	—	—	1.65
IV (188)	231.5	16630	—	4.36	1.44	—
	277	14500	0.48	—	—	4.32
	361	16900	0.36	—	—	1.89
BA	222	16500	—	—	—	—
	262	17200	—	—	—	—
	318	7350	—	—	—	—

[a] I = *p*-phenylenediamine-*N*-*N*'-dibenzylidene; II = *p*-phenylenediamine-*N*-*N*'-dipyrilidene-2-2'; III = *p*-phenylenediamine-*N*-*N*'-dipyrilidene-3,3'; IV = *p*-phenylenediamine-*N*-*N*'-dipyrilidene-4,4'; BA = benzylideneaniline. The melting points are given in parentheses.

[b] The oscillator strengths are evaluated according to Mulliken (see ref. 15).

[c] a is the cavity; μ_g (in anhydrous benzene solution at 25 ± 1 °C) and μ_e are the ground and excited state dipole moments respectively.

The IR spectra, in potassium bromide pellets, show the strong characteristic band of the CN group at about 1620 cm^{-1}. The UV spectra and the dipole moments were determined as previously[4,5]; for the latter the Guggenheim-Smith method was used[6]. The dipole moments of the first two excited states were obtained by means of the solvent shift theory[7], by applying the Amos and Burrows equation[8]; the cavity radius, a, was evaluated from the molecular volume[9]. Figure 1 shows the maxima of the absorption bands against $\Phi(D)$ (defined as $\Phi(D) = (D - 1)/(D + 2)$, where D is the dielectric constant of the solvent). The physical properties of the solvents are those previously utilized[10,11].

The INDO/S method, parameterized as described in ref. 12, was employed in order to rationalize the experimental absorption bands; 120 monoexcited configurations were considered in the CI treatment. Referring to the molecular scheme we have taken into account four possible conformations: *over-over-trans*, *over-over-cis*, *over-under-trans* and *over-under-cis* with respect to the central phenyl ring.

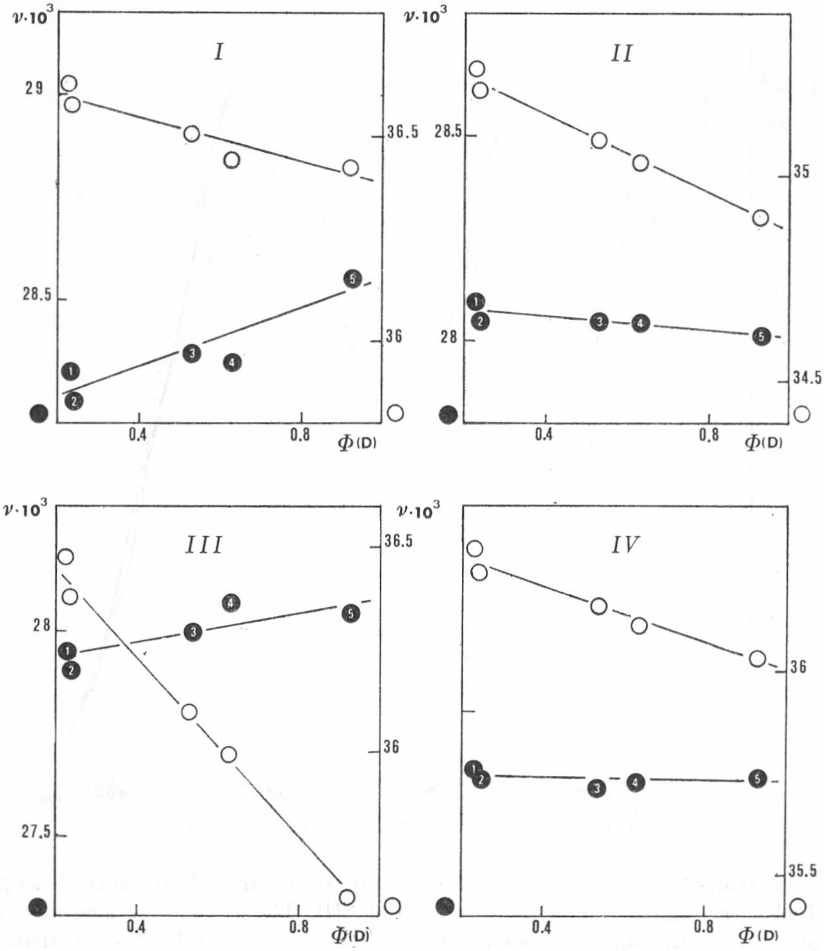


Figure 1. Plots of ν_{max} against Φ(D): ● C band; ○ B band. Solvents: 1) *n*-pentane; 2) *n*-hexane; 3) ethyl ether; 4) ethyl acetate; 5) acetonitrile; 6) dimethylformamide; 7) methanol; 8) ethyl alcohol (abs).

DISCUSSION

The UV spectra of the studied compounds (figure 2) show three absorption bands in the range 230—240 nm (band A); 275—285 nm (band B) and 355—360 nm (band C). Table 2 shows the theoretical transition energies and relative composition for compound *I*. Comparison of the spectra shows no remarkable difference on passing from the parent molecule to its aza-derivatives, except in the shape of band A. With respect to the corresponding band of BA, it can be seen that the A and B bands undergo only moderate changes in intensity and energy, while the C band shifts remarkably to longer wavelengths and greatly increases its intensity. This behaviour could be explained by assuming that the C band is prevalently due to a $\pi^* \leftarrow \pi$ transition involving the whole π-system. On the contrary, the solvent shift results clearly attributes to it the characteristic behaviour of a $\pi^* \leftarrow n$ transition. In fact, while an increase of the excited state dipole moments is observed for band B (as expected for

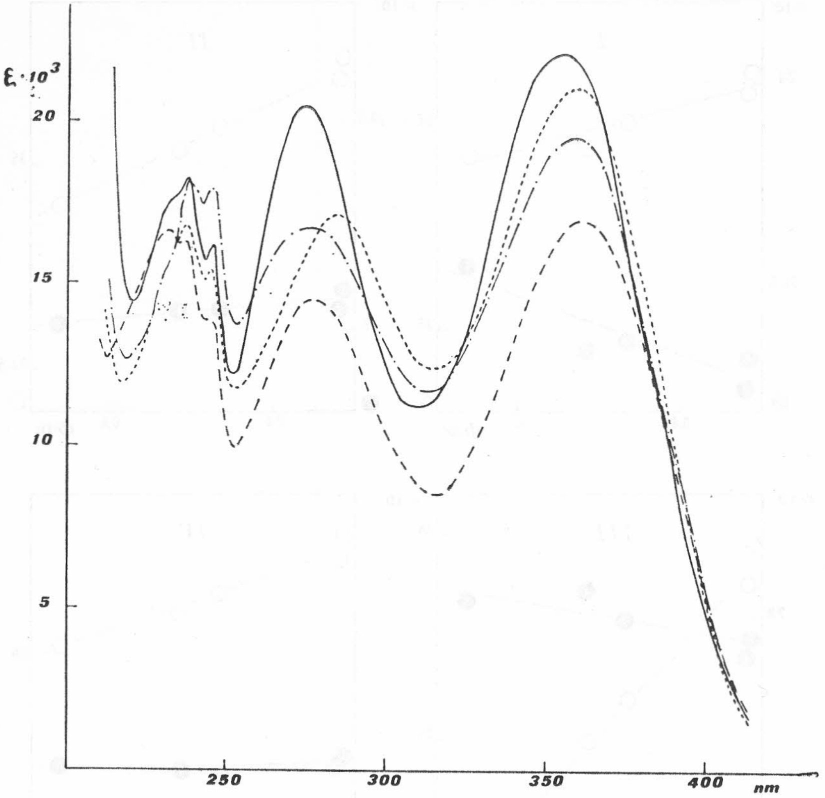


Figure 2. UV spectra in cyclohexane solution: I ——; II — — —; III —·—·—·—; IV - - - - - - -.

a $\pi^* \leftarrow \pi$ transition), the $\Delta\mu$ values for band C are about zero (compounds *II* and *IV*) or negative (compounds *II* and *III*). These results become comprehensible by assuming a superimposition of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions. This is confirmed by the theoretical data since the first two calculated transitions, attributable to the C band, have both a $\pi^* \leftarrow \pi$ and a $\pi^* \leftarrow n$ nature in comparable weight. On the other hand a $\pi^* \leftarrow n$ transition at about 346 nm was hypothesized for BA on the basis of a Gaussian resolution of its spectrum[13]. Band B and band A, assigned to the transitions calculated at 4.77 eV and 5.60 eV, are confirmed to have a $\pi^* \leftarrow \pi$ nature. The weakly allowed transitions predicted at 4.49 eV and 4.69 eV are not evident in the experimental spectrum probably because they are submerged by the strong absorption at 4.77 eV. It is interesting to point out that, from an analysis of the involved MOs, the theoretical transition at 4.49 eV is almost exclusively the benzenic *p* band. The two weak transitions calculated at 5.10 eV and 5.62 eV are experimentally found as a little maximum at 5.04 eV and a shoulder at 5.31 eV.

Apart from the calculated dipole moment values, which however were somewhat overestimated, the calculated spectrum does not change in the four examined conformations. A vectorial composition, assuming the benzylideneaniline or the benzylidenemethylamine dipole moment[14] as the group moment for the C-N bond and assigning equal probability for all the possible limit

TABLE II

Electronic Spectrum of p-Phenylendiamine-N-N'-dibenzylidene (OOC form[a])

ΔE/eV	f	Pol.	Nature	Sym.	Composition (%)[b]	Exp.	f[c]	MO	ε_i	Sym.	Nat.	Mainly located on
3.62	0.053	x	$\pi^* \leftarrow \pi, n$	A″	$30V_{53}^{54}$; $23V_{47}^{55}$; $12V_{46}^{54}$			46	—10.32	a″	n	N atoms
3.66	0.100	— 43[d]	$\pi^* \leftarrow \pi, n$	A′	$24V_{53}^{55}$; $27V_{47}^{54}$; $12V_{46}^{55}$	3.50	0.51	47	—9.88	a′	n	N atoms
4.49	0.021	4	$\pi^* \leftarrow \pi$	A′	$62V_{53}^{58}$; $21V_{51}^{59}$			48	—9.49	a″	π	phenyls A and C
4.69	0.008	x	$\pi^* \leftarrow \pi$	A″	$22V_{48}^{54}$; $23V_{49}^{55}$; $22V_{52}^{56}$; $16V_{50}^{57}$			49	—9.49	a′	π	phenyls A and C
4.69	0.004	45	$\pi^* \leftarrow \pi$	A′	$22V_{49}^{54}$; $22V_{52}^{57}$; $24V_{48}^{55}$; $16V_{50}^{56}$			50	—9.24	a″	π	delocalized
4.77	1.414	x	$\pi^* \leftarrow \pi$	A″	$49V_{53}^{54}$; $13V_{52}^{55}$; $10V_{53}^{59}$; $10V_{50}^{54}$	4.52	0.63	51	—9.21	a′	π	phenyl B
5.10	0.040	54	$\pi^* \leftarrow \pi$	A′	$58V_{53}^{55}$; $10V_{47}^{54}$; $11V_{52}^{54}$	5.04		52	—9.09	a′	π	phenyl A and C
5.60	0.384	x	$\pi^* \leftarrow \pi$	A″	$19V_{53}^{59}$; $16V_{50}^{54}$; $16V_{52}^{55}$; $15V_{46}^{54}$; $10V_{53}^{54}$	5.23	(4.30)	53	—8.14	a″	π	phenyl B and N atoms
5.62	0.011	54	$\pi^* \leftarrow \pi$	A′	$41V_{52}^{54}$; $28V_{50}^{55}$; $10V_{47}^{54}$	5.32_{sh}		54	—0.80	a′	π*	delocalized
								55	—0.67	a″	π*	phenyls A and C + N atoms
								56	—0.04	a″	π*	phenyls A and C
								57	—0.04	a′	π*	phenyls A and C
								58	+0.22	a″	π*	phenyl B
								59	+0.33	a′	π*	phenyl B + weak deloc.

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[a] The calculated electronic spectrum for the remaining conformations (here not reported) shows no appreciable variations.

[b] Only configurations with weight equal to or greater that 10% are reported.

[c] Value in parentheses is log ε.

[d] Angle between the transition moment and the Y axis in the YZ plane.

structures, gave a value of 2.06 D for the dipole moment of *I*, in good agreement with the experimental value of 1.90 D. Nevertheless this is not a valid basis for determining the most probable conformation because nearly equal figures are obtained for both planar and perpendicular structures. On the other hand the planar form is to be excluded since both *cis* and *trans* conformations are improbable due to steric hindrance, while the perpendicular one opposes the conjugation, in contrast to the experimental evidence of the UV spectrum (band C). The results as a whole allow us to conclude that the assumed geometry is acceptable and appears to be the most probable.

Since the experimental spectra of the pyridinic derivatives are similar to those of PPDD no detectable structural variation is to be expected, so that no theoretical calculations have been performed. Differences are to be expected only in the dipole moment values, which, logically, must be lower in the *p-p'*-derivatives and higher in the *meta* and *ortho* ones. This expectation is confirmed by the experimental values.

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SAŽETAK

Elektronski spektri i dipolni momenti *p*-fenilendiamin-*N,N'*-dibenzilidena i njegovih aza-derivata

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Opisana je priprava triju aza-derivata *p*-fenilen-diamina-*N,N'*-dibenzilidena. Njihovi su spektri asignirani na temelju spektralnih pomaka u raznim otapalima i teorijskih računa provedenih pomoću INDO/S CI metode. Dane su i eksperimentalne vrijednosti dipolnih momenata u temeljnom stanju i u prva dva pobuđena stanja. Računske vrijednosti dipolnih momenata su nešto veće od eksperimentalnih. Predviđena je i konformacija studiranih molekula.

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