

ELECTRONIC STRUCTURE OF ARYLAMINES. ELECTRONIC SPECTRA AND CHARGE DISTRIBUTIONS

P. ZACH and S. NEŠPŮREK

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

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By using the HMO and Pariser-Pople-Parr methods, the electronic spectra of some oligoaniline donors were studied, and the results were compared with the experiment. The distributions of electron densities in the ground state and excited singlet states were calculated. For a molecule of diphenylamine, the amount of charge transfer in the decomposition of several lowest singlet excited states was determined.

The problem of electrical conductivity of aniline black and its salts, and also of complexes of *p*-phenylenediamine and its *N*-alkyl derivatives has been dealt with in several papers¹⁻³. The same can be said about linear oligoaniline derivative and their complexes⁴⁻⁸. The donor activity of oligomers increases with the length of the chain to a certain limit value. The same dependence in connection with the decrease of the ionization potential of bases is exhibited also by the electrical conductivity of complexes in which they represent the donor component. It is evident that oligomers which are extended in the sense of their homologous series represent a suitable model for an investigation of a polymer having the same structural unit⁵.

At present, data on the electronic structure and spectral properties of bases alone are lacking, with certain exceptions⁹⁻¹¹. The present paper is devoted to an investigation of the electronic spectra and the localization of the π -electron charge on molecules of polyaniline compounds, both experimentally and theoretically, using the HMO method, and in some cases also using a method of limited configuration interaction (LCI) of monoexcited configurations set up with the aid of selfconsistent molecular orbitals.

The compounds were prepared by a method described earlier⁵. Aniline was purified by distillation *in vacuo* (pressure 10^{-2} Torr), the other amines by crystallizing several times from ethanol or dioxane (the solution was bubbled through with hydrogen in the presence of 5% palladium on charcoal). The solutions in spectrally pure ethanol and cyclohexane were prepared in an argon atmosphere directly before measurement. The samples in the solid state were prepared in the form of thin layers, deposited by sublimation on uvial glasses *in vacuo* (pressure 10^{-5} Torr). The ultraviolet absorption spectra were recorded with a recording spectrophotometer CF-4 Optica Milano. The molar extinction coefficients, $\epsilon(\nu)$, were determined from Lambert-Beer's law; no substantial deviations from this law could be observed within the concentration range under investigation. The oscillator strength of the electronic transition characterized by the extinction curve $\epsilon(\nu)$ was determined¹²⁻¹⁴ from the equation $f = 4.32 \cdot 10^{-9} \int_0^{\infty} \epsilon(\nu) d\nu$, in which the value of the inte-

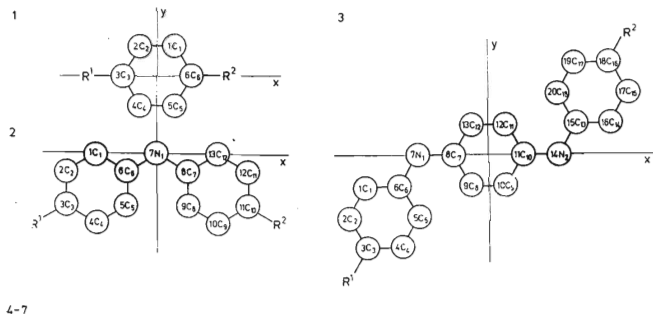
gral was approximated by the expression $\epsilon_{\max} \cdot \Delta\nu$, where ϵ_{\max} is the optical extinction in the maximum, and $\Delta\nu$ is the band halfwidth in cm^{-1} .

RESULTS AND DISCUSSION

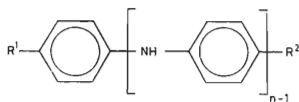
Experimental Data

The experimental absorption electronic spectra of the compounds under investigation presented formally in Scheme 1 in the planar *trans*-conformation along with the numbering of atoms introduced to simplify the presentation of results are shown in Fig. 1. Cyclohexane was used as solvent in the spectral measurements; in the series A, ethanol was used, since the higher members ($n \geq 4$) are little soluble in cyclohexane.

The spectra thus recorded exhibit three characteristic bands at 200, 230–265 and 280–320 nm, similarly to the monosubstituted derivatives of benzene (200, 230–254, 286–296 nm)¹³. The absorption intensity of bands increases with the increasing chain length in the homologous series if the same molar concentration is preserved. The positions of the absorption maxima suggest that in the case of this increase, and starting from a certain member of the series, there is no substantial improvement in the partial conjugation of the π -electron system of the molecules (Table I). As a rule, the inclusion of the electrons of the end substituents into the π -electron system of the molecule



4-7



- A: $R^1, R^2 = \text{H}$, $n = 2-7$
- B: $R^1, R^2 = \text{NH}_2$, $n = 1-3$
- C: $R^1 = \text{H}$, $R^2 = \text{NH}_2$, $n = 1-3$
- D: $R^1, R^2 = \text{Cl}$, $n = 2$
- E: $R^1, R^2 = \text{N}(\text{CH}_3)_2$, $n = 2, 3$

SCHEME 1

is reflected in an increase in the molar extinction coefficient and a drop in the energy of the first spectral transition.

The effect of polarity of the solvent on the positions of the maxima of long-wave bands is not large and indicates a relatively weak interaction between the solvents employed and the compounds under investigation. The maximum deviation in the position of the maximum of the long-wave band of the absorption spectra of compound dissolved in hexane, cyclohexane, 1,4-dioxane, ethanol and methanol is ± 3 nm. Analogously, the fact that the interaction between molecules of the compound itself in the solid state is not too strong is corroborated by the low shift range of the absorption maximum toward the red region going from the solution to the solid state.

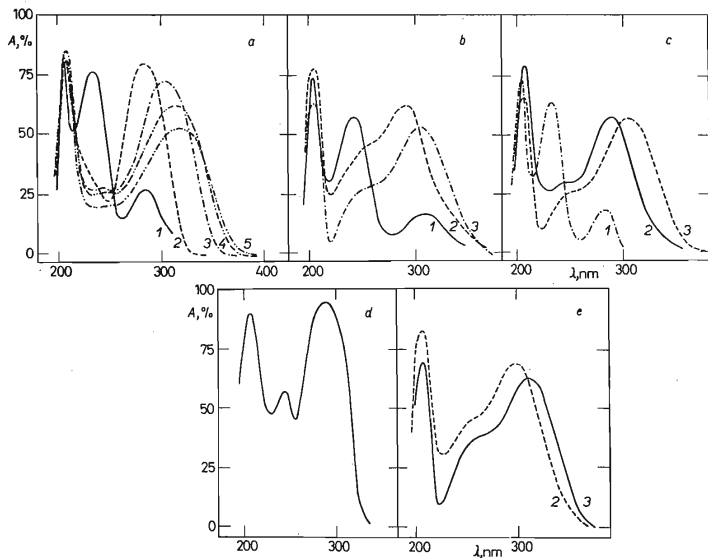


FIG. 1

Absorption Electronic Spectra of Compounds A–E (*a–e*) in Cyclohexane

Concentrations of the benzene rings in the measuring cell are approximately constant and correspond to a concentration $c = 1.3 \cdot 10^{-5} \text{ mol l}^{-1}$ of compound X_3 (A–E). Numerical designation of curves is identical with the index n in the chemical formula (Scheme 1). Anomaly: *a* ethanol as solvent, $c = 1.9 \cdot 10^{-5} \text{ mol l}^{-1}$, A₁ aniline; *d* D₂, $c = 4.2 \cdot 10^{-5} \text{ mol l}^{-1}$.

The difference between the absorption spectra recorded in solution and in the solid state for compounds of the series A is given in Table II.

TABLE I

Positions of the Absorption Maxima and the Corresponding Values of Molar Extinction Coefficients of Amines under Investigation

Amine	λ_1 nm	$\epsilon_1 \cdot 10^{-3}$ mol	λ_2 nm	$\epsilon_2 \cdot 10^{-3}$	λ_3 nm	$\epsilon_3 \cdot 10^{-3}$	Solvent	$c \cdot 10^5$ mol l ⁻¹
A ₂	284	21.3			207		ethanol	1.9
A ₂ ^a	286	24.0	237	5.2			ethanol	
A ₂ ^b	282	20.0			207	21		
A ₂ ^c	286	19.5			207	21.4	ethanol	
A ₂ ^d	286	24	230	7.6			hexane	
A ₃	304	27.5	243		208		ethanol	1.9
A ₃ ^e	304	27					ethanol	
A ₄	315	30.1	246		208		ethanol	1.4
A ₅	318	31.0	248		208		ethanol	1.1
A ₇	328						1,4-dioxane	
B ₁	309	1.9	243	8.7	206		cyclohexane	3.9
B ₂	290	22.1			206		cyclohexane	1.9
B ₃	305	26.0			206		cyclohexane	1.3
C ₁ ^f	287	2.0	234	8.9	201		cyclohexane	4.0
C ₁ ^f	281	1.4	230	8.2	196	34.5	buffer pH 8.0	
C ₂	288	17.7	246		206		cyclohexane	1.9
C ₃	304	29.8	252		206		cyclohexane	1.3
D ₂	290	20.8	244	6.2	208		cyclohexane	2.1
E ₂	299	26.1			208		cyclohexane	2.0
E ₃	311	33.4			208		cyclohexane	1.3

^a Ref.²⁵, ^b ref.²⁶, ^c ref.²⁷, ^d ref.¹³, ^e ref.²⁸, ^f ref.²⁹

TABLE II

Change in the Position of the Absorption Bands (λ , nm) going from the Ethanol Solution to the Solid State

Compound	Solution		Solid state	
	λ_1	λ_2	λ_1	λ_2
A ₂	284	230	290	253
A ₃	304	243	313	270
A ₄	315	246	350	305

Calculations

Calculations presented in this paper are of double type. For all compounds investigated here they were carried out using a simple HMO method. In this way, basic information was obtained, and it was possible to make some comparisons. Moreover, the compounds C_1 (aniline), A_2 (diphenylamine) and A_3 (N,N'-diphenyl-*p*-phenylenediamine) were studied in more detail using the LCI SCF LCAO-MO method. The programme employed was verified by comparing the results obtained with those published by other authors for compound C_1 (ref.⁹) and partly also A_2 (ref.¹⁰), and used to find the change in the bond orders and the π -electron charge distributions of molecules A_2 , A_3 by excitation. Using the calculated positions of the absorption maxima, respective values of the oscillator strengths and estimated band halfwidths (after their preliminary assignment), simplified theoretical absorption spectra for the singlet-singlet transitions were simulated with a computer.

The HMO Method

As it is usual, in the calculations of this type, it is assumed for the α resonance and β coulomb integrals, that $\alpha_X = h_X\beta + \alpha_C$, $\beta_{XY} = k_{XY}\beta$ (where β is the so-called β -unit equal to β_{CC} for the benzene bond and α_C is identified with the zero of the energy scale). The parameters h , k were chosen as follows: $h_N = 1.5$, $k_{CN} = 0.8$ for the amine group, $h_{Cl} = 2$, $k_{CCl} = 0.4$ for a chlorine atom¹²; for the group $R = N(CH_3)_2$, the values $h_R = 1$, $k_{CR} = 0.8$ were used, which proved to be useful in our previous calculations employing for this case the inductive hyperconjugation model.

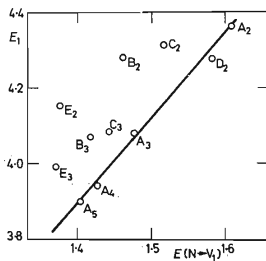


FIG. 2

Relation between the Energy of the First Intense Spectral Transitions E_1 (eV) and the Difference of the HMO Energies of the First Unoccupied $e(-1)$ ($|\beta|$) and highest Occupied $e(+1)$ ($|\beta|$) Molecular Orbitals $E(N \rightarrow V_1)$ ($|\beta|$) for Compounds under Investigation with the Exception of the Terms of the Series Having an Index $n = 1$

A regression line has been drawn through the points corresponding to compounds of the series A.

The HMO energies, $\epsilon(+1)$ ($|\beta|$), $\epsilon(+2)$ ($|\beta|$) of the two highest energy occupied MO and $\epsilon(-1)$ ($|\beta|$), $\epsilon(-2)$ ($|\beta|$) of the two lowest energy unoccupied MO are given in Table III. In accordance with the data in Table I, the decrease in $\epsilon(+1)$ ($|\beta|$) connected with an increase in the index of members of the individual series diminishes steeply. Using the experimental energy values E_1 (eV) of the first intense singlet-singlet spectral transitions listed in Table I, and putting $E(N \rightarrow V_1) = \epsilon(-1) - \epsilon(+1)$, it is possible to investigate the mutual correlation of these quantities for the compounds under investigation. The regression line corresponding to their dependence for the compounds of the A series and described by the equation $E_1 = 2.273E(N \rightarrow V_1) + 0.709$ is represented in Fig. 2. The respective correlation is statistically important on the 0.1% level. An estimate of E_1 for compound A₆, as yet unsynthesized, gives 3.86 eV (321 nm).

The calculated bond orders $p_{\mu\nu}$ (in the units 10^{-3}) and the net π -charges (in the units $10^{-3} |e|$), localized on the individual π -centres for the singlet state of molecules C₁, A₂ and A₃ with the lowest energy are added to Scheme 2. For types of molecules

TABLE III

Energies of the Highest Occupied $\epsilon(+i)$ ($|\beta|$) and Lowest Unoccupied $\epsilon(-j)$ ($|\beta|$) HMO Orbitals of Compounds under Investigation

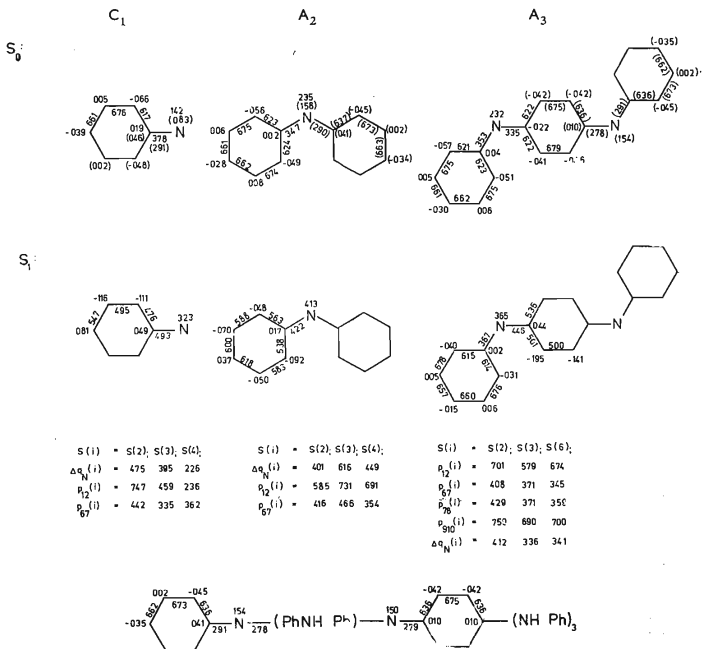
Experimental energy values of the first intense spectral transitions E_1 . $E(N \rightarrow V_1) = \epsilon(-1) - \epsilon(+1)$.

Compound	$\epsilon(+2)$	$\epsilon(+1)$	$\epsilon(-1)$	$\epsilon(-2)$	$E(N \rightarrow V_1)$	E_1 , eV
A ₂	-1.0000	-0.6074	1.0000	1.0000	1.6074	4.36
A ₃	-0.7591	-0.4778	1.0000	1.0000	1.4778	4.08
A ₄	-0.6074	-0.4269	1.0000	1.0000	1.4269	3.94
A ₅	-0.5258	-0.4022	1.0000	1.0000	1.4022	3.90
A ₆	-0.4778	-0.3884	1.0000	1.0000	1.3884	—
A ₇	-0.4474	-0.3779	1.0000	1.0000	1.3799	—
B ₁	-1.0000	-0.5762	1.0000	1.0000	1.5762	4.01
B ₂	-0.7438	-0.4619	1.0000	1.0000	1.4619	4.28
B ₃	-0.5919	-0.4187	1.0000	1.0000	1.4187	4.07
B ₄	-0.5144	-0.3975	1.0000	1.0000	1.3975	—
C ₁	-1.0000	-0.7438	1.0000	1.0833	1.7438	4.36
C ₂	-0.8792	-0.5144	1.0000	1.0000	1.5144	4.31
C ₃	-0.6625	-0.4415	1.0000	1.0000	1.4415	4.08
C ₄	-0.5541	-0.4094	1.0000	1.0000	1.4094	—
D ₂	-0.9497	-0.5803	1.0000	1.0000	1.5803	4.28
E ₂	-0.5856	-0.3748	1.0000	1.0000	1.3748	4.15
E ₃	-0.4813	-0.3688	1.0000	1.0000	1.3688	3.99
E ₄	-0.4361	-0.3656	1.0000	1.0000	1.3656	—

studied these values did not vary on the end rings and substituents with an accuracy of 10^{-4} when the chain was extended by a further unit, starting from $n = 4$; near the centres of the molecules, the same holds for $n = 5$. The values of the above quantities for compound A_7 are given for comparison.

The LCI SCF LCAO-MO Method

The approximations used in the present work to solve the problem of motion of the π -electrons in the field of the molecular σ -skeleton and the way of selecting semiempirical parameters correspond to a procedure commonly known as the Pariser-Pople-Parr method¹⁴.



SCHEME 2

TABLE IV

Lowest Energy Singlet States of Molecules of Compounds C_1 , A_2 and A_3

Symmetry of the models used, energy of the ground state $E_0^S(0)$, excitation energy $E_k^S = E_n^S(k) - E_0^S(0)$, its equivalents ν_k , λ_k , components of the transition moment $(M_{ok})_{x,y}$, and oscillator strength values f_k . Experimentally determined wavelengths λ_k^e corresponding to the absorption maxima and measured oscillator strengths f_k^e . Cyclohexane as solvent, cell thickness 1 mm, concentration (in mol^{-1}) 0.0038 (C_1), 0.00019 (A_2) and 0.00013 (A_3). Terms represented in the expansion of wave functions by less than 5% are omitted.

State	Symmetry	Wave function
Molecule C_1 , classification according to C_{2v}		
S(0)	S_0	
S(1)	A_1	0.8587 S(4 → 5) - 0.4993 S(3 → 6) + ...
S(2)	B_2	- 0.9572 S(4 → 6) - 0.2617 S(3 → 5) + ...
S(3)	A_1	0.5041 S(4 → 5) + 0.7867 S(3 → 6) - 0.3527 S(2 → 5) + ...
S(4)	B_2	0.2265 S(4 → 6) - 0.9391 S(3 → 5) + ...
S(4)	A_1	
Molecule A_2 , classification according to C_2		
S(0)	S_0	
S(1)	A	0.8218 S(7 → 10) + 0.2770 S(6 → 11) + 0.3744 S(5 → 8) - 0.3158 S(4 → 9) + ...
S(2)	B	- 0.8018 S(7 → 9) - 0.4156 S(6 → 8) - 0.2952 S(5 → 11) + 0.3062 S(4 → 10) + ...
S(3)	A	0.9704 S(7 → 8) + ...
S(4)	B	- 0.9268 S(7 → 11) + 0.2302 S(6 → 10) + 0.2423 S(5 → 9) + ...
S(5)	A	- 0.5564 S(7 → 10) + 0.3352 S(6 → 11) + 0.5688 S(5 → 8) - 0.4220 S(4 → 9) + ...
S(6)	B	0.5767 S(7 → 9) - 0.4989 S(6 → 8) - 0.3052 S(5 → 11) + 0.5095 S(4 → 10) + 0.2240 S(3 → 9) + ...
S(7)	A	
S(8)	B	
Molecule A_3 , classification according to C_i		
S(0)	S_0	
S(1)	A_g	0.7186 S(11 → 13) + 0.5354 S(11 → 15) - 0.2670 S(7 → 12) + ...
S(1)	A_u	

S(2)	A _u	-0.9446 S(11 → 12) + 0.2614 S(10 → 16) + ...
S(3)	A _u	-0.4169 S(11 → 13) + 0.5634 S(11 → 15) - 0.4990 S(10 → 14) - 0.2697 S(9 → 12) - 0.3122 S(8 → 16) + ...
S(4)	A _g	
S(5)	A _g	
S(6)	A _u	0.8395 S(11 → 17) - 0.3284 S(10 → 16) - 0.2263 S(7 → 13) + ...
S(7)	A _g	
S(8)	A _u	-0.3339 S(11 → 13) + 0.5522 S(11 → 14) + 0.2532 S(10 → 14) + 0.2498 S(9 → 12) + 0.3467 S(8 → 16) + 0.2434 S(7 → 12) + 0.2251 S(6 → 13) - 0.3079 S(6 → 15) + ...
S(9)	A _g	
S(10)	A _g	
S(11)	A _u	-0.3978 S(11 → 13) + 0.2757 S(9 → 12) - 0.6078 S(7 → 12) + 0.2949 S(7 → 17) - 0.2896 S(6 → 13) - 0.2995 S(6 → 15) + ...
S(12)	A _u	0.3518 S(11 → 17) + 0.4979 S(10 → 16) - 0.2945 S(9 → 15) - 0.4030 S(8 → 14) - 0.4594 S(6 → 12) + ...

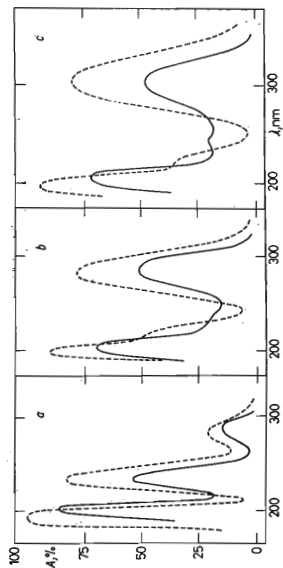


Fig. 3

Spectrum of Compounds C₁(a), A₂(b) and A₃(c) for the Case of the Gaussian Shape of the Extinction Curves
 Cyclohexane as solvent (*c* in 10⁻⁴ mol l⁻¹), *d* = 0.1 cm, *h* in 10³ cm⁻¹ (— experimental, constructed). *a*: *c* = 3.8, *h*₁ = 3.73, *h*₂ = 4.02, *h*₃ = *h*₄ = 2.70; *b*: *c* = 1.9, *h*₁ = *h*₂ = *h*₇ = *h*₈ = 3.00, *h*₄ = 3.5, *h*₅ = *h*₆ = 4.90; *c*: *c* = 1.3, *h*₁ = 3.00, *h*₂ = 5.20, *h*₃ = *h*₆ = *h*₈ = 4.00, *h*₁₁ = *h*₁₂ = 6.10.

TABLE IV
(Continued)

State	Symmetry	$E_{\pi}^{S(0)}$ eV	E_{π}^S eV	ν_k 10^3 cm^{-1}	λ_k nm	$(M_{ok})_x$ D	$(M_{ok})_y$ D	f_k	λ_k nm	f'_k
Molecule C_{1v} , classification according to C_{2v}										
S(0)		-219.76	0							
S(1)	A ₁		4.386	35.38	282.65	0	-0.345	0.046	287 ^a	0.03
S(2)	B ₂		5.278	42.57	234.90	0.898	0	0.372	234 ^b	0.15
S(3)	A ₁		6.329	51.05	195.88	0	-0.981	0.533	201 ^c	
S(4)	B ₂		6.498	52.41	190.80	-1.196	0	0.814		
S(4)	A ₁									
Molecule A_2 , classification according to C_2										
S(0)		-491.48	0							
S(1)	A		4.336	34.98	285.91	-0.069	0	0.002		
S(2)	B		4.345	35.05	285.32	0	-0.332	0.042	284	0.37
S(3)	A		4.428	35.72	279.96	1.355	0	0.712		
S(4)	B		5.520	44.52	224.60	0	-0.291	0.041	^d	
S(5)	A		5.786	46.67	214.27	0.511	0	0.132	203	
S(6)	B		4.873	47.37	211.11	0	0.637	0.209	203	
S(7)	A		6.255	50.46	198.19	0	-0.167	0.015	203	
S(8)	B		6.272	50.59	197.66	1.103	0	0.667		
Molecule A_3 , classification according to C_i										
S(0)		-935.49	0							
S(1)	A _g		4.010	32.34	309.20	-0.124	0.308	0.039		
S(2)	A _u		4.088	32.97	303.27	1.570	0.946	1.202	302	0.6
S(3)	A _u		4.281	34.53	289.57	0.369	-0.206	0.067		
S(4)	A _g		4.28	forbidden transition						
S(5)	A _g		4.83	forbidden transition						
S(6)	A _u		5.476	44.17	226.39	-0.017	-0.355	0.061		

S(7)	A _g	5.53	forbidden transition					
S(8)	A _u	5.539	44.67	223.84	0.433	-0.201	0.110	243
S(9)	A _g	5.57	forbidden transition					
S(10)	A _g	5.59	forbidden transition					
S(11)	A _u	5.958	48.06	208.08	-0.240	-0.681	0.272	205
S(12)	A _u	6.147	49.58	201.70	-0.189	-0.153	0.032	

^{a-c} Ref. ²⁹; ^a 281, ^b 230, ^c 196; ^d ref. ¹³; 230.

TABLE V

Comparison of Depression of the π -Electron Charge on the Nitrogen Atom $d_N(k)$ with the Percentual Amount of the (CT)-Transitions in the Wave Functions of Excited Singlet States S(k)

Symbol (l.p. $\rightarrow \tilde{1} \tilde{\varphi}_{h(k)}$) denotes the charge-transfer transition of an electron from the (l.p.) orbital to the $\tilde{1} \tilde{\varphi}_{h(k)}$ molecular orbital of the benzene ring I.

Compound	State	(CT) = (l.p. $\rightarrow \tilde{1} \tilde{\varphi}_{h(k)}$) %	(CT) _{tot} %	$d_N(k)$ e
Aniline	S(1)	19.89	19.89	0.181
	S(2)	37.82	37.82	0.333
	S(3)	26.42	26.42	0.253
	S(4)	7.73	7.73	0.084
Diphenylamine	S(1)	10.12	20.24	0.178
	S(2)	9.92	19.84	0.166
	S(3)	17.84	35.68	0.381

To determine the coulomb integrals γ , Mataga's approximation¹⁵ $\gamma_{\mu\nu} = 14.3994 : (a_{\mu\nu} + r_{\mu\nu})$ was used, where $a_{\mu\nu}$ is a constant characteristic of the given pair of AO χ_μ, χ_ν and the valence-state of atoms μ, ν ; $r_{\mu\nu}$ denotes the distance between the centres $\mu\nu$.

The system of Hartree-Fock's equations was solved by the method of successive approximations; the zero approximation $\mathbf{C}^{(0)} = (C_{\mu j}^{(0)}) (\mu = 1, 2, \dots, M, j = 1, 2, \dots, M)$ of the matrix of eigenvectors $\mathbf{C} = (C_{\mu j})$ was set up from the HMO molecular orbitals. The iterative process was terminated when for certain m for all MO (i) the condition $|\varepsilon_i^{(m+1)} - \varepsilon_i^{(m)}| < 10^{-4}$ eV was fulfilled for the values of the orbital energies ε_i (eV).

The values of parameters $Y_\mu, Z_\mu, a_{\mu\nu}, \beta_{\mu\nu}$ for the carbon atoms of benzene rings and nitrogen atoms of diphenylamine and N,N'-diphenyl-*p*-phenylenediamine were taken from Klessinger's paper dealing with the molecule of aniline⁹, similarly as it was done by Tyutyulkov, Fratev and Petkov¹⁰ for conjugated amines:

$$\begin{aligned} a_{CC} &= 1.2996 \text{ \AA}, & a_{CN} &= 1.2043 \text{ \AA}, \\ a_{NN} &= 1.1220 \text{ \AA}, & \beta_{CC} &= -2.3194 \text{ eV}, \\ \beta_{CN} &= -2.30 \text{ eV}, & Y_C &= -11.16 \text{ eV}, \\ Y_N &= -22.63 \text{ eV}, & Z_C &= 1. \\ Z_N &= 2, \end{aligned}$$

It should be mentioned that Y_μ is equivalent to $W_\mu - \sum_{\mu \neq \nu} (\mu | U_\nu | \mu)$ from the paper by Klessinger and Z_μ denotes the number of electrons by which the centre contributes to the π -system of the molecule.

For the bond length C—N in compounds A_2, A_3 we used the value determined by the X-ray analysis for 4,4'-dichlorodiphenylamine¹⁶, $r_{CN} = 1.45$ \AA. For the molecule of aniline, also given here to facilitate comparison, the value $r_{CN} = 1.43$ \AA was left, similarly to Klessinger. The molecules under investigation were idealized as planar. The bond angle at the nitrogen atom was chosen 120° . The position of the axes XY can be seen from Scheme 1.

In the case of the molecules of aniline and diphenylamine, all SCF LCAO-MO were included into interaction of monoexcited configurations; for N,N'-diphenyl-*p*-phenylenediamine, only those configurations $K = (v \rightarrow j)$ were used for which it holds $4 \leq v \leq 11 \leq j \leq 17$. Wave functions $S(k)$ for singlet excited states with lowest energies were determined by diagonalization. They are summarized in Table IV, along with the values $E_k^S = E_n^S(k) - E_n^S(0)$, where $E_n^S(0)$ denotes the π -electron energy of the ground state S_0 . Moreover, the Table includes values of the important quantity f_k , the oscillator strength, which for a spectral transition with the frequency ν_{0k} (cm^{-1})

is given by $f_k = 1.085 \cdot 10^{11} \nu_{0k} |\mathbf{M}_{0k}|^2$; \mathbf{M}_{0k} denotes the transition moment $\mathbf{M}_{0k} = [S(0) | \sum_t e_t \mathbf{r}_t | S(k)]$; \mathbf{r}_t is the position vector of a particle having an index t . Table IV also contains equivalents of the values E_k^S , ν_{0k} (cm^{-1}), λ_k (nm), as well as positions of the absorption maxima λ'_k (nm) and oscillator strengths f'_k determined experimentally.

If we keep the notation used in the preceding text and in Figures, it holds for the relative absorption $A(\nu)$

$$A(\nu) = 100[1 - 10^{-cd} \epsilon(\nu)], \quad (1)$$

where c is concentration of solution (mol/l) and d is thickness of the absorbing layer of solution (cm). A rough theoretical construction of the absorption spectra by means of the calculated values of ν_k (cm^{-1}), f_k and estimated half-widths of the corresponding bands h'_k (cm^{-1}) allowing an overall comparison of the recorded spectra and calculated results, is based on an assumption of the Gaussian shape of the extinction curves corresponding to the individual spectral transitions.

$$\epsilon_k^G(\nu) = \epsilon_k^G(\text{max}) \exp \left\{ -4(\ln 2) \left[\frac{(\nu - \nu_k)}{h'_k} \right]^2 \right\}; \quad (\epsilon_k^G(\nu_k) = \epsilon_k^G(\text{max})). \quad (2)$$

We obtain, by numerical calculations,

$$\int_0^\infty \epsilon_k^G(\nu) d\nu = 1.0645 h'_k \epsilon_k^G(\text{max}), \quad (3)$$

so that it follows from the assumption made about the shape of the extinction curve $f_k = 4.32 \cdot 10^{-9} \cdot 1.0645 h'_k \epsilon_k^G(\text{max})$.

If after a preliminary assignment of bands we make an estimate of the half-widths h'_k , we can determine the individual $\epsilon_k^G(\text{max})$ and thus also the shape of the functional dependence $\epsilon_k^G(\nu)$. By superposition of the extinction curves of all bands under consideration and using the expression for $A(\nu)$ we obtain the final shape of the absorption curve.

The values of f_k , ν_k necessary for the construction of the theoretical UV spectra of solutions of compounds C_1 , A_2 , A_3 were taken from Table IV. The resulting spectra were retransformed into the scale of wavelengths λ (nm) for the respective compounds and compared with the corresponding spectra obtained by measurements (Fig. 3). The agreement between the experimental and the constructed spectra is comparatively good, even in the case of spectral transitions of the type $S(0) \rightarrow S(3)$, $S(4)$ for diphenylamine which, as can be seen from Scheme 2, show a particularly large charge transfer from the nitrogen atom. This is an argument in favour of parameters chosen for its description.

For a singlet wave function $S = s_0 S_0 + \sum_{K=(\nu \rightarrow j)} s_K S_K$ the bond orders $p_{\mu\nu}$ or the

π -electron charges $q_\mu = p_{\mu\mu}$, already investigated in the HMO calculations, have their correspondence in the representation of the first order density matrix $P_S^{(1)}(r'_1 | r_1)$ in the space of atomic orbitals χ_μ , $P_S^{(1)}(v|\mu)$ defined by^{19,20}

$$\begin{aligned} N \int S^*(x'_1, x_2, \dots, x_N) S(x_1, x_2, \dots, x_N) dx_2 \dots dx_N = \\ = \frac{1}{2} P_S^{(1)}(r'_1 | r_1) \alpha(1) \alpha^*(1') + \frac{1}{2} P_S^{(1)}(r'_1 | r_1) \beta(1) \beta^*(1'), \\ P_S^{(1)}(r'_1 | r_1) = \sum_{v,\mu} P_S^{(1)}(v | \mu) \chi_\mu^*(r'_1) \chi_v(r_1). \end{aligned} \quad (4)$$

$P_S^{(1)}(v | \mu)$ can be written in an abbreviated form as $p_{\mu\nu}(k)$. A formula needed for numerical calculations is contained in a well-known paper by McCoy and Ross¹⁷. Scheme 2 gives a survey of the important values of the net π -charges $\Delta q_\mu = Z_\mu - q_\mu(|e|)$ and bond orders for the wave functions of the lowest energy singlet states of molecules C_1 , A_2 , A_3 . It also makes possible a comparison between the values of these quantities obtained by the SCF method for the state S_0 and those calculated by the HMO method.

In all cases described above an excitation of molecules of compounds C_1 , A_2 , A_3 leads to a decrease in the π -electron charge $q_N(k)$, localized on the $2p_z$ orbital of the nitrogen atom. In the case of compound C_1 , this finding is in full agreement with the general conclusion about the behaviour of electrons of the donor substituents in similar cases as published by Bertrán, Chalvet and Daudel¹⁸. These authors explain the decrease in the electron density on the π -orbital of the atom yielding electrons when the molecule is excited by means of the perturbation calculus, discussing the magnitude of the coefficient of this atomic orbital in the expansions of the individual molecular orbitals. In zero approximation, they take as a basis the molecular orbitals of a hydrocarbon and a separate substituent; in this case, it is a lone pair on the nitrogen atom. If we proceed in a similar manner with diphenylamine, that is, if we construct its molecular orbitals from the molecular orbitals of both benzene rings and the lone pair of the amino group, the explanation given in the above paper can be used as a guideline also in our case. Such an approach to the problem, which is adequate to the idea of separated electron groups¹⁹, allows to decompose — after a preliminary compactization of expansions by means of natural orbitals^{20,21} — the wave functions $S(k)$ of the excited singlet states and to determine the percentual amount of the charge transfer (CT) transition from the nitrogen atom to the respective benzene rings in these functions. This amount is given by squares of coefficients of the singlet wave functions ${}^k S_{K(k)}$, $K(k) = (\text{l.p.} \rightarrow {}^k \tilde{\varphi}_{h(k)})$ (ref.⁹) in the expansion of the wave function $S(k)$, where ${}^k \tilde{\varphi}_{h(k)}$ is a molecular orbital close to the orbital $\varphi_{h(k)}$ of an unperturbed benzene ring.

The results thus obtained for aniline⁹ (Table V) are closely connected with a depression of the π -electron charge on the nitrogen atom, $d_N(k) = q_N(0) - q_N(k)$,

due to excitation. The percentual amount of the (CT) transitions in the wave functions $S(k)$ of diphenylamine with the depression $d_N(k)$ (ref.^{22,23}) is compared in the same Table.

For the carbon atoms, an agreement between the charges, both calculated and determined experimentally, was demonstrated by Klessinger for the $S(1)$ state of aniline with an accuracy of 0.03 e. If a similar agreement is assumed also for the other cases, and the net π -charges on the atoms are accepted as a guideline for the determination of the centres of the nucleophilic and electrophilic reactions¹⁰, we can follow, in Scheme 2, the rearrangement of these centres by the transitions from the ground to the excited states.

The knowledge of changes of the bond orders also yields a valuable information about the trend of their length changes. A considerable increase in the bond order of the C—N bond in the $S(3)$ state of compound A_2 obviously signalizes its appreciable contraction, etc.

In conclusion we should like to add a note about the basicity of compounds under investigation. Tyutyulkov, Fratev and Petkov¹⁰ found an excellent correlation, close to linear proportionality, between the calculated magnitude of the π -electron charge on the nitrogen atom, and the experimental value of the constant pK_a , of several aromatic amines, including also compounds C_1 , A_2 . They used this correlation in their paper also to make a prognosis of the values of the constant pK_a for the excited states. If we notice that the calculated values of $q_N(0)$ for compounds A_2 , A_3 differ but slightly, we can expect the same for the constants $pK_a(1)$, which characterize the basicity of the corresponding amine groups. The constant pK_a for A_2 is approximately 0.9 (ref.²⁴).

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