Experimental and Theoretical Determination of Electronic State Energies of Naphthanilides

M. Brozis[a], J. R. Heldt[b], and J. Heldt[a]

[a] Institute of Physics, Pomeranian Pedagogical Academy,
ul. Arciszewskiego 22 B, 76-200 Słupsk, Poland
[b] Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland

Reprint requests to Dr. J. R. H.; Fax: (048)(058) 341-31-75; E-mail: fizjh@julia.univ.gda.pl

Z. Naturforsch. **56 a,** 841–848 (2001); received August 27, 2001

Experimental absorption spectra of α- and β-naphthanilide derivatives in the vapour phase and in MCH solution are interpreted on basis of calculations performed using the INDO/S-CI method. The ground state geometries have been optimised with the PM3 parameterisation method. The calculated values of the lowest triplet state T_1 as well as energy differences of the $T_1 \rightarrow T_n$ transitions have been compared with measured data determined from the phosphorescence and picosecond transient absorption spectra. For $S_0 \rightarrow S_n$ and $T_1 \rightarrow T_n$ transitions, a good agreement is noticed between the experimental and calculated energy values. An additional band observed in the total luminescence spectrum at 77 K, is interpreted as due to the emission of the double H-bonded imidol dimer formed in the excited state. – PACS: 31.70 Dk, 33.50 Dg

Key words: Naphthanilides; Absorption; INDO/S Calculations; Luminescence Spectrum.

1. Introduction

Naphthanilide derivatives consist of two chromophores (naphthalene and benzene) linked by the peptide bridge –CON<, as indicated in Figure 1. The bichromophor molecules play an important role in quantum optics as dye lasers [1], optoelectrical switches [2] or light frequency converters [3]. In the molecules studied, three flexible bonds (N1-C2, C2-C4 and N1-R1 see Fig. 1) allow rotation. As a result, the transition moments of the separated chromophores can have different space orientations in the ground and excited state. Therefore in some solutions naphthanilides like benzanilide derivatives can exhibit dual fluorescence [4]. The absorption and normal fluorescence (LE) spectra of the naphthanilide derivatives have been analysed on the basis of the naphthalene spectra [5]. It appears that the β- and α-substituted derivatives of naphthanilide compose molecules possessing an extended conjugation in the longer or the shorter axis of the parent naphthalene molecule. This causes respective shifts of the observed absorption and fluorescence bands [6].

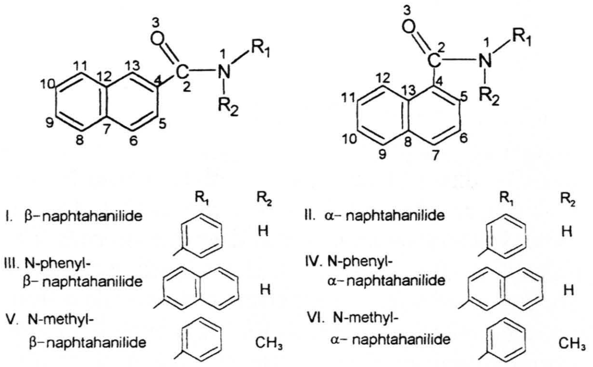

Fig. 1. The chemical structure of the naphthanilide derivatives under study.

In the present work we report experimental data of steady state spectroscopic measurements which are compared with theoretical calculation of electronic state energies. The WinMOPAC computer program was used in the performed calculation. Geometrical structures of the investigated molecules have been determined using the PM3 parameterisation procedure [7]. The INDO/S semi-empirical method was used in calculations of the electronic singlet and triplet state energies. The calculations were conducted for the neutral, free molecule (closed-shell) in the gas phase. The theoretical data of the electronic singlet states are compared with experimental values determined from the absorption spectra measured in

0932–0784 / 01 / 1200–0841 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

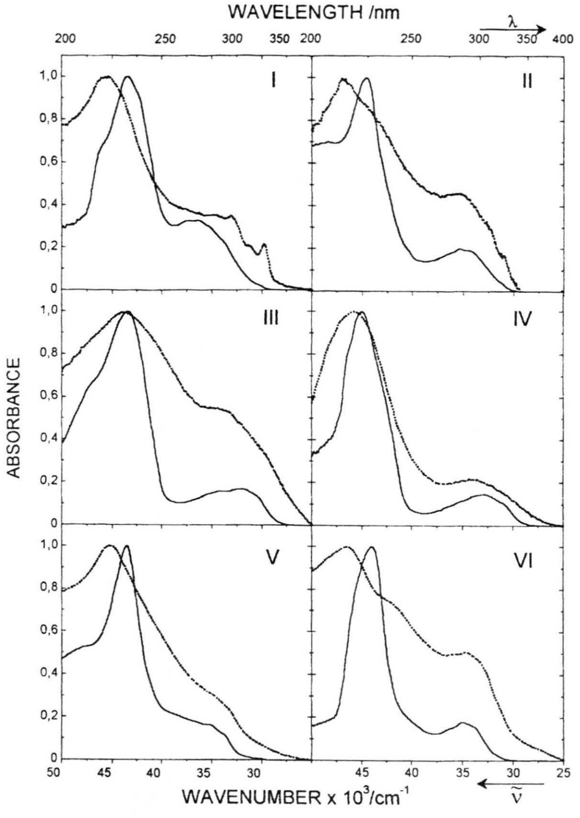

Fig. 2. The absorption spectra of the molecules I-VI measured for vapor (···) and in MCH solution (—).

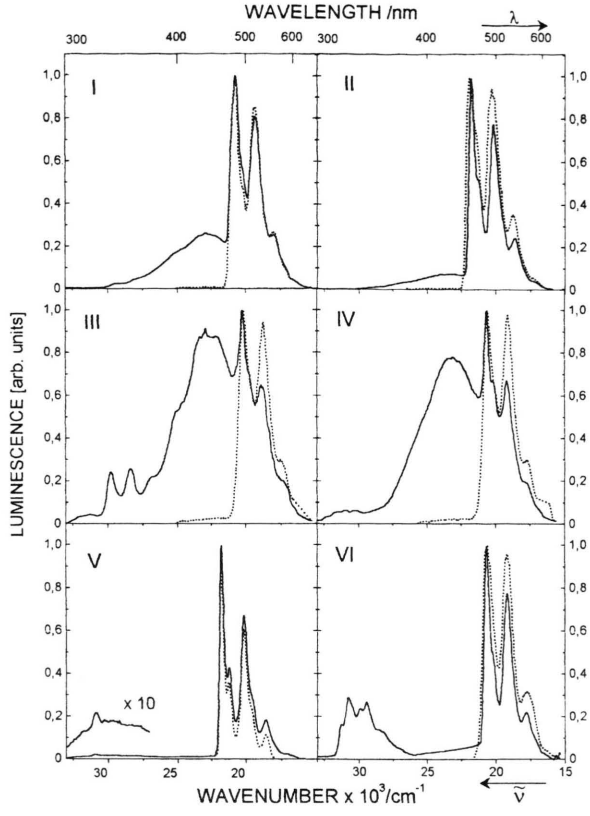

Fig. 3. The total luminescence (fluorescence + phosphorescence —) and phosphorescence (···) spectra of the molecules I-VI at 77 K in diethylether / toluene / ethanol 2:1:1 v/v rigid glass.

methylcyclohexane solution and in the gas phase. The calculated energy values of the lowest triplet state are compared with the experimental data taken from phosphorescence spectra and for higher triplet levels from the time-resolved picosecond transient absorption spectra measurements.

2. Experimental Details

Naphthanilide derivatives under study (presented in Fig. 1) have been synthesized and purified as described in [8]. The UV-visible absorption spectra of naphthanilide derivatives were recorded with a Shimadzu UV-2401 PC recording spectrophotometer in methylcyclohexane (MCH) and vapour phase. The absorption measurements in the vapour phase were carried out using 10 cm Suprasil tube heated by resistant wire. Argon was used as carrier gas for the molecules in vapour phase. The temperature of the absorption tube was held below the melting point of naphthanilide derivatives, i. e. in range of 360 - 450 K. Fluorescence and phosphorescence spectra of these molecules at 77 K in a mixture of diethylether / toluene / ethanol (DTE, 2:1:1 v/v) rigid glass were measured with a Shimadzu spectrofluorophotometer RF-5301 PC. The concentration of the molecules in MCH and DTE solvents was about 10^{-4} M. The luminescence light was observed perpendicular to the direction of the excited beam from a 2 mm diameter quartz tube placed inside a finger quartz dewar. A mechanical tope chopper was employed as a phosphoroscope. Before use the MCH solvent was distilled from a sodium potassium amalgam to ensure that it is clean and free of water. The used solvents did not show any traces of luminescence being excited at $\lambda_{ex} \sim 300$ - 320 nm. Figure 2 shows the absorption spectra of molecules studied in the vapour phase and in MCH solvent. The total luminescence (fluorescence + phosphorescence) and the phosphorescence spectrum

Table 1. Torsion and space angles of the compounds I-VI.

Torsion angle (°)	I	II	III	IV	V	VI
C2N1-planeR1	10.8	55.2	128.3	128.7	90.1	91.7
N1C2C4C5	43.9	87.3	70.1	92.6	88.2	88.7
C4C2N1R1	178.7	164.9	164.6	163.6	179.8	176.0
O3C2N1R1	0.7	19.2	18.1	18.5	14.3	14.9
O3C2C4C5	136.7	92.2	107.6	91.5	88.8	90.1
O3C2N1R1	179.4	175.9	177.3	178.0	180	178.8

of these molecules in DTE rigid glass are presented in Figure 3.

3. Calculations

The large number of atoms originating in the molecules under study (more then 32) puts some restrictions on the calculation method used. The only useful and practical method for this case is the semi-empirical PM3 and INDO/S approach. Since in the literature we did not find any data concerning the bond length and angles describing the space structure of naphthanilide and its derivatives, we calculated them using the PM3 method. As it is shown in Fig. 1, the naphthanilide molecules possess three flexible bonds allowing free rotation of the separated chromophores towards the plane of the peptide group.

In order to determine the space structure of the molecules under study, the following procedure has been adapted. Firstly, we optimised the internal energy of the molecules by putting a fixed value for the torsion angles C4C2N1R1 and N1C2C4C5, taking the third angle C2N1-planeR1 as a free running parameter along with bond lengths between all atoms and other geometrical parameters, i.e. angles between the bonds in benzene and naphthalene rings. In the second step, the torsion angles C4C2N1R1 and C2N1-planeR1 were fixed while N1C2C4C5 was a free running parameter. In the last step the angles N1C2C4C5 and C2N1-planeR1 were fixed while C4C2N1R1 was a free running parameter et cetera. The iteration procedure was continued until the minimum internal energy of molecules was found. The torsion angles determined in this way are collected in Table 1.

The energy levels of the singlet (S) and triplet (T) electronic states as well as the oscillator strengths of the transition between the corresponding levels $S_0 \rightarrow S_n$ of the compounds I-VI were determined by semi-empirical INDO/S-CI computation method using WinMOPAC software. Atom coordinates of the molecules studied for the INDO/S calculations were obtained from minimum energy for the optimised space geometry of the molecules. The configuration interaction (CI) calculations were performed using wave functions including all electronic state which are generated by singly exciting all electronic states electrons in the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. In our calculations 90 singly excited configurations were taken into account. The calculated state energies were cut-off at 6 eV.

Calculated energy values of the singlet states and the oscillator strength of the corresponding transitions $S_0 \rightarrow S_{\text{ex}}$ are listed in Table 2. The triplet states energies determined in respect to the ground S_0 state are given in Table 3.

4. Results and Discussion

4.1. Absorption and Emission Spectra

Figure 2 shows the absorption spectra of β- and α-naphthanilides in MCH solution and in the gas phase. Two main bands in the 210 - 250 nm and 260 - 330 nm regions can be distinguished. The bands dispossess vibration structure, they compose a superposition of many transitions forming two distinct bands only. The absorption spectrum of the molecules studied in gas phase is broadened in comparison to that in MCH and only the band in the 200 - 250 nm region has a distinct shape.

The long-wave band in the region 260 - 330 nm, as it was shown in [10], comprises a very weak $n\pi^*$ transition appearing at $\tilde{\nu} \cong 30770$ cm^{-1} ($\lambda \cong 325$ nm). This and earlier studies [9, 10] show that the absorption spectrum of the β- and α-naphthanilides consists of three main absorption bands with maxima at $\tilde{\nu} = 30488$ cm^{-1} (328 nm), 34965 cm^{-1} (286 nm), and 45455 cm^{-1} (220 nm), respectively. In comparison to naphthalene these bands correspond to the $^1\text{L}_\text{b}$ ($^1\text{B}_{3\text{u}}^- \leftarrow {}^1\text{A}_{1\text{g}}$, 32151 cm^{-1}), $^1\text{L}_\text{a}$ ($^1\text{B}_{2\text{u}}^+ \leftarrow {}^1\text{A}_{1\text{g}}$, 36365 cm^{-1}) and $^1\text{B}_\text{b}$ ($^1\text{B}_{3\text{u}}^+ \leftarrow {}^1\text{A}_{1\text{g}}$, 45250 cm^{-1}) transitions [5], respectively. It shows that the anilide chromophor at β- and α-position of the naphthalene ring compose a bichromophoric molecule with an extended conjugation primarily along the longitudinal or along the perpendicular axis of the parent molecules. These substituents cause not only band shifts and intensity changes of the corresponding transitions but also promote new transitions. They proceed as a result of symmetry changes of the molecules

Table 2. Excitation energies (eV and cm^{-1}) and oscillator strengths (f) of singlet transitions of the molecules I-VI. The naphthalene data are given for comparison only.

State	Naphthalene			Molecule I			Molecule II			Molecule III			Molecule IV			Molecule V			Molecule VI		
	eV	cm^{-1}	f	eV	cm^{-1}	f	eV	cm^{-1}	f	eV	cm^{-1}	f	eV	cm^{-1}	f	eV	cm^{-1}	f	eV	cm^{-1}	f
1	4.02	32392	0.004	3.81	30753	0.001	3.86	31131	0.001	3.81	30746	0.002	3.76	30367	0.003	3.90	31472	0.005	3.84	30951	0.001
2	4.26	34339	0.147	3.89	31376	0.003	3.87	31247	0.008	3.85	31091	0.002	3.91	31553	0.005	4.24	34239	0.154	3.88	31313	0.009
3	5.32	42941	1.625	4.23	34099	0.133	4.17	33615	0.203	3.89	31378	0.003	3.98	32082	0.009	4.44	35825	0.029	4.21	33977	0.228
4	5.39	43446	0.000	4.50	36268	0.007	4.54	36601	0.003	4.33	34908	0.052	4.33	34918	0.249	4.67	37686	0.584	4.51	36360	0.005
5	5.53	44603	0.000	5.02	40511	0.738	5.16	41617	0.661	4.34	34961	0.248	4.37	35285	0.239	5.18	41773	0.959	5.19	41843	1.056
6	5.57	44912	0.578	5.19	41856	1.317	5.19	41902	0.545	5.02	40498	2.977	5.02	40492	0.793	5.27	42558	0.436	5.25	42372	0.132
7	6.09	49105	0.000	5.34	43099	0.065	5.23	42174	0.261	5.28	42607	0.236	5.17	41751	1.009	5.35	43148	0.165	5.27	42473	0.411
8	6.19	49903	0.000	5.38	43371	0.055	5.27	42526	0.070	5.33	42969	0.086	5.32	42944	0.473	5.37	43269	0.043	5.31	42833	0.008
9				5.40	43540	0.326	5.37	43336	0.062	5.38	43366	0.032	5.36	43230	0.179	5.46	44041	0.063	5.37	43292	0.019
10				5.41	43672	0.160	5.45	43924	0.649	5.39	43472	0.128	5.38	43383	0.653	5.49	44273	0.074	5.49	44281	0.228
11				5.63	45432	0.127	5.71	46052	0.010	5.45	43944	0.003	5.43	43819	0.129	5.52	44556	0.461	5.50	44364	0.407
12				5.90	47599	0.039	5.82	46959	0.148	5.45	43962	0.092	5.45	43965	0.294	5.86	47262	0.557	5.57	44918	0.194
13				5.91	47679	0.209	5.87	47374	0.057	5.48	44161	0.297	5.51	44408	0.004	5.89	47545	0.046	5.69	45901	0.005
14				5.94	47904	0.543	5.97	48175	0.207	5.56	44877	0.799	5.53	44629	0.136	5.96	48104	0.052	5.78	46587	0.023
15				5.98	48203	0.313	5.99	48330	0.562	5.57	44966	0.131	5.58	44974	0.444	5.97	48197	0.082	5.82	46943	0.046
16				6.05	48833	0.007	6.03	48666	0.619	5.61	45245	0.022	5.75	46357	0.428	6.00	48429	0.322	6.01	48459	0.848
17										5.86	47272	0.022	5.86	47282	0.002						
18										5.91	47637	0.000	5.92	47736	0.008						
19										5.97	48203	0.056	5.97	48173	0.003						
20										6.06	48906	0.009	6.07	48973	0.002						

Table 3. Triplet excitation energies (eV and cm^{-1}) of the molecules I-VI. The naphthalene data are given for comparison only.

State	Naphthalene		Molecule I		Molecule II		Molecule III		Molecule IV		Molecule V		Molecule VI	
	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}
1	2.91	23449	2.63	21172	2.59	20868	2.60	20975	2.59	20918	2.69	21735	2.59	20880
2	4.06	32757	3.23	26049	3.25	26201	2.63	21173	2.60	20970	3.38	27273	3.24	26163
3	4.20	33906	3.60	29062	3.56	28752	3.55	28669	3.55	28667	3.69	29728	3.55	28646
4	4.56	36821	3.68	29692	3.66	29498	3.60	29064	3.56	28715	3.77	30428	3.66	29548
5	4.72	38030	3.95	31824	3.97	31986	3.67	29601	3.67	29598	4.04	32583	3.98	32124
6	5.10	41099	4.10	33082	4.11	33117	3.68	29693	3.67	29601	4.17	33614	4.11	33174
7	6.18	49831	4.12	33209	4.15	33503	3.88	31295	3.88	31300	4.20	33892	4.12	33243
8	6.33	51033	4.18	33746	4.20	33883	3.95	31826	3.99	32142	4.23	34123	4.19	33819
9			4.22	34031	4.26	34361	4.09	32961	4.09	32960	4.31	34760	4.26	34394
10			4.46	35949	4.47	36039	4.10	33079	4.12	33241	4.57	36862	4.46	36011
11			4.72	38066	4.72	38104	4.22	34043	4.23	34129	4.80	38683	4.59	37039
12			4.76	38411	4.76	38390	4.43	35768	4.43	35768	4.85	39146	4.74	38257
13			5.55	44756	5.57	44899	4.46	35951	4.47	36067	5.64	45493	5.57	44938
14			5.83	47056	5.91	47664	4.77	38461	4.77	38473	5.93	47843	5.92	47747
15			5.95	47969	6.00	48426	5.51	44430	5.51	44433	5.94	47915	5.98	48223
16			6.07	48918	6.00	48432	5.55	44755	5.57	44959	6.14	49504	6.00	48406
17			6.11	49291	6.07	48973	5.76	46437	5.76	46437	6.19	49901	6.07	48992
18			6.17	49762	6.18	49856	5.83	47058	5.93	47793	6.35	51252	6.16	49709
19			6.32	50996	6.20	50033	6.03	48619	6.01	48504	6.36	51296	6.19	49928
20			6.39	51544	6.28	50630	6.07	48918	6.03	48612	6.38	51479	6.20	50020

studied in comparison to naphthalene. The shifts of the ^1L_b, ^1L_a, and ^1B_b absorption band maxima equal to about 3600 cm^{-1}, 900 cm^{-1} and 1300 cm^{-1} for molecule I in comparison to the position in naphthalene. The shifts of the corresponding bands of individual molecules differ somewhat.

Analysing the absorption spectra of the molecules studied (see Fig. 2) it follows that:

a) The absorption spectra of β- and α-naphthanilides are less structured than these of naphthalene. Nevertheless three absorption regions can be distinguished. They are determined by the spectrum structure and supported by the extinction coefficient differences.

b) The $\tilde{\nu}_{\text{onset}}$-values of the $^1\text{L}_\text{b}$ band in solution and in the gas phase follow the inequality $\tilde{\nu}_{\text{sol}} > \tilde{\nu}_{\text{gas}}$ or $\lambda_{\text{gas}} > \lambda_{\text{sol}}$. It indicates that the $^1\text{L}_\text{b}$ band of the studied molecules has a pronounced $n\pi^*$ admixture. This finding is in agreement with the $\tilde{\nu}_{\text{max}}$-changes observed for the $n\pi^*$ transition by changing the environment from gas phase to liquid solvents [11].

c) In the absorption spectrum of β- and α-naphthanilides the $\tilde{\nu}_{\text{max}}$ value of the $^1\text{B}_\text{b}$ band follows the relation $\tilde{\nu}^{\alpha}_{\text{max}} < \tilde{\nu}^{\beta}_{\text{max}}$, whereas in the case of the $^1\text{L}_\text{b}$ and $^1\text{L}_\text{a}$ bands an opposite dependence is noted, i. e. $\tilde{\nu}^{\beta}_{\text{max}}(^1\text{L}_\text{b}) < \tilde{\nu}^{\alpha}_{\text{max}}(^1\text{L}_\text{b})$ and $\tilde{\nu}^{\beta}_{\text{max}}(^1\text{L}_\text{a}) < \tilde{\nu}^{\alpha}_{\text{max}}(^1\text{L}_\text{a})$. This dependence is in agreement with the well known substituent effects [5, 17].

d) The band $^1\text{B}_\text{b}$ of β- and α-naphthanilides consists of two transitions. They are well visible in the vapour phase absorption spectra and less pronounced in solutions.

Figure 3 shows the total luminescence (fluorescence + phosphorescence) and only the phosphorescence spectra of molecules I-VI at 77 K in DTE rigid glass. The fluorescence and phosphorescence bands show clear vibration structure. The most intense peak in the phosphorescence spectrum originates from the 0-0 transition of $S_0 \leftarrow T_1$ band at $\tilde{\nu}_{0\text{-}0} \cong 20700\ \text{cm}^{-1}$. As can be seen from the total luminescence spectra, the intersystem crossing ratio, defined as ratio of quantum yields of phosphorescence to fluorescence under steady excitation, possesses a value $\chi = \Phi_{\text{Ph}}/\Phi_{\text{F}} \gg 1$ for all molecules under study. This indicates that the fluorescence emission from the S_1 state follows the conditions of the $n \rightarrow \pi^*$ transition [15]. It supports the former findings concerning a blue shift of the $\tilde{\nu}_{\text{onset}}(^1\text{L}_\text{b})$ value by changing the environment of the absorbing molecules from the vapour phase to solvent. As can be seen in Fig. 3 at 77 K the total luminescence spectra of the molecules I-IV besides the fluorescence and phosphorescence bands possess a third unstructured band with $\tilde{\nu}_{\text{max}}$ at about $24000\ \text{cm}^{-1}$ ($\lambda \sim 440$ nm). This unstructured band originates from the cis-imidol tautomer emission. Its intensity is higher for the β substituted molecules (I and III), and it is dominating in the spectra of N-naphthalene α- and β-naphthanilides. For the molecules under study the cis-imidol tautomers and excimers are created in molecular films and rigid glasses [10, 12, 13]. The excited excimers facilitate occurrence of a double excited state proton transfer reaction in which the imidol form of these molecules is created [12]. The emission band of this form is unstructured and shifted to lower $\tilde{\nu}$ values (longer wavelength) [11 - 14]. The low temperature luminescence spectra of molecules V and VI do not show this unstructured band (see Fig. 3), since the N-methyl substituent prohibits this reaction. The above finding supports the existence of H-bonded dimers of naphthanilides which can give rise to concerted biprotonic transfer and the cis-imidol tautomer formed in I-IV compounds.

4.2. Results of Chemical Structure and Excited State Energies Calculation

As mentioned earlier, the PM3 method has been employed for the ground state (S_0) geometry optimisation of studied compounds. Table 1 collects the values of the rotation angles as well as the space angles between the plane of the peptide linkage –CON<, substituted naphthalene and benzene rings. Figure 4 shows fully optimised chemical structures of molecules I, II, V and VI calculated keeping the bond lengths, the angles of rotation around the flexible bonds: N1-C2, N1-R1 and C2-C4 as variable parameters. The molecular structures shown in Fig. 4 dispose the chemical structure of the molecule in a way that the peptide linkage is situated in the plane of the page (a) and perpendicular to it (b). The computer-drawn chemical structures as well as the space angles collected in Table 1 point out that for molecules V and VI planes of the chromophores, i. e. phenyl and naphthyl are parallel to each other and compose an angle of about 90° to the plane of the peptide bridge. For the other molecules where the N-methyl substituent is replaced by the H atom (I and II), a distinct differences from 90° is noted. The differences in the space structure of the studied molecules are reflected in the computed energy values of the excited singlet (S) and triplet (T) electronic states.

Analyzing the data collected in Table 2 and 3 it follows that for the molecules under study in the 6 eV excitation region there appear more levels than listed for naphthalene. Distinct differences between the oscillator strengths of the molecules studied and that calculated for naphthalene are also noted. It concerns particularly the absence of strictly forbidden transi-

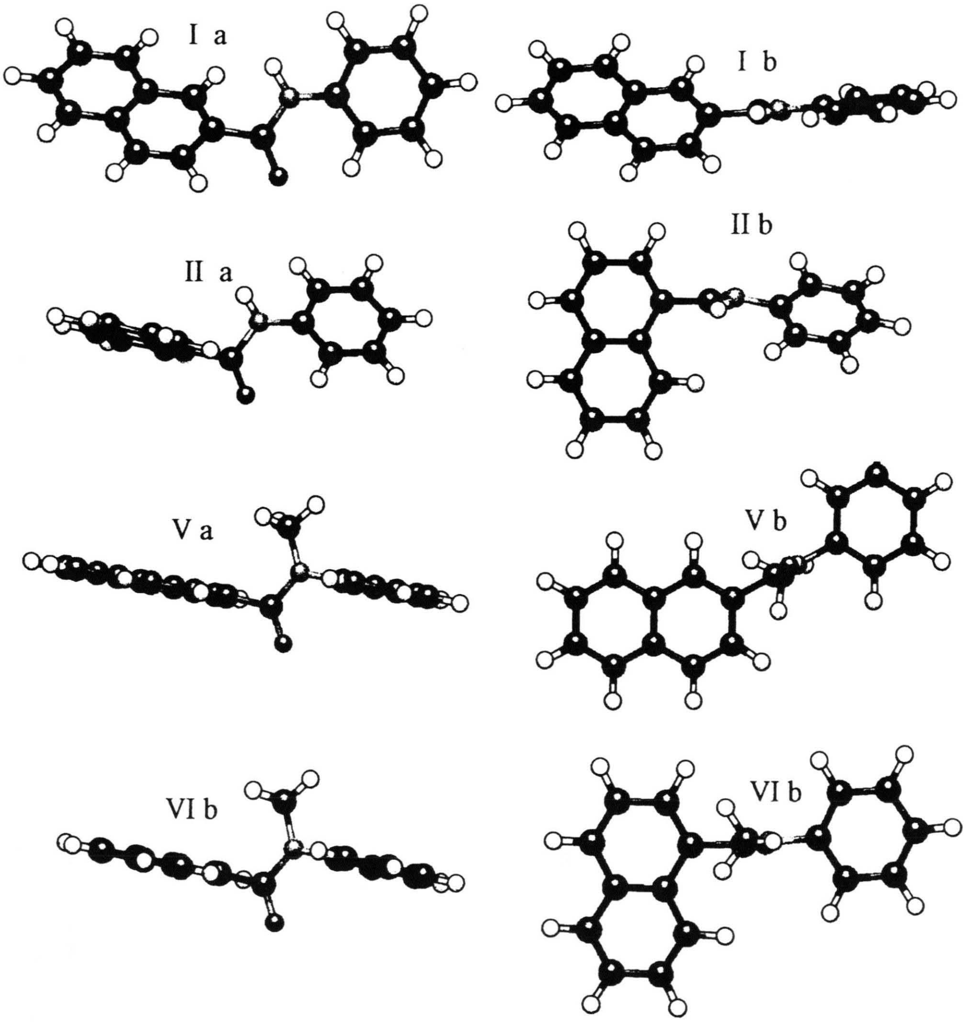

Fig. 4. The chemical space structures of the molecules I, II, V and VI. a) given so that the peptide linkage is seen from above, b) perpendicular to it.

tions, which appear in the naphthalene spectrum. It is a consequence of the symmetry changes of the molecules studied in comparison to that of naphthalene (D_{2h}).

Generally, in the molecules studied the weak long-wave transition at 30000 - 32000 cm^{-1} (in naphthalene the ^1L_b transition for which the oscillator strength $f(^1L_b) = 0.003$) is accompanied by one or two transitions of similar strength. The stronger transition at $\tilde{\nu}$ = 34000 - 35000 cm^{-1} (corresponding to the ^1L_a band in naphthalene with $f(^1L_a) = 0.166$) is followed up by two transitions for which the oscillator strength are of the order 0.01 - 0.60. These transitions do not appear in naphthalene. The main absorption band of naphthalene ^1B_b at 42771 cm^{-1} has a corresponding band in the measured spectra at $\tilde{\nu}$ = 41856, 41617, 40498, 41751, 41773, and 41843 cm^{-1} for the molecules I, II, III, IV, V, and **VI**, respectively (see Table 2). The oscillator strengths of these transitions are smaller in comparison to naphthalene. Additionally, for the molecules studied this transition is accompanied by several close lying bands possessing non-zero oscillator strengths. In naphthalene these transitions are forbidden (see Table 2 and [16]).

It must be noted that in the 5.4-6 eV (230 - 200 nm) excitation region there appear some more intense absorption bands $S_0 \rightarrow S_n$, e. g., at $\tilde{\nu}$ = 47904, 48330, 48429, and 48459 cm^{-1} for the molecules I, II,

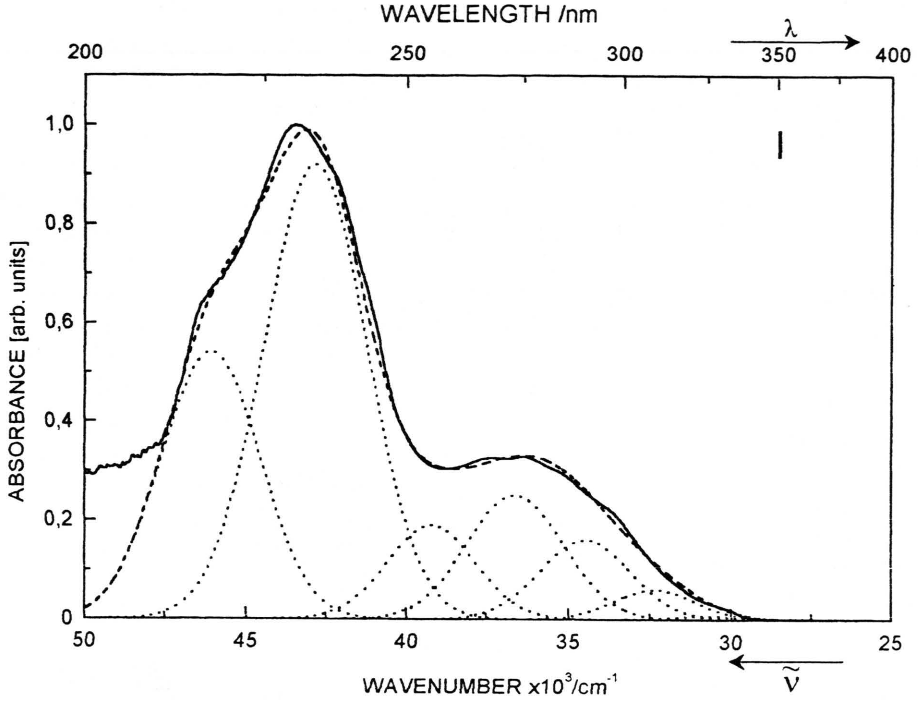

Fig. 5. Absorption spectrum of (β-naphthanilide (I) in MCH solution decomposed into six bands.

Table 4. Lowest energies (in cm^{-1}) of the singlet and triplet states of the molecules I-VI.

Comp.	Singlet states				Triplet states			
		Calc.	Exp.	ΔE / %		Calc.	Exp.	ΔE / %
Naph-	S_0	0	0	–				
thalene	S_1	31367	32051	648 / 2.0	T_1	23449	21348	2101 / 8.9
					T_2	32757		
I	S_0	0	0	–				
	S_1	30753	31056	303 / 1.0	T_1	21172	20747	425 / 2.0
					T_2	26048		
					T_{13}	44756	43683	1073 / 2.4
II	S_0	0	0	–				
	S_1	31131	31258	127 / 0.3	T_1	20869	20833	35 / 0.2
					T_2	26201		
					T_{13}	44899	42110	2789 / 6.2
III	S_0	0	0	–				
	S_1	30746	30850	104 / 0.3	T_1	20975	20242	733 / 3.5
					T_2	28669		
IV	S_0	0	0	–				
	S_1	30367	30770	403 / 1.3	T_1	20918	20233	685 / 3.4
					T_2	28666		
V	S_0	0	0	–				
	S_1	31472	32790	1318 / 4.2	T_1	21735	20833	902 / 4.1
					T_2	27273		
					T_{13}	45493	43969	1724 / 3.9
VI	S_0	0	0	–				
	S_1	30951	32560	1609 / 5.2	T_1	20879	20661	218 / 1.0
					T_2	26163		
					T_{13}	44938	41938	3000 / 7.1

V, and VI, respectively. These bands correspond to the $2^1B^*_{2u} \leftarrow^1 A_{1g}$ transition in naphthalene at $\tilde{\nu}$ = 47989.7 cm^{-1} (f = 0.268) [16], such intense bands do not appear for molecules III and IV in this excitation region.

Analyzing the data collected in Table 3 it follows that the density of the triplet energy states per eV is higher than in the singlet manifold. The calculated energy of the T_1 state of studied compounds is in a very good agreement with experimental values determined from the 0-0 vibrational transition of the phosphorescence spectrum (see Table 4). Also, it must be noted that for these molecules the energy of the T_2 state is smaller than that of the S_1 level, contrary to that for naphthalene. This explains the intensive phosphorescence emission appearance at 77 K for these molecules. We would like to notice that in the row of calculated triplet state energies we found a corresponding state for which the difference $E(T_m) - E(T_1)$ has a corresponding peak in the picosecond transient absorption spectrum [10]. The energy of this state, energy difference $E(T_m) - E(T_1)$ and the corresponding experimental $\tilde{\nu}_{T-T_1}$-values are listed in Table 4.

Figure 5 shows decomposition of the absorption spectrum of β-naphthanilide (I) in MCH into separate bands with some assumptions which simplify the calculations. As it has been mentioned earlier, the energy values of some theoretically obtained levels show very small difference. Such states have been counted as one with a sum of all oscillator strengths. As can be seen in Fig. 5, the sum of individual bands obtained from the decomposition of the experimental absorption profile gives a spectrum which is in a good agreement with the measured one. In the decomposition procedure the individual bands possess a Gauss profile of equal half-width and adjusted height (intensity). The areas under the individual band not in all cases follow the calculated oscillator strengths.

5. Conclusions

The performed spectroscopic and quantum-mechanical studies of the α and β-naphthanilide derivatives have shown that:

- The experimental unstructured absorption spectrum can be decomposed into separate bands taking into account results of theoretical computation. Its sum gives the experimental profile with a good approximation.
- For the compounds studied the number of electronic states in the region up to 6 eV, obtained from the INDO/S calculations is larger than for naphthalene. All $S_0 \rightarrow S_n$ transitions possess an oscillator strength differing from zero, while in naphthalene, where some transitions are forbidden by the symmetry rule.
- Changing the molecular environment from the vapour to the solvent phase, the onset $\tilde{\nu}$-value of the long-wave ($S_0 - S_1$) absorption band changes in the following way: $\tilde{\nu}_{\text{onset}}^{\text{vapor}} > \tilde{\nu}_{\text{onset}}^{\text{solvent}}$ (or $\lambda_{\text{onset}}^{\text{vapor}} > \lambda_{\text{onset}}^{\text{solvent}}$). The above finding, the fact that the phosphorescence has intensity many times higher than the fluorescence indicate that the $S_0 \leftarrow S_1$ and $S_0 \leftarrow T_1$ transitions are of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ type, respectively.
- The calculated energy values of the lower singlet and triplet states are in a good agreement with the experimental data, the differences do not exceed 5%.
- At 77 K, the compounds I-IV show an additional broad unstructured band besides the structured fluorescence and phosphorescence bands. It is considered to be emitted by a cis-imidol tautomer. This tautomeric form of the molecules is created in an excited bi-protonic reaction of the H-bonded dimer.

The chemical space structure optimization procedure allows determination the permanent dipole moments in the ground and excited states of compounds under study. These results with respective experimental data will be published in a separate paper.

Acknowledgements

The authors are grateful to Dr hab. Józef Liwo (from the Institute of Chemistry of the University of Gdańsk) for many helpful discussions concerning the quantum-chemistry calculations. This work was partially supported by the research grants of the Pomeranian Pedagogical Academy at Słupsk, Project NW/6/76/01 and the University of Gdańsk, Project BW-5200-5-0206-1 and KBN 203/P03/2001/21.

[1] K. H. Drexhage, in F. P. Schafer (Ed.), Structure and Properties of Laser Dyes, in: Dye Lasers, ed. Springer Verlag, Berlin 1973.
[2] J. M. Warman et al., Chem. Phys. Lett. **210**, 397 (1993).
[3] J. Bourson, J. Mugnier, and B. Valeur, Chem. Phys. Lett. **92**, 430 (1982).
[4] J. Heldt and M. Kasha, J. Mol. Liquids **41**, 303 (1989).
[5] R. N. Jones, J. Amer. Chem. Soc., **67**, 2127 (1945).
[6] E. Lipczynska-Kochany, J. Photochem. Photobiol. A Chem. **41**, 187 (1988).
[7] J. J. P. Steward, J. Comp. Chem. **10**, 209 (1989).
[8] E. Lipczynska, Monatsh. Chem., **114**, 1009 (1983).
[9] E. Szatan J. R. Heldt, and J. Heldt, J. Photochem. Photobiol. A Chem. **115**, 27 (1998).
[10] J. Heldt, J. Photochem. Photobiol. A Chem. **60**, 183 (1991).
[11] M. Kasha, J. Chem. Soc. Faraday Trans. **82**, 2379 (1986).
[12] E. Lipczynska-Kochany, Some New Aspects of Hydroxamic Acids Chemistry, Wydawnictwo Politechniki Warszawskiej, Warszawa 1988.
[13] G.-Q. Tang, J. MacInnis, and M. Kasha, J. Amer. Chem. Soc. **109**, 2531 (1987).
[14] D. P. Bandyopadhyay, D. Majumdar, S. P. Bhattacharyya, and K. K. Das, J. Mol. Structure (Theochem.) **367**, 127 (1996).
[15] M. Kasha, Faraday Soc. Discussion **9**, 14 (1950).
[16] T. Hashimoto, H. Nakano, and K. Hirao, J. Chem. Phys. **194**, 6244 (1996).
[17] J. N. Murrell, The Theory of the Electronic Spectra of Organic Molecules, John Wiley & Sons Inc. New York 1963, Chapt. 7-11.