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Calculated and Experimental Spectra of some 1,8-Naphthalimide Derivatives

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This paper is dedicated to Prof. Dr Nikolai Tyutyulkov on the occasion of his 70th birthday.

ABSTRACT

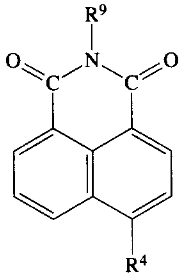
The influence of different electron donating substituens on the absorption of 1,8-naphthalimide derivatives was studied and compared with the theoretically (AM1,PPP-SCF-CI) calculated predictions. It was shown that the experimental results and the calculated electronic transitions are in good agreement, assuming that in relation to the solvent polarity the possible mesomeric forms contribute to a different extent. In cases where a labile hydrogen atom is present, tautomerism takes place. © 1997 Elsevier Science Ltd

INTRODUCTION

Derivatives of 1,8-naphthalimides attract interest in view of their practical application as fluorescent dyes, laser active media, solar energy collectors, etc [1]. Some of them show solvatochromic effects and it is known that the well known influence of solvents on UV–Vis spectra is an indication of possible non-linear optical activity [2]. An essential advantage of these dyes is their thermo- and photostability, which make it of interest for technological use. This group of compounds, as typical of the carboximide dyes, were given general characterisation by Fabian [3]. Although some 1,8-naphthalimide derivatives have been intensively investigated in the last years [4], there is still a lack of theoretical and experimental data for the basic parameters of these dyes such as the dipole moments, the electronic transition energies, the oscillator strengths, etc. The aim of the present work is to get further information about the basic electronic properties of some 1,8-naphthalimide dyes. This is done by comparing the experimentally determined absorption bands and oscillator strength with the corresponding calculated values.

EXPERIMENTAL

The compounds under study were of general formula:



Dye	R^4	R^9
1	$-NH_2$	$-C_2H_5$
2	$-NH_2$	$-CH_2CH_2OH$
3	$-NHC_2H_5$	$-CH_2CH_2OH$
4	$-N(CH_3)_2$	$-CH_2CH_2OH$
5	morpholino	$-CH_2CH_2OH$
6	piperidino	$-CH_2CH_2OH$
7	pyrrolidino	$-CH_2CH_2OH$

The synthesis and the structure characterization of the compounds investigated were reported earlier [5].

The absorption spectra were measured at room temperature on a Perkin–Elmer Lambda 2 UV–Vis spectrophotometer, using spectral grade solvents. The dye concentration was $4.76–8.3 \times 10^{-5}$ mol l^{-1}. In view of the insolubility of some dyes in nonpolar solvents, it was only possible to record their spectra in saturated hexane solutions of unknown concentration. However, this has no influence on the dye spectra interpretation.

Colour measurements of dyed polyamide fabrics were carried out on a Texflash 3881 ACS/Datacolor spectrophotometer at dye concentration 0.5% w/w and fluorescence calibration.

Methods of calculation

The influence of the substituents in position R^4 on the geometry of the π-electronic fragment was evaluated by means of the AM1 method [6]. The results for the optimized geometry were used for calculation of electron spectra within the PPP–CI-method including all the mono-excited configurations. Standard parameters for dye molecules were used [7]:

X	$U_x[eV]$	$\gamma_x[eV]$	$\beta^0_{cx}[eV]$	$R_{cx}[\AA]$
C	10.84	11.47	2.318	1.40
$\dot{N}$	13.73	11.88	2.576	1.36
$\ddot{N}$	22.31	11.88	2.350	1.43
$\dot{O}$	14.84	14.519	2.670	1.22
$\ddot{O}$	26.84	14.519	2.550	1.36

The Mataga approximation [8] was used for γ_{cx}, and the Mulliken formula [9]

$$\beta(R) = \beta_o.S(R)/S_o$$

accounted for the dependence of resonance integrals β on bond lengths R (S stands for overlap integrals).

The labelling of the atoms is given in Fig. 1

RESULTS AND DISCUSSION

Molecular structure and spectral data

The AM1 optimized geometrical data collected in Tables 1–3 reveal the specific effect of substituents.

It is easily seen (Table 1) that the bond lengths of the seven molecules are very close in value. Some characteristic deviations are observed with **4** where

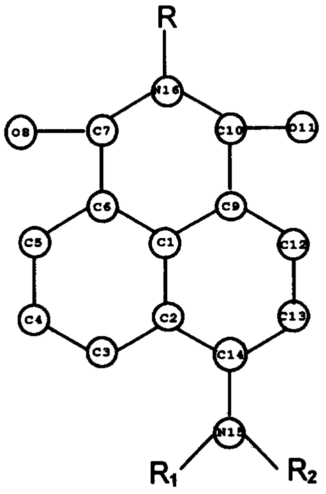


Fig. 1. Atomlabelling.

TABLE 1
AM1-computed Bond Lengths (Å)

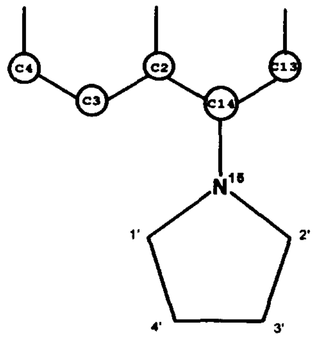
Comp. bond	*1*	*2*	*3*	*4*	*5*	*6*	*7*
C1—C2	1.417	1.419	1.419	1.420	1.433	1.433	1.427
C1—C6	1.425	1.424	1.423	1.423	1.426	1.426	1.425
C1—C9	1.418	1.418	1.418	1.420	1.417	1.416	1.417
C2—C3	1.421	1.419	1.420	1.421	1.419	1.419	1.419
C2—C14	1.448	1.448	1.451	1.447	1.464	1.466	1.455
C3—C4	1.375	1.377	1.377	1.378	1.377	1.378	1.378
C13—C14	1.404	1.408	1.404	1.397	1.416	1.417	1.416
C4—C5	1.411	1.410	1.409	1.410	1.404	1.403	1.406
C12—C13	1.399	1.396	1.400	1.405	1.391	1.390	1.392
C5—C6	1.381	1.381	1.381	1.381	1.380	1.381	1.381
C9—C12	1.384	1.386	1.382	1.379	1.380	1.380	1.384
C6—C7	1.482	1.483	1.483	1.486	1.484	1.484	1.483
C9—C10	1.476	1.473	1.476	1.476	1.473	1.473	1.473
C7—N16	1.404	1.405	1.405	1.406	1.403	1.405	1.404
C10—N16	1.409	1.409	1.408	1.406	1.406	1.407	1.407
C7—O8	1.246	1.246	1.246	1.246	1.247	1.247	1.247
C10—O11	1.246	1.248	1.248	1.247	1.248	1.249	1.249
C14—N15	1.384	1.370	1.387	1.412	1.388	1.388	1.378

TABLE 2
AM1-optimized Valence Angles (α)

				Dye			
α	*1*	*2*	*3*	*4*	*5*	*6*	*7*
C1—C2—C3	119.3	118.4	118.2	118.3	115.1	114.9	116.7
C2—C3—C4	120.4	121.2	121.4	121.1	123.6	123.7	122.4
C3—C4—C5	120.5	120.5	120.3	120.5	120.5	120.7	120.6
C4—C5—C6	120.4	119.8	120.0	119.7	118.7	118.6	119.2
C5—C6—C7	119.7	119.3	119.4	119.4	117.7	117.5	118.4
C6—C7—O8	121.3	121.5	121.7	121.6	121.3	121.2	121.5
C2—C1—C9	121.1	120.7	120.4	120.7	121.6	121.7	121.2
C1—C9—C10	120.5	120.5	120.3	120.5	122.1	122.1	121.3
C9—C10—O11	121.9	122.2	122.3	122.0	122.1	122.0	122.1
C1—C9—C12	119.7	119.8	119.9	119.5	118.9	118.9	119.5
C9-C12-C13	120.6	120.9	120.9	120.9	120.6	120.6	120.7
C12—C13—C14	121.4	121.2	121.2	121.5	124.0	124.2	122.5
C2—C14—N15	121.1	121.3	120.1	119.6	126.9	127.1	125.2
C6—C7—N16	118.5	118.7	118.4	118.6	118.9	118.9	118.7

the bond C14—N15 is noticeably longer (1.41Å) compared to the rest of the compounds ($\sim$1.38Å). The deviations of the valence angles from the ideal value of 120° is insignificant (2–3°). The bulkier the substituent at site 14, the larger the angle C2—C14—N15, to avoid the proximity of the H-atom at C3 (Table 2). Here again **4** makes an exception—the longer bond C14—N15 allows for some torsion and instead of increase in the bond angle here the

TABLE 3
Some AMl-optimized Dihedral Angles (Θ°) of **7**

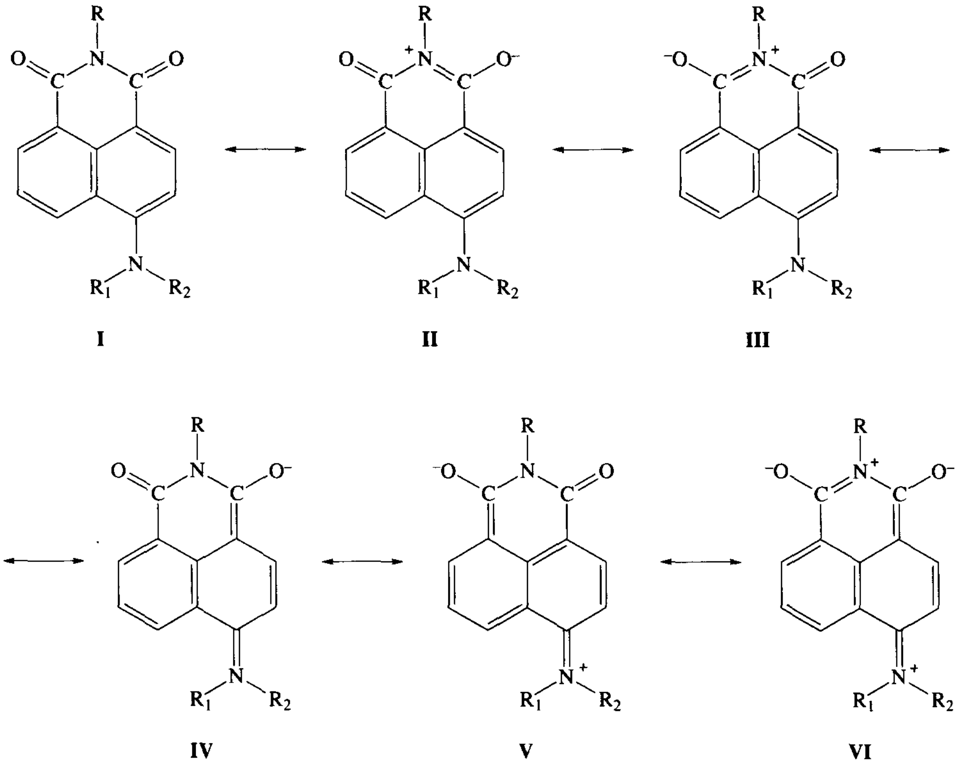


Dihedral angle (θ°)	
C3C2C14C15	−1.18
C2C14C15*C1'*	0.33
C13C14C15*C2'*	−0.65
C1'C15C2'C3'	0.23
C2'C15C1'C4'	1.25

overlap is avoided by twisting of the CH_3-groups out-of-plane. The planarity of compounds **1**–**3** and **7** is perfect (Table 3), whereas **4**–**6** deviate to a different degree. The calculated geometry is in good agreement with the X-ray data for naphthalimide [10]. The results for the longest wavelength absorption λ_{max}, with respective oscillator strength f, and the dipole moments μ_0 of the ground state of each form of compounds **1**–**7** are collected in Table 5. Table 4 contains the experimental data of the UV–Vis absorption spectra taken in solvents of different polarity.

The spectra in Fig. 2(a,b and c) show that for all the compounds a series of bands in the range 340–440 nm are recorded. However, the quantum–chemical calculations for the basic form I (see Table 5), do not reproduce the experimental spectral series. With increase of solvent polarity [Fig. 2(b)], both bathochromic shift and most often hyperchromic effect of the longest wavelength absorption is observed, whereas the shorter wavelength peaks undergo only a hypochromic change. This may be due to tautomerism and/or to the stabilization of more polar forms resulting from intramolecular redistribution of electron density. Polar forms contribute only a small part to the ground state, but they make a large contribution to the excited state. In connection with this, the long wavelength can be a result of co-operation of different forms [11]. For example, in ethanol λ_{max} undergoes a bathochromic shift in relation to the band in non-polar solvents because the energy of exitation is lowered by ionic forms. Thus the ground state of the compounds under investigation could be described as a resonance hybrid of the six most probable canonical structures presented in Scheme 1.

Solvents with increasing polarity tend to stabilize charge-transfer structures; the limiting case corresponds to a charge transfer of one electron from


I II III IV V VI

Scheme 1.

the donating to the accepting group [12]. The use of different solvents, at least in principle, allows for the modulation of the structure of the nonpolar form I, so that one of the mesomeric forms, the zwitterionic II–V or the tetrapolar VI would predominate.

From a theoretical viewpoint it is possible to mimic solvent effects in terms of redistribution of electron density in the molecule. This was accounted for by means of appropriate choice of parameters reflecting the respective valence state of the heteroatoms in the PPP—CI calculations. In Table 5 are presented the results of the latter for λ_{max}, f and μ_0 of the structures I–VI in the ground state.

The results obtained correlate nicely with the experimental data from Table 4.

In hexane, the dyes are not solvated with the solvent and form I, for which the dipole moment is the lowest and the absorption is at shortest wavelengths, should be responsible for the colour. However, the π-electron energy of form I is higher than any of the polar forms II–VI, so that even in hexane the polar mesomeric forms contribute. With the increase of solvents polarity

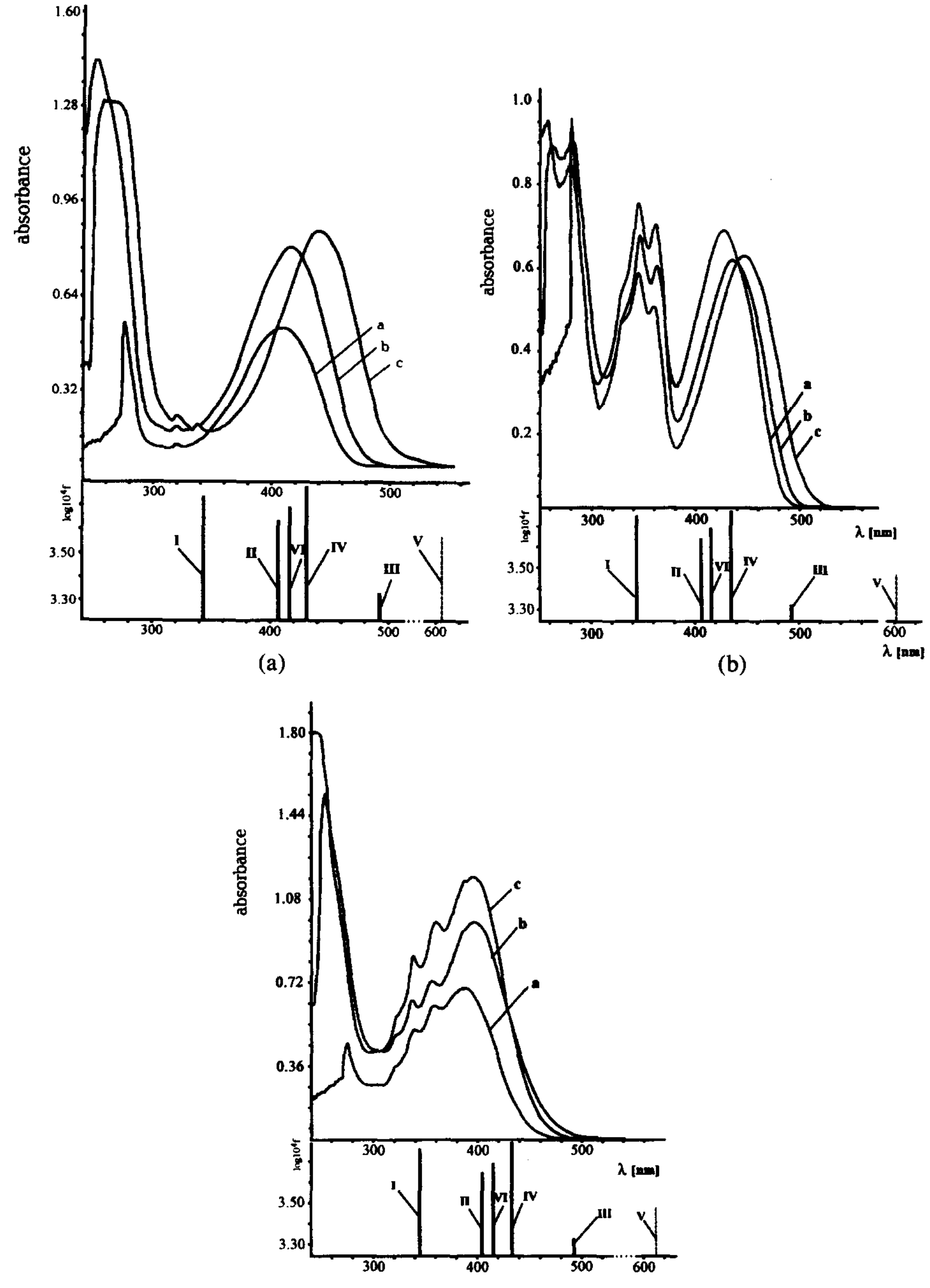
TABLE 4
Experimental Spectral Data

Dye	C_6H_{14}	$PhCH_3$		$CHCl_3$		C_2H_5OH		$(CH_3)_2SO$		R_{min}
	λ_{max} (nm)	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε	(nm)
1		327		326	3.322			326	3.491	
		342						342	3.380	
	386	412	3.883	420	3.859	430	4.161	440	4.176	440
2		327		326				326	3.588	
		342						343	3.439	
	398	410	3.825	414	3.602	430	4.037	442	3.923	445
3	327	329	3.654	328	3.613	322	3.890	328	3.633	
	341	345	3.783	345	3.740	339	3.984	344	3.724	
	356	360	3.753	362	3.690	350	3.921	358	3.663	
	400	425	3.763	432	3.763	436	4.039	444	3.778	445
4	327	327	3.322	328	3.255			328	3.255	
	342	342	3.431	344	3.303			342	3.230	
	396	424	4.033	424	4.064	412	4.029	428	4.025	440
5	326	329	3.638	328	3.699	328	3.635	328	3.643	
	340	345	3.814	344	3.851	344	3.756	344	3.763	
	356	366	3.900	364	3.934	362	3.833	364	3.833	
	382	394	3.959	396	4.025	397	3.968	404	3.973	400
6	326	328	3.256	328	3.287			328	3.421	
	341	344	3.367	344	3.314			343	3.432	
	395	405	3.935	420	3.978	412	4.004	415	4.050	420
7		332		331	3.257			331	3.415	
		347		346	3.111			347	3.301	
	426	442	4.182	450	4.257	443	4.290	454	4.322	455

a structure described by forms II and III resulting from the imide resonance should be favored (in terms of dipole moments).

However, the UV–Vis spectra give no evidence for contribution of form III. Apparently, the proximity of N15 stabilizes the negative charge at O11, while for O8 this route is much longer to be effective. Next in polarity comes the tetrapolar form VI, which actually occurs from superposition of forms III and IV and, accordingly, its dipole moment has an intermediate value between those of III and IV. This is the mesomeric form predominating in the structure in solvents of intermediate polarity.

Solvents of high polarity favour form IV where a charge transfer from the electron-donating N15-atom to the electron-accepting O11-atom occurs. This form features the largest dipole moment and it describes best the longest wavelength absorption registered in the experimental spectra. In none of the latter, though, was traced an absorption band corresponding to form V. A possible reason for this is that in form V the route of charge redistribution is the longest possible in the molecule and with poor conjugation (Table 1).



(a) (b)

(c)

Fig. 2. UV–Vis-spectra in toluene (a), chloroform (b) and DMSO (c), compared with the theoretically predicted 0–0 transitions of the mesomeric forms (Scheme 1). Fig 2a — compound 2. 2b — compound 3. 2c — compound 5.

TABLE 5
PPP–SCF–CI-calculated Spectral Characteristics

Dye	*Form*	λ_{max} (nm)	f	μ_0(D)	*Dye*	*Form*	λ_{max} (nm)	f	μ_0 (D)
1	I	343	0.53	4.23	**4**	I	343	0.53	4.23
	II	407	0.43	10.33		II	407	0.42	10.33
	III	488	0.22	9.65		III	490	0.21	9.70
	IV	435	0.60	15.78		IV	436	0.60	16.07
	V	603	0.29	19.33		V	599	0.29	19.51
	VI	417	0.49	13.65		VI	416	0.49	13.86
	VII	372	0.80	5.51	**5**	I	345	0.56	4.40
	VIII	556	0.25	15.15		II	406	0.44	10.67
2	I	344	0.56	4.79		III	493	0.21	9.70
	II	407	0.43	10.44		IV	430	0.63	15.80
	III	493	0.21	9.73		V	612	0.29	19.75
	IV	434	0.60	15.70		VI	420	0.48	13.92
	V	604	0.29	19.27	**6**	I	347	0.55	4.38
	VI	418	0.48	13.58		II	410	0.44	10.73
	VII	375	0.83	6.28		III	499	0.21	9.75
	VIII	556	0.25	15.16		IV	431	0.63	15.67
3	I	343	0.53	4.25		V	614	0.29	19.62
	II	407	0.43	10.41		VI	422	0.48	13.79
	III	493	0.21	9.73	**7**	I	347	0.54	4.35
	IV	435	0.60	15.82		II	409	0.44	10.66
	V	602	0.29	19.32		III	499	0.21	9.75
	VI	417	0.49	13.68		IV	431	0.62	15.54
	VII	375	0.83	6.28		V	613	0.29	19.40
	VII	375	0.83	6.28		V	613	0.29	19.40
	VIII	556	0.25	15.15		VI	421	0.47	13.61

On the highly polar polyamide, where additional stabilization of the zwitterionic structures, due to the possibility of H-bonding occurs, form IV is again the predominating one (Fig. 3). The analysis of the IR spectra of compounds 1–7 showed that ν_{anti} and ν_{symm} each appear as a doublet, giving four bands for the C = O groups in the range 1699–1634 cm^{-1}. This observation supports the idea of four possible resonance structures [13].

The compounds under study have as substituent R^4 (C14 in our labelling) a primary (**1**, **2**), a secondary (**3**) and a tertiary amino group (**4** – **7**). Thus, for compounds **1–3** the possibility for tautomerism should be taken into account Scheme 2.

In Table 5 are presented the calculated values for λ_{max}, f and μ_o of the optimized tautomeric forms (VII and VIII) of compounds 1–3. For the form VIII of compounds 1–3 (with optimized geometry) were obtained identical values of λ_{max} with low f (0.2) and large μ_o (15.15 D). The experimental absorption spectra give no evidence for the presence of this form. Our arguments to rule out this form are the same as those applied to mesomeric form V (see above).

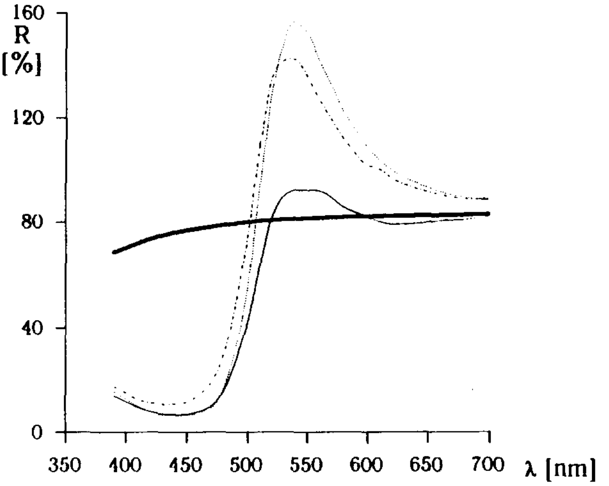
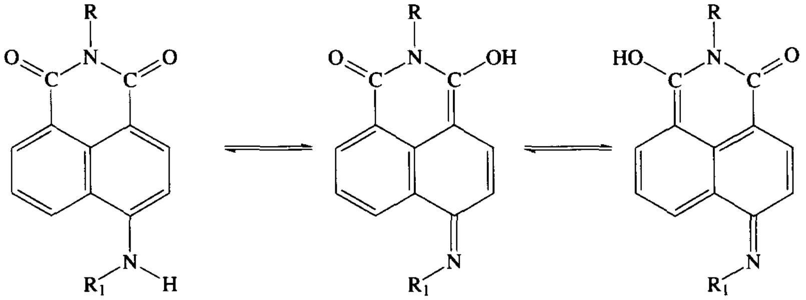


Fig. 3. Reflection spectra on polyamide of compound **2**(——), **3**(······) and **4** (–·–·–).



I VII VIII

Scheme 2.

Experimentally the presence of tautomerism was demonstrated by means of UV–Vis, IR- and ^{1}H-NMR - spectroscopy [14]. As can be seen in Fig. 4, the increase of the solvent polarity results in a hypochromic shift of the short wavelength maxima compensated usually by a hyperchromic effect of the long wavelength ones. The isobestic point is at $\sim$380 nm. Bearing in mind that the π-electron energy of the tautomeric forms VII of 1–3 is lower compared to the basic form (I) and the dipole moments of forms I and VII are pretty close and much lower than the rest of the forms (II–VI), it seems that even in non-polar solvents the tautomeric form is the one responsible for the longest wavelength absorption, alongside with some contribution of form II. The experimental results obtained convincingly confirm the possibility for tautomerism of compounds **1–3**, containing labile hydrogen atom in R^4, as initially predicted by quantum-chemical calculations.

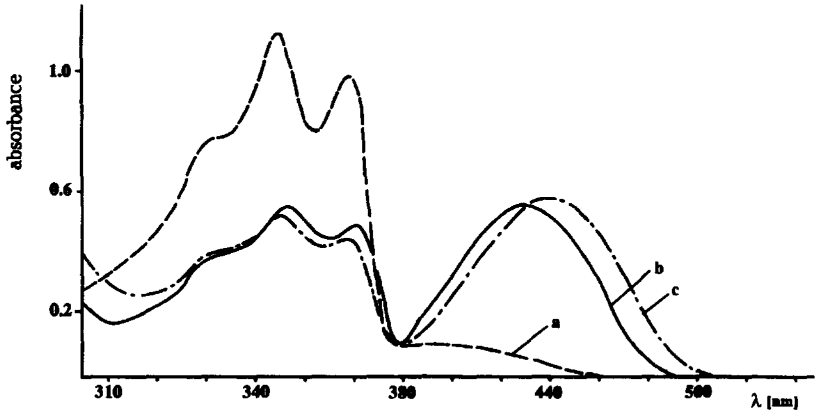


Fig. 4. Test for tautomerism—UV-/Vis -spectrum of isomolar solutions of 3 in tetrachloromethane (a), chloroform (b) and DMSO (c).

Colour—constitution correlation

The major advantage of quantum-chemical studies on dyes is the possibility of establishing a correlation between colour and constitution. According to the order of increasing of the electron-donating properties of the substituents at R^4, the bathochromic shift of the longest wavelength transition should follow the substituent order [15]:

NH_2 < NHEt < morpholino < $N(CH_3)_2$ < pyrrolidino < piperidino

However, the experimental data (Table 4) show that the deepening of the colour follows a somewhat different sequence:

morpholino < piperidino < HN_2 < $N(CH_3)_2$ < NHEt < pyrrolidino

The results for λ_{max} of 1–7 calculated by means of the PPP–SCF–CI-method do not differ substantially, since the π-electron system is essentially the same. Deviation of the experimental λ_{max} from the theoretically predicted values can be interpreted in terms of structural differences of the compounds, partly evidenced by the data in Tables 1–3.

Compounds 1 and 2 differ only in an OH-group at the R^9 substituent. The ratio of their λ_{max} varies depending on the solvent used: in aprotic solvents $\lambda_{max}(\mathbf{1}) < \lambda_{max}(\mathbf{2})$, whereas in protic ones holds the opposite, $\lambda_{max}(\mathbf{1}) > \lambda_{max}(\mathbf{2})$.

The reason for this effect is probably the formation of intramolecular H-bond between the oxygen atoms of the OH-group at R^9 and the carbonyl oxygen 011 [15]. This interatomic distance is 2.9Å (AM1) and allows for the occurrence of H-bonding. In ethanol, where the intermolecular H-bonding of solvent molecules is strong, the two compounds absorb at equal wavelength.

The increase of λ_{max} in **3** is in conformity with the higher electron-donating properties of the NHEt-group compared to that of the NH_2-one. Otherwise, the geometry of **1**, **2** and**3** is practically the same.

For compound **4** is recorded a substantial hypsochromic shift of λ_{max} compared to **3**, regardless of the fact that the electron-donor character of the dimethylamino-group is greater than that of the ethylamino-group. In this case, however, the steric hindrance results in twisting about the C14—N15 bond to reduce steric crowding, removing the nitrogen atom $2p_z$ AO from optimum position of overlap with the aromatic π-electron cloud to a position of reduced overlap.

Of special interest are compounds **5**–**7**, where N15 is part of a saturated cycle. The optimized geometry shows that in **5** and **6** the morpholino and pyperidino cycles are in a chair conformation, whereas the pyrrolidino derivative is perfectly planar. The steric effect in **5** and **6** results in substantial increase of the valence angle C2—C14—N15 (Table 4), which affects the planarity of the naphthalimide fragment. Such an effect does not occur in **7**. The lack of planarity in **5** and **6** disturbs the conjugation, hence, the hypsochromic effect. The further hypsochromic shift resultant in the morpholino derivative is relatable to the -I effect of the additional heteroatom in the γ-position [16], and the degree of shift increases with the increased strength of the inductive effect making the polar forms less favored.

Surprisingly, the optimized geometry of **7** is perfectly planar (Table 3), but still this cannot explain the significant bathochromic shift of its absorption compared to that of the rest. Most probably, here occurs *σ-p* hyperconjugation, which practically means an extension of the conjugated system, hence, the shift to longer wavelengths [17].

The reflection spectra of the compounds under study are again in support of the influence of planarity on spectral behaviour. In the adsorbed state, the torsions are hindered and constraint improvement of planarity occurs, hence, the systematic bathochromic shift of R_{min}-values on polyamide compared to λ_{max} in any of the solvents used.

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REFERENCES

1. Wintgens, V., Valat, P., Kossanyi, J., Biczok, L., Demetar, A. and Berus, T., *Journal of the Chemistry Society Faraday Transcripts*, 1994, **90**, 411.
2. Long, N., *Angewehr Chemie*, 1995, **107**, 37.
3. Fabian, J. and Hartmann, H., *Light Absorption of Organic Colorants*. Springer, Berlin, 1980, p.80.
4. Baumann, D., Haneman, T. and Wolarz, E., *Zeitschrift Naturforschung*, 1994, **499**, 671.
5. Philipova, T., *Journal of Practical Chemistry*, 1994, **336**, 587.
6. Stewart, J. J. P., *MOPAC: A General Molecular Orbital Package (Vers. 6.0)*. Q.C.P.E., 1994, **455**, 10.
7. Fabian, K. and Hartmann, H., *Theoretica Chimica Acta*, 1968, **12**, 319.
8. Mataga, N. and Nishimoto, K., *Zeitschrift Physics and Chemie*, 1957, **13**, 140.
9. Mulliken, R. S., *Journal of Chemistry and Physics*, 1949, **46**, 497 675.
10. Grigorieva, L.P., Chetkina, L. A., Neugaus, M. G. and Goldar, G. A., *Christallographie* (russ.), 1975, **20**, 33.
11. Wojciechowski, K., *Dyes and Pigments*, 1993, **22**, 239.
12. Zuliani, P., Del Zoppo, M., Castiglioni, C., Zerbi, G., Marder, S. and Perry, J., *Journal of Chemistry and Physics*, 1995, **103**, 1.
13. Philipova, T., Karamancheva, I. and Grabchev, I., *Dyes and Pigments*, 1995, **28**, 91.
14. Tadjer, A., Karamancheva, I., Philipova, T. and Madjarova, G., (to be published)
15. Gordon, P. and Gregory, P., *Organic Chemistry in Colour*. Springer, Berlin, 1983, 141–147.
16. Peters, A. T. and Bide, M., *Dyes and Pigments*, 1985, **6**, 349.
17. Silverstein, R., Bassler, G. and Morril, T., *Spectrometric Identification of Organic Compounds*. John Wiley & Sons, NY, 1974, p.443.