Electronic Spectral Investigations upon the Photochemical Transformations of Some Substituted 1-(N,N-bisacyl)amino-4,5-diphenyl-1,2,3-triazoles

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The objective of this report is to investigate the steady state and dynamic photophysical and photochemical properties of 1-(N,N-bisacyl)amino-4,5-diphenyl-1,2,3-triazoles in solvents of different polarity at room temperature and in frozen matrix at 77 K. On the basis of the comparison of their UV absorption and luminescence spectra with those of 4,5-diphenyl-1,2,3-triazole and dibenzamide (model compounds), cleavage of the N-N bond in the title compounds after irradiation with polychrome UV light is proved.

Key words: 1-(N,N-bisacyl)amino-1,2,3-triazoles; Absorption; Luminescence; UV Irradiation; N-N Bond Cleavage.

Introduction

Photochemical reactions of both aromatic and aliphatic N-substituted phthalimides result mainly in cyclic products [1, 2] or fission of the N-CO bond [3]. In the literature [4 - 8] there are also a few examples which represent a formal β-cleavage reactions [4] involving carbonyl compounds beside those reported for ketones containing good radical leaving groups at α-carbon [6]. In [7] the first examples of photoinduced β-elimination of the triazole group in 1-(N,N-bisacyl)amino-1,2,3-triazoles are reported and the proposed mechanism rested basically on product isolation. The application of 1-(N,N-bisbenzoyl-amino)-4,5-diphenyl-1,2,3-triazole as a photoinitiator in photopolymerization of methyl methacrylate is reported in [8].

The aim of the present work is to prove the reported cleavage of the N-N bond in 1-(N,N-bisacyl)-amino-1,2,3-triazoles [7] and the concomitant formation of 4,5-diphenyl-1,2,3-triazole and dibenzamide after irradiation with polychrome UV light on the basis of their photophysical and photochemical properties. For that purpose a detailed study of the UV ab-
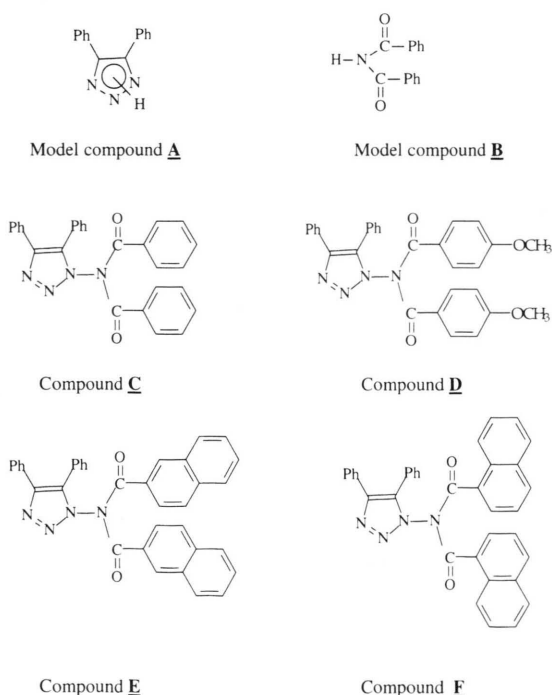

Fig. 1. Structure of the model compounds **A** and **B** and the investigated compounds **C**, **D**, **E**, and **F**.

Table 1. Spectral characteristics of the model compounds **A**, **B** and the investigated compounds **C**, **D**, **E**, and **F** in ethanol, cyclohexane and acetonitrile at 300 K. ν_{abs} and ν_{fl}: absorption and fluorescence Franck-Condon transitions in [cm^{-1}], ε: molar extinction coefficient in [l/mol·cm], Q_{fl}: fluorescence quantum yield, τ: natural lifetime in [ns], K_r: radiative rate constant calculated from τ and Q_{fl}.

Comp.	— Ethanol —						— Cyclohexane —					— Acetonitrile —				
	ν_{abs}	ε	ν_{fl}	Q_{fl}	τ	K_r	ν_{abs}	ν_{fl}	Q_{fl}	τ	K_r	ν_{abs}	ν_{fl}	Q_{fl}	τ	K_r
A	39 600	14 200	28 570	0.04	1.34	0.029	39 600	29 410	0.02	1.36	0.015	39 600	27 780	0.03	1.90	0.016
B	41 600	16 100	/	/	/	/	43 410	/	/	/	/	41 600	/	/	/	/
C	40 820, 35 000 s	33 600	/	/	/	/	40 820, 35 000 s	/	/	/	/	40 000, 35 000 s	/	/	/	/
D	36 500, 33 000 s	11 500	24 390	0.01	1.80	0.005	36 530, 34 480 s	/	/	/	/	35 710, 32 260 s	22 730	0.01	1.22	0.008
E	41 230, 33 540 s, 28 770 s	99 700 23 800	23 500	0.03	3.30	0.009	40 410, 32 390 s, 28 770 s	26 320	0.01	1.32	0.008	42 080, 33 540 s, 28 350 s	23 260	0.02	3.20	0.006
F	41 230, 32 770, 30 620 s	98 500	21 620	0.09	12.60	0.007	41 230, 32 770, 31 090 s	23 260	0.02	6.02	0.003	41 230, 32 770, 30 620 s	20 830	0.06	10.60	0.006

sorption, and steady state and dynamic luminescence properties of differently substituted 1-(N,N-bisacyl)amino-1,2,3-triazoles-compounds **C**, **D**, **E** and **F** (Fig. 1) in solvents with different polarity at room temperature and in frozen matrix at 77 K was performed. The spectral results of compounds **C**, **D**, **E** and **F** are discussed in comparison with those of the model compounds **A** and **B** (Fig. 1) which are considered as the two main fragments in the investigated structures.

Experimental

The investigated compounds (Fig. 1) were synthesized according to procedures described in [9, 10]. The absorption spectra were recorded on a Specord UV-VIS (Carl Zeiss, Jena). The solvents used were of fluorescence grade. The corrected fluorescence spectra were recorded on a Perkin Elmer MPF 44 spectrofluorimeter. The fluorescence quantum yields (Q_{fl}) were measured in relation to 3-aminophtalimide ($Q_{fl} = 0.6$ in ethanol) [11]. The fluorescence decay curves (10 000 counts in the maximum, 512 channels, 0.1 ns/chan) were collected at 300 K on a nanosecond Single Photon Counting spectrofluorimeter System PRA 2000, using a nitrogen filling flash lamp with λ_{ex} 313 nm and an emission wavelength corresponding to the maxima of the emission bands. The natural lifetime τ was estimated by a standard deconvolution procedure, the accuracy of the fit was controlled by the weight residuals, the autocorrelation function of the residuals and the reduced χ^2. The quantum-chemical calculations were carried out with AM1 approximation, taking into consideration all single and double excited configurations among 10 molecular orbitals and simulating solvent effects in the ground and excited state [12]. The irradiation (up to 30 min) was made in solutions with optical density (OD) at 250 nm in quartz cells, using a medium pressure Hg lamp (150 W) up to no further changes in the electronic spectra. The freezing of the solutions at 77 K was made after their irradiation. Thin-layer chromatography (TLC) was performed on 4 × 10 cm plates coated with Silicagel 60$_{F 254}$ (Merck). The solvent system that produced a reliable separation was Heptane-Acetone, 5:2 (v:v). The compounds were applied as 5 µl aliquots of 10^{-3} M ethanol solutions.

Results and Discussion

1. Absorption and Luminescence of Non-irradiated Solutions

1.1. Absorption at 300 K

The longest wavelength absorption bands both of the investigated differently substituted 1-(N,N-bisacyl)amino-1,2,3-triazoles, compounds **C**, **D**, **E** and **F**, as well as the model compounds **A** and **B** (Fig. 1) are in the UV region (Table 1, Fig. 2). On Fig. 2 the absorption spectra of the compounds **C**, **D**, **A** and **B** in ethanol at 300 K are shown, the vertical lines indicate the calculated electron transitions of **C** and **D**.

The maxima of the longest wavelength absorption bands of the model compounds **A** and **B** in ethanol are at 39 600 cm^{-1} ($\varepsilon = 14 200$ l/mol·cm) and 41 600 cm^{-1} ($\varepsilon = 16 100$ l/mol·cm), respectively (Table 1, Fig. 2). In the case of compound **A** the increase in the solvent polarity does not influence the energy of the absorption maxima, indicating a very low dipole moment in the ground state. For compound **B**, a bathochromic shift of about 1 800 cm^{-1} from cyclohexane to ethanol is observed, which should be
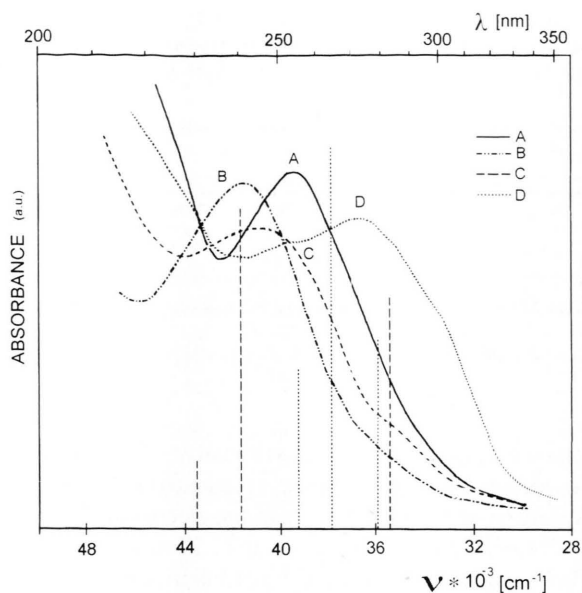
Fig. 2. Absorption spectra of compounds **A**, **B**, **C** and **D** in ethanol at 300 K. The vertical lines denote the computed energies of the $\pi\pi^*$ transitions and the corresponding oscillator strengths of **C** and **D**.
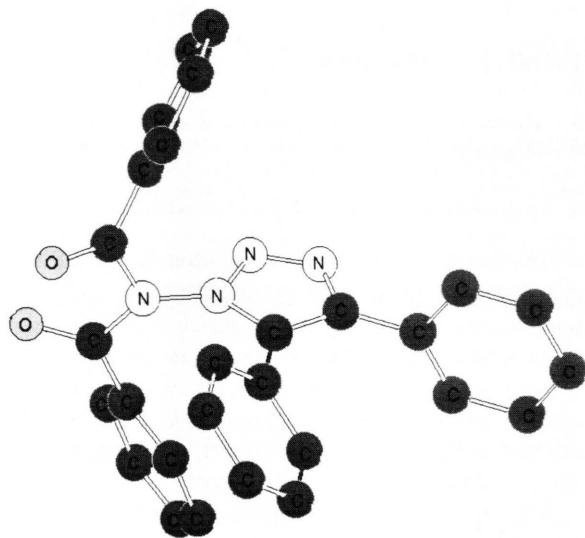

Fig. 3. Structure of compound **C** with optimized geometry in ground state.

attributed to the presence of both carbonyl and phenyl groups in the structure of **B**.

In the absorption spectrum of compound **C** in ethanol there is one well-defined absorption band with a maximum at 40 820 cm^{-1} ($\varepsilon = 33\,600$ l/mol·cm) (Fig. 2) and a weak shoulder in the region of

35 000 cm^{-1}. The results from quantum-chemical calculations show that the shoulder corresponds to the S_0-$S_1(\pi\pi^*)$ transition (Fig. 2) with oscillator strength $f = 0.46$, while the more intensive well-defined absorption band is due to the S_0-$S_2(\pi\pi^*)$ transition ($f = 0.70$). The lower energy of the S_0-$S_1(\pi\pi^*)$ transition in **C** in comparison to those in the fragments **A** and **B** indicates that the two fragments are interacting although they are out of plane, as it is seen on Figure 3.

With introducing the -OCH$_3$-group (compound **D**) in imide fragments of the molecule (Fig. 1), the longest wavelength absorption maxima shift to the red both in non-polar and in polar solvents (Table 1) in comparison to compound **C**. This is related to the interaction between the electron-donating substituent -OCH$_3$ group and the electron-accepting carbonyl groups in the molecule. Similar effects are observed also with the introdution of β-naphthalene- (compound **E**) and α-naphthalene- (compound **F**) groups at the same position (Table 1).

1.2. Fluorescence at 300 K

The model compound **A** fluoresces in all solvents used (Table 1), and the fluorescence maxima shift bathochromically with increasing solvent polarity; ν_{fl} is 29 410 cm^{-1} and 28 570 cm^{-1} in cyclohexane and ethanol, respectively. There are three N-atoms in the molecule of **A** (Fig. 1), one of them is pyrrole-type and not connected with the nπ^*-states, while the other two are pyridine-type nitrogens. According to [13], if both types of nitrogen atoms are present in a molecule, a tautomeric equilibrium between two or more forms may exist. In the case of 1,2,3-triazole (**A**) the thermodynamic parameters of the equilibrium in solution at room temperature were calculated [14] and a predominance of the (2H)-1,2,3-triazole tautomer (83%) over (1H)-1,2,3-triazole (17%) was found. Consequently,the two pyridine-type N-atoms in **A** are not adjacent, and because of that it is reasonable to compare the energy of the nπ^*-levels in compound **A** to that in the molecules of s-triazine (36 770 cm^{-1} [15, 16]) or pyrimidine (33 300 cm^{-1} [16]). There are not enough arguments to decide which one is more relevant for the investigated structure **A**, but in both cases the lowest singlet excited state in the energy diagram of the model compound **A** should be of nπ^* type because its first singlet $\pi\pi^*$ is at 39 600 cm^{-1} (Table 1). Hence the observed fluorescence of 4,5-di-

phenyl-1,2,3-triazole (Q_{fl} = 0.04 in ethanol) is of $n\pi^*$-type, similarly to other aza heterocycles [17, 18].

The carbonyl containing model compound **B** does not fluoresce in any solvent. According to literature data [19, 20], the lowest singlet excited state of $n\pi^*$-type in the energy diagram of a compound with similar structure, N-methylphtalimide is at 34 000 cm^{-1} and no fluorescence is observed in that case. Based on the structural analogy of the model compound **B** to N-methylphtalimide it is reasonable to refer the same energy of the $n\pi^*$-state in both compounds. The maximum of the longest wavelength $\pi\pi^*$ absorption band of **B** in ethanol is at 41 600 cm^{-1} (Table 1) and similarly to N-methylphtalimide the fluorescence from the first singlet excited $\pi\pi^*$-state is quenched by internal conversion through the lower lying $S_1(n\pi^*)$ level.

Bearing in mind that the energy of the localized $n\pi^*$-levels depends weakly on the prolongation of the π-system [21, 22], the energy of the first singlet $n\pi^*$-state in compounds **C**, **D**, **E** and **F** conforms to the data of the model compounds **A** and **B**. Hence the lowest singlet $n\pi^*$-state in **C**, **D**, **E** and **F** is in the spectral region 33 300 - 34 000 cm^{-1}, corresponding to the energy of the $n\pi^*$-levels in pyrimidine or N-methylphtalimide, respectively.

The lowest lying singlet $\pi\pi^*$- state in compound **C** is at about 35 000 cm^{-1} (Table 1), so the first singlet excited state in the energy diagram is of $n\pi^*$-type, and this explains the lack of fluorescence in **C**.

Compound **D** does not fluoresce in non-polar solvents and fluoresces in polar ones (Table 1). In cyclohexane the first singlet excited $\pi\pi^*$-state is at about 34 500 cm^{-1}, and similarly to **C** it is again deactivated through the close lying $S_1(n\pi^*)$ state. Increasing solvent polarity (cyclohexane - ethanol) shifts the longest wavelength absorption maximum bathochromically by about 1500 cm^{-1}, consequently in polar solvents the lowest singlet excited state is of $\pi\pi^*$-type and this fact clarifies the observed fluorescence. The fluorescence bands of **D** in ethanol and acetonitrile, which are with maxima at 24 390 cm^{-1} (Q_{fl} = 0.01) and 22 730 cm^{-1} (Q_{fl} = 0.01), respectively, differ completely (as to energy and shape of the band) from the fluorescence of the model compound **A**, and therefore this emission should be assigned to fluorescence from the whole conjugated system of compound **D**.

The hypothesis for the quenching of the emission through $S_1(n\pi^*)$ states in **C** and **D** (in non-polar solvents) is supported also by the observed fluorescence of compounds **E** and **F** in all solvents used (Table 1).

Table 2. Spectral characteristics in ethanol at 77 K. ν_{fl}: absorption and fluorescence Franck-Condon transitions in [cm^{-1}], ν_{ph}: phosphorescence Franck-Condon transitions in [cm^{-1}], τ_{ph}: phosphorescence lifetime in [s].

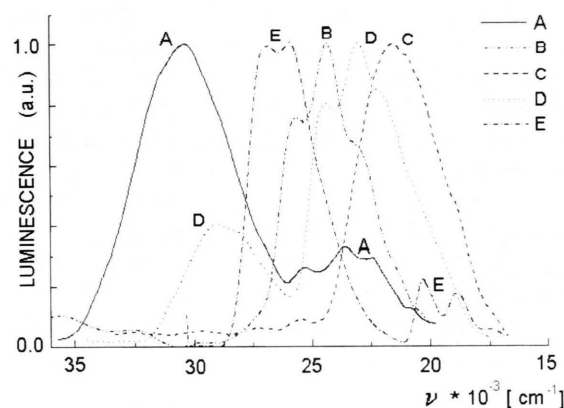| Compound	ν_{fl}	ν_{ph}	τ_{ph}
A	30 300	23 600	2.1
B	/	24 330	1.3
C	/	21 450	1.3
D	28 990	23 000	1.3
E	25 970	20 240, 18 800	1.3
F	26 110	19 920, 18 420	1.3

Fig. 4. Luminescence spectra of compounds **A**, **B**, **C**, **D** and **E** in ethanol at 77 K (normalized to 1).

As it is seen from these data, the $S_1(\pi\pi^*$ states both in non-polar and polar media for **E** and **F** have ower energy than 33 300 cm^{-1}, and consequently they are not influenced by the higher lying singlet $n\pi^*$-levels.

The maxima of the fluorescence bands ν_{fl} strongly depend on the nature of the substituent and shift bathochromically in the order -OCH$_3$, β-naphthalene, α-naphthalene. The bathochromic shift of the Franck-Condon fluorescence transition of compound **F** in comparison to compound **E** agrees with the data in [23], where a bathochromic shift of fluorescence maxima is also observed with replacement of β-naphthalene by α-naphthalene in arylethylene.

1.3. Luminescence at 77 K

The luminescence spectrum of model compound **A** in frozen ethanol matrix at 77 K consists of two emission bands (Table 2, Fig. 4). The prompt shorter wavelength luminescence with a maximum at 30 300 cm^{-1} is blue shifted by about 1 700 cm^{-1} against the corresponding emission of **A** at room temperature, similarly to the effects described in [16]. On the basis of

these characteristics this band should be assigned to the fluorescence of **A** at 77 K. The second luminescence band has a maximum at $23\,600$ cm^{-1}, the band is wide ($26\,000 - 20\,000$ cm^{-1}) and long-lived, the lifetime is 2.1 s. Based on the energy and the lifetime, this emission band should be considered as the phosphorescence of the model compound **A**. The fact that the excitation spectrum of this band is identical to the one of the prompt fluorescence excludes impurities in the matrix.

Contrary to the solutions of **B** at room temperature, where no emission is observed, the frozen ethanol matrix of **B** is characterized by one emission band with well defined vibrational structure in the region $30\,300 - 20\,000$ cm^{-1} and maximum at $24\,330$ cm^{-1} (Table 2, Fig. 4). The lifetime of this emission is 1.3 s, its intensity decreases proportionally to the decrease in concentration, and consequently it is not connected with aggregation. So this band should be considered as phosphorescence of Model compound **B**. The excitation spectrum of the phosphorescence band is identical to the absorption one.

In the luminescence spectrum of compound **C** the single emission band has a maximum at $21\,450$ cm^{-1}, lifetime 1.3 s, and this emission should also be assigned to phosphorescence (Table 2, Fig. 4). The phosphorescence of **C**, which is bathochromically shifted in relation to the phosphorescence of the model compounds **A** and **B** (Table 2, Fig. 4) should be considered as an additional proof for the interaction between the two fragments **A** and **B** in the molecule **C**.

The luminescence spectrum of **D** in frozen ethanol matrix consists of two emission bands (Table 2, Fig. 4). The maximum of the prompt fluorescence (lifetime in the order of nanoseconds) is at $28\,990$ cm^{-1} and is blue shifted against the fluorescence maximum of **D** in ethanol at 300 K. The second emission band with a lifetime of about 1 s, clear vibrational structure, and a maximum of the longest wavelength vibrational band in the region $21\,740 - 20\,400$ cm^{-1} is due to the phosphorescence transition.

In the luminescence spectra of **E** and **F**, similarly to the spectrum of **D**, two emission bands are observed (Table 2, Fig. 4). The maxima of the prompt fluorescence bands in both compounds are almost with the same energy and only a negligible difference in the vibrational structure is registered. The Franck-Condon fluorescence transitions for both compounds are hypsochromically shifted against the corresponding

fluorescence maxima at 300 K. The long-lived phosphorescence bands (lifetime about 1.3 s) in **E** and **F** have a well defined vibrational structure with two maxima (Figure 4).

The effect of substituents in imide fragments of the molecule upon the phosphorescence maxima is similar to the effect upon the fluorescence maxima at 300 K: bathochromic shift in the order -OCH$_3$, β-naphthalene, α-naphthalene.

2. Absorption and Luminescence of Irradiated Solutions

2.1. Absorption at 300 K

In [7, 8] the result caused by irradiation of 1-(N,N-bisacyl)amino-4,5-diphenyl-1,2,3-triazole (**C**) with polychromatic light is explained with cleavage of the N-N bond and formation of 1,2,3-triazolyl and imidyl radicals which after hydrogen abstraction form the final stable photoproducts 4,5-diphenyl-1,2,3-triazole (model compound **A**) and dibenzamide (model compound **B**).

Our experimental results show that after irradiation with polychromatic light only a slight decrease in the optical density in the region of the longest wavelength absorption bands of compounds **C**, **D**, **E** and **F** in all solvents used is registered. Furthermore, it is very difficult to estimate the exact changes after irradiation only from the absorption data because of the overlapping of all absorption spectra in the region $48\,000 - 28\,000$ cm^{-1} (Fig. 2) and the less intensive longest wavelength absorption bands of the two possible photoproducts **A** ($\varepsilon = 14\,200$ l/mol·cm) and **B** ($\varepsilon = 16\,100$ l/mol·cm) in comparison to that of **C**, **D**, **E** and **F** (Table 1).

2.2. Fluorescence at 300 K

Similarly to the absorption, the fluorescence properties of both model compounds **A** and **B** are not influenced by irradiation with UV light.

In contrast to the non-irradiated cyclohexane solutions of compounds **C** and **D**, where no fluorescence is observed, fluorescence bands with maxima at $29\,410$ cm^{-1} both for **C** and **D** are registered in the irradiated solutions. The shapes of the bands and the energies of the maxima are identical with the fluorescence band of **A** in cyclohexane. This supports the hypothesis of the cleavage of the N-N bond after
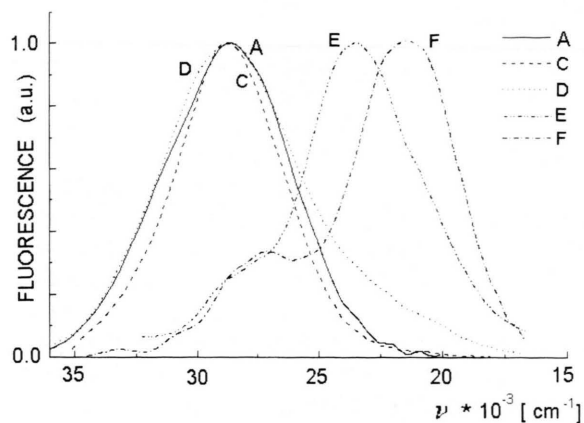
Fig. 5. Fluorescence spectra of with UV light irradiated (30 min) ethanol solutions of compounds **C**, **D**, **E**, **F** and model compound **A** at 300 K (normalized to 1).

Fig. 7. Luminescence spectra of with UV light irradiated (30 min) ethanol solutions of compounds **C**, **D**, **E** and model compounds **A** and **B** at 77 K (normalized to 1).
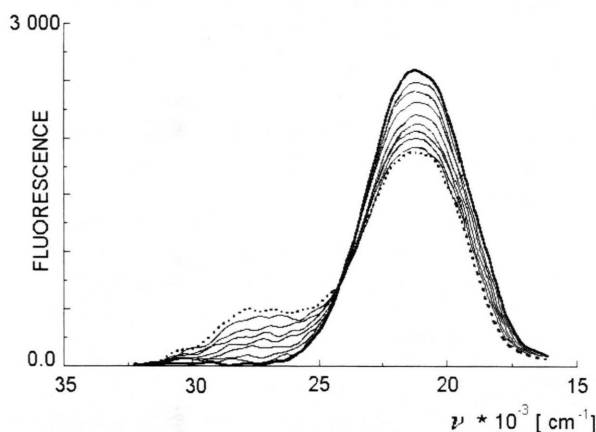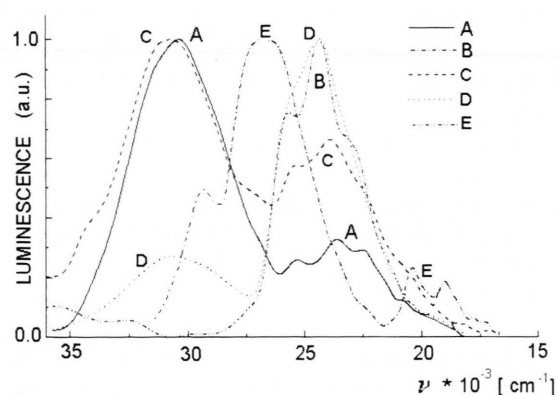

Fig. 6. Influence of polychrome irradiation on the fluorescence spectrum of **F** (ethanol, 300 K). Solid line: 0 min irradiation, dotted line: 30 min irradiation.

the emission band which is due to the model compound **A** appears (Figure 5). In the case of irradiated solutions of **E** and **F** the intensity of the fluorescence bands at 23 500 cm^{-1} (**E**) and 21 620 cm^{-1} (**F**) decrease slightly after 30 min irradiation, and a weak shoulder in the region of the fluorescence bands of **A** in the corresponding solvents is observed (Figure 5).

Depending on the substituents in imide fragments, the solutions of the investigated structures show different photostability, which could be followed by decrease in intensity of the fluorescence bands in **D**, **E** and **F** after irradiation in the same conditions. The photostability of the solutions increases in the same order as the maxima of the fluorescence shift to the red. On Fig. 6, the changes in the fluorescence spectrum of compound **F** in ethanol at 300 K in relation to the irradiation time are shown.

2.3. Luminescence at 77 K

The irradiation does not influence the luminescence spectra of the frozen irradiated ethanol solutions of model compounds **A** and **B**.

After irradiation the intensity of the phosphorescence band of **C** decreases and two new bands appear in the luminescence spectrum of the ethanol matrix. The first band with maximum at 30 300 cm^{-1} corresponds totally to the prompted fluorescence band of **A** at 77 K (Figure 7). The second band is long-lived (in order of 1 s) with maximum at about 23 800 cm^{-1}, which is in the same spectral region as the phosphorescence bands of **A** and **B**. Consequently, after

irradiation and the formation of 4,5-diphenyl-1,2,3-triazole (**A**) and dibenzamide (**B**). Since compounds **B**, **C** and **D** are non-fluorescent in non-polar solvent, only the emission of compound **A** should be observed in the irradiated solutions of **C** and **D**. This statement agrees also with the TLC results. On the TLC chromatogram with the samples of model compound **B**, non-irradiated **C** and irradiated **C** it could be seen that, while non-irradiated **C** produces only one spot, irradiated **C** splits into two, and the one which is held stronger matches exactly the spot of the model compound **B**.

In the fluorescence spectra of irradiated ethanol solutions of **D** the own fluorescence of **D** diminishes, and after sufficiently long irradiation (30 min) only

irradiation the emission spectrum of **C** is a superposition of the luminescence spectra of **A** and **B** (Fig. 7) including the prompt fluorescence of **A** and the phosphorescence of **A** and **B**.

Two bands, a prompt fluorescence band having the same shape and maximum as that of the model compound **A**, and a phosphorescence band, similar to **C**, produced by overlapping of the phosphorescence bands of **A** and **B** (Fig. 7) are distinguished in the luminescence spectrum of frozen irradiated ethanol matrix of **D**.

In the luminescence spectra of compounds **E** and **F** only a weak shoulder in the region of the prompt fluorescence of **A** arises after irradiation (Figure 7). The luminescence characteristics at 77 K of irradiated frozen solutions of **E** and **F** are the least influenced in comparison to the other compounds similarly to the fluorescence of the irradiated solutions at 300 K.

Conclusions

Steady state and dynamic photophysical investigations on the 1-(N,N-bisacyl)amino-4,5-diphenyl-1,2,3-triazoles, as well as quantum-chemical calculations indicate a conjugation between the two main fragments in the structure. All the investigated compounds have phosphorescence with τ_{ph} in the order of 1s. On the basis of a comparative study of the electronic spectra in solution and in frozen matrix of the compounds **C**, **D**, **E** and **F** with those of the two model compounds **A** and **B**, hypothesis for the cleavage of the N-N bond and formation of 1,2,3-triazole and dibenzamide after irradiation with polychromatic UV light is proved.

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