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Sensing pH-dependent fluorescence in a hydrocarbon solvent with 2,6-diphenylpyridine

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Abstract

Fluorescence measurements of 2,6-diphenylpyridine in cyclohexane indicate the formation of a 1:1 hydrogen bonded complex upon addition of trifluoroacetic acid, with a formation constant of $1.23 \pm 0.07 \times 10^3$ M^{-1}, which increases the molecular fluorescence quantum yield from 0.014 to 0.61 for the complex. This behavior is potentially useful for sensing pH-dependent processes and acid generation in a hydrocarbon solvent, and occurs via an intermolecular hydrogen bond transfer in the excited state since the dielectric constant of the solvent is too low to support the excited-state proton transfer. MOPAC calculations correctly predict the formation of the 1:1 complex with an intermolecular N–H bond distance of 2.51 Å, and a stabilization energy of 3.6 kcal/mol.

Keywords: Excited-state H-bond transfer; Hydrogen-bonded complex; pH-dependent fluorescence; Photoacid sensor; 2,6-Diphenylpyridine

1. Introduction

In recent reports we have shown that the mono-phenylpyridines fluoresce only after undergoing an excited-state proton transfer (ESPT) from water [1,2]. This behavior is well understood in terms of the increased basicity of aromatic azines in the excited singlet state. Specifically these molecules are not fluorescent in hydrocarbons, polar organic solvents, and in alkaline aqueous solutions. In contrast, preliminary experiments with 2,6-diphenylpyridine (2,6-DPP) have shown that it does not undergo an ESPT and exhibits fluorescence in a hydrocarbon solvent due to inverting n,π and π,π singlet states, with the latter lying lower. In view of these marked differences in the fluorescence behavior of the 2,6-diphenyl derivative, relative to 2-, 3-, and 4-phenylpyridine, we have initiated this fluorescence study of 2,6-DPP. Chakravorti et al. [3] have investigated the *N*-heteroaromatic effect in a photophysics study comparing 2,6-DPP, *m*-terphenyl, and 2,6-lutidine; however, the influence of ground-state protonation, hydrogen bonding and molecular complexation on the fluorescence of this molecule have not been investigated. Some of the specific issues we wanted to address include: (i) the influence of an acid and molecular complexation on its fluorescence; (ii) the relationship of its ground-state pK_a to the ESPT observed with the mono-phenylpyridines; (iii) can we distinguish between an ESPT and a hydrogen bond transfer in the excited state? (iv) what do semiempirical calculations predict regarding the optimum geometry of the ground state? (v) what is the effect of the second phenyl group substitution? and (vi) can the fluorescence be enhanced by formation of a molecular complex? It was in the framework of the above questions that this study was undertaken.

2. Experimental details

2.1. Materials

2,6-diphenylpyridine was obtained from Aldrich Chemical and purified by recrystallization from hexane and ethyl alcohol. Glass-distilled water and spectrograde solvents were used after verifying that they did not contain any fluorescence impurities. Sealed 1-ml ampules of trifluoroacetic acid, (TFA), from Aldrich Chemical were used as received. The solution concentrations employed covered the range 10^{-5}–10^{-7} M, and were not degassed, since measurements confirmed that the fluorescence was not sensitive to dissolved oxygen.

2.2. Apparatus and procedures

Fluorescence measurements were carried out using 300 nm excitation with a Perkin-Elmer LS-50 spectrofluorometer

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and UV absorption data were obtained with an HP-8452A diode array spectrophotometer. The excitation and emission band widths were held constant at 2.5 nm. Optical densities at the excitation wavelength were typically 0.05 per cm, and the fluorescence quantum yield was measured relative to the value $\phi_F = 0.19$ for 4-phenylpyridine in water [1,2]. Semiempirical torsional potential energy calculations, using the AM1 Hamiltonian, for the ground state of 2,6-DPP, and for its complexation with trifluoroacetic acid were done with the MOPAC 6.0 quantum mechanical program from Serena Software, Bloomington, IN.

3. Results

The fluorescence of 2,6-DPP was measured with 300 nm excitation in a variety of solvents, and a summary of the quantum yield dependence is given in Table 1. The fluorescence of the neutral molecule appears at 342 nm in organic, hydrocarbon and polar solvents, shifting to 350 nm in a hydrogen bonding solvent such as water, while the corresponding 2,6-diphenylpyridinium ion fluoresces at 396 nm. The invariant absorption and fluorescence peak observed for the first five solvents is consistent with a π,π^* lowest singlet. Collectively, these results indicate that there is no ESPT occurring in water for this molecule as is the case with the monophenyl pyridines. This was also confirmed by the observation that the fluorescence yield is the same in H_2O and D_2O. The low fluorescence yield in cyclohexane is attributed to a π,π^* lowest singlet resulting from the inverting n,π and π,π levels induced by the second phenyl substitution on the pyridine ring.

The pK_a for 2,6-DPP was determined from pH-dependent absorption and fluorescence measurements to be 3.7 ± 0.1, and is unexpectedly low, due to the steric hindrance from the two phenyl rings attached *ortho* to the pyridine nitrogen.

Table 1
Summary of fluorescence quantum yield [a] data for the 2,6-diphenylpyridine (p$K_a = 3.7 \pm 0.1$) [b] in various solvents ($\lambda_{exc} = 300$ nm)

Solvent	Absorption, λ_{max} (nm)	Fluorescence, λ_{max} (nm)	ϕ_F
Cyclohexane	302	342	0.014
Dioxane	304	342	0.024
Tetrahydrofuran	302	342	0.020
Acetonitrile	302	342	0.026
Ethyl alcohol	302	342	0.030
Water	298	350	0.16
0.1 N NaOH	298	350	0.16
0.02 N H_2SO_4	320	396	0.67
0.01 N Trifluoroacetic acid (in cyclohexane)	326	396	0.61

[a] Quantum yield measured relative to the value $\phi_F = 0.19$ for 4-phenylpyridine in water [1,2].
[b] pK_a value for the 2,6-diphenylpyridinium ion determined from the pH dependence of the absorption and fluorescence spectra.

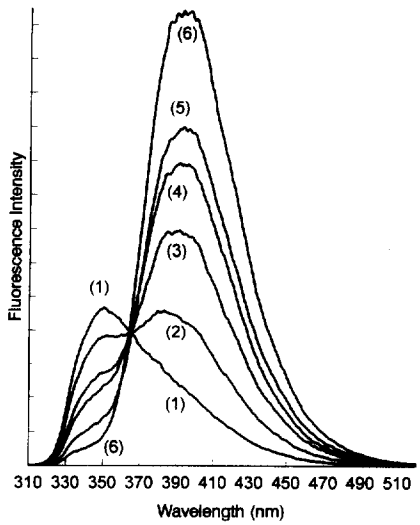


Fig. 1. pH dependence of the fluorescence spectrum of 3.0×10^{-6} M 2,6-diphenylpyridine with varying aqueous concentrations of sulfuric acid ($\lambda_{exc} = 300$ nm): (1) 0, (2) 6.1×10^{-5} N, (3) 1.8×10^{-4} N, (4) 3.0×10^{-4} N, (5) 6.1×10^{-4} N, (6) 1.8×10^{-3} N.

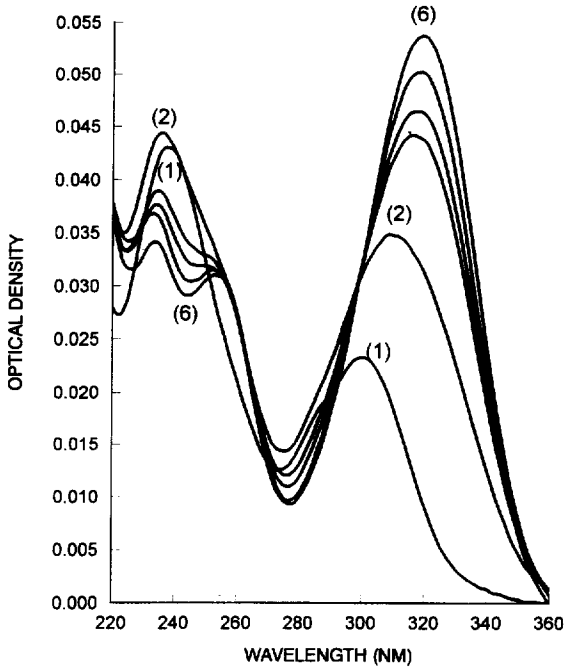


Fig. 2. pH dependence of the absorption spectrum of 3.2×10^{-6} M 2,6-diphenylpyridine with varying aqueous concentrations of sulfuric acid ($\lambda_{exc} = 300$ nm): (1) 0, (2) 2.0×10^{-4} N, (3) 6.5×10^{-4} N, (4) 1.0×10^{-3} N, (5) 2.0×10^{-3} N, (6) 6.5×10^{-3} N.

When compared to the pyridinium ion pK_a* of 9.0 ± 0.5 for the mono-phenylpyridines [1,2], the absence of an ESPT can be readily understood, i.e., the pK_a of 3.7 for 2,6-DPP is lower than the values for 2-phenylpyridine (p$K_a = 4.2$), 3-phenylpyridine (p$K_a = 4.8$) and 4-phenylpyridine (p$K_a = 5.3$). A significant increase in fluorescence is observed upon ground-state protonation, as is seen in Fig. 1, which also indicates an isoemissive point at 365 nm. The corresponding pH dependence of the absorption spectrum is given in Fig. 2, where a

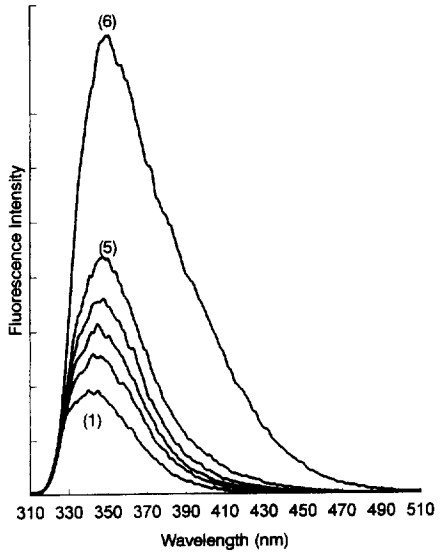


Fig. 3. Influence of water addition on the fluorescence of 3.0×10^{-6} M 2,6-DPP in ethyl alcohol. Percent water: (1) 0%, (2) 40%, (3) 50%, (4) 60%, (5) 70%, (6) 100%.

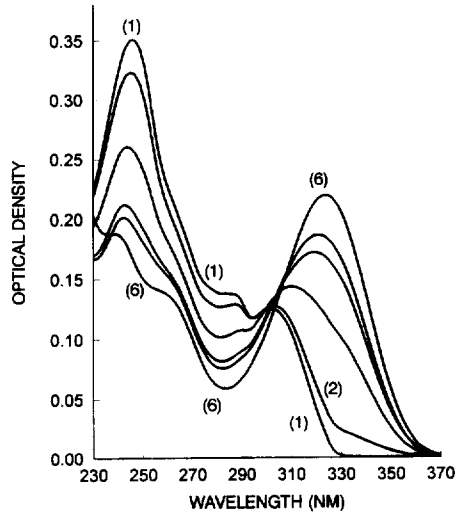


Fig. 4. Influence of TFA addition on the absorption spectrum of 1.0×10^{-5} M 2,6-DPP in cyclohexane. Concentration of TFA: (1) 0, (2) 3.0×10^{-4} N, (3) 9.0×10^{-4} N, (4) 1.2×10^{-3} N, (5) 1.5×10^{-3} N, (6) 6.0×10^{-3} N.

wavelength shift from 298 to 320 nm is evident, when increasing sulfuric acid concentration is added to a 3.2×10^{-6} M aqueous solution of 2,6-DPP. The acidic solutions appear to show an isosbestic point at 298 nm.

The significance of hydrogen bonding on the fluorescence of 2,6-DPP can be gleaned from Fig. 3, which shows that water addition to ethyl alcohol results in a five-fold increase in the fluorescence yield, while shifting the fluorescence wavelength maximum from 342 to 350 nm, as the molecule becomes hydrogen bonded to water. A marked increase occurs when the water content exceeds 70%. No protonation occurs in water since the pK_a for 2,6-DPPH$^+$ is 3.7. Noteworthy is that the fluorescence yield in 0.1 N NaOH is identical to the value measured in water, i.e., hydrogen bonding occurs even in a basic solution, whereas complete fluorescence quenching occurs in the case of 2-, 3- and 4-phenylpyridine, which require an ESPT to fluoresce.

In view of the increased fluorescence in acid solutions, resulting from ground-state protonation, we also investigated the fluorescence of 2,6-DPP in the presence of trifluoroacetic acid, TFA, ($pK_a=0.3$) employing cyclohexane as the solvent. The formation of the 1:1 H-bonded complex is readily seen from the absorption spectra presented in Fig. 4, where an isosbestic point is evident at 303 nm. An isoemissive point at 353 nm can be seen in Fig. 5 and is also consistent with formation of the complex between 2,6-DPP and TFA. In addition to the enhanced fluorescence observed in 0.02 N aqueous H_2SO_4 ($\phi_F=0.67$), we determined that the fluorescence yield of 2,6-DPP enhanced by complexation with 0.01 N TFA in cyclohexane is 0.61, with an emission wavelength maximum at 396 nm. In cyclohexane the uncomplexed molecule has a quantum yield of $\phi_F=0.014$ and an emission wavelength maximum at 342 nm. The dependence of the fluorescence intensity of 2,6-DPP in cyclohexane on the concentration of TFA is shown in Fig. 5, where a significant increase is observed upon TFA addition. Clearly the weak fluorescence of the neutral molecule at 342 nm. is replaced with that of the H-bonded complex resulting in a fluorescence maximum at 396 nm. From spectral absorption data and a plot of the integrated fluorescence area vs. TFA concentration it was determined that the 50% complexation point corresponds to a formation constant of $1.23\pm0.07\times10^3$ M^{-1}. There is a difference of 6 nm in the absorption wavelength maximum between 2,6-DPPH$^+$ and the H-bonded complex, which is most likely due to a solvent effect and distinguishable species. The fluorescence wavelength maximum at 396

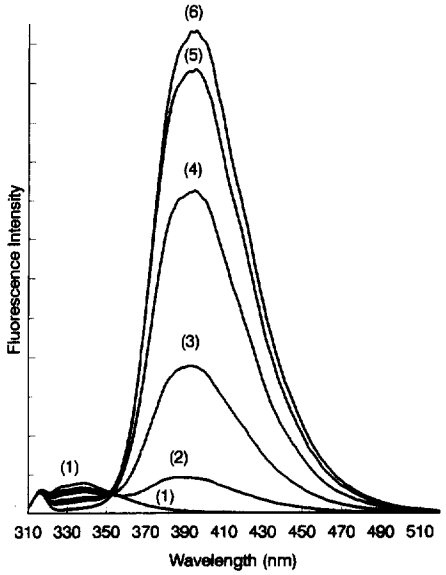


Fig. 5. Influence of TFA addition on the fluorescence spectrum of 1.0×10^{-6} M 2,6-DPP in cyclohexane. Concentration of TFA: (1) 0, (2) 3.0×10^{-4} N, (3) 6.1×10^{-4} N, (4) 1.1×10^{-3} N, (5) 1.5×10^{-3} N, (6) 4.6×10^{-3} N.

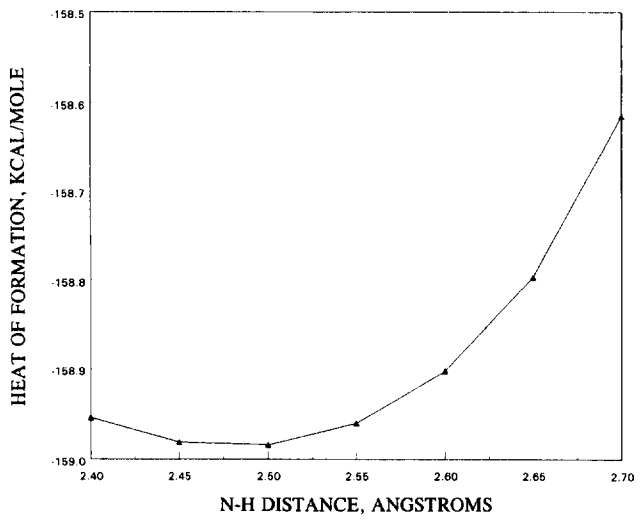


Fig. 6. MOPAC calculations illustrating the hydrogen-bonded complex between 2,6-DPP and TFA with an energy minimum at 2.51 Å. The N–H distance is the hydrogen-bonded distance between the two molecules in the complex.

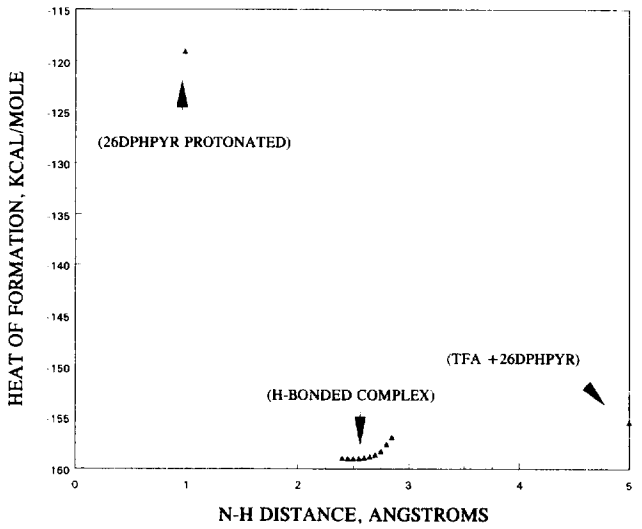


Fig. 7. MOPAC summary for the heats of formation of: (i) separated 2,6-DPP and TFA; (ii) hydrogen-bonded complex between 2,6-DPP and TFA; and (iii) protonated 2,6-DPP.

nm, however, appears to be the same for the two species. Experiments involving 0.05 M chloroacetic acid (pK_a = 2.85), 0.1 M trifluoroethanol (pK_a = 12.4), and 0.1 M trimethylacetic acid (pK_a = 5.0) were also attempted with the aim to enhance the fluorescence of 2,6-DPP, and in none of these cases did we observe any evidence of an H-bonded complex. Trifluoroethanol has been shown to quench indole fluorescence in neat solvent and in aqueous mixtures by an excited-state proton transfer [4].

3.1. MOPAC calculations

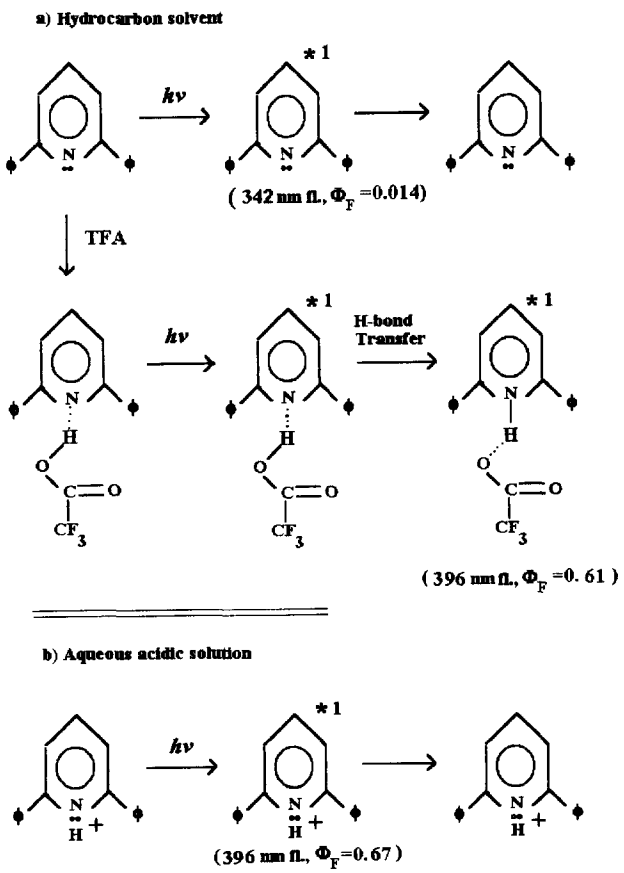
The optimized geometry for ground-state 2,6-DPP was determined to have both phenyl rings at a 41° torsional angle relative to the pyridine plane.

Since the fluorescence of 2,6-DPP is significantly enhanced by formation of the 1:1 H-bonded complex, we have also modelled this process, which predicts a ground state complex with a N–H distance of 2.51 Å, as is shown in Fig. 6. A summary of the calculations for the protonation and H-bonded complexation are presented in Fig. 7, where it is clearly seen that the optimized N–H bond distance is significantly larger than the 1.0 Å distance predicted for the protonation of 2,6-DPP. The calculated stabilization energy of the H-bonded complex is 3.6 kcal/mol relative to the two separated molecules, and also shows that the H-bonded complex is energetically favored over the protonated species.

4. Discussion

The results presented above clearly demonstrate a significant fluorescence enhancement for 2,6-DPP when hydrogen bonded to TFA in cyclohexane. Although the increased fluorescence also occurs by ground state protonation of the molecule in water, the option of sensing an acid in a nonpolar environment appears attractive in cases where chemical events generate acids. It can be envisioned that the reverse situation, namely sensing acid generation by first dissolving 2,6-DPP in a nonpolar solvent such as cyclohexane, where $\phi_F = 0.014$, or other nonpolar media, would upon irradiation respond to acid release, and induce fluorescence from the H-bonded complex, which has a quantum yield of 0.61. Preliminary experiments, using visual observation, in a 1-cm cuvette with 3×10^{-6} M 2,6-DPP, testing this procedure with a pulsed nitrogen laser (337 nm) excitation, where 2,6-DPP does not absorb, showed no fluorescence for the uncomplexed molecule; however, addition of 10 μl of 0.01 M solution of TFA (6×10^{16} molecules) forms the complex, whereupon fluorescence from the complex becomes easily visible to the eye. The acid forms the complex with 2,6-DPP, shifts the new absorption band into the region of the nitrogen laser and causes fluorescence to appear. At this diluted concentration of 2,6-DPP in cyclohexane 6×10^{16} molecules of generated acid would readily be detected. Electronic photodetection would significantly increase by several orders of magnitude the ability of 2,6-DPP to sense small quantities of generated acid.

The enhanced fluorescence of 2,6-DPP in the presence of TFA can be described by an excited-state process which involves either an intermolecular proton transfer or a hydrogen bond transfer, which should be distinguishable. In a recent study of the Mannich base, 3,5,6-trimethyl-2(*N*,*N*′-diethyl(aminomethyl)phenol it was shown that the excited-state intramolecular proton transfer does not occur for polar solvents when the dielectric constant is <6.3 [5]. Instead the excited- state intramolecular hydrogen bond transfer is favored in a solvent such as cyclohexane ($\epsilon = 2.01$). In view of the fact that dielectric constant for cyclohexane is 40 times smaller than it is for water, and the stabilization of ions in solution are inversely proportional to this parameter, we con-



Scheme 1.

sider the proton transfer to be very unlikely, and suggest that the enhanced fluorescence is due to an excited-state hydrogen bond transfer as is shown in Scheme 1, i.e., from the configuration (N···H–O)* to (N–H···O)*, consistent with the increased basicity of an azine in the excited singlet state. During this process the N–H bond is shortened, while the O–H bond is lengthened. The calculated MOPAC results presented in Fig. 7 provide further evidence that the H-bond transfer is favored over a proton transfer by ~40 kcal/mol in a hydrocarbon solvent. It is noteworthy that in a recent study of the electroreduction of quinones in aprotic solvents it was shown that a hydrogen bonded reduction could be distinguished from that of a protonated species [6]. The differences between a hydrogen bond and a proton transfer in the excited singlet state were discussed in a fluorescence study involving the interaction between β-naphthol and triethylamine, where it was shown that the formation of ion pairs and proton transfer is unlikely in cyclohexane [7].

In summary, we have shown that 2,6-DPP in cyclohexane forms an efficient 1:1 H-bonded H-bonded complex with TFA, enhances its fluorescence by a factor of 44 via an intermolecular hydrogen bond transfer in the excited singlet state, and can be used to sense the generation of an acid in a nonaqueous environment. The addition of the second phenyl group to the pyridine ring has essentially turned off the ESPT in water, that is essential for the fluorescence of 2-, 3- and 4-phenylpyridines, and results in an unexpectedly low pK_a for the pyridinium ion, due to steric hindrance.

References

[1] S. Hotchandani, A.C. Testa, J. Photochem. Photobiol. A 55 (1991) 323.
[2] J. Kubin, A.C. Testa, J. Photochem. Photobiol. A 83 (1994) 91.
[3] S. Chakravorti, S.K. Sarkar, P.K. Mallick, Chem. Phys. Lett. 187 (1991) 93.
[4] Y. Chen, B. Liu, M. Barkley, J. Am. Chem. Soc. 117 (1995) 5608.
[5] A. Szemik-Hojniak, A. Koll, J. Photochem. Photobiol. A 72 (1993) 123.
[6] N. Gupta, H. Linschitz, J. Am. Chem. Soc. 119 (1997) 6384.
[7] N. Mataga, Y. Kaifu, Mol. Phys. 7 (1963) 134.