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Acid–base interaction of 2,3-dimethyl-6-phenylimidazo-[1,2-b]-1,2,4-triazine in the ground and excited states

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Abstract

The acid–base interaction of 2,3-dimethyl-6-phenylimidazo-[1,2-b]-1,2,4-triazine (DMPIT) in the ground and excited states was studied. The electronic structures of 6-phenylimidazo-[1,2-b]-1,2,4-triazine and its cations were calculated by the CNDO/S and MNDO methods. The ground state protonation of the DMPIT molecule proceeds at the N_5 atom of the imidazole ring. In hydrocarbon solvents, a hydrogen-bonded 1 : 1 complex and 1 : 2 ionic pair of DMPIT with trifluoroacetic acid are formed. In polar and basic solvents, a 1 : 1 ionic pair is formed ($pK_a = 2.76$). On excitation of DMPIT, the basicity of the N_5 atom decreases ($pK_a{}^* = -0.88$) and that of the N_4 atom increases. In the excited state, the dissociation of N_5-protonated DMPIT takes place. The rate of dissociation increases as the solvent basicity increases. This reaction induces a radiationless deactivation (quantum yield of adiabatic reaction $\phi_r = 0.46$ in water). In dioxan, ethanol and water, excited DMPIT is protonated by an acid at the N_4 atom by a dynamic mechanism. In hydrocarbon solvents, the phototautomerization of the N_5 cation to the N_4 cation takes place in the hydrogen-bonded 1 : 2 ionic pair. This photoreaction is similar to that in the 7-azaindole–solvent complex.

Keywords: Acid-base interaction; 2,3-Dimethyl-6-phenylimidazo-[1,2-b]-1,2,4-triazine; Ground state; Excited state

1. Introduction

The basicity of azines and azoles increases on excitation. The excited state protonation of these compounds has been studied extensively [1]. However, only a few papers have been devoted to the investigation of the reverse photodissociation of the protonated forms [2]. Information on the rate of the reverse reaction and on the radiationless deactivation induced by this reaction is of great importance for an understanding of the proton transfer mechanism. Compounds whose basicity decreases on excitation are most suitable for the study of photodissociation. From this point of view, the multiacidic nitrogen bases of the imidazo-[1,2-b]-1,2,4-triazine (imitrine) series are of interest since they consist of electron-donor (imidazole) and electron-acceptor (triazine) rings. It is expected that the basicity of these compounds will decrease on excitation if the first excited state is a charge transfer state. In addition, imitrine is a neutral analogue of deprotonated 7-azaindole and an investigation of imitrine photoreactions can shed light on the mechanism of intramolecular proton transfer in 7-azaindole complexes [3]. Imitrines are also of interest due to their lasing ability [4] and biological activity [5]. They can serve as fluorescent probes to study the environment of proteins.

In this paper, the acid–base interaction of 2,3-dimethyl-6-phenylimidazo-[1,2-b]-1,2,4-triazine (DMPIT, Fig. 1), having several basic centres (N_1, N_4 and N_5 atoms), with strong acids in various solvents has been studied.

2. Experimental details

The excited state electronic structures and spectra of 6-phenylimidazo-[1,2-b]-1,2,4-triazine (PIT, Fig. 1) were calculated by the CNDO/S-CI technique, taking into consideration 81 singly excited configurations formed by electron transition from nine highest occupied molecular orbitals (MOs) to nine lowest unoccupied MOs, and by the SCF method in combination with the MNDO technique, taking into account one excited configuration formed by electron transition from the highest occupied MO to the lowest unoccupied MO

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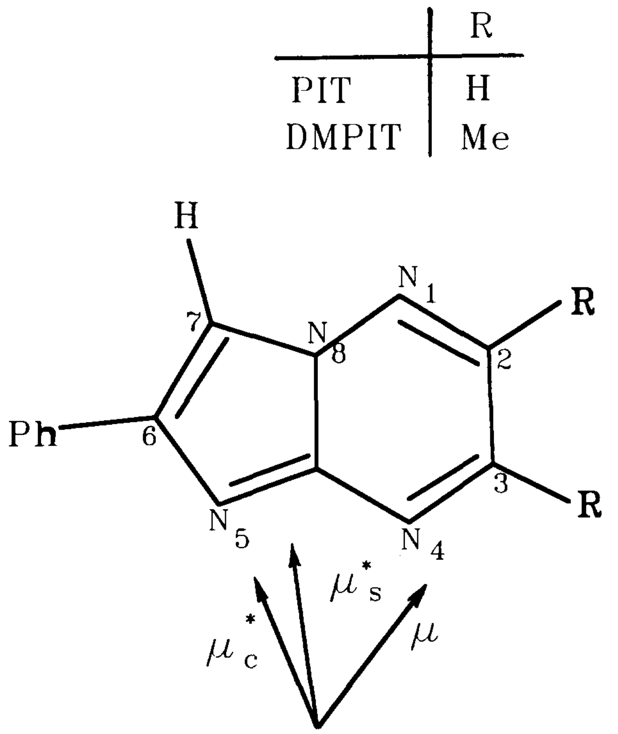


Fig. 1. Structures of imidazo-[1,2-b]-1,2,4-triazines, dipole moments of PIT in the ground (μ) and excited (μ_C*) states calculated by the MNDO method and dipole moment of DMPIT in the excited state (μ_S*) obtained by the spectral shift method.

[6]. The calculations were carried out by means of VIKING software [7]. The bond lengths, valence and dihedral angles of imidazo-[1,2-b]-1,2,4-triazine in the ground state were obtained by the MNDO technique. The geometry of the phenyl ring was taken from Ref. [8]. The proton affinity (PA) of PIT was determined from the formation heats of PIT and its cations calculated by the MNDO technique, taking the heat of proton formation (1530.6 kJ mol^{-1}) as the sum of one-half of the hydrogen molecule atomization energy and the hydrogen atom ionization potential.

The acid–base equilibrium constants and spectral characteristics of the products were calculated by the home-generated software EQUILI based on a multidimensional, non-linear, least-squares method [9], using the optical densities and/or fluorescence intensities of 8–12 solutions at 8–10 wavelengths. The concentration of DMPIT was equal to 10^{-4}–10^{-5} M. The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer, and the fluorescence spectra were recorded on an Elumin-2M spectrofluorometer. The fluorescence quantum yield (ϕ) was measured by comparing the areas under the corrected fluorescence spectra of solutions of quinine bisulphate in 1 N H_2SO_4 ($\phi = 0.546$ [10]) and of the studied compound. The synthesis of DMPIT is described in Ref. [11]. The methylated derivative of DMPIT was obtained by boiling 0.1 g of DMPIT in a 10 ml mixture of CH_3I and MeCN (1 : 1) for 2–4 h. The reaction products were separated by thin layer chromatography. Hexane, toluene (MePh), dioxan (DXN), acetonitrile (MeCN), ethanol (EtOH), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and trifluoroacetic acid (CF_3COOH) were purified and dried according to well-known methods [12].

3. Results

The charges on the nitrogen atom and the imidazole, triazine and phenyl rings of PIT in the ground and excited states and the wavelengths and oscillator strengths of the S_1–S_0 transition of PIT and its cations, calculated by the CNDO/S-CI method, are given in Table 1. The dipole moment (μ) and the angle between μ and the C_9–N_8 axis of PIT (β), calculated by the CNDO/S-CI method, are equal to 4.594 D and 46.4° in the ground state and 8.243 D and −63.4° in the excited state respectively. The calculations by the MNDO method give $\mu = 3.181$ and $\beta = 38.3°$ for the ground state and $\mu = 2.724$ D and $\beta = 22.9°$ for the excited state (Fig. 1).

The maximum wavelengths of the DMPIT absorption (λ_a) and fluorescence (λ_f) spectra in various solvents are given in Tables 2 and 3. The absorption spectrum is shifted to shorter wavelengths and the fluorescence spectrum is shifted to longer wavelengths as the solvent polarity increases. In the presence of strong acid, a short-wavelength shift of the absorption spectrum and an increase in the extinction coefficient (in MeCN, the values of ϵ_{max} are equal to 12 000 and 15 000 M^{-1} cm^{-1} for DMPIT and its cation respectively) are observed (Table 2, Figs. 2(a)–2(c)).

The quantum yield of DMPIT fluorescence (ϕ_0) is rather high and is not dependent on the solvent (Tables 2 and 3). In hydrocarbon solvents (hexane and MePh), an increase in acid concentration ($[CF_3COOH] < 1 \times 10^{-3}$ M) results in a long-wavelength shift of the fluorescence spectrum without a change in intensity. If $[CF_3COOH] > 1 \times 10^{-3}$ M, fluorescence quenching is observed and a weak short-wavelength fluorescence band appears. In polar and basic solvents, an increase in acid concentration leads to a short-wavelength shift of the spectrum, which is accompanied by fluorescence quenching (DXN, DMF, DMSO, EtOH and H_2O, Figs. 2(a) and 2(b)) or by a fluorescence intensity increase (MeCN, Fig. 2(c)). The fluorescence intensity of the DMPIT–CF_3COOH system in DXN and DMF increases if $[CF_3COOH] > 1.7$ M (Fig. 2(b)). In hexane, DXN, EtOH and H_2O, the fluorescence quenching of DMPIT by acid is accompanied by the appearance of a weak long- wavelength fluorescence band ($\lambda_f = 550$ nm, Figs. 2(a) and 2(b)). The intensity of the short-wavelength fluorescence band increases

Table 1
Charges at the nitrogen atoms (q_1, q_4, q_5) and the imidazole (q_{Im}), triazine (q_{Tr}) and phenyl (q_{Ph}) rings and the wavelengths (λ) and oscillator strengths (f) of the S_1–S_0 transition for the PIT molecule and its cations in the ground and excited states calculated by the CNDO/S-CI method

	q_1 (10^4 e)	q_4 (10^4 e)	q_5 (10^4 e)	q_{Im} (10^4 e)	q_{Tr} (10^4 e)	q_{Ph} (10^4 e)	λ (nm)	f
B	−1457	−2276	−3225	−456	654	−1679	382	0.316
B*	−4116	−4039	−3187	4984	−5226	−590		
$B_{N1}H^*$	−542	−1294	−2375	2234	3505	−739	525	0.656
$B_{N1}H^{+*}$	−1416	−3178	−3152	2765	−283	2545		
$B_{N4}H^+$	−548	−698	−276	1564	5055	−659	570	0.464
$B_{N4}H^{+*}$	−3163	−1961	−2620	5334	−1355	1784		
$B_{N5}H^+$	−1078	−2234	−1381	352	367	−86	406	0.430
$B_{N5}H^{+*}$	−3038	−2660	−2058	464	−283	253		

Table 2
Maximum wavelengths of the absorption (λ_a, nm) and fluorescence (λ_f, nm) spectra, fluorescence quantum yields (ϕ) for the neutral form of DMPIT (B), hydrogen-bonded DMPIT–acid complex ($B_{N5}HA$) and ionic pairs ($B_{N5}H^+AHA^-$ and $B_{N4}H^+AHA^-$) in hydrocarbon solvents and equilibrium constants of reactions (3)–(5) in the ground and excited states of DMPIT

Solvent	B			$B_{N5}HA$					$B_{N5}H^+HA_2^-$					$B_{N4}H^+HA_2^-$	
	λ_a	λ_f	ϕ	λ_a	λ_f	ϕ	log K_1	log K_1*	λ_a	λ_f	ϕ	log K_2	log K_2*	λ_f	ϕ
Hex [a]	392	450	0.38	383	478	0.40	3.31	2.19	349	440	0.01	3.08	−2.33	535	0.01
MePh	386	462	0.54	370	473		3.24	0.77	363	–	–	2.24	1.23	–	–

[a] Hexane.

Table 3
Maximum wavelengths of the absorption (λ_a, nm) and fluorescence (λ_f, nm) spectra, fluorescence quantum yields (ϕ) for DMPIT (B) and its cations ($B_{N5}H^+$, $B_{N5}Me^+$ and $B_{N4}H^+$) in basic and protic solvents and equilibrium constants of reaction (5) in the ground and excited states of DMPIT

Solvent	B			$B_{N5}H^+$ [a]			$B_{N4}H^+$ [a]		$B_{N5}Me^+$		log K	log K*
	λ_a	λ_f	ϕ	λ_a	λ_f	ϕ	λ_f	ϕ	λ_f	ϕ		
DXN	377	473	0.69	349	455	0.13	540	0.04	456	0.56	1.32	−3.23
MeCN	374	464	0.54	347	452	0.85	–	–	451	0.50	4.02	−0.42
DMF	377	468	0.65	350	458	0.43	–	–			1.57	−2.79
DMSO	378	472	0.63	356	472	0.11	–	–			1.98	−1.51
EtOH	375	477	0.65	348	467	0.16	550	<0.01	462	0.58	2.91	−1.50
EtOH [b]	378	437	0.75	350	421	0.90	–	0.01				
H_2O	371	481	0.41	347	480	0.12	550		468	0.56	4.50	0.53

[a] 96% of DMPIT protonated in the ground state.
[b] 77 K.

and the long-wavelength band disappears as the temperature of the acidic DMPIT solution in EtOH is decreased.

In hexane and MePh solutions of DMPIT ($[CF_3COOH] = 2 \times 10^{-2}$ M) at 77 K, two intense fluorescence bands ($\lambda_f = 440$ and 540 nm) are observed. Excitation spectra of the short-wavelength (in all studied solvents at 293 K, in hexane and EtOH at 77 K) and long- wavelength (in hexane, H_2O and DXN at 293 K, in hexane at 77 K) fluorescence bands of the DMPIT–acid system coincide with the absorption spectra at high acid concentration.

The absorption and fluorescence spectra of the methylated DMPIT cation are shifted to shorter wavelengths relative to the corresponding DMPIT spectra. This cation fluoresces strongly in all solvents (Table 3).

4. Acid–base interaction in the ground state

4.1. Site of DMPIT protonation

It is probable that the N_1, N_4 and N_5 atoms are the strongest proton-accepting centres in the DMPIT mol-

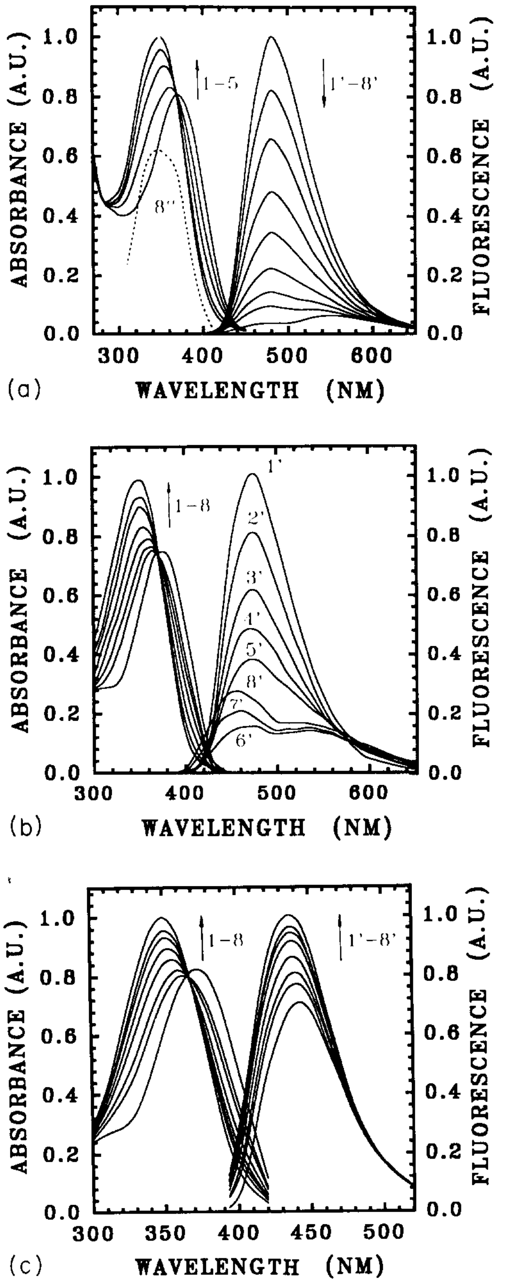


Fig. 2. (a) Absorption (1–5), fluorescence (1'–8') and fluorescence excitation (8") spectra of DMPIT in H_2O. [H_2SO_4] (M): 0 (1, 1'); 4.26×10^{-4} (2, 2'); 1.21×10^{-3} (3, 3'); 3.75×10^{-3} (4, 4'); 7.70×10^{-3} (5, 5'); 2.21×10^{-2} (6'); 9.51×10^{-2} (7'); 3.85×10^{-1} (8', 8"). (b) Absorption (1–8) and fluorescence (1'–8') spectra of DMPIT in DXN. [CF_3COOH] (M): 0 (1, 1'); 0.058 (2, 2'); 0.171 (3, 3'); 0.281 (4, 4'); 0.441 (5, 5'); 1.16 (6, 6'); 2.85 (7, 7'); 4.41 (8, 8'). (c) Absorption (1–8) and fluorescence (1'–8') spectra of DMPIT in MeCN. [CF_3COOH] (M): 0 (1, 1'); 6.1×10^{-4} (2, 2'); 9.1×10^{-4} (3, 3'); 1.35×10^{-3} (4, 4'); 1.79×10^{-3} (5, 5'); 2.70×10^{-3} (6, 6'); 3.51×10^{-3} (7, 7'); 4.41×10^{-3} (8, 8').

ecule. The basicity of these centres can be estimated from the PA values of PIT and from atomic charges (Table 1) [13]. In the ground state, PA is equal to 724.7, 811.4 and 883.0 kJ mol^{-1} for N_1, N_4 and N_5 centres respectively. The greatest PA of the N_5 atom is in agreement with the greatest negative charge on this atom (Table 1). The calculated λ_a value for N_5-protonated PIT is in best agreement with the experimental λ_a value for protonated DMPIT (Table 1). It can be concluded that the most probable protonation site of DMPIT is the N_5 atom.

The protonation of azaindolizines, whose structure is similar to that of imitrine, proceeds at the nitrogen atom of the five-membered ring [14,15]. This reaction is accompanied by a short-wavelength shift of the absorption spectrum and by an increase in ϵ_{max}. It was assumed that DMPIT is protonated at N_5 ($pK_a=0.35$) [16]. It has been shown by the ^{13}C nuclear magnetic resonance (NMR) technique that protonation of 6-(2'-methoxy-4'-methylsulphenyl)phenylimidazo-[1,2-b]-1,2,4-triazine proceeds at the N_5 atom [17].

4.2. Mechanism of acid–base interaction

The number of distinct components in the spectrum of the DMPIT–acid–solvent system, calculated by the Wallace–Katz method [18], is equal to three for hydrocarbons and to two for other solvents. In polar and basic solvents (S), the protonation of DMPIT (B) is carried out by an acid–solvent complex SHA ($SHA=H_3O^+$ for H_2O, HA is acid)

$$HA+S \rightleftharpoons SHA \qquad K_S \tag{1}$$

$$B+SHA \rightleftharpoons B_{N5}H^+ + A^- + S \qquad K \tag{2}$$

In non-basic and non-polar (hexane and MePh) solvents, CF_3COOH solvation is weak and CF_3COOH dimerization should be taken into account ($K_d=192$ and 2.63 M^{-1} in cyclohexane and benzene respectively [19]). Acid–base interaction in these solvents is well described by the following scheme

$$2HA \rightleftharpoons (HA)_2 \qquad K_d \tag{3}$$

$$B+HA \rightleftharpoons B_{N5}HA \qquad K_1 \tag{4}$$

$$B_{N5}HA+HA \rightleftharpoons B_{N5}H^+HA_2^- \qquad K_2 \tag{5}$$

The calculated absorption spectra of $B_{N5}H^+A^-$ and $B_{N5}H^+HA_2^-$ (Fig. 3) are similar to the absorption spectrum in H_2O in the presence of H_2SO_4 and differ markedly from the DMPIT absorption spectrum (Tables 2 and 3). Thus it can be concluded that DMPIT protonation is carried out by one CF_3COOH molecule (cation $B_{N5}H^+$) in polar and basic solvents and by two CF_3COOH molecules (ionic pair $B_{N5}H^+AHA^-$) in hydrocarbon solvents. The addition of one CF_3COOH molecule to DMPIT in hexane and MePh results in the formation of a hydrogen-bonded complex (reaction (4)). The values of K, K_1 and K_2 for the DMPIT–CF_3COOH system are given in Tables 2 and 3.

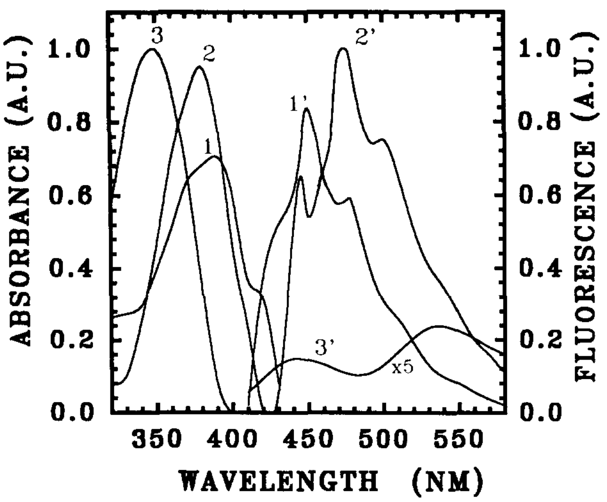


Fig. 3. Experimental (1, 1') and calculated (2, 3, 2', 3') absorption (1–3) and fluorescence (1'–3') spectra of DMPIT (1, 1'), hydrogen-bonded 1 : 1 complex (2, 2') and 1 : 2 ionic pair (3, 3') in hexane.

5. Excited state proton transfer reactions of DMPIT

5.1. Basicity of DMPIT in the excited state

The short-wavelength shift of the absorption spectrum on DMPIT protonation indicates that the acidity of the $B_{N5}H^+$ cation increases on excitation. The equilibrium constants of DMPIT protonation in the first excited state, determined by the Förster thermodynamic cycle [20], indicate (Tables 2 and 3) that the excited $B_{N5}H^+$ cation is more acidic ($pK_a = 2.76$ and $pK_a^* = -0.88$) than CF_3COOH ($pK_a = -0.04$ [21]).

According to CNDO/S-CI calculations, the electron density on the N_4 and N_1 atoms and on the triazine ring increases, but on the N_5 atom and the imidazole and phenyl rings decreases (Table 1) on excitation of PIT. The PA values of PIT at N_1, N_4 and N_5 sites increase and are equal to 930.7, 1019.5 and 929.9 kJ mol^{-1} respectively. Hence the most basic centre of excited PIT is the N_4 atom. The increase in $B_{N5}H^+$ acidity on excitation, determined by the Förster cycle, does not agree with the increase in PA and decrease in the calculated S_0–S_1 transition energy on protonation, but correlates with the reduction of the electron density on the imidazole ring.

The estimation of the dipole moment change of DMPIT by means of the spectral shift method [22] is consistent with the calculated electron density redistribution in PIT on excitation. The absolute value of the DMPIT dipole moment is unchanged but its direction varies. The angle between the dipole moment vectors in the ground and excited states has a different value when μ values calculated by the CNDO/S-CI and MNDO methods are used: 71°±2° and 46°±3° respectively (Fig. 1).

5.2. Excited state dissociation of DMPIT cation

The maximum wavelengths of the $B_{N5}Me^+$ fluorescence spectrum and the short-wavelength fluorescence band of the DMPIT–acid system (99% of $B_{N5}H^+$ in the ground state) are similar (Table 3). The excitation spectrum of this short- wavelength band coincides with the absorption spectrum of N_5-protonated DMPIT. Therefore this band can be attributed to the $B_{N5}H^+$ cation ($B_{N5}H^+AHA^-$ in hexane).

Since the fluorescence spectra of B and $B_{N5}H^+$ overlap strongly, only the sum of the fluorescence quantum yields of these species (ϕ_S) can be determined correctly. At 96% ground state protonation, the value of ϕ_S in a polar weakly basic solvent (MeCN) is close to ϕ_0, but in non- polar (hexane and MePh), basic (DXN, DMF and DMSO) and protic (EtOH and H_2O) solvents $\phi_S \ll \phi_0$ (Table 3). The dependence of ϕ_S in DXN and DMF on the acid concentration exhibits a minimum (Fig. 2(b)). Thus the fluorescence quantum yield of the $B_{N5}H^+$ cation depends strongly on the nature of the solvent and the acidity of the solution. The fluorescence quantum yield of the $B_{N5}Me^+$ cation (ϕ'_0) is high in all solvents (Table 3). The Stern–Volmer constant of DMPIT fluorescence quenching in EtOH and H_2O ($K_q^B[S] < 16\,000 \pm 300$ in H_2O at $[H_2SO_4] < 1.3 \times 10^{-3}$ M) is less than the ground state protonation constant (Table 3). This means that a process resulting in the formation of excited neutral DMPIT takes place. These results can be interpreted in terms of the acidic photodissociation of the $B_{N5}H^+$ cation. This photodissociation results in a low fluorescence efficiency of the $B_{N5}H^+$ cation in basic solvents.

The low value of ϕ_S in basic and hydrocarbon solvents in comparison with both ϕ_0 and ϕ'_0 values (Table 3) indicates that, during dissociation, only some (ϕ_r) of the excited $B_{N5}H^+$ cations are converted to excited neutral DMPIT molecules ($\phi_r < 1$). In other words, the formation of excited neutral DMPIT (rate constant k_1) is accompanied by radiationless deactivation of excited molecules induced by reaction (rate constant k_2). This conclusion is unusual for the NH–acid photodissociation reaction. It has been shown that the photodissociation of 2-naphthylamine, 2-aminoanthracene and 1-aminopyrene cations is not accompanied by induced radiationless deactivation ($\phi_r = 1$) [23]. The dependence of the $B_{N5}H^+$ fluorescence intensity on the solvent may be caused by a change in either k_1 or k_2 in different solvents.

The increase in the $B_{N5}H^+$ fluorescence intensity in DXN and DMF with an increase in CF_3COOH concentration above 1 M (95% and 92% ground state protonation of DMPIT in DXN and DMF respectively) seems to be a result of a decrease in the photodissociation rate. This may be caused by a decrease in the proton acceptor (anion CF_3COO^- or solvent molecule) concentration or its accepting ability as a result of specific interaction with acid. The decrease in the amine cation photodissociation rate at high acid concentration has been explained similarly [23].

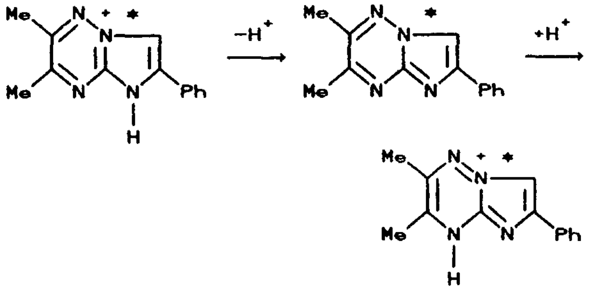
5.3. Excited state protonation of DMPIT

The excitation spectra of the long-wavelength fluorescence band of DMPIT in hexane, H_2O and DXN at acid concentrations corresponding to more than 99% ground state protonation coincide with the absorption spectrum of the $B_{N5}H^+$ cation ($B_{N5}H^+HA_2^-$ in hexane). Therefore this fluorescence band can be attributed to the product of the $B_{N5}H^+$ reaction in the excited state. Since the N_4 atom is the most basic site in the excited DMPIT molecule, we can assume that the N_4-protonated cation ($B_{N4}H^+$) is the product of this reaction. This interpretation agrees with the decrease in the S_0–S_1 transition energy on N_4 protonation of PIT, calculated by the CNDO/S-CI and MNDO methods, and with the long-wavelength shift of the fluorescence spectra on proton addition to the nitrogen atom of six-membered heterocycles [24].

5.4. Excited state double proton transfer in DMPIT cation in basic solvents

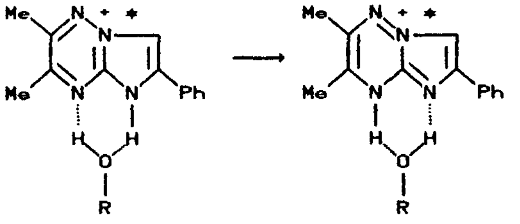
The Stern–Volmer constant of DMPIT fluorescence quenching in DXN ($K_q{}^B[S] > 85 \pm 5$ at [CF_3COOH] < 0.28 M) exceeds the ground state protonation constant (Table 3). In this solvent, the long-wavelength fluorescence band of the $B_{N4}H^+$ cation is observed. This indicates that protonation of DMPIT by acid in DXN proceeds via both static and dynamic mechanisms. In polar basic (DMF, DMSO) and weakly basic (MeCN) solvents, the dynamic reaction and $B_{N4}H^+$ fluorescence are absent. We can assume that the excited $B_{N4}H^+$ cation is formed by the interaction of the excited DMPIT molecule with acid.

The $B_{N4}H^+$ cation can be formed from the $B_{N5}H^+$ cation by two sequential processes (sequential intermolecular mechanism) (Eq. (6)): (i) the formation of an excited neutral DMPIT molecule by $B_{N5}H^+$ cation photodissociation and (ii) protonation of the neutral excited molecule by acid



(6)

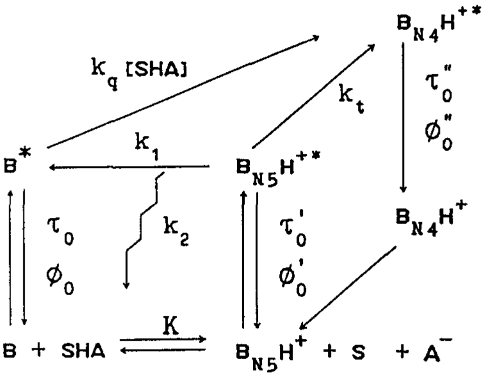
The $B_{N4}H^+$ cation can also be produced from the excited $B_{N5}H^+$ cation by double proton transfer in the hydrogen-bonded complex of DMPIT with a protic solvent (synchronous intramolecular mechanism) (Eq. (7))



(7)

Similar processes are known for aromatic nitrogen heterocycles. Excited state proton transfer from the imidazole to the pyridinium ring in acidic solutions of 2-(2′-pyridyl)-benzimidazole proceeds by a sequential mechanism consisting of (i) the protonation of the monocation and (ii) the dissociation of the dication [25]. Double proton transfer in the hydrogen-bonded complex of 7-azaindole (neutral analogue of DMPIT cation) with protic solvents takes place by a synchronous intramolecular mechanism [26,27].

The ground and excited state processes in the DMPIT–acid–basic solvent system are given by the scheme



(8)

where k_q is the rate constant of bimolecular DMPIT fluorescence quenching by the SHA complex, k_t is the double proton transfer rate constant and τ_0, τ'_0 and τ''_0 are the lifetimes of B^*, $B_{N5}H^{+*}$ and $B_{N4}H^{+*}$ respectively in the absence of photoreaction. If $C_{HA} < C_S$, where C_S and C_{HA} are the analytical concentrations of solvent and acid respectively, $[SHA] \approx C_{HA}$ ($[SHA] = [H_3O^+]$ if $S \equiv H_2O$).

The fluorescence spectra of B and the $B_{N5}H^+$ cation overlap strongly and cannot be registered separately. According to Eq. (8)

$$\frac{F_0}{F_S} = \frac{(1+KC_{HA})(1+k_q\tau_0C_{HA})(1+k_q\tau_0')}{1+k_r\tau_0'+KC_{HA}[k_1\tau_0'+(1+k_q\tau_0C_{HA})F_0'/F_0)]} \tag{9}$$

where $k_r = k_1 + k_2 + k_t$ and F_0, F'_0 and F_S are the integral fluorescence intensities (400–470 nm) of B, the $B_{N5}H^+$

cation in the absence of photoreaction and the B–HA system respectively. The analogous integral intensity of the $B_{N5}Me^+$ cation was used instead of the F'_0 value. In the absence of dynamic quenching

$$\frac{F_0}{F_S}=\frac{1+KC_{HA}}{1+KC_{HA}(k_1\tau_0'+F_0'/F_0)/(1+k_r\tau_0')} \quad (10)$$

The dependence of F_0/F_S on C_{HA} (C_S is constant) is described adequately by expression (9) for EtOH and H_2O (Fig. 4) and by expression (10) for DMSO. Eqs. (9) and (10) are not valid for solutions in DXN and DMF. As mentioned above, the fluorescence intensity of $B_{N5}H^+$ increases in DXN ($[CF_3COOH] > 1.2$ M) and DMF ($[CF_3COOH] > 1.7$ M) (Fig. 2(b)) as the acid concentration increases. This means that the photodissociation rate decreases. Let us consider the various proton-acceptor agents for the photodissociation of $B_{N5}H^+$: the solvent molecule and the CF_3COO^- anion. In the first case, the photodissociation rate should be proportional to the concentration of free solvent molecules. At the acid concentrations used, $[S] = C_S^0(1-C_{HA}/C_{HA}^0) - C_{HA}$, where C_S^0 and C_{HA}^0 are the concentrations of solvent and acid as neat liquids respectively. The substitution of k_r by $k'_r[S]$ does not result in an adequate description of the experimental data by expressions (9) and (10) if $\phi'_0 < 1$. If the CF_3COO^- anion is the proton acceptor, the decrease in the photodissociation rate may be caused by complexation of the anion with acid. Such complexation is well known for carboxylic acids [28] and results in a decrease in anion basicity [29]

$$B_{N5}H^+A^- + SHA \rightleftharpoons B_{N5}H^+AHA^- + S \quad K' \quad (11)$$

If the efficiency of proton transfer in the excited product of this reaction is low, the inclusion of reaction (11) into Eq. (8) allows us to describe both the fluorescence quenching of DMPIT and the fluorescence increase of the $B_{N5}H^+$ cation in DXN and DMF (Fig. 4). The K' values are 3.9 ± 0.4 and 0.92 ± 0.02 for DXN and DMF respectively.

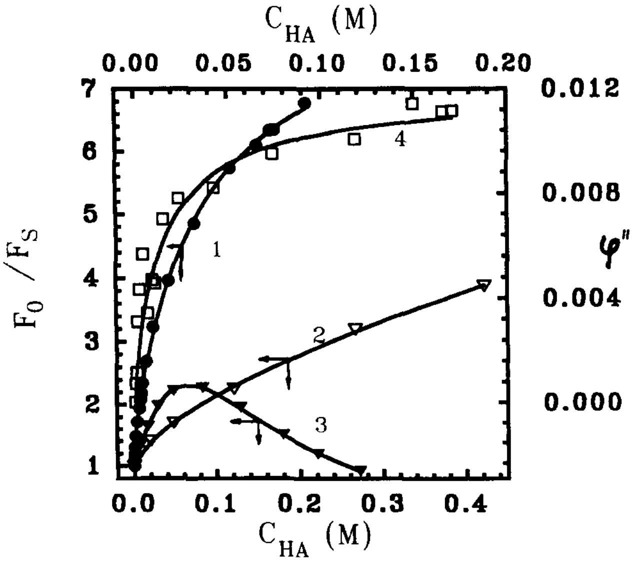


Fig. 4. F_0/F_S (1–3) and ϕ'' (4) vs. C_{HA} for DMPIT in H_2O (1, 4), EtOH (2) and DMF (3).

In the absence of dynamic quenching of DMPIT fluorescence (DMF and DMSO), the following combination of constants $(k_1\tau'_0+F'_0/F_0)/(1+k_r\tau'_0)$ can be obtained by means of expression (10). This ratio is equal to 0.184 ± 0.004 and 0.24 ± 0.01 in DMF and DMSO respectively. Assuming that $k_r\tau'_0 \gg 1$, we can estimate $k_r\tau'_0$ and ϕ_r values. Since the k_r value in MeCN is low compared with the rate constant of $B_{N5}H^+$ emission, the value of ϕ_S is rather high: $k_r\tau'_0 \ll \phi_S$. The values of $k_r\tau'_0$, $k_q\tau_0$ and $k_1\tau'_0$ are presented in Table 4.

The fluorescence quantum yield of the $B_{N4}H^+$ cation (ϕ'') can be approximately calculated by the expression: $\phi'' \approx \phi_S - \phi_0F_S/F_0$. According to Eq. (8)

$$\phi''=\frac{1}{1+KC_{HA}}\left[\frac{\phi_0''k_q\tau_0C_{HA}}{1+k_q\tau_0C_{HA}}\times\left(1+\frac{KC_{HA}k_1\tau_0'}{1+k_r\tau_0'}\right)+\frac{\phi_0''k_t\tau_0'KC_{HA}}{1+k_r\tau_0'}\right] \quad (12)$$

If $\phi''_0k_q\tau_0 = 1.2 \pm 0.2$ M and $\phi''_0k_t\tau'_0 = 0$, the dependence of ϕ'' on $[H_3O^+]$ for DMPIT in H_2O is satisfactorily described by expression (12) using previously determined values of $k_q\tau_0$, $k_r\tau'_0$, $k_1\tau'_0$ and K (Fig. 4). Thus the dynamic protonation of excited DMPIT is the main path of formation of the excited $B_{N4}H^+$ cation in basic solvents.

The increase in the k_r value on going from MeCN to basic solvents is consistent with the increase in the $B_{N5}H^+$ cation acidity in the ground ($1/K$) and excited ($1/K^*$) states (Table 3). This result agrees with the increase in the photodissociation rate of the 1-aminopyrene cation in the sequence of solvents MeCN < MeOH < DMSO < H_2O [30]. The low dissociation efficiency of $B_{N5}H^+$ in MeCN is due to the low basicity of this solvent. The $k_q\tau_0$ value increases in the following sequence of solvents DMF, DMSO ≪ DXN ≈ EtOH < H_2O. This can be explained

Table 4
Kinetic parameters $k_q\tau_0$, $k_r\tau_0'$, $k_1\tau_0'$ and ϕ_r for DMPIT–CF_3COOH (H_2SO_4 for H_2O) system. $\tau_0 = 5.5$ ns and $\tau_0' = 4.45$ ns in MeCN

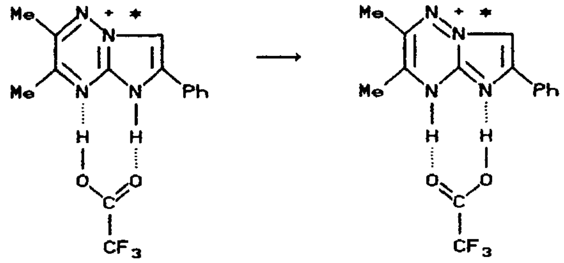
Solvent	$k_q\tau_0$ (M^{-1})	$k_r\tau_0'$	$k_1\tau_0'$	ϕ_r
DXN	4.4 ± 0.2	19 ± 2	–	–
MeCN	–	< 0.85	–	–
DMF	–	> 8	–	< 0.18
DMSO	–	> 6	–	< 0.24
EtOH	4.1 ± 1.6	14 ± 7	6.4 ± 3.2	0.30 ± 0.15
H_2O	52 ± 6	20.1 ± 0.5	8.9 ± 0.5	0.46 ± 0.04

by the increase in the DMPIT photoprotonation efficiency as the acidity of the protonating agent (SHA complex; H_3O^+ for H_2O) increases.

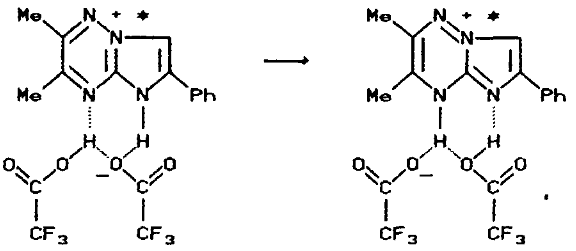
Since the $B_{N5}Me^+$ cation fluoresces strongly at 293 K, the temperature-activated radiationless process of the $B_{N5}H^{+*}$ cation is caused by its photodissociation. The activation energy of the radiationless process in the 293–130 K region is equal to 12.3±0.5 kJ mol^{-1}. This value is close to the activation energy of the EtOH bulk viscosity (14.2 kJ mol^{-1} [31]) and apparently characterizes the dynamic reorientation of the solvent molecules which is necessary for $B_{N5}H^{+*}$ dissociation. It has been shown for excited state double proton transfer in 7-azaindole that temperature-activated solvent reorientation is necessary for the formation of a six-membered reaction complex of 7-azaindole with alcohol and water with non-linear H bonds [26,27].

5.5. Excited state double proton transfer in DMPIT cation in hydrocarbon solvents

The calculated fluorescence spectra of individual $B_{N5}HA$ and $B_{N5}H^+HA_2^-$ in hexane are shown in Fig. 3; their spectral data are given in Table 2. The Stern–Volmer constants of B and $B_{N5}HA$ fluorescence quenching by acid monomer ($K_q^B = 2090 \pm 15$ M^{-1} and $K_q^{BHA} = 1130 \pm 10$ M^{-1} in hexane) coincide with the K_1 and K_2 constants respectively (Table 2). A similar agreement is observed for MePh: $K_q^B = 1170 \pm 480$ M^{-1} and $K_1 = 1080 \pm 1400$ M^{-1}. This means that, in these solvents, only static interaction of B and $B_{N5}HA$ with acid takes place and $B_{N4}H^{+*}$ is produced only by reaction in the $B_{N5}H^+HA_2^{-*}$ ionic pair. The intense fluorescence of $B_{N5}H^+HA_2^-$ and $B_{N4}H^+HA_2^-$ ionic pairs at 77 K in non-glassy hexane and glassy MePh indicates that the tautomerization of $B_{N5}H^+HA_2^{-*}$ has a low activation energy and does not require essential rearrangement of this complex. It is probable that the dissociation of $B_{N5}H^{+*}$ and the formation of $B_{N4}H^{+*}$ cations in the $B_{N5}H^+HA_2^{-*}$ ionic pair proceeds by double proton transfer via H bonds in eight-membered (Eq. (13)) or six-membered (Eq. (14)) rings



(13)



(14)

In excited 7-azaindole dimer [32], a double proton transfer in the eight-membered ring with two linear hydrogen bonds has a low activation energy. In the six-membered ring of the 7-azaindole–solvent complex with two non-linear H bonds, this reaction has a rather high activation energy. Similarly, the activation energy for reaction (13) may be lower than that for reaction (14).

6. Conclusions

The ground state protonation of DMPIT proceeds at the N_5 atom of the imidazole ring. On interaction of DMPIT with acid, a hydrogen-bonded 1 : 1 complex and 1 : 2 ionic pair in hydrocarbon solvents and a 1 : 1 ionic pair in polar and basic solvents are formed.

On DMPIT excitation, charge transfer from the imidazole to the triazine ring takes place; the basicity of the N_5 atom decreases and that of the N_4 atom increases.

The excited $B_{N5}H^+$ cation dissociates to form neutral excited DMPIT. This reaction induces a radiationless deactivation. The low quantum yield of $B_{N5}H^+$ fluorescence in basic solvents is caused by the photodissociation of this cation.

Excited DMPIT is protonated by acid at the N_4 atom by a dynamic mechanism in H_2O, EtOH and DXN.

In hydrocarbon solvents, the dissociation of the $B_{N5}H^{+*}$ cation and the formation of the $B_{N4}H^{+*}$ cation proceed intramolecularly in the hydrogen-bonded complex $B_{N5}H^+HA_2^{-*}$ and have a low activation energy.

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