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PHOTOCHEMISTRY OF PYRIDINIUM SALTS 1. INTRAMOLECULAR CHARGE TRANSFER IN *N*-AMINO-SUBSTITUTED PYRIDINIUM CATIONS

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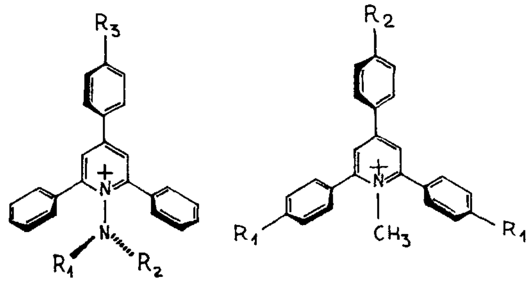
The photophysics and photochemistry of *N*-amino-substituted pyridinium salts were investigated. Electron transfer from the amino group to the pyridinium ring takes place in the singlet excited state. The fluorescence quenching and photoreactivity of these compounds is conditioned by this process. Irradiation of *N*-aminopyridinium salts in solution leads to novel fused heterocycles or to triphenylpyridine, depending on the concentration of the initial compound. Free radical intermediates are involved in the photoreaction.

INTRODUCTION

Aryl-substituted pyridinium salts are convenient substrates for the investigation of several different photoinduced processes, such as fluorescence with anomalous Stokes shift (ASS), intramolecular charge and energy transfer and photochemical reactions. These processes are strongly coupled to photo-induced structural relaxation in the excited state.[1] We regard the structural relaxation as the motion of the molecule along the reaction coordinate toward the minimum of its one-minimum potential energy surface in the excited state. This minimum can correspond to either a coplanar structure with maximum overlap of the orbitals of the interacting chromophores [an intramolecular charge-transfer (CT) state] or to a TICT structure with a minimum overlap of the orbitals of the nearly orthogonal coupling chromophores.[2] It has been established previously that in aryl-substituted pyridinium salts the first singlet excited state has the intramolecular CT nature. Aromatic substituents become coplanar to the pyridinium ring in the excited state.[1]

In the development of these ideas, in this work we investigated some photo-induced processes in 1-amino-2,4,6-triaryl-substituted pyridinium perchlorates (**1**–**4**) which contain strong electron-donor groups at the nitrogen atom. *N*-Methyl-substituted compounds **5**–**8** were used as the models.



1 $R_1 = R_2 = R_3 = H$
2 $R_1 = R_3 = H$, $R_2 = CH_3$
3 $R_1 = R_2 = CH_3$, $R_3 = H$
4 $R_1 = R_2 = H$, $R_3 = OCH_3$

5 $R_1 = R_2 = H$
6 $R_1 = H$, $R_2 = OCH_3$
7 $R_1 = OCH_3$, $R_2 = H$
8 $R_1 = R_2 = OCH_3$

EXPERIMENTAL

General. Electronic absorption and luminescence spectra were recorded on a Specord M-40 (GDR) spectrophotometer and an Elumin 2M (USSR) spectrofluorimeter, respectively. The fluorescence decay time was measured with an SP-70 (Applied Photophysics) nanosecond spectrometer. Distilled

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ethanol was used as a solvent. For preparative photochemical reactions, a quartz photoreactor of 0·5 dm^3 volume with a 230 W unfiltered high-pressure mercury lamp was used. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer. Proton chemical shifts in acetonitrile-d_3 are reported in ppm downfield from HMDS as an internal standard. IR spectra were recorded on a Specord IR-75 (GDR) spectrophotometer and mass spectra on a Finnigan 4021 instrument. Transient absorption was measured by conventional flash photolysis, $\tau = 20\ \mu s$.[3]

Compounds **1**–**3** were synthesized as previously reported.[4] Salt **4** was prepared according to the literature.[5] All methyl-substituted cations were obtained from appropriate pyrylium salts in the usual way.[6]

Procedure for photochemical syntheses. 1,3-Diphenyl-[4a,10]-dihydropyrido[1,2-*b*]-2*H*-indazole (**9**) was prepared as follows. A solution of salt **1** (20 mg) in 500 ml of ethanol was irradiated at room temperature for 5 min in a photoreactor. A low concentration of reactant was used to prevent bimolecular processes. The solvent was removed under reduced pressure and the residue was washed with hexane. The solution was then evaporated and the solid was recrystallized from hexane to yield **9**, a yellow crystalline solid, m.p. 127–129 °C (decomp.), yield 60–70 per cent. ^1H NMR, δ 7·10–8·10 (m, 13H, aromatic), 8·65 (s, H-3, pyridinium ring) 8·67 (s, H-5, pyridinium ring); IR (Nujol), 1650, 1620, 1600, 1560, 1505, 1415, 1220, 1180, 1090, 1050, 880, 780, 760, 735 and 710 cm^{-1}; MS, *m/z* (relative intensity) 320 (100, M^+), 319 (71, $M-1$), 243 (5), 77 (12). Analysis for $C_{23}H_{16}N_2$: calculated, C 86·26, H 5·00, N 8·74; found, C 85·90, H 5·02, N 8·69%.

1-Phenyl-3-(*p*-methoxyphenyl)-[4a,10]-dihydropyrido[1,2-*b*]-2*H*-indazole (**10**), prepared by the same procedure, is a brown crystalline solid, m.p. 81–83 °C (decomp.), yield 50–60%. ^1H NMR, δ 3·87 (s, 3H, OCH_3), 7·10–8·10 (m, 13H, aromatic), 8·54 (s, H-3, pyridinium ring), 8·56 (s, H-5, pyridinium ring); IR (Nujol), 1650, 1615, 1585, 1560, 1525, 1505, 1430, 1310, 1270, 1195, 1115, 1050, 850, 800 and 710 cm^{-1}; MS, *m/z* (relative intensity) 350 (16, M^+), 349 (85, $M-1$), 336 (85), 77 (38). Analysis for $C_{24}H_{18}N_2O$: calculated, C 82·30, H 5·14, N 7·99; found, C 81·66, H 5·18, N 7·87%.

RESULTS AND DISCUSSION

Absorption spectra of *N*-amino-substituted compounds **1**–**3** and **4** are similar to those of corresponding *N*-methyl-substituted cations **5** and **6** (Figure 1). There is no observable band associated with intramolecular CT between directly connected strong electron-donor and -acceptor groups. This is attributed to the high π-electron density on the pyridinium nitrogen atom,[7] and also the orthogonality of the amino group to the pyridinium ring which results from steric hindrance.

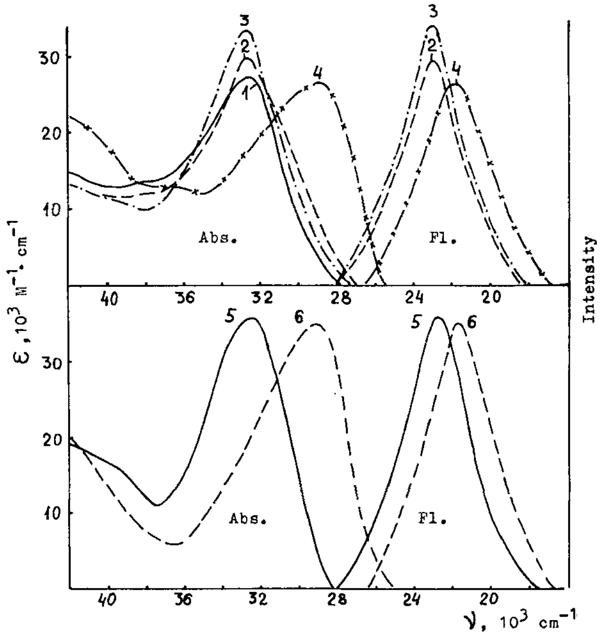


Figure 1. Spectral properties of compounds 1–6 at 293 K in ethanol (numbers on the curves are the compound numbers)

Table 1. Fluorescence properties of pyridinium salts **1**—**6**

Compound	293 K				77 K:
	λ_{max}, (nm)	Φ_f	τ_f, (ns)	K_f (10^9 s^{-1})	λ_{max}, (nm)
1	—	—	—	—	385
1 (dication)	439	0·001	—	—	—
2	435	0·009	—	—	375
3	435	0·29	1·4	0·21	375
5	435	0·32	1·4	0·23	375
4	460	0·025	0·3 (0·5)	0·83 (0·05)	395
6	460	0·2	1·58	0·13	405

Compound **1** does not fluoresce at room temperature, in contrast to model **5** (Table 1). However, the fluorescence quantum yields increase as methyl substituents are introduced into the amino group, and approach that of **5** in the case of cation **3**. At the same time, the fluorescence spectra of **2** and **3** are identical with that of cation **5** (Figure 1). ASS fluorescence belongs to the intramolecular CT structure with coplanar 2,6-phenyl rings, as has been observed previously in **5**.[1] Fluorescence quenching is associated with the competitive process of the formation of the non-fluorescent intramolecular CT state, resulting from torsional twisting of the amino group in the excited state, accompanied by electron transfer from the amino group to the pyridinium ring. The efficiency of formation of the non-fluorescent CT state decreases strongly in the series of compounds **1**–**3** as steric hindrance for structural relaxation increases (Table 1). It is interesting that the strongest electron donor, the dimethylamino group, causes the smallest perturbation of the fluorescent transition. Compounds **3** and **5** have almost identical fluorescent spectra, quantum yields and rate constants (Table 1). Electron-transfer efficiencies are expected to decrease as the pyridinium ring electron-acceptor ability decreases. Introduction of the electron-donor OCH_3 group into the molecule (**4**) leads to a decrease in the electron-acceptor ability of the pyridinium ring in comparison with cation **1**. As a result, **4** is fluorescent at room temperature, unlike salt **1**.

Protonation of the amino group leads to appearance of biscation **1** fluorescence at room temperature (Table 1) and also to an increase in the fluorescence intensity of biscation **2** in comparison with the cation. Neither the fluorescence spectrum nor the quantum yield of **3** is affected by the acidity of the solution. Therefore, it is probable that protonation of the cation **3** does not take place under the experimental conditions, i.e. in a 1 M ethanolic solution of sulphuric acid. The last result is in good agreement with the previously reached conclusions about the low basicity of sterically hindered dimethylamino groups (cf., e.g. Ref. 8).

If intramolecular CT in the excited state occurs, there is also the possibility of fluorescence quenching by intermolecular electron transfer.[9] Model compounds **5**–**8** were investigated and triethylamine (TEA) was used as an electron donor. We failed to detect any changes in the long-wavelength absorption band as the concentration of TEA increased to 0·01 M. However, the possibility of fluorescence quenching by ground-state complex formation (static mechanism) was taken into account by using the equation[10]

$$I_0/I = (1 + K[\mathrm{D}])(1 + K_q\tau_0[\mathrm{D}]) \qquad (1)$$

where [D] is TEA concentration, I_0 and I are fluorescence intensities in absence and presence of TEA, respectively, τ_0 is the excited state lifetime when [D] = 0 and K and K_q are measured static and dynamic quenching constants, respectively. If it is remembered that

$$1 + K_q\tau_0[\mathrm{D}] = \tau_0/\tau \qquad (2)$$

where τ is the lifetime of the S_1 state in the presence of TEA, one can calculate K and K_q, measuring I_0/I and τ_0/τ independently.

The experimental results are given in Table 2 and Figure 2. The observed decrease in the dynamic quenching constant K_q in the series of compounds **5**–**8** is in good agreement with the decrease in the electron-accepting ability of the pyridinium ring within the series, as determined by the number and positions of the donor substituents. Static quenching takes place only in the most electron-accepting triphenylpyridinium cation **5**. The dynamic constant in this case approaches the diffusion-controlled rate ($K_{\mathrm{dif}} \approx 6 \times 10^9$ l mol^{-1} s^{-1}).

It was also of interest to investigate the quenching of the fluorescence of dimethylamino-substituted compound **3** by TEA. The observed increase in the static quenching constant in comparison with model compound **5** is attributable to the σ-accepting influence of the sterically hindered dimethylamino group. The bulky dimethylamino group also hinders the electron transfer from the TEA molecule to the cation. As a result, the dynamic quenching constant for **3** is less than that for **5**.

We conclude that the formation of the non-fluorescent intermolecular CT state is characteristic for *N*-amino-substituted pyridinium cations. The efficiency

Table 2. Constants of dynamic (K_q) and static (K) quenching of the fluorescence of the pyridinium salts by triethylamine

	Compound				
Constant	**8**	**7**	**6**	**5**	**3**
K_q (10^9 l mol^{-1})	1.93	2.16	3.0	5.2	3.6
K l mol^{-1})	—	—	—	2.8	3.5

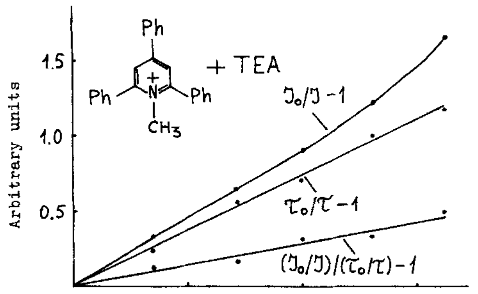
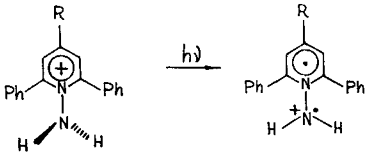


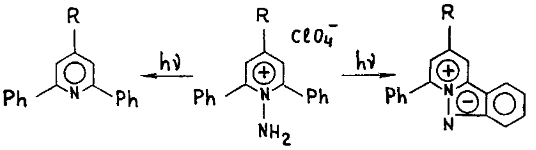
Figure 2. Quenching of the fluorescence of compound **5** by triethylamine in ethanol

of this process depends on both electronic and steric factors. The mechanism we suggested is in good agreement with that proposed by Mariano[9] for electron-transfer fluorescence quenching in pyridinium and related aza aromatic salts, containing electron-rich olefins as *N*-substituents.

Let us now look at the same process from another point of view. Electron transfer leads to a biradicaloid electronic configuration in the singlet excited state (Scheme 1). Such a structure is expected to have a high reactivity.[9,11] Indeed, irradiation of dilute solutions of **1** or **4** results in irreversible changes in the absorption spectra (Figure 3), corresponding to photoconversion to fused photoproducts **9** or **10**, respectively (Scheme 2).



Scheme 1



11 R = C_6H_5 9 R = C_6H_5

12 R = p-$C_6H_4OCH_3$ 10 R = p-$C_6H_4OCH_3$

Scheme 2

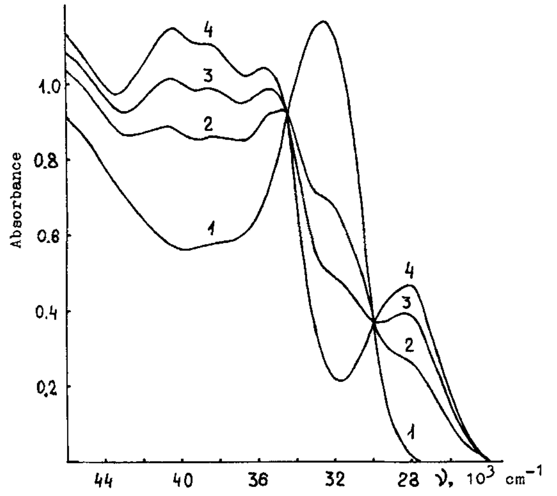
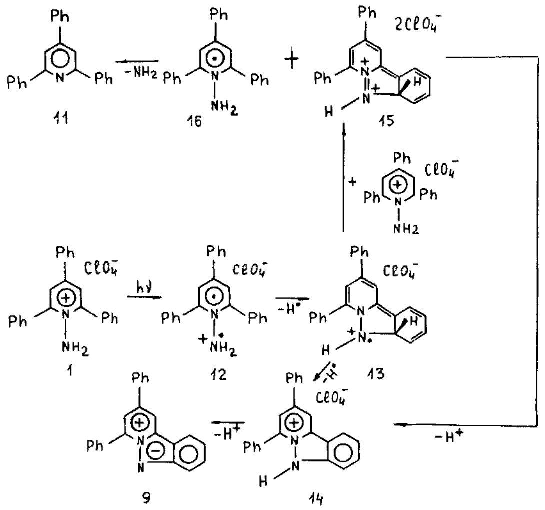


Figure 3. Photo-induced transformation of compound **1**: absorption spectrum. Curves 1, 2, 3 and 4, 0, 30, 60 and 90 s of irradiation with the 313 nm line of a mercury lamp, respectively; $C = 4 \times 10^{-5}$ M

Novel 1,3-diaryl-[4a,10]-dihydropyrido[1,2-*b*]-2*H*-indazoles **9** and **10** were isolated. Elemental analysis data and mass spectra confirmed the molecular formulae. Compounds **9** and **10** are bases soluble in alkanes. There are no characteristic bands of the amino group or perchlorate anion in the IR spectra, but there is a new band of the C$\overset{...}{=}$N bond in the strained five-membered ring (1650 cm^{-1}). In ^{1}H NMR spectrum of **9** there are only signals of the aromatic protons, whereas in the spectrum of **10** there is an additional signal of the methyl group (3·87 ppm). Symmetry breaking in **9** and **10** leads to non-equivalence of the 3,5-pyridine protons. Their signals in the region of 8·64 and 8·55 ppm for **9** and **10**, respectively, are a pair of singlets with chemical shifts difference of about 0·02 ppm. According to quantum-chemical calculations on the condensed polycyclic part of the molecule by the INDO method,[12] the electronic structure of the photoproduct is of the betainic N^+—N^- type. This is confirmed by the UV absorption spectrum, which is similar to that of a pure betaine resulting from salt **1** in basic media.

Photoproducts **9** and **10** are accompanied by 2,4,6-triarylpyridines **11** and **12**. The yield of side-products increases as the initial concentration rises. Increasing the concentration of initial compound **1** from 2×10^{-5} to 2×10^{-3} M leads to a dramatic increase in the triphenyl pyridine yield from 0 to 57 per cent. Because the pathway of the phototransformations of *N*-amino-substituted pyridinium cations depends on concentration, the photoreaction mechanism must involve both mono- and bimolecular processes. Quenching of the triplet state of the cation **1** ($E_t = 22\,000$ cm^{-1}) by naphthalene ($E_t = 21\,000$ cm^{-1}; $C = 0{\cdot}1$ M) shows that the photoreaction **1**→**9** proceeds only via a singlet excited state. The triplet level energy was determined by recording the phosphorescence, which proved to be of a biphenyl type, as with other 4-phenyl substituted cations.[1] Flash photolysis of the cation **1** indicates that a reaction intermediate with a broad long wavelength absorption (λ 450–650 nm, τ 12 ms) exists. On the other hand, flash photolysis of the photostable model compounds **5** and **3** showed no evidence for any transient absorption.

According to all the experimental data available one can suggest the mechanism of photoinduced processes shown in Scheme 3. The singlet-excited biradicaloid structure **12** (cf. Ref. 9) transforms with elimination of a hydrogen atom into free-radical intermediate **13** (as in Ref. 13), which can be observed in the flash-photolysis experiment. Its lifetime decreases from 12 to 7 ms as the concentration of the initial compound increases from 2×10^{-5} to 2×10^{-4} M. Radical cation **13** may disappear by two routes. Depending on the initial compound concentration, a unimolecular pathway leads to cation **14**, which is unstable in pure ethanol and converts to final photoproduct **9**. Cation **14** may be observed by means of the UV spectrum of **9** in a 0·3 M ethanolic



Scheme 3

solution of perchloric acid. A competitive bimolecular pathway proceeds via electron transfer from radical cation **13** to cation **1**, resulting in the appearance of biscation **15** and radical **16**. Antiaromatic biscation **15** transforms readily into cation **14** and then into base **9**. Radical **16**, after the elimination of the amino group, gives 2,4,6-triphenylpyridine (**11**). The evidence for the last reaction was proved by conversion of salt **1** to the pyridine **11** on reduction on a sodium mirror.

CONCLUSION

The results confirm the bichromophoric nature[1] of *N*-substituted pyridinium cations in which the *N*-substituent does not interact with the remainder of the molecule in the ground state. Photoexcitation leads to structural relaxation and the formation of the highly reactive intramolecular CT state responsible for the fluorescence quenching. Such an approach gives an opportunity to explain both the photophysical and the photochemical properties of *N*-substituted pyridinium cations from a common viewpoint.

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