PYRIDINIUM SALTS: LUMINESCENT SPECTROSCOPY AND PHOTOCHEMISTRY

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Abstract – The electronic absorption and emission properties of pyridinium cations are summarized and rationalized in terms of their molecular structure. Photochemical processes of pyridinium salts are surveyed with particular reference to cyclization reactions and the effect on reaction modes and rates of structural variations. The various photophysical and photochemical processes are formulated in a general scheme of photoinduced excitation and relaxations.

INTRODUCTION

There has been great interest recently in both the fundamental and the applied aspects of the photochemistry of heterocyclic cations.   Investigations of the excited states of π-iso-electronic pyrylium and pyridinium cations have led to fundamental and detailed conclusions on photoinduced processes in heteroaromatic compounds.   The photochemical synthesis has been achieved of unusual heteroaromatic systems, often beyond the reach of traditional methods, which include new and unique luminescent materials. The uv-spectroscopy of pyrylium salts has been previously[1] reviewed in detail, but the spectroscopy of pyridinium salts is not yet summarized, and the photochemistry of pyridinium cations has been covered only partially in more general reviews.[2,3] The photochemistry, and especially the luminescent spectroscopy, of pyridinium cations possess their own intrinsic interest: we have therefore summarized and critically analyzed the available results.

The first two parts of the present review are devoted to the absorption and emission of pyridinium cations in relation to their molecular structure.   The third part summarizes photochemical investigations of pyridinium salts. The final section deals with the general scheme

of photoinduced processes in aryl-substituted pyridinium cations, the compounds most completely investigated.

## 1. ELECTRONIC ABSORPTION SPECTRA AND MOLECULAR STRUCTURE OF PYRIDINIUM SALTS.

The electronic absorption bands of the parent pyridinium cation (PC) were assigned by comparisons of the π-iso-electronic aromatic systems, benzene, pyridine and pyrylium cation.[4-6] The $\pi\pi^*$ absorption bands of benzene (^1L_a and ^1L_b) also occur in the azaheterocycle spectra.[4,5] The lower molecular symmetry of the azines (C_{2v}) in comparison with benzene (D_{6h}) renders the S_1-S_o transition more permitted. The intensity of the long-wavelength ^1L_b band, due to the symmetry forbidden A_{1g}-B_{2u} transition,[6] increases considerably in the azines, and even more in the case of the pyridinium cation. There is also a noticeable decrease of the vibronic structure of the pyridinium cation absorption spectrum[5] in comparison with those of benzene and pyridine.[7]

Theoretical calculations of the pyridinium cation electronic absorption energies[8-10] are in good agreement with experimental values for the two long-wavelength transitions: ^1L_a-$^1A_1$ and ^1L_b-$^1A_1$.[7] The pyridinium cation electronic distribution in the ground state is predicted by theoretical analysis[10-12] to localize the positive charge mostly on the 2-, 4-, and 6-carbon atoms. The electronic density distributions in singlet excited states have been also investigated.[10]

Introduction of methyl groups into the pyridinium cation ring does not drastically change its absorption spectrum; their influence on the position and intensity of the long-wavelength absorption band ^1L_b has been investigated.[13,14] Theoretical and experimental results agree that the 2- and 6-positions are most sensitive towards substitution, causing a (7 nm) long-wavelength spectral shift. A CH_3-group in the 4-position leads to a short-wavelength displacement of the lowest absorption band. Unlike methyl substituents, the donor NH_2 group interacts strongly with the pyridinium π-system and causes a noticeable long-wavelength shift (45-60 nm).[15] The lowest energy bands in the absorption spectra of the aminopyridines are probably intramolecular charge-transfer transitions (CT); the excited states of the corresponding neutral aminopyridines are also in large measure CT.[16]

Investigations of the absorption and luminescence spectra of aryl substituted pyridinium salts have been connected with the study of their molecular structure. The conformations of simple phenyl substituted pyridinium cations are determined by a combination of conjugative and steric effects, as in biphenyl.[17] As shown by nmr-spectroscopy,[18] the torsional angle between the aromatic rings in 2-phenylpyridine (30°) increases considerably in the protonated molecule. The structures of more complex 2,4,6-triphenylsubstituted pyridinium cations have also been investigated by NMR:[19,20] the torsional angles between the 2,6-phenyl rings and the pyridinium ring increase passing from the corresponding pyridine to the pyridinium and the N-methylpyridinium

cations, attaining 60°-70° in the last case.   Variation of the N-substituent has little effect of
the torsional angles of the 4-phenyl rings.
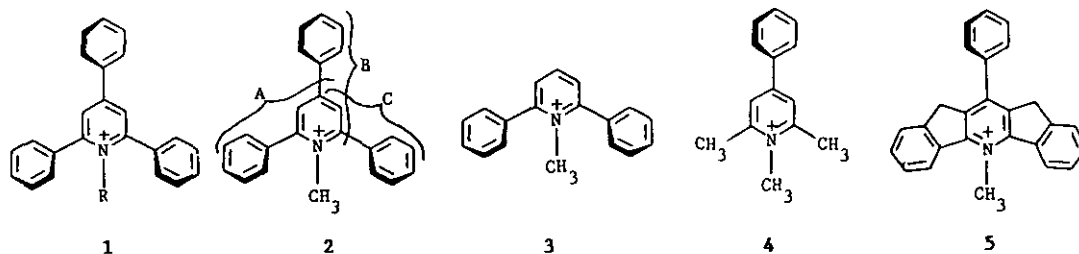
The geometrical structures of N-aryl-substituted pyridinium cations are important for the
interpretation of their spectroscopic and photochemical properties. *The torsional angle between an
N-phenyl substituent and a pyridinium ring increases from 47° for the simple 1-phenylpyridinium
cation[21] to 57° for 1-(2,5-dihydroxyphenyl)pyridinium cation[22] and to 84° for 1-phenyl-2,4,6-
trimethylpyridinium cation.[23] The values of the torsional angles in 1,2,4,6-tetraaryl-substituted
pyridinium salts determined by X-ray analyses[24,25] are in good agreement with nmr data in
solutions.[26]* Aryl substituted pyridinium cations thus possess a significantly non-coplanar
structure because of steric interactions.

As phenyl groups are introduced into 2,4,6-positions of the pyridinium ring, the lowest
absorption band undergoes bathochromic shifts and intensity changes, which can be large if the
phenyl rings contain donor substituents (for example OCH_3[29]).

The spectral transitions of aryl-substituted pyridinium cations were assigned by Knyazhanskii
et al.[30] by investigation of the 2,4,6-triphenylpyridinium cation 1 and model compounds 3-5.
Cation 2 possesses the weakly-conjugated non-coplanar biphenyl fragments A, B, and C, and the
short-wavelength bands (max ≈ 40,000 cm^{-1}) in the absorption spectra (Fig. 1a) are attributed to
the superposition of ^1L_a-$^1A_1$ transitions of biphenyl type.   As seen in the circular dichroism
spectrum (Fig. 1c), the long-wavelength absorption band (max = 33,000 cm^{-1}) is complex: it is a
superposition of two different electronic transitions.   The band of longer-wavelength is connected
with CT from the 2,6-phenyl rings to the electron-accepting pyridinium ring and that of shorter-
wavelength with the analogous CT from the 4-phenyl substituent. Analysis of the absorption spectra
of model compounds, including cations 3 and 4, confirms this assignment. Replacement of the N-
methyl group by N-phenyl,[28,30] or by N-naphthyl,[31] leaves the absorption spectra almost unchanged,
because of the previously mentioned non-coplanar orientation of the N-aryl substituent together
with the high electronic density on the heterocyclic nitrogen atom.[10,11] Hence N-aryl-substituted
pyridinium cations should be regarded as bichromophoric systems in which the π-systems of the N-
aryl substituent and of the pyridinium fragment hardly interact in the ground state. This

separation of the chromophores is achieved solely by steric and electronic factors without using aliphatic spacers.
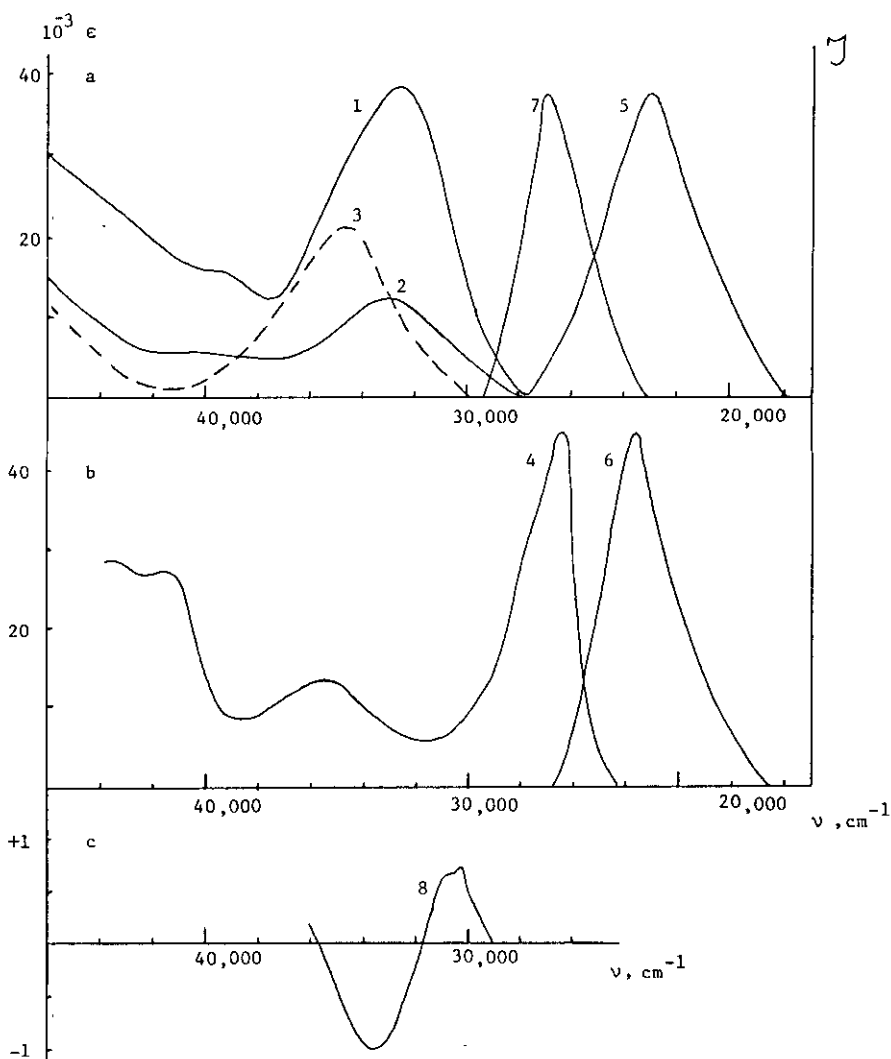

Fig. 1   Absorption (Curves 1 – 4), fluorescence at 293°   (Curves 5, 6) and at 77° (Curve 7), and circular dichroism (Curve 8) spectra of cations 2 (Curves 1, 5, 7, 8), 3 (Curve 2), 4 (Curve 3), and 5 (Curves 4, 6) in ethanol.

However, a new weak long-wavelength CT band appears when donor substituents are introduced into the N-phenyl group.[28,32] Analogous CT bands have also been observed in N-aralkylpyridinium cations 6[33] where the two chromophores are separated by an aliphatic chain.

6

(R = H, COOCH$_3$, CN)

7

(R=H, SO$_3$H, 5-Phenyloxazol-2-yl)
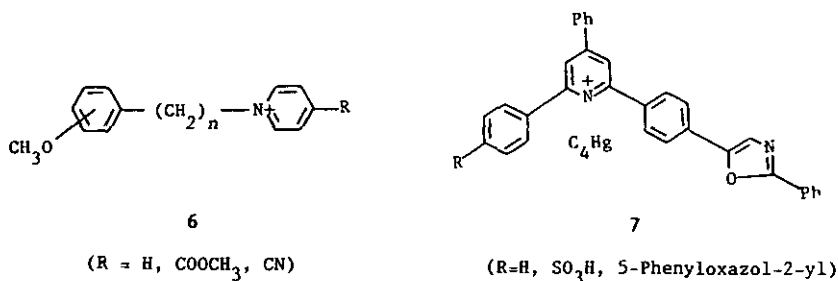
2. LUMINESCENT PROPERTIES OF PYRIDINIUM CATIONS.

The unsubstituted pyridinium cation was long considered as non-luminescent; however comparatively recently a weak phosphorescence (η_{Ph} = 0.04, λ_{max} = 334 nm, τ_{Ph} = 3,5 s) has been reported.[34] Methyl substituents have little effect on the luminescence, but amino and dimethylamino substituents significantly perturb the heterocycle π-system and such cations have strong UV luminescence at 293 and 77°.[15,35] Pyridinium salts also become decidedly luminescent when aryl-substituents are introduced into a 2-, 4- or 6-position of the pyridinium ring. As the number of phenyl substituents increases, the fluorescence quantum yield also increases, reaching 0.3 for 1-methyl-2,4,6-triphenylpyridinium cation.[28] Methoxy groups in the para-positions of substituent phenyl rings lead to long-wavelength shifts of the fluorescence band (λ_{max} = 460 to 520 nm), together with increased fluorescence quantum yield reaching 1 in the case of 1-methyl-2,6-di(4-methoxyphenyl-4-phenylpyridinium cation.[29] Katritzky et al. have recently reported[36] the fluorescent properties of water-soluble aryl-substituted pyridinium salts containing an oxazole fragment (7).

Anomalous fluorescence Stokes shifts (ASS) are characteristic for aryl-substituted pyridinium cations,[29,37] but the reason for ASS appearance in the 2,2'-dipyridyl monocation[37] is not clear. ASS was attributed[29] to the change of the localization of the N-proton in the equilibrium excited state of the 2,4,6-triphenylpyridinium cation. However, such proton transfer would lead to the corresponding pyridine, which has a shorter-wavelength fluorescence. Reinterpretation of the ASS fluorescence in 2,4,6-triarylpyridinium cations ($\Delta\nu$ = 10,000 cm^{-1}) has shown that ASS was intramolecular in nature and was caused by the adiabatic twist of 2,6-aryl substituents in the S_1-state ("structural relaxation"). A near planar conformation of the 2,6-substituents with the pyridinium ring plane is the emitting structure, the fluorescence of cation 2 at 293 K is thus similar to that of model compound 5. At the same time the fluorescence band is shifted considerably to the shorter wavelength region *when structural relaxation is hindered* (at 77 K) (Fig. 1a, b).

The luminescent properties of pyridinium cations change when an N-alkyl substituent is replaced by N-aryl and depend considerably on the nature of the N-aryl introduced. Compounds 8a

and **8b** are not fluorescent at room temperature, while the fluorescence of cation **8c** is very weak (η_{fl} 10^{-3}).[32] Interestingly, the mechanism of the fluorescence quenching is different in all three cases. In compound **8b**, a very rapid S–S intramolecular energy transfer to the weakly conjugated non-luminescent nitrobenzene chromophore with its low S_1 state (λ_{abs} = 340 nm[32]) takes place. However, when donor OCH_3-substitutents were introduced into 2,6-phenyl rings, the energy of the pyridinium chromophore S_1 state for **9** becomes lower than that of **8b**, and correspondingly cation **9** is fluorescent. In compounds of type **8c**, the absorptions of the N-aryl and pyridinium chromophores become coupled and a weakly permitted long wavelength CT transition from the N-aryl group ($\varepsilon \leq$ 3000[32]) is responsible for the weak fluorescence.
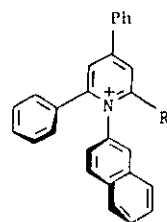

8
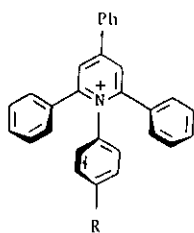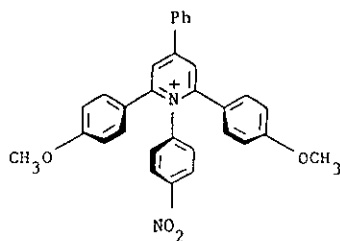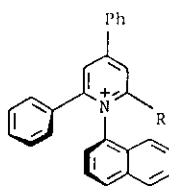
a: R = H,   b: R = NO_2

   c: R = OCH_3, NH_2

9

10

a: R = H

b: R = Ph

11

a: R = H

b: R = Ph

The complete quenching of the fluorescence of cation 8a at room temperature was considered to be the result of photocyclization,[32] as described below. However, with the help of the comparative analysis of the spectra and radiative fluorescence lifetimes of series of photostable p-methoxyphenyl substituted compounds, it has been shown[38] that photophysical processes also play a role in the fluorescence quenching. The N-aryl and the pyridinium chromophores do not interact in the ground state, but their interaction in the excited state results in fluorescence quenching by a CT mechanism. Hence, the complete fluorescence quenching of cation 8 at room temperature is a result of both photochemical and photophysical processes.

N-Naphthyl-substituted cations (10, 11) have very large fluorescence Stokes shifts ($\Delta\nu$ = 13,000–14,000 cm^{-1}).[31] This ASS at 293 K results[31,39] from torsional twisting the S_1-state of the N-naphthyl group which is almost perpendicular to the pyridinium ring in the ground state. Compounds 10 and 11 can undergo two types of torsional relaxation in the S_1-state relaxations of the N-naphthyl and of the 2,6-phenyl substituents. These two allowed structural relaxations are reflected in the complex dependence of the fluorescence maxima on solvent viscosity.[39]

Analogous plots of ν^{fl}_{max} against solvent viscosity for 1-methyl-2,4,6-triaryl-substituted cations have a simple S-like form.[40] This structural relaxation model has allowed[41] a satisfactory explanation of the unexpected short-wavelength shift with increased concentration found for the

lazer generated and superfluorescence spectra of some aryl-substituted pyrylium and pyridinium salts. Use of this effect has been suggested for the identification of structural mobility in luminophores. ASS fluorescence ($\Delta v \simeq$ ca 20,000 cm^{-1}) has been also observed for simple N-methylpyridinium salts, but explained by Brigleb et al. as electron transfer from anion to cation in the excited state.[42] Electron transfer between different molecular fragments was also used to explain the fluorescence quenching of pyridinium cations with anthryl[43] and heteroaromatic substituents.[44]

Few papers deal with pyridinium cation phosphorescence. In addition to that of the unsubstituted pyridinium cation (mentioned above), there are data concerning long-lived (τ_{ph} = 1.3 - 2 s) phosphorescence of amino and dimethylamino substituted salts, most intensive for 4-substituted compounds which are non-fluorescent even at 77 K.[35]

Interesting phosphorescence occurs for aryl-substituted pyridinium cations: that of 1-methyl-2,4,6-triphenylpyridinium cation 2 is similar to biphenyl (Fig. 2). The emitting transition is localized on the structural fragment including the 4-phenyl group.[30] 4-Unsubstituted cation 3 is non-phosphorescent. The type of phosphorescence does not change even for p-methoxyphenyl substituted cations, and confirms that polyaryl-substituted pyridinium cations should be regarded as aggregates of weakly conjugated biphenyl fragments.

Replacement of the N-methyl group by N-phenyl does not change the phosphorescence wavelength, but increases the intensity.[32] If this is caused by increased intersystem crossing, it must be regarded as another efficient way of quenching the fluorescence of cation 8a. The situation is significantly different when an N-naphthyl substituent is introduced: the almost unperturbed triplet state of the naphthyl chromophore, populated by triplet-triplet energy transfer from the pyridinium chromophore,[31] is responsible for the phosphorescence. The naphthalene phosphorescence has been intermolecularly sensitized in cation 10b (Fig. 3). The phosphorescence data confirm the separation of π-systems of the non-coplanar N-naphthyl and pyridinium fragments.

Hence in the aryl-substituted pyridinium cations the emitting singlet and triplet states always correspond to different molecular orbitals.

3. PHOTOCHEMISTRY OF PYRIDINIUM SALTS

Some photochemical reactions of pyridinium cations have been discussed previously in reviews on the photochemistry of quaternary salts of aromatic heterocycles (Eltsov et al.[2]) and of iminium salts (Mariano[3]). Here, we attempt to summarize all the main types of photochemical reactions of pyridinium salts. Special attention will be given to the photochemistry of aryl-substituted pyridinium salts which were hardly discussed in the previous reviews.

The well-investigated photoreactions of pyridinium salts include photorearrangements. Valence bond isomerizations are characteristic for pyridinium salts as well as for their π-isoelectronic
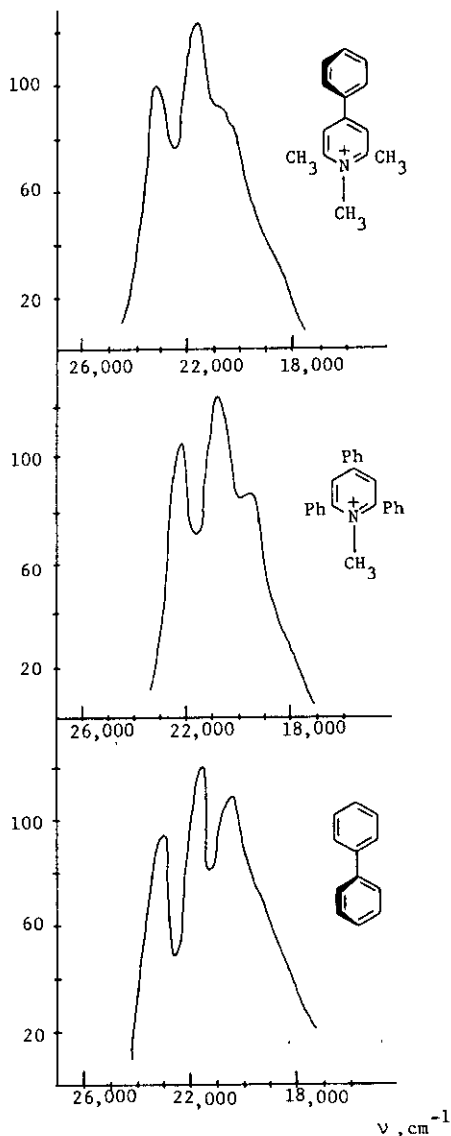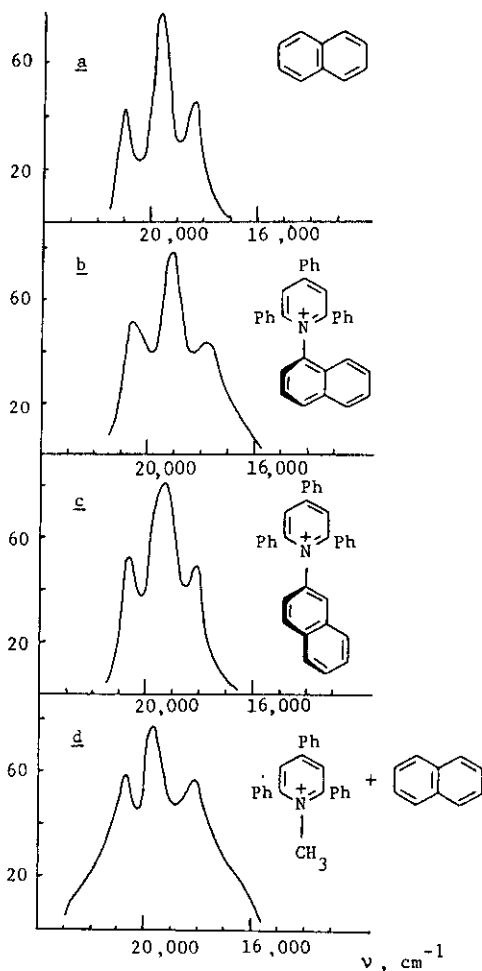
Fig. 2   Phosphorescence spectra at 77 K in ethanol.

Fig. 3 Phosphorescence (Curves a–c) and sensitized phosphorescence spectra of naphthalene (Curve d) (λ_{ex} 340 nm) at 77K in ethanol.

analogs benzene and pyridine. Irradiation of aqueous solutions of 1-methylpyridinium chloride, and of corresponding methyl and dimethyl homologs **13**, affords high quantum yields of 6-azabicyclo[3.1.0]hex-3-enes **12**.[45] Irradiation of 1-methylpyridinium perchlorate in methanol gives a high yield (80%) of a trans-trans-dimethoxycyclopentenylamine **15**, probably as a result of a secondary solvation of a protonated bicycloaziridine **14**.[46]

| 12 | 13 | 14 | 15 |
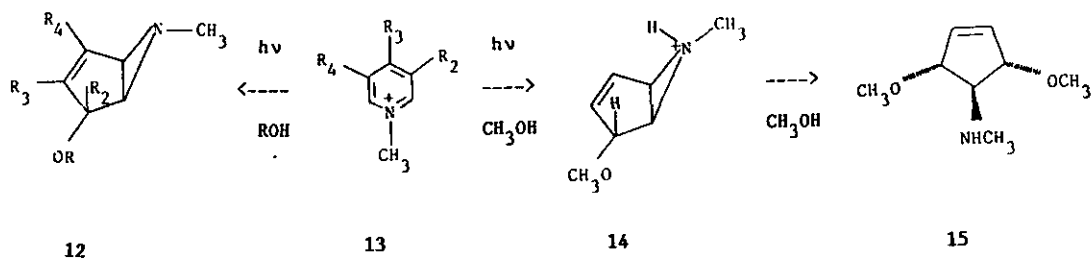
Irradiation of 1-phenyl-3-oxidopyridinium **16** at 350 nm[47] similarly gives compound **17**, together with a photo-dimer **18**.


| 16 | 17 | 18 |
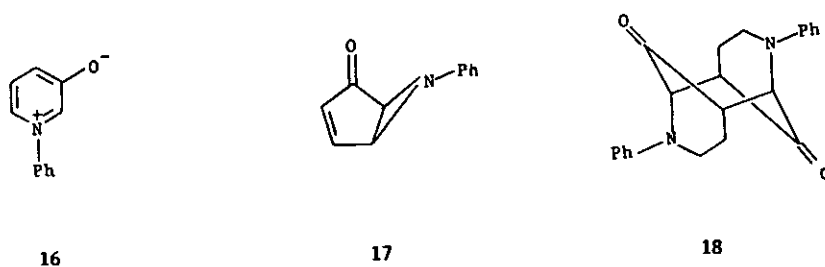
Dimer forming $4\pi + 4\pi$ cycloadditions are characteristic for pyridinium salts which are π-isoelectronic analogs of aromatic hydrocarbons: thus, irradiation of the 2-amino-5-substituted pyridinium salt **19** leads to photo dimer **20**.[48]


| 19 | 20 | 21 | 22 |
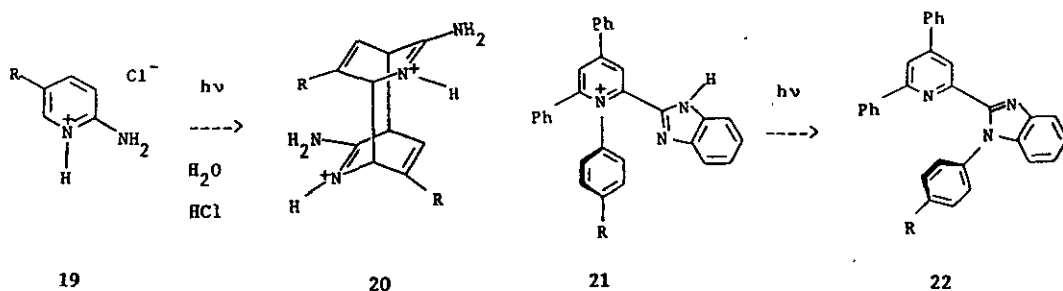
The interesting intramolecular 1,4-photochemical aryl shift **21** --> **22** occurs in high yield.[49] Photolysis of 1-substituted 4,6-diphenylpyridinium-2-carbonyl azides leads to a variety of products via intra- or intermolecular reaction of the corresponding nitrenes.[50] Photohydrolysis of one of the pyridinium rings in biscation system **23** results in the eventual formation of the isonicotinic acid derivative **24**.[51] Photoreaction of the parent pyridinium cation with water leads to ring-opening with formation of glutaconic aldehyde.[51]

23   **24**
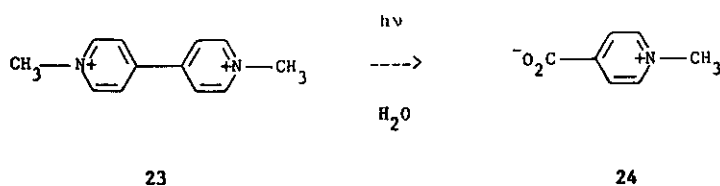
Photoaddition of alcohols and ethers to pyridinium salts is a well-defined reaction. The 1,2-dihydropyridine **25** results from irradiation of compound **26a** in methanol. Methyl homologs of **26a** give a somewhat different photoproduct (**26b** --> **27**) or are photostable (**28**).[52]

     25   **26**   **27**   **28**

a: R = H, b: R = Ph
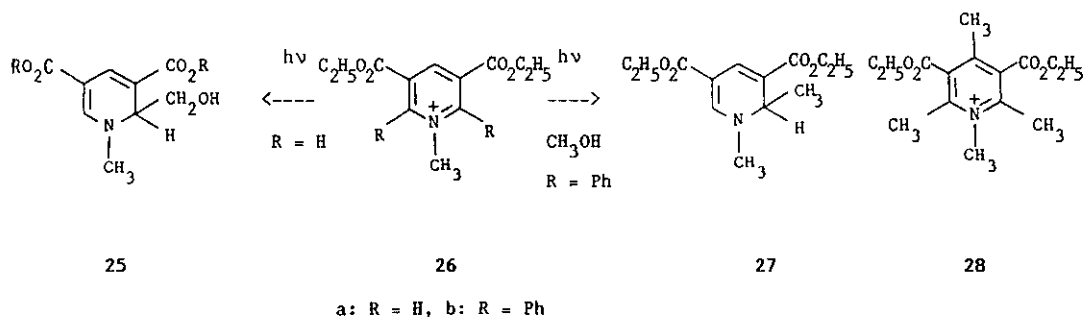
The electron deficient nature of pyridinium cations allows their photoreduction, thus biscation system **29** with primary or secondary alcohols gives the cation-radical.[53]

       29   **30**
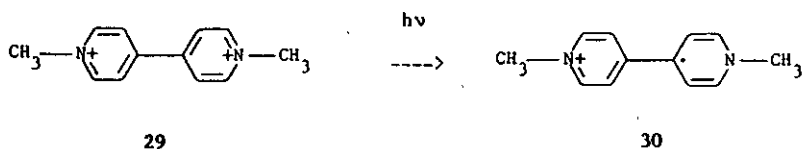
Photoreduction of cation **32** in presence of diethylamine leads to bispyridine **33** with a yield of 19%,[54] perhaps by dimerization of radicals resulting from electron phototransfer of the diethylamine-cation **32** in charge-transfer complex. The corresponding thermal reaction forms adduct **31**.

R = CH_2Ph

     31   **32**   **33**
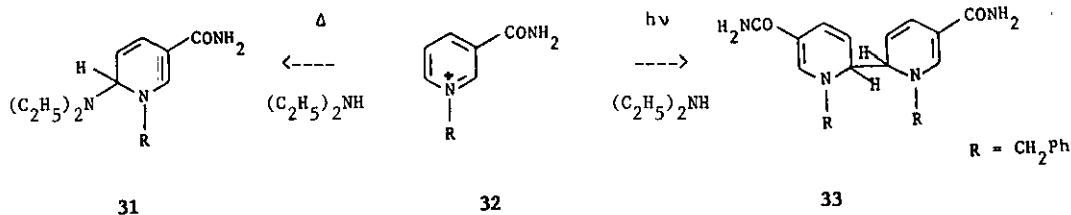
trans-cis-Photoisomerizations about C=C bonds, and the influence of solvent polarity and pH on them, have been investigated.[55]   Certain halofuryl substituted pyrylium and pyridinium salts photodimerize with halogen elimination.[56]   The photodimers are efficient luminophores with luminescence quantum yields approaching unity.
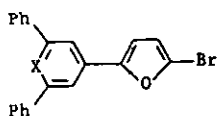

34   X = N, NH$^+$, O$^+$
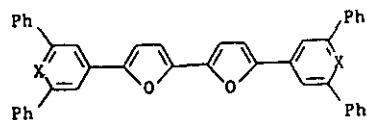
35

Photocyclizations with rearomatization by dehydrogenation or dehalogenation are common for aryl-substituted pyridinium salts. Reactions of this type have been much investigated from the preparative point of view in the styryl and benzyl substituted heterocycle series.   Irradiation of ethanolic solutions of 1-styrylpyridinium salts and their derivatives **36** in presence of iodine results in dehydrogenation and formation of condensed salts **37** (25-60%).[57]
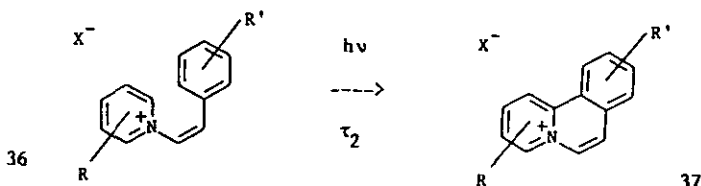

Photocyclization rates and yields hardly vary on introducing CH_3, C_6H_5, or halogen substitutuents into different positions of the pyridinium and benzene rings of **36**. The orientation of the styryl group largely determines the possibility of photocyclization:[58]   2- and 4-Styrylpyridinium cations are quite stable to prolonged irradiation unlike the corresponding neutral molecules which readily give azaphenanthrenes.   Photocyclization of the 3-styrylpyridinium cation is less efficient in comparison with that of the neutral styrylpyridines.[58]   These regularities are predicted by the theoretical analysis of reactivity of these compounds.[59]   Free valence indices of the singlet state, and overlap population were chosen as measures of the reactivity of 2-styrylpyridine and its cation.   The calculations predict the low reactivity of 2-styrylpyridinium cation to photocyclization.

The influence of structural and electronic factors on photocyclization have been investigated for 1-(halogenarylmethyl)pyridinium salts. An extended series of substituted 1-benzylpyridinium salts 38 has been converted in good yields into the novel pyrido[2,1-a]isoindolium derivatives 39.[60,61] The photocyclization rate of the isomer (38, R'=halogen, R=H) is lower and the yield is less. The lower reactivity of halogen in the benzene ring is confirmed by elimination of bromine from pyridinium ring during the photocyclization of the dibromo derivative (38, R = R' = Br). The non-substituted salt (R = R' = H) does not photocylize. Additionally, the photocyclization reaction with halogen elimination does not proceed when both aromatic chromophores are electron acceptors, as shown[61] for substituted 1-(2-halo-3-quinolylmethyl)pyridinium salts 40. This clarifies why Bradsher et al.[60] failed to photocyclize 1-benzylpyridinium cations with an NO_2 group in the benzyl ring.
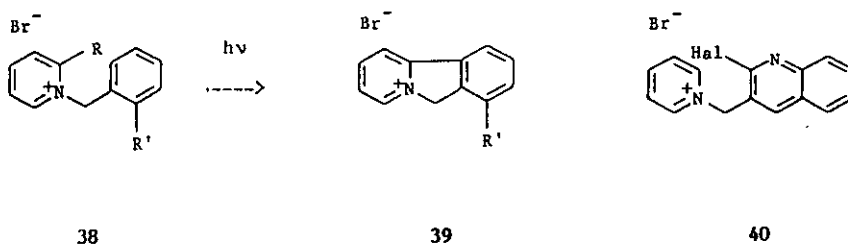
In the N-phenacylpyridinium molecule 41 where there is no conjugation between the aromatic fragments, the cyclic product 42 can be obtained only if a halogen atom is present on the pyridinium ring (as in 43[60]), just as for N-benzyl-substituted pyridinium cations.
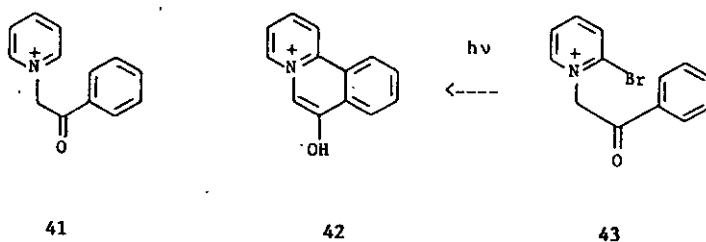

Quaternary heterocycles with large π-systems can be obtained by the photocyclization of condensed pyridinium derivatives as in 44 --> 45[62] and 46--> 47.[63]

44   45   46   47
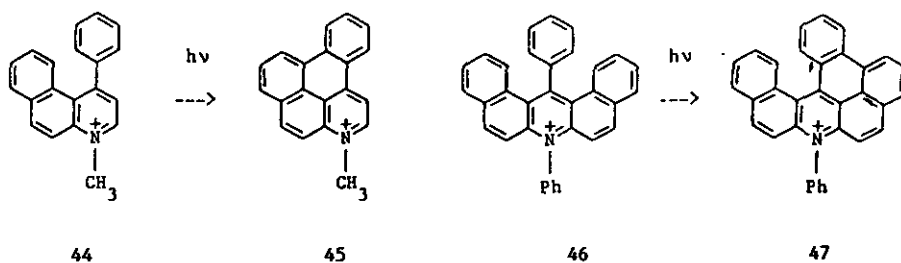
The photocyclodehydrogenation reactions of N-aryl-substituted pyridinium cations have been intensively investigated recently. This reaction was first reported by *Dorofeenko* et al.[64], but an incorrect structure was suggested for one of the photoproducts. The correct structure was elucidated by Katritzky et al.[65,66] These early papers investigated the photocyclizations of 48 and 50.

48   49
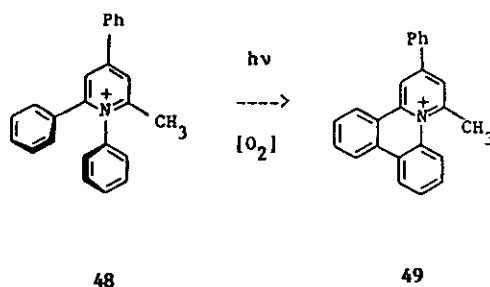
The appearance of absorption and fluorescence in the visible spectrum is characteristic for this reaction. Transformation 50 --> 52 involves the formation of intermediate 51, which was long preparatively inacessible. However, it was recently reported that photolysis of a degased methanol solution of compound 50 at -80°C leads in good yield only to photoproduct 51. The reaction can be also stopped at the monocyclization stage by electronic (meta-halogen in the N-phenyl ring[67]) or steric effects a (3-methyl group in the pyridinium ring[32]). 2,6-Diphenyl-N-naphthyl pyridinium cations (10b, 11b, R ≠ H) are photostable, but decreased steric hindrance in the 2-unsubstituted analog (10a, 11a, R = H) allows efficient photocyclizations (53a --> 54, 55 --> 56) in yields of 60-70%.[31] The structure of photoproduct 56 was determined by Atovmyan, Aldoshin et al.[24] by X-ray analysis: the higher reactivity of the naphthalene α- compared to the β-position determines the orientation despite the resulting non-planar sterically-hindered structure.

Ph   hν   Ph   hν   Ph

[O₂]   [O₂]

50   **51**   **52**

Ph   hν   Ph   Ph   hν   Ph

53   **54**   **55**   **56**
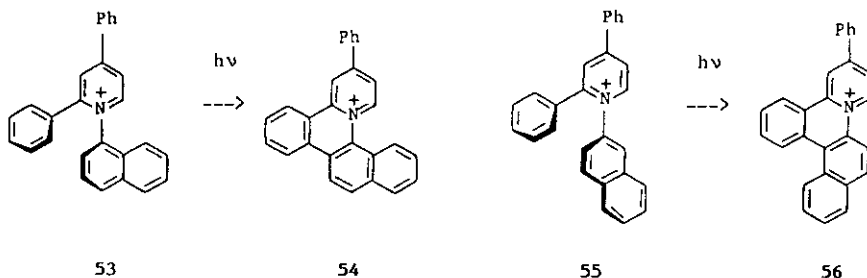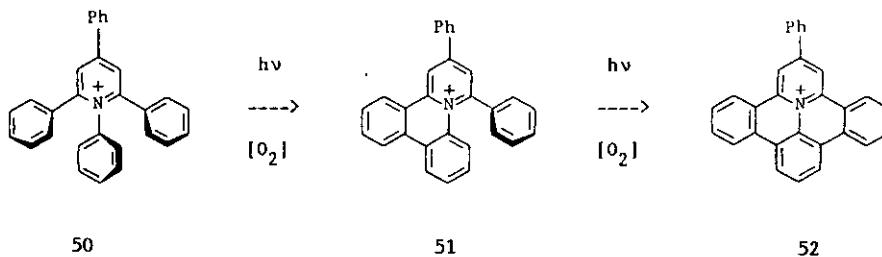
Numerous novel condensed polycyclic systems have been obtained by the photocyclizations of 1- and 2-heteroaryl (pyridyl, tetrazolyl, benzothiazolyl, etc.) substituted pyridinium cations.[66,68] Photocyclization of N-3-(p-nitrobenzylideneamino)phenyl]-2,4,6-triphenylpyridinium cation (57 --> 58 + 59) also succeeded.[69]

Ph   hν   Ph   Ph

Ph   Ph   ----->   Ph   Ph

Argon

N=CH   NH₂

NO₂

57   **58**   **59**
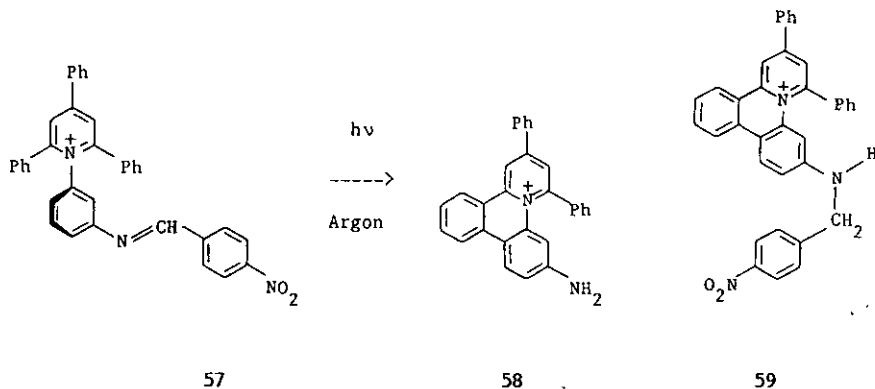
Photocyclization of symmetric bis(aryl pyridinium biscations) affects only one of the potential photoactive pyridinium fragments.[32,70,71] The excited state of the second fragment deactivates only by intramolecular S-S energy transfer (λ_{ss} = 10^{12} ÷ 10^{13} s^{-1}). Energy transfer efficiency can be varied as in pyridinium salts with azomethine chromophore (L)[70,72]. Here the energy transfer rate constant depends strongly on the nature of the substituent R. Pyridinium salts with 0-oxyazomethine substituents have efficient photochromic properties.[73]
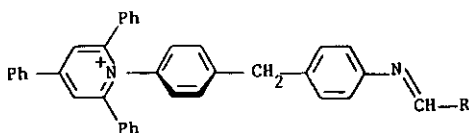
60

R = phenyl, o-hydroxyphenyl, 2-hydroxynaphthyl

Investigation of the photocyclization mechanisms of N-aryl pyridinium cations showed that photoexcitation led to the formation of a short lived ($\tau \approx 100$ ms) intermediate which was oxidised by dissolved oxygen into the final photoproduct.[74,75] This conclusion is based on flash-photolysis experiments and because intermediate compounds, absorbing in a long-wavelength spectral range ($\lambda \geq$ 450 nm), have been observed by photolysis of degased solutions. These intermediates were long regarded as condensed dihydro derivatives, as in the case of the photocyclization of some neutral systems, based on UV-spectroscopy, however, ESR experiments[76] indicate that they may have a radical nature, and we consider that the matter requires further investigation.

4. POLYARYLSUBSTITUTED PYRIDINIUM CATIONS: PATHWAYS OF EXCITED STATE DEACTIVATION

In the previous sections of this review various mechanisms for the relaxation of the excited states of pyridinium salts have been discussed. The whole complexity of different photoinduced processes in pyridinium salts is of special interest. Substituted N-arylpyridinium cations have received the most complete investigation, and for these there are considerable photochemical and luminescent data. Because the photochemical and photophysical processes are connected closely, we have attempted the formulation of a general scheme of the photoinduced processes of substituted N-arylpyridinium salts. As a very general example, we examine the N-naphthyl-2,4-diphenylpyridinium cation, which has been investigated in detail.[31,75] Fig. 4 gives a section of the potential energy surface along the most interesting reaction co-ordinate, the torsional angle ϕ between the planes of pyridinium and N-naphthyl fragments. The transition energies correspond to those of cation **61**.
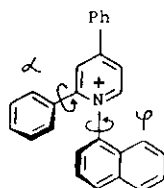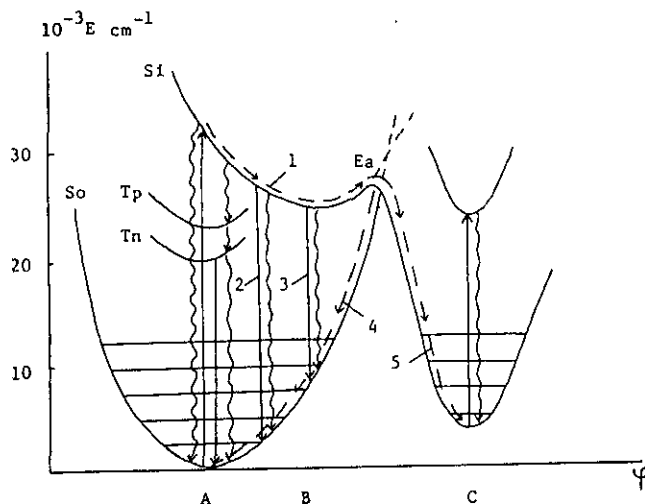

61

Fig. 4 Pathways of excited state deactivations in
N-naphthyl-2,4-diphenylpyridinium cations.

After photoexcitation into the S_1-state of the initial non-coplanar structure, structural relaxation 1 (decrease of the torsional angle ϕ) begins. This relaxation is accompanied by radiationless energy loss and by fluorescence; depending upon the solvent viscosity, structures with more or less co-planar N-naphthyl and pyridinium fragments are fluorescent (fluorescence processes 3 and 2).[39] Simultaneously with the structural relaxation of the N-naphthyl substituent, torsional twists of the α-phenyl rings take place; solvent viscosity and temperature affect only weakly the efficiency of this process. The molecule can overcome a potential barrier E_a during further motion along the reaction co-ordinate. Vibronic relaxation to the initial non-coplanar structure competes with this process. At 77 K, the potential barrier cannot be overcome and there is no photoreaction.

Solvent viscosity hinders structural relaxation as well as the return from the planar structure to the initial non-coplanar one, but the rates of these processes depend differently on the solvent viscosity. This results in the characteristic extreme dependence of the photocyclization quantum yield on solvent viscosity.

Population of the naphthyl fragment triplet state T_n proceeds by intramolecular T-T energy transfer from the pyridinium chromophore triplet state T_p. Energy transfer as well as phosphorescence emission proceeds from a structure with non-coplanar N-naphthyl, α-phenyl and pyridinium fragments. The photoinduced processes in substituted N-phenylpyridinium cations differ from that last-mentioned only by the absence of fluorescence at room temperature.

The molecular orbitals of the triplet state of aryl-substituted pyridinium cations thus differ considerably from those of the singlet excited state. In substituted N-phenyl compounds, the biphenyl type triplet level is phosphorescent. The almost unperturbed triplet state of the N-naphthyl chromophore populated by intramolecular energy transfer is phosphorescent in substituted N-naphthyl cations.

We wish to stress once more that structural relaxation in the singlet excited state plays a major role in influencing the fluorescent and photochemical properties of aryl-substituted pyridinium salts. Hence the photophysical and photochemical processes of excitation energy degradation can be examined from a common viewpoint.

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