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PHOTOCYCLIZATION OF 1,2-DIARYL- AND PHOTOBICYCLIZATION OF 1,2,6-TRIARYLPYRIDINIUM CATIONS*

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New 1,2-diaryl- and 1,2,6-triarylpyridinium salts, containing various five- and six-membered heteroaromatic substituents in the 1, 2, and 6-positions of the pyridinium ring, were synthesized. New tetra- and hexacyclic compounds were prepared by photocyclization of the cations of these salts. Photocyclization proceeds through a singlet excited state with nonadiabatic formation of a dihydro intermediate, followed by its oxidative dehydrogenation. The structure and quantum yield of the formation of photoproducts are determined by steric and electronic effects of the substituents, and in bichromophore compounds by the presence of S—S intramolecular interfragment energy transfer.

The present article represents a generalization of results on the reaction of photocyclization of polyaryl-substituted pyridinium cations and consists of two parts. The first includes the results of preparative photosynthesis of new heterosubstituted systems, conducted at the laboratory of the University of East Anglia and Florida under the supervision of Prof. A. R. Katritzky. The second part discusses the structural and energy metabolism of the photoreaction, as well as the photophysical processes that compete with it. The results of this part of the work were obtained at the laboratory of photochemistry of the Scientific-Research Institute of Physical and Organic Chemistry of Rostov State University.

1. PHOTOCYCLIZATION AS A METHOD OF PRODUCING NEW HETEROCYCLIC COMPOUNDS

The work on the photocyclization of 1,2-diaryl-cations (I → II) and the photobicyclization of 1,2,6-triarylpyridinium cations (I → III) was conducted by A. R. Katritzky's group [1] and followed the work of G. N. Dorofeenko et al. [2], in which these photoconversions were detected for the first time. This section presents the results of a broader investigation of photocyclization for pyridinium cations with various heteroaryl substituents.

Most of the pyridinium derivatives were produced from the corresponding pyrylium salts and amines by conventional methods (Table 1). The yields were good except for the case of Ic, where adverse steric and electronic effects are associated with the presence of an ortho-carboxy group.

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*The article is dedicated to the memory of Professor G. N. Dorofeenko.

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TABLE 1. Aryl-Substituted Pyridinium Salts I

Compound[a]	R^1	R^2	R^3	R^4	Method	mp (dec.), °C[b]	Found, %			Gross formula[c]	Calculated, %			Yield, %
							C	H	N		C	H	N	
Ia	Ph	Ph	Ph	Ph	A	241—242	73,4	4,7	3,0	$C_{29}H_{22}BF_4N$	73,9	4,7	3,0	90
Ib	Ph	4-C_6H_4F	4-C_6H_4F	4-C_6H_4F	B	206—209	66,4	3,6	2,7	$C_{29}H_{19}BF_7N$	66,3	3,6	2,7	86
Ic	2-$C_6H_4CO_2Me$	Ph	Ph	Ph	A	166—168	69,8	4,8	2,6	$C_{31}H_{24}BF_4NO_2$	70,5	4,4	2,7	35
Id	2-$C_6H_4CO_2H$	Ph	Ph	Ph	A	272—273[d]	68,5	4,4	2,4	$C_{30}H_{22}ClNO_6$	68,3	4,2	2,6	70
Ie	2-$C_6H_4CO_2^-$	Ph	Ph	Ph	—	295—298	83,7	5,3	5,6	$C_{30}H_{21}NO_2$	84,1	4,9	5,3	93
If	4-Pyridyl	Ph	Ph	Ph	A	207—209	70,5	4,7	5,9	$C_{28}H_{21}BF_4N_2$	71,1	4,5	6,0	70
Ig	1-Pyrrolyl	Ph	Ph	Ph	A	237—241	70,4	4,6	6,1	$C_{27}H_{21}BF_4N_2$	70,4	4,6	6,1	74
Ih	3-Me-5-Isothiazolyl	Ph	Ph	Ph	A	219—221	65,7	4,0	5,6	$C_{27}H_{21}BF_4N_2S$	65,9	4,3	5,7	90
Ii	4-vic-Triazolyl	Ph	Ph	Ph	A	197—200	64,8	4,1	12,4	$C_{25}H_{19}BF_4N_4$	64,9	4,1	12,1	63
Ij	4-symm-Triazolyl	Ph	Ph	Ph	A	231—234	65,1	4,0	12,1	$C_{25}H_{19}BF_4N_4$	64,9	4,1	12,1	71
Ik	5-Tetrazolyl	Ph	Ph	Ph	A	211—217	62,4	3,8	14,7	$C_{24}H_{18}BF_4N_5$	62,4	3,9	15,1	79
I*l*	2-Benzothiazolyl	Ph	Ph	Ph	A	219—223	68,0	4,2	5,5	$C_{30}H_{21}BF_4N_2S$	68,2	4,0	5,3	63
Im	Ph	CO_2Et	Ph	Ph	B	186—187	59,3	4,5	3,0	$C_{26}H_{22}BF_4NO_2$	59,4	4,5	3,0	97
In	Ph	CH=CHPh	Ph	Ph	—	253—255	74,1	4,9	2,9	$C_{31}H_{24}BF_4N$	73,5	4,9	2,8	87
Io	Ph	2-Pyridyl	Ph	Ph	B	228—231	71,3	4,6	5,6	$C_{28}H_{21}BF_4N_2$	71,2	4,5	5,9	86
Ip	Ph	4-MeC_6H_4	Ph	4-MeC_6H_4	A	239—242	74,2	5,2	2,8	$C_{31}H_{26}BF_4N$	74,6	5,2	2,8	88
Iq	Ph	2-Benzothiazolyl	Ph	Ph	A	241—246	68,5	4,0	5,0	$C_{30}H_{21}BF_4N_2S$	68,2	4,0	5,3	76
Ir	Ph	2-Thienyl	Ph	2-Thienyl	B	220—230	60,0	3,5	2,8	$C_{25}H_{18}ClNO_4S_2$	60,5	3,6	2,8	94
Is	4-MeC_6H_4	Ph	CO_2Et	Ph	B	183—185	67,2	5,1	2,9	$C_{27}H_{24}BF_4NO_2$	67,3	5,0	2,9	85
It	4-Pyrazolyl	Ph	Ph	Ph	A	195—198	56,9	3,9	8,1	$C_{26}H_{21}B_2F_8N_3$	56,8	3,8	7,7	61
Iu	3-Me-4-Isothiazolyl	Ph	Ph	Ph	B	208—210	66,1	4,2	5,8	$C_{27}H_{21}BF_4N_2S$	65,9	4,3	5,7	90
Iv	4-MeC_6H_4	Ph	CO_2^-	Ph	—	287—289	82,3	5,0	3,7	$C_{26}H_{19}NO_2$	82,2	5,2	3,8	90
Iw	4-MeC_6H_4	Ph	H	Ph	—	174—179	70,6	4,8	3,5	$C_{24}H_{20}BF_4N$	70,4	4,9	3,9	30
Ix	Ph	Me	Ph	Ph	A	214	68,6	4,9	3,6	$C_{24}H_{20}ClNO_4$	68,3	4,7	3,3	96

[a] BF_4^- anions, with the exception of those noted separately. Compounds Id, r, and x are perchlorates. [b] Ir: from acetic acid, the rest from alcohol; Ib, m: in the form of needles, the rest in the form of prisms. [c] The composition of compounds Ih, *l*, q, r, and u was also confirmed by determining the sulfur content. [d] According to the data of [3], mp 269-272°C.

TABLE 2. Products of Photocyclization of Pyridinium Salts

Irradiated compound[a]	Photo-product[b]	mp (dec.) °C[c]	Found, %			Gross formula[d]	Calculated, %			Yield, %
			C	H	N		C	H	N	
Ia	IIIa	307—310	74,5	3,8	2,9	$C_{29}H_{18}BF_4N$	74,5	3,9	2,9	75
Ib	IIIb	325	64,5	3,0	2,5	$C_{29}H_{16}BF_7 \cdot H_2O$	64,5	3,1	2,6	76
Id	IIId	342 [1]	71,0	3,7	2,8	$C_{29}H_{18}ClNO_4 \cdot 1/2H_2O$	71,2	3,9	2,9	75
If	IIIf	312	71,1	3,7	5,8	$C_{28}H_{17}BF_4N_2$	71,6	3,8	6,0	70
Ih	IIh	301—305	65,7	3,9	5,6	$C_{27}H_{19}BF_4N_2S$	66,1	3,9	5,7	86
Ii	IIi	216—219	65,5	3,8	12,0	$C_{25}H_{17}BF_4N_4$	65,2	3,7	12,2	89
Im	IIm	250—253	66,8	4,4	2,9	$C_{26}H_{20}BF_4NO_2$	67,1	4,3	3,0	80
Io	IIIo	261—264	71,3	3,7	—	$C_{28}H_{17}BF_4N_2$	71,6	3,8	—	68
Ip	IIIp	330	75,6	4,7	3,0	$C_{31}H_{22}BF_4N$	75,2	4,4	2,8	89
Iq	IIq	330	68,5	3,4	4,8	$C_{30}H_{19}BF_4N_2S$	68,4	3,6	5,3	80
Ir	IIIr	340	59,6	2,9	2,8	$C_{25}H_{14}ClNO_4S_2$	59,9	3,0	2,8	80
Is	IIIs	275—278	67,4	3,5	3,1	$C_{26}H_{18}BF_4NO_2$	67,4	3,9	3,0	75
It	IIIt	330	57,0	3,1	7,9	$C_{26}H_{17}B_2F_8N_3$	57,3	3,1	7,7	93
Ix	IIx	244	68,3	4,6	3,2	$C_{24}H_{18}ClO_4N$	68,7	4,3	3,3	80
IV	V	289—293	71,9	4,1	2,7	$C_{31}H_{20}ClO_4N \cdot 1/2H_2O$	72,3	4,1	2,7	35

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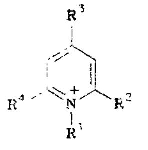
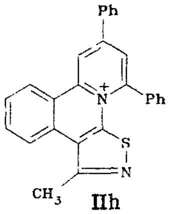
[a] The irradiation procedure is cited in the experimental section. Compounds Id, r and IIId, r represent perchlorates; the rest are tetrafluoroborates. [b] Compounds IIIa, b, d, f, o, s, IIm, x crystallize in the form of yellow needles, IIh as orange needles, IIi, q, IIIp, r, t as yellow prisms, and V as green needles. [c] Compounds IIh, i, q, and V were crystallized from ethanol, IIx, IIIa, d, f from a mixture of acetonitrile and ethanol, and the rest from methanol. [d] The composition of compounds IIh, q and IIIr was also confirmed by determining the sulfur content.

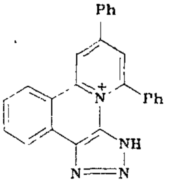
The characteristics of the photocyclization products are cited in Table 2. In the photocyclization of the perchlorate of the N-o-carboxyphenyl derivative (Id), as a result of elimination of carbon dioxide, 2-phenylbenzo[1,2]quinolyzino[3,4,5,6-def]phenanthridinium perchlorate is formed, identical with a specimen previously obtained photochemically [1] from 1,2,4,6-tetraphenylpyridinium perchlorate. The elimination of CO_2 also occurs in the photolysis of betaine Ie [1], the photoproduct of which is a bicarbonate of the same cation as the perchlorate IIId and the tetrafluoroborate IIIa. As was expected, the photocyclization of the salts Ib, p, and s proceeds smoothly (Table 2).



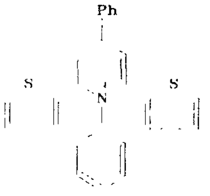
I



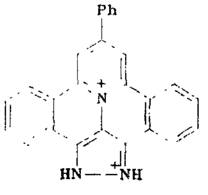
IIh



IIi



IIIr



IIIt

According to the data of [1], aza-substitution does not affect photocyclization as a result of which photoproducts of the type of IIIa are formed. In agreement with this, pyridyl analogs If, o cyclize with high yields and lead to compounds IIIf, o. The bisthienyl derivative IIIr was formed particularly easily in the irradiation of Ir.

Attempted monocyclization (irradiation for one week in various solvents) of the 1-(o-methoxycarbonylphenyl)derivatives (Ic) was not successful; however, the photoreactions of 2-ethoxycarbonyl- and 2-(2-benzothiazolyl)-substituted cations (Im, q) led to products of photomonocyclization IIm and IIq, respectively. Monocyclization is also effective when the 1-substituent is a heteroaromatic five-membered ring: isothiazole in Ih and vic-triazole in Ii (Table 2). The N-(4-pyrazolyl) derivative (It) photocyclizes to a new triazahexacycle IIIt.

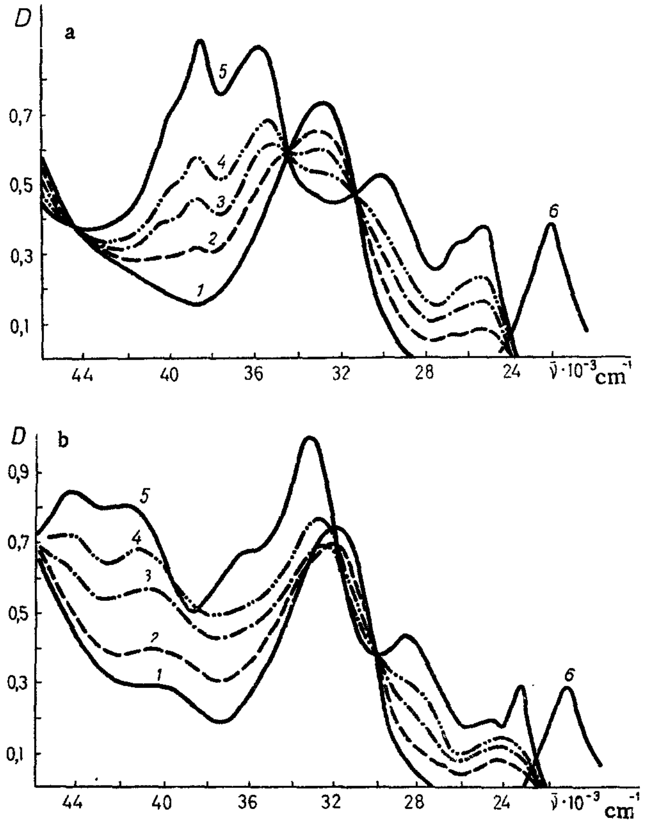
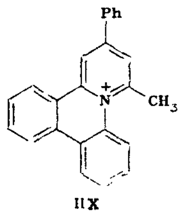
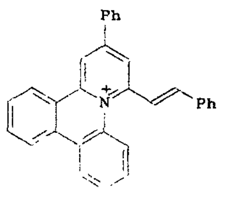


Fig. 1. Photoinduced changes in the absorption spectra (1–4) of N-aryl-substituted pyridinium cations ($2\cdot10^{-5}$ M in ethanol, 293°K, λ of irradiation 313 nm) and absorption (5) and fluorescence spectra (6) of the photoproducts: a) irradiation of 2-methyl-1,4,6-triphenylpyridinium perchlorate for 0, 10, 20, and 35 min (1–4); of 2-phenyl-4-methylpyrido[1,2-f]phenanthridinium perchlorate (5, 6); b) irradiation of 1,2,4,-6-tetraphenylpyridinium perchlorate for 0, 3, 8, and 13 min (1–4); of 2-phenylbenzo[1,2]quinolyzino-[3,4,5,6-def]phenanthridinium perchlorate (5, 6).

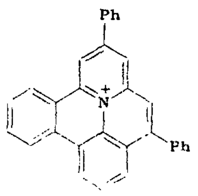
The 6-phenyl-2-styryl derivative (In) is unchanged after a week of irradiation in methanol, acetic acid, or DMSO. In view of this, we synthesized the possible intermediate IV from the methyl-substituted tetracycle Ix [1]. Compound IV is completely converted to compound V by irradiation for 24 h in methanol. Additional investigations are being conducted to determine the electronic or steric factors leading to the absence of photocyclization of compound In.



IIX



IV



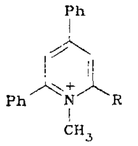
V

Irradiation of pyridinium derivatives Ig and Ij, containing heteroaryl groups (pyrrole and symm-triazole) in the 1-position, linked through the nitrogen atom, leads only to resinification. In the case of 1-(5-tetrazolyl)- and 1-(2-benzothiazolyl)-substituted pyridiniums (Ik, *l*), in which the heteroatoms occupy both reactive positions, there is no photocyclization. Attempts to oxidize compound Iw in alcohol medium to obtain the corresponding 4-oxo-compounds failed.

Some of the cyclic products contained water of crystallization, which is difficult to remove. Its presence is confirmed by the data of IR and NMR spectroscopy and by analyses according to Fischer.

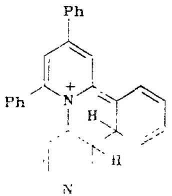
2. MECHANISM OF THE PHOTOCYCLIZATION REACTION AND COMPETING PROCESSES

For a study of the mechanism of photocyclization reaction we selected the simplest representatives of N-aryl-substituted pyridinium cations (Ia, x) and their N-methyl analogs VIa, b.

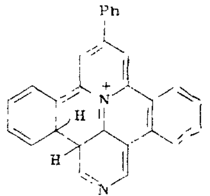


VIa, b

a $R=CH_3$; b $R=Ph$



VII



VIII

Compounds Ia, x do not fluoresce in solutions at room temperature, in contrast to compounds VIa, b. At the same time, at 77°K their spectralfluorescent properties are virtually identical ($\bar{\nu}_{max} \approx 32{,}000\ cm^{-1}$, $\bar{\nu}_{max\text{-}fl} \approx 27{,}000\ cm^{-1}$, $\bar{\nu}_{max\text{-}fl} \approx 21{,}000\ cm^{-1}$), and the calculated deactivation constants of their excited states are close ($\varphi_{fl} \approx 0.47\text{-}0.53$, k_{fl} $5 \cdot 10^8\ sec^{-1}$, $k_{st} \approx 5 \cdot 10^8\ sec^{-1}$). The sharp change in the fluorescent properties at 293°K is associated with the appearance of the possibility of photochemical deactivation of the energy of excitation under these conditions. Irradiation in the long-wave absorption band of the cations Ia, x leads to an irreversible modification of their absorption spectra (Fig. 1). The isobestic points in the spectra of Ix during irradiation (Fig. 1a) indicates the existence of a single stable photoproduct in the irradiated solution, for which a tetracyclic structure IIa was established in [1, 2]. The photoconversions of the cation Ia are more complex (Fig. 1b). In the course of the photoreaction, intense fluorescence arises ($\varphi_{fl} \approx 0.3$), the excitation spectra of which repeat the form of the photoinduced absorption. The fluorescent individual end products of the photoreaction were isolated preparatively with yields exceeding 80% [1, 2]. A comparison of the spectral characteristics of the photoproducts from the cations Ia, x indicate the possibility of a process of bicyclization of the cation Ia, rather than monocyclization. Actually, the hexacyclic structure IIIa of the photoproduct was demonstrated by an x-ray crystallographic method [1].

The nature of the intermediates in the photocyclization of 1,2,6-triarylpyridinium cations was investigated on the example of the photobicyclization of the cation If [4]. In stationary photoirradiation of degasified solutions, the compound VII is formed, with a more long-wave absorption ($\bar{\nu}_{max} \approx 18{,}000\ cm^{-1}$) than the final hexacyclic cation IIIf ($\bar{\nu}_{max} \approx 23{,}000\ cm^{-1}$). Oxidation by molecular oxygen converts compound VII to the tetracyclic compound IIf. A short lived product ($\tau_e \approx 100$ msec), absorbing close to $18{,}000\ cm^{-1}$, is also observed under conditions of pulsed photolysis in the presence of atmospheric oxygen. The results obtained permit us to consider the intermediate VII as the 13a,13b-dihydroderivative of the tetracycle IIf. The spectral data also indicate the possibility of a process of oxidative dehydrogenation of the intermediate VII in an excited singlet state.

In photoexcitation in the region of the absorption of the tetracycle IIf, modification of the absorption spectra indicates the formation of a different intermediate (VIII), which absorbs in an even longer-wave spectral region ($\bar{\nu}_{max} \approx 14{,}000\ cm^{-1}$). Oxidation of compound VIII leads to the formation of the final hexacyclic cation IIIf. The absorption spectra and fluorescent properties of the π-isoelectronic cations IIIa and IIIf are entirely identical. Under conditions of pulsed photolysis of nondegasified solutions of the cation If, the formation both of the intermediate VII and of a short-lived product ($\tau_e \approx 100$ msec), absorbing in the region of $14{,}000\ cm^{-1}$, is observed. The data obtained provide a basis for considering compound VIII as the 3a,3b-dihydroderivative of the hexacyclic cation IIIf.

Thus, the photobicyclization reaction in 1,2,6-triaryl-substituted pyridinium cations includes an intermediate step forming a tetracyclic cation. At the stages of mono- and bicyclization the corresponding dihydro-intermediates are formed. To determine the mechanism of the photocyclization reaction, it is of great importance to establish the nature of the S_0-S_1 transition. The long-wave band in the absorption spectra of Ia, x, VIa, b is complex in the region of $32{,}000\ cm^{-1}$. Investigations of aryl-substituted benzene, pyridine, and py-

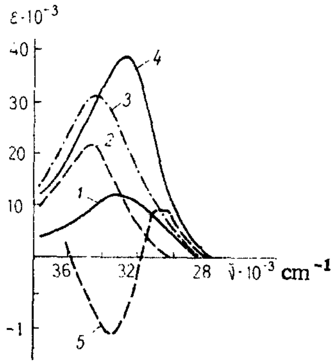
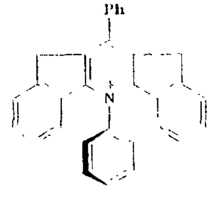


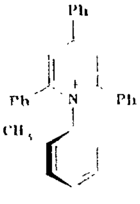
Fig. 2. Long-wave bands in the absorption spectra of aryl-substituted pyridinium cations (ethanol, 293°K): 1) 1-methyl-2,6-diphenylpyridinium perchlorate; 2) 1,2,6-trimethyl-5-methylpyridinium perchlorate; 3) additive spectrum 1 and 2; 4, 5) absorption and circular dichroism spectra of 1-methyl-2,4,6-triphenylpyridinium perchlorate (VIb).

ridinium derivatives showed that this band arises only in the spectra of heteroaromatic molecules. Its intensity increases with increasing electron donor capacity of the heteronucleus, while an intensification of the electron donor properties of the aromatic substituents (incorporation of the OCH_3 group) leads to a sharp long-wave shift, which is characteristic of transitions of the type of intramolecular charge transfer (ICT).

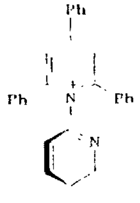
From a comparison of the absorption and circular dichroism spectra it also follows that the band represents a superposition of two electronic transitions (Fig. 2). Just as in the π-isoelectronic 2,4,6-triphenylsubstituted pyrylium cation [5], in the cations I and VI the more long-wave of these transitions is associated with ICT from the 2,6-substituent in the heteroring, while the short-wave transition is associated with ICT from the 4-phenyl substituent to the heteroring. Such a nature of the compound band, in particular, is confirmed by the possibility of representing it in the form of an approximated superposition of the absorption of 1-methyl-2,6-diphenylpyridinium and 1,2,6-trimethyl-4-phenylpyridinium, which are models of fragments with these substituents (Fig. 2). The absence of bands of ICT from the N-phenyl substituent is associated with the substantially increased electron density on the nitrogen atom of the heterocycle in comparison with the 2,4,6-carbon atoms and the substantial acoplanarity of the N-phenyl ring [6].



IX



X



XI

Consequently, electronic excitation S_0-S_1 in N-phenyl-substituted pyridinium cations is localized on a fragment of the molecule including the 2,6-phenyl rings and does not affect the N-phenyl ring that deviates from the plane. Therefore, the rotation of the N-phenyl ring necessary for photocyclization is due to its steric interaction with the mobile 2,6-phenyl rings. Such a structural mechanism is confirmed by the absence of photocyclization of the model compound IX, in which rotation of the 2,6-phenyl substituents is excluded.

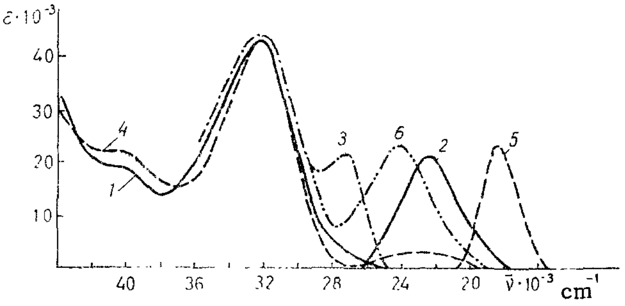
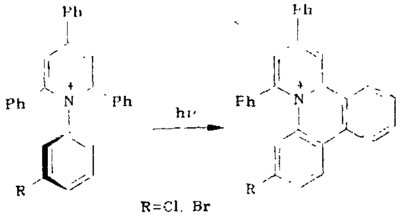


Fig. 3. Spectral fluorescent properties of 1-(4-R-phenyl)-2,4,6-triphenylpyridinium perchlorates (ethanol, 293°K): 1, 4) absorption; 2, 5) fluorescence; 3, 6) excitation of fluorescence (1-3, R=OCH_3, 4-6, R=NH_2).

It can be assumed that the adiabatic process of formation of a fluorescent structure with an anomalous Stokes shift in the S_1 state, with a flattened arrangement of the 2,6-phenyl rings relative to the pyridinium ring system, competes with the initial step of photocyclization of the cations I (formation of a dihydro intermediate). Actually, compounds X and XI, in which the quantum yield of the photoreaction is sharply reduced (to zero in X), possess fluorescence with an anomalously large Stokes shift. The assignment of this fluorescence at 293°K to a structure with coplanar 2,6-phenyl rings relative to the pyridinium ring is confirmed by the coincidence of the fluorescence spectra of compounds X, XI with the fluorescence of the model compound IX.

In 1-(3-R-phenyl)-2,4,6-triphenylpyridinium cations (R = Cl, Br), steric factors permit stoppage of the photoreaction at the step of monocyclization without significantly decreasing its quantum yield in the absence of fluorescence with an anomalously large Stokes shift. These results, taken together, cannot be achieved by introducing substituents into the ortho- or para-position of the N-phenyl ring (see part 1 and [1]). The results of spectral investigations of the photoreaction and the data of x-ray crystallographic analysis of the preparatively isolated photoproduct (R = Cl, 60% yield) [7] provide evidence of the formation of stable end products of monocyclization — 2,4-diphenyl-7-R-pyrido[1,2-f]phenanthridinium perchlorates (R = Cl, Br).

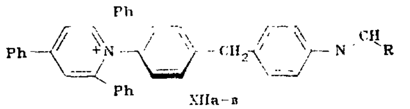


Steric hindrance of rotation of one of the 2,6-phenyl rings in 3-methyl-1,2,4,6-tetraphenylpyridinium also leads only to monocyclization, while the cation with still another methyl group in the 5-position — 3,5-dimethyl-1,2,4,6-tetraphenylpyridinium — is photochemically stable and does not exhibit fluorescence with an anomalous Stokes shift.

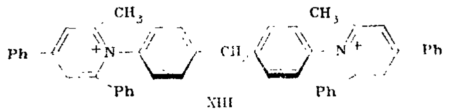
Most of the substituents of various electronic types (CH_3, $COCH_3$, Cl, Br, F) in the para-position of the N-phenyl ring of compound I do not introduce any appreciable spectral changes; however, they substantially lower the quantum yield of photobicyclization (see also [1]). In contrast to the substituents mentioned, when electron donor groups OCH_3 and NH_2 are incorporated, supplementary low-energy transitions in the absorption and emission appear, possessing the characteristics typical of ICT — an increase in the intensity and a long-wave shift when the electron donor capacity of the substituent is enhanced (Fig. 3). The states of ICT that arise lead to an intensive deactivation of the singlet state, associated with rotation of the 2,6-phenyl rings. As a result of this, both the photoreaction and fluorescence with an anomalously large Stokes shift are absent.

When a NO_2 group is introduced into the meta- or para-position of the N-phenyl ring, no spectral characteristics of new compounds, associated with the electronic effect of the substituent, are observed. And yet, the position of the acoplanar nitrobenzene fragment, extremely close to the heteroring (0.5 nm), and the presence of a low-lying S_0-$S_{\pi*}$ transition in the absorption, overlapping with the fluorescence of the acoplanar form of the 2,4,6-triphenylpyridinium fragment, create favorable conditions for the effective interfragment singlet-singlet (S-S) emissionless transfer of energy from the pyridinium fragment to the nitrobenzene substituent. As a result of this process there is no photocyclization, and there is a complete quenching of fluorescence at 293 and 77°K.

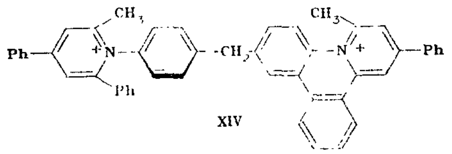
Quenching of the triplet state of the cations Ia, x ($E_t \approx 23{,}000$ cm^{-1}), which appears at 77°K in the form of sensitized phosphorescence of naphthalene ($\lambda_{excit} > 340$ nm), does not lead to any decrease in the quantum yield of photocyclization at 293°K. Together with the data cited, this indicates that the photocyclization reaction proceeds exclusively through the lower singlet state. In view of this, the influence of intramolecular emissionless energy transfer on the photocyclization reaction was investigated in specially synthesized bichromophore systems XII [8].



XIIa–в



XIII



XIV

Compound	XIIa	XIIb	XIIc
R	2-hydroxyphenyl	2-hydroxynaphthyl-1	phenyl
$E_{S_1} \cdot 10^{-3}$, cm^{-1} [8]	29	23	32

The data obtained in a study of the fluorescence properties in solutions at 77°K provide evidence of the existence in systems XIIa, b of an intramolecular S-S energy transfer from the pyridinium to the azomethine fragment, which competes successfully with the intercombinational conversions (S_1-T_1) in the pyridinium portion of the molecule. In accordance with the value of the Förster overlapping integral, the transfer constants are equal to $2.3 \cdot 10^{10}$ (XIIa) and $6 \cdot 10^{11}$ sec^{-1} (XIIb) and are close to the values obtained experimentally. In system XIIc there is no energy transfer as a result of the unfavorable position of the singlet states of the fragments. An investigation of the photochemical behavior of bichromophore molecules XIIa-c at room temperature shows that the presence of azomethine fragments affects the quantum yield of the photoreaction in accordance with the established effectiveness of the S-S energy transfer. The addition of benzalaniline (XIIc) has virtually no effect on the quantum yield of the photocyclization of the pyridinium fragment ($\Phi = 0.01$). In the molecule with salicylalaniline (XIIa) the quantum yield is significantly reduced ($\Phi = 0.003$), and, finally, in system XIIb the photoreaction practically is not observed.

According to the data obtained, it might be expected that singlet-singlet energy transfer, leading to a rather high rate, will determine photocyclization in the symmetrical bicationic system XIII. The structure of the single photoproduct obtained preparatively corresponds to the structure of the cation XIV. This is indicated by the data of comparative spectral-fluorescent investigations of the photoproduct and of compound IIx. Deactivation of the reactive state of the noncyclizing fragment occurs as a result of the extremely high rate ($k \approx 10^{12}$ sec^{-1}) of the intramolecular S-S energy transfer to the cyclic fragment formed as a result of the photoreaction.

The data presented are convincing evidence that S-S energy transfer in bichromophore systems can affect both the quantum yields of the photocyclization and the structure of the final photoproducts.

We should mention that the summary quantum yield of photocyclization and fluorescence for all the systems studied in the work proved to be significantly less than one ($\Phi \leqslant 0.05$). This is an indication of the existence of a reverse process of formation of the ground state of the initial acoplanar form, occurring with high probability. This process may occur through intermediate nonequilibrium structures, representing the nonadiabatic formation of a dihydro intermediate. Such degradation of the energy of excitation is extremely characteristic of photochemically unstable systems and may be considered as one of the types of photochemically induced processes of emissionless deactivation, the mechanism of which has recently been actively discussed.

EXPERIMENTAL

The electronic absorption spectra were obtained on a Specord UV-vis spectrometer, the circular dichroism spectra on a Jasko-20 spectropolarimeter. The fluorescent measurements were performed on a Fotolyum spectrofluorometer. A DRSh-250 mercury lamp with replaceable glass filters was used as the source of photoactive light.

For preparative photochemical reactions we used Rayonet photoreactors with a volume of 200 ml and a quartz photoreactor with immerscible DRL-1000-2 mercury lamp with a volume of 1 liter. The spectral study of the photochemical processes in solutions at 293°K in the absence of oxygen was conducted in a special evacuated cuvette. The solutions were preliminarily degasified at 77°K at a pressure of about 10^{-4} mm. Intermediate short-lived products were registered on a pulse lamp photolysis setup.

Aryl-substituted pyridinium salts (I, Table 1). A. A mixture of 12 mmoles of primary amine and 10 mmoles of the corresponding pyrylium salt in 20 ml of ethanol was boiled with a reflux condenser for 6-90 h until the fluorescence disappeared; then the solvent was removed at reduced pressure and the residue was triturated with ether.

B. The pyrylium salt and amine were mixed in 50 ml of methylene chloride at room temperature for 2 h, the solvent evaporated, and the residue triturated with ether.

2-(2,4,6-Triphenylpyridinium)benzoate (Ie). To a solution of 5.28 g (10 mmoles) pyridinium perchlorate Id in 25 ml of ethanol, 0.56 g (10 mmoles) potassium hydroxide was added, mixed for 25 min, and the potassium perchlorate that precipitated was filtered off. The solution was concentrated at reduced pressure, diluted with ether, and left overnight in a refrigerator. The crystals that precipitated were filtered off and recrystallized from ethanol. Yield 3.58 g (91%).

1-(4-Methylphenyl)-2,6-diphenylpyridinium tetrafluoroborate (Iw). The 4-ethoxycarbonylpyridinium salt (Is) was subjected to hydrolysis by an aqueous alcohol solution of potassium hydroxide according to a procedure analogous to that described above. The betaine that precipitated, 1-(4-methylphenyl)-2,6-diphenylpyridinium-4-carboxylate (Iv), mp 287-290°C (according to unpublished data of S. Kato, mp 288-289°C), was mixed for 2 h at room temperature with 10 ml of 40% HBF_4, and the tetrafluoroborate filtered off. The latter was heated for 12 h at 120°C in quinoline with a catalytic amount of copper powder. The decarboxylation product (Iw) was precipitated from a cooled quinoline solution with twice the amount of ether. Recrystallization from 5 ml of acetic acid yielded white crystals of Iw.

2-Phenyl-4-styrylpyridol[1,2-f]phenanthridinium perchlorate (IV). To a suspension of 0.15 g (0.375 mmole) 2-phenyl-4-methylpyrido[1,2-f]phenanthridinium perchlorate (IIx) in 10 ml of ethanol we added 16 mg (0.187 mmole) piperidine and 40 mg (0.375 mmole) benzaldehyde, boiled with a reflux condenser for 30 min, cooled, and the green precipitate that formed (0.198 mmole, 53%) was recrystallized from ethanol. Mp 270-273°K. Found: C 71.9; H 4.4; N 2.7%. $C_{33}H_{22}ClNO_4 \cdot 1/4H_2O$. Calculated: C 72.0; H 4.4; N 2.7%.

1,4,6-Triphenyl-2-styrylpyridinium tetrafluoborate (In, Table 1) was produced analogously from 2-methyl-1,4,6-tetraphenylpyridinium tetrafluoroborate.

Photocyclization of pyridinium salts. A solution (0.2 or 1 liter) of the pyridinium salt in methanol or ethanol (1 mg in 1 ml) was irradiated with monochromatic light 300 nm or with the summary light of a mercury lamp in a photoreactor during passage of air or oxygen. The time of irradiation was determined by the cessation of changes in the absorption spectra and was from 1 to 72 h. The reaction mixture was concentrated at reduced pressure, the residue dissolved with a mixture of acetonitrile-ether, and recrystallized.

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TAUTOMERISM OF A SERIES OF SUBSTITUTED 9-ACRIDINETHIONES

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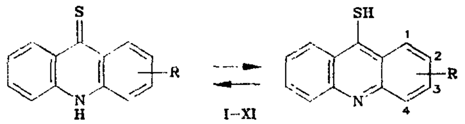
UDC 547.835.5 + 541.623 + 543.51

A quantitative estimation of thione-thiol tautomerism in a series of substituted 9-acridinethiones was performed by methods of IR, UV, and mass spectrometry as a function of the aggregated state, temperature, and solvent. It was shown that the thione form predominates in the crystal and gas phase; the position of the equilibrium is ambiguous in solutions.

This work presents the results of a quantitative study of the tautomeric (thione-thiol) equilibrium in a series of substituted 9-acridinethiones (I-X), depending on the change in the polarity of the solvent, temperature, aggregated state, and ionic strength of the solution.

The following compounds were investigated:



I R=H; II R=2-Cl; III R=3-Cl; IV R=4-Cl; V R=2-OCH_3; VI R=2-OC_2H_5; VII R=4-OCH_3; VIII R=4-OC_2H_5; IX R=2-NO_2; X R=3-NO_2; XI 10-methyl-9-acridinethione

Thione-thiol tautomerism of 9-acridinethione was recorded back in 1944 [1]. Spectral evidence of the existence of thione–thiol equilibrium in solution for compound I was obtained in [2]. However, the numerated studies and later ones [3, 4] were qualitative; there is no quantitative estimation of the dynamic tautomeric equilibrium. In all the investigations indicated above, the influence of the nature of the solvent, the electronic effect of the substituent R, the temperature, and the phase state of the substance on the ratio of the tautomeric forms in this heterocyclic system were not discussed.

For a quantitative estimation of the position of the tautomeric equilibrium in the series of acidinethiones I-X we used UV and IR spectroscopy and mass spectrometry. The use of UV spectroscopy was due to a difference in the electronic absorption spectra of 10-methyl-9-acidinethione XI and 9-methylmercaptoacridine [2] (the method of model compounds [5]). The presence of an absorption band of the thione group ($\nu C=S = 1230 \pm 5\ cm^{-1}$ [2]) in the IR spectrum also permits the use of this method for the quantitative determination of the thione form.

First let us consider the influence of the nature of the solvent on the prototropic equilibrium in the system of 9-acridinethione (Table 1). The results of the investigation showed that the polarity of the organic solvent has no significant influence on the position of the tautomeric equilibrium. Table 1 presents comparative data for nonpolar solvents –

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