ether was boiled for 3 h. After the ether and thionyl chloride were distilled off, 3.53 g (48 mmoles) diethylamine was added to the residue, and it was heated with boiling for 2 h. The excess diethylamine was distilled off, 30 ml of water was added, and soda was added to pH 10. The reaction products were extracted with ether and then chromatographed; the eluent was ether. Yield 0.2 g (35%) of compound IX; mp 158-159°C (from a 1:2 mixture of hexane and benzene). IR spectrum: 1650 cm$^{-1}$ (CONR$_2$). Found: C 77.9; H 7.6; N 9.1%; M$^+$ 614. $C_{40}H_{46}\cdot N_4O_2$. Calculated: C 78.1; H 7.5; N 9.1%; M 614.

## LITERATURE CITED

1. N. S. Prostakov, V. P. Shalimov, and V. P. Zvolinskii, Khim. Geterotsikl. Soedin., No. 12, 1668 (1972).
2. N. S. Prostakov, B. Kh. Sisimbina, S. A. Soldatova, V. P. Shalimov, K. G. Montenegro, N. I. Leonova, and L. A. Murugova, Khim. Geterotsikl. Soedin., No. 12, 1668 (1982).
3. N. S. Prostakov, I. R. Vaskes, N. M. Mikhailova, and B. N. Anisimov, Izv. Vyssh. Uchebn. Zaved., Khim. i Khim. Tekhnol., 22, 920 (1977).
4. I. D. Rubin and E. I. Becker, J. Org. Chem., 22, 1623 (1957).
5. H. E. Fritz, D. W. Peck, M. A. Eccles, and K. E. Atkins, J. Org. Chem., 30, 2540 (1965).

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# FLUORESCENCE AND PHOTOCYCLIZATION OF N-NAPHTHYL-SUBSTITUTED PYRIDINIUM CATIONS

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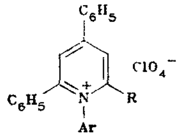
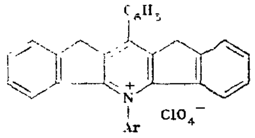
The spectral-fluorescent and photochemical properties of 1-naphthyl-2,4-di- and 2,4,6-triphenylpyridinium perchlorates were investigated in solutions at 293 and 77°K. The anomalously large Stokes shift of the fluorescence was due to the adiabatic change in the structure of the molecules as a result of rotations of the C- or N-aryl substituents. The observed phosphorescence arises as a result of intramolecular T-T transfer of energy to the N-naphthyl radical. 1-Naphthyl-2,4-diphenylpyridinium cations are capable of photocyclization with the formation of intensely fluorescent derivatives of benzo[b or c]pyrido[1,2-f]phenanthridinium, isolated with high yields in preparative photolysis.

In arylsubstituted pyridinium cations, deactivation of the lower excited singlet state occurs both as a result of the formation of photochemically stable coplanar structures that fluoresce with an anomalous Stokes shift and as a result of a competing process of photocyclization with the participation of the N-phenyl substituent. The relative rates of these reactions depends substantially on steric and electronic factors [1, 3]. The purpose of this work was to study the processes of deactivation of the excited states of N-naphthyl-substituted pyridinium cations and to perform a photochemical synthesis of new polycyclic heteroaromatic systems with directed variation of the structure of the initial compounds. The objects of investigation were N-naphthylpyridinium perchlorates I-IV and model compounds V and VI.



I-IV



V,VI

I, II, V Ar=1-napthyl III, IV, VI Ar=2-napthyl; I, III R=$C_6H_5$; II, IV R=H

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Scientific Research Institute of Physical and Organic Chemistry at M. A. Suslov Rostov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1528-1532, November, 1984. Original article submitted August 3, 1983. Revised April 3, 1984.

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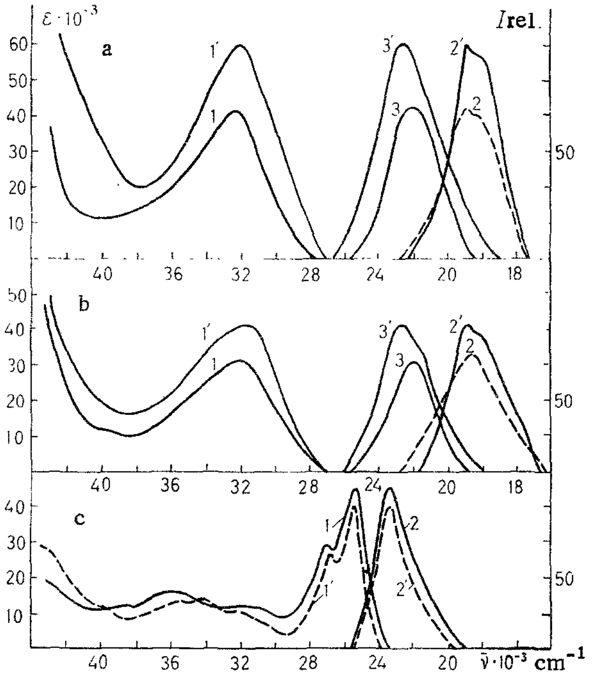


Fig. 1. Absorption spectra (1, 1'), fluorescence at 293°K (2, 2') and 77°K (3, 3') of ethanol solutions of compounds I-VI ($\lambda_{excit}$ 313 nm). a) I (1-3), II (1'-3'); b) III (1-3), IV (1'-3'); c) V (1', 2'), VI (1, 2).

At 293°K in solutions of compounds I-IV, fluorescence ($\varphi_{fl} \approx 0.015$-$0.03$) with an extremely large Stokes shift (12,000-13,000 $cm^{-1}$) is observed (Fig. 1a, b). The parameters of the fluorescence are virtually independent of the concentration and solvent, which is evidence of an intramolecular mechanism of the formation of the anomalous Stokes shift. According to the data of [4, 5], in polyaryl-substituted pyridinium cations, the N-phenyl substituent is virtually orthogonal to the plane of the pyridinium ring. An analogous structure should be expected, all the more, for the cations I-IV with voluminous N-naphthyl fragments. Consequently, it can be assumed that flattened structures, formed as a result of rotation of the N-naphthyl substituents, are responsible for the appearance of an anomalously shifted fluorescence.

The proposed mechanism is confirmed in an examination of model molecules — bisindenopyridinium derivatives (V, VI) with a fixed coplanar arrangement of the 2,6-phenyl rings. In such structures rotation of the N-naphthyl ring is rather improbable on account of the extremely large potential barrier, due to steric hindrances. As a result of this, the fluorescence with an anomalous Stokes shift associated with rotation of the N-naphthyl substituents is absent and only the fluorescence characteristic of cations with coplanar 2,6-substituents is observed [3, 4] (Fig. 1c). In solutions frozen down to 77°K, for compounds I-IV with unchanged absorption spectra, fluorescence with a somewhat lower Stokes shift, modeled by the fluorescence of the cations V and VI, is observed. Consequently, the formation of the Stokes shift under these conditions is associated with rotation not of the N-naphthyl but of the 2,6-phenyl substituents in the excited state.

The data cited are evidence that the fluorescence of N-naphthyl derivatives, in contrast to N-methyl- and N-phenyl-substituted pyridinium cations [2, 3], under any conditions, possess an anomalous Stokes shift, which is due to adiabatic variation of the structure of the molecules as a result of rotation of the C- or N-aryl substituents.

In the case of excitation of compounds I-IV in the system of levels of the pyridinium chromophore, together with the fluorescence of the pyridinium fragment with coplanar 2,6-phenyl rings, the characteristic structural fluorescence of naphthalene is observed ($\tau_{fl} \approx$ 2.4 sec), which, however, is somewhat bathochromically shifted (Fig. 2). A certain lowering of the triplet level of naphthalene is associated with the perturbing influence of the pyridinium ring, close in electron acceptor properties to the nitro group [6, 7]. The extremely

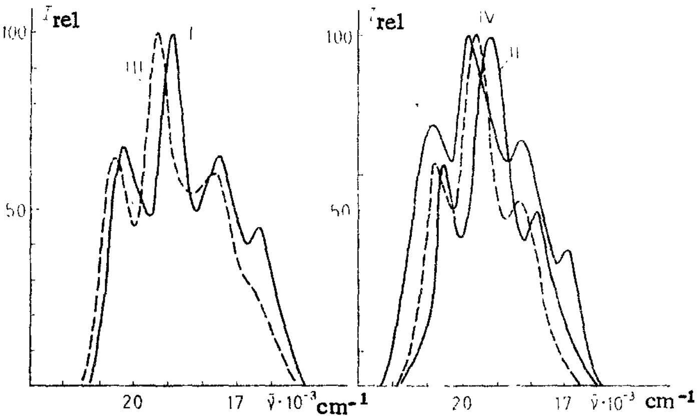
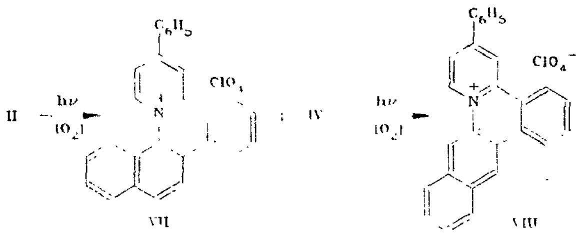


Fig. 2. Fluorescence spectra of compounds I-IV and naphthalene (1) (ethanol, $10^{-5}$ M, 77°K, $\lambda_{excit}$ 313 nm).

small distance between the orthogonal π-systems and the profitable arrangement of their triplet states (in pyridinium ∿22,000 cm$^{-1}$, in naphthalene ∿21,000 cm$^{-1}$) permit us to suggest a population of the triplet level of naphthalene by interfragmentary T-T transfer of energy from the pyridinium chromophore.

As is well known [8], the presence of an intermolecular T-T transfer of energy is direct evidence of such a process. Actually, when the N-methyl-2,4,6-triphenylpyridinium cation is used as a donor of triplet energy ($c_d$ $2\cdot10^{-4}$ M), while naphthalene ($c_a$ 0.1 M) is used as the acceptor, in the case of excitation of the levels of the cation in the system ($\lambda_{excit}$ > 340 nm) in solutions at 77°K, sensitized phosphorescence of naphthalene was observed. The detected effective intramolecular T-T transfer of energy can serve as still another evidence of the virtually complete orthogonality of the N-naphthyl and pyridinium fragments in excited molecules I-IV at 77°K.

Now let us consider the photochemical pathway of deactivation of excited states of N-naphthyl-substituted cations, which compete at room temperature with the formation of anomalously shifted fluorescence. In the case of voluminous N-naphthyl substituents, the main factor determining the effectiveness of the photocyclization reaction is steric interaction, manifested in the process of the formation of a coplanar polycyclic structure of the photoproducts. Actually, the 2,6-diphenyl-substituted cation I is photostable on account of substantial steric hindrance to the coordinated rotation of the 1,2,6-aryl substituents, necessary for photocyclization. Two ways of reducing the indicated steric interactions are possible: isomeric addition of a N-naphthyl fragment (cation III) and/or synthesis of 6-unsubstituted cations (cations II, IV). As was shown by spectral-fluorescent investigations, irradiation of solutions of compounds II and IV induces a substantial modification of their absorption and fluorescence spectra (Fig. 3), typical of the photocyclization process [9]. A conclusion on the most probable structure of the photoproduct VIII was drawn on the basis of the results of [9] on the selective photocyclization of pyridinium cations with substituents nonsymmetrical with respect to the C-N bond.



Preparative photochemical synthesis of new heterocyclic systems — derivatives of benzo[c or b]pyrido[1,2-f]phenanthridinium (VII, VIII) — was performed in a quartz photoreactor. The spectral-fluorescent characteristics of the individual photoproducts VII and VIII, isolated with yields of 76 and 63%, respectively, are cited in Fig. 3. High final yields were obtained despite the extremely low quantum yields of the photoreactions (0.04 and <0.01 for compounds II and IV, respectively). The absence of a correlation in this case between the

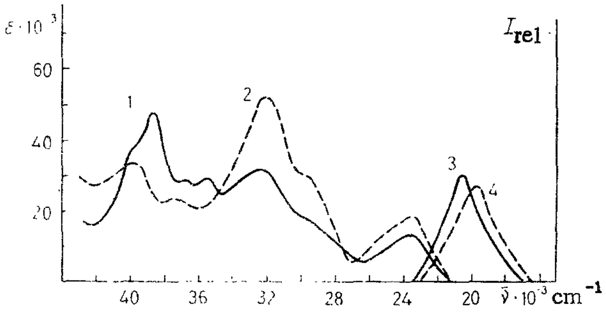


Fig. 3. Absorption (1, 2) and fluorescence spectra (3, 4) of compounds VII (1, 3) and VIII (2, 4) (ethanol, 293°K, $\lambda_{excit}$ 400 nm).

rate of the photoreaction and steric hindrances is evidence of the necessity of considering differences in the reactivity of the nonequivalent carbon atoms of the naphthyl fragment.

In a comparison of the fluorescence spectra of the initial (II, IV) and final (VII, VIII) compounds, the unusual shorter-wave position of the fluorescence bands of the photoproduct is noteworthy (Figs. 1 and 3). It can be assumed that such a pecularity is associated with a certain noncoplanarity of the structure of the photoproducts, analogous to that described in [9]. In contrast to the initial compounds, the photoproducts represent stable luminophores with a quantum yield of fluorescence $\varphi_{fl} \approx 0.3$, which permitted the use of compound VIII to obtain generation in the case of pumping with a nitrogen laser.

Thus, variation of the structure of polyaryl-substituted pyridinium cations, considering possible steric interactions, permits a directed influence on the pathways of deactivation of excited states. As a result, the possibility emerges for effective photochemical synthesis of new polycyclic heteroaromatic compounds, inaccessible by other synthetic methods.

## EXPERIMENTAL

The electronic absorption spectra were recorded on a Specord UV-vis spectrophotomer; the fluorescent measurements were performed on a Fotolyum instrument. The quantum yields of the fluorescence ($\varphi_{fl}$) were measured according to the Parker procedure relative to 9,10-diphenylanthracene in toluene ($\varphi_{fl}$ = 0.72) [10].

The quantum yields of the formation of photoproducts were determined according to the initial portions of the kinetic curves of the increase in the optical density in the long-wave absorption band of the photoproduct formed. Photoexcitation was performed with the mercury line 313 nm, isolated by a glass light filter from the spectrum of a DRSh-250 lamp.

1-(1-Naphthyl)-2,4-diphenylpyridinium perchlorate (II). A mixture of 0.38 g (1 mmole) of 2-carboxy-4,6-diphenylpyrylium perchlorate and 0.14 g (1 mmole) of 1-naphthylamine in 10 ml glacial acetic acid was boiled for 4 h. After cooling the precipitate was filtered off and washed with ether. The yield was quantitative; mp 244-245°C (dec.) after three recrystallizations from a 5:1 mixture of ethanol and acetonitrile. Found: C 70.8; H 4.5; Cl 7.7; N 3.0%. $C_{27}H_{20}ClNO_4$. Calculated: C 70.9; H 4.4; Cl 7.8; N 3.1%.

1-(2-Naphthyl)-2,4-diphenylpyridinium perchlorate (IV). Produced from 2-carboxy-4,6-diphenylpyrylium perchlorate and 2-naphthylamine according to the procedure described above with a yield of 80%. Mp 255-256°C (dec.) after three recrystallizations from a 5:1 mixture of ethanol and acetonitrile.

1-(1- or 2-Naphthyl)-2,4,6-triphenylpyridinium (I, III) and 5-(1- or 2-naphthyl)-11-phenyl-9H,12H-5-azoniandeno[2,3-b]fluorene (V, VI) perchlorates were produced by the reaction of equimolar amounts of the corresponding pyrylium salts and naphthylamines with boiling in ethanol for 1 h. The data of elementary analysis correspond to the gross formulas cited. I: mp 278-280°C (dec.), from ethanol, $C_{33}H_{24}ClNO_4$. III: mp 298-300°C (dec.) from ethanol $C_{33}\cdot H_{24}ClNO_4$. V: mp 244-245°C (dec.) from acetonitrile, $C_{35}H_{24}ClNO_4$. VI: mp 310-312°C (dec.) from acetonitrile, $C_{35}H_{24}ClNO_4$.

Preparative photocyclization at 25°C was conducted in a photoreactor with a volume of 0.5 liter with a DRT-220 immersible mercury lamp with a power of 220 W with intensive purging with oxygen.

3-Phenylbenzo[c]pyrido[1,2-f]phenanthridinium perchlorate (VII). A solution of 0.5 g of the perchlorate II in 0.5 liter of ethanol was irradiated for 6 h. The reaction mixture was evaporated to 50 ml and 0.38 g (76%) of compound VII was filtered off. Mp 300-302°C (dec.), from acetonitrile. Found: C 71.2; H 4.0; Cl 7.9; N 3.1%. $C_{27}H_{18}ClNO_4$. Calculated: C 71.2; H 4.0; Cl 7.8; N 3.1%.

6-Phenylbenzo[b]pyrido[1,2-f]phenanthridinium perchlorate (VIII). A solution of 0.35 g of the perchlorate IV in 0.5 liter of a 1:1 mixture of ethanol and chloroform was irradiated for 8 h. The reaction mixture was evaporated to 50 ml, and 0.22 g (63%) of compound VIII was obtained. Mp 263-265°K (dec.), from a 1:1 mixture of acetonitrile and ethanol. Found: C 71.2; H 3.9; Cl 7.6; N 3.2%. $C_{27}H_{18}ClNO_4$. Calculated: C 71.2; H 4.0; Cl 7.8; N 3.1%.

## LITERATURE CITED

1. Ya. R. Tymyanskii, M. I. Knyazhanskii, Yu. P. Andreichikov, G. E. Trukhan, and G. N. Dorofeenko, Zh. Org. Khim., 12, 1126 (1976).
2. M. I. Knyazhanskii, Ya. R. Tymyanskii, Summaries of the Third Symposium on Photochemistry [in Russian], Potsdam, German Democratic Republic (1982), p. 2.
3. M. I. Knyazhanskii, Izv. Akad. Nauk SSSR, Ser. Fiz., 47, 1309 (1983).
4. S. M. Aldoshin, Ya. R. Tymyanskii, O. A. D'yachenko, L. O. Atovmyan, M. I. Knyazhanskii, and G. N. Dorofeenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2270 (1981).
5. R. M. Claramunt and J. Elguero, Collect. Czech. Chem. Commun., 46, 584 (1981).
6. S. McGlynn, T. Azumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice-Hall (1969).
7. C. Toma and A. T. Balaban, Tetrahedron, Suppl. 7, 27 (1966).
8. Emissionless Transfer of Energy of Electronic Excitation [in Russian], Nauka, Leningrad (1977), p. 176.
9. Ya. R. Tymyanskii, S. M. Aldoshin, M. I. Knyazhanskii, O. A. D'yachenko, A. I. Pyshchev, and L. O. Atovmyan, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 535 (1982).
10. C. Parker, Photoluminescence of Solutions, Elsevier (1968).

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# THERMAL DECOMPOSITION OF 1,2-DIMETHYL-3(5)-(4-R-STYRYL)-PYRAZOLIUM IODIDES

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The reaction of 1,2,3(5)-trimethylpyrazolium iodide with aromatic aldehydes yielded the series of 1,2-dimethyl-3(5)-(4-R-styryl)pyrazolium iodides (R = H, $NMe_2$, $NO_2$). The quantitative ratio of 1-methyl-3- and -5-(4-R-styryl)pyrazoles formed in the thermal decomposition of the above-mentioned pyrazolium iodides depends on steric factors in the initial compounds and on the electronic influence of the substituent R. A simple method was proposed for the production of trans,trans-1,4-bis(1-methyl-3-pyrazolylvinyl)benzene and 1-methyl-3,5-distyrylpyrazole, which possess fluorescent properties.

Earlier we described the synthesis of trans-1-methyl-3- and -5-(4-R-styryl)pyrazoles (R = $NO_2$, $NH_2$) and trans,trans-1,4-bis(1-methyl-3- (I) and -5-pyrazolylvinyl)benzenes (II). However, the multistep nature of the synthesis and the low yields hinder searches for ways of practical utilization of compounds I and II, which possess intense fluorescence in solutions and in the solid state [1]. The methyl group in the 3(5)- position of 1,2,3(5)-trimethylpyrazolium iodide (III) is active in the reaction of condensation with aldehydes, and certain 1,2-dimethyl-3(5)-(R-styryl)pyrazolium iodides have been produced by the reaction of compound III with aromatic aldehydes [2]. Thus, we synthesized 1,2-dimethyl-3(5)-(4-R-

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