Photochemical properties and the structure of 6-methyl-2,4-diphenyl-1-(*p*-tolyl)pyrimidinium perchlorate and the product of its photocyclization

N. I. Makarova,[a] M. I. Knyazhanskii,[a] O. S. Filipenko,[b] D. S. Bulgarevich,[a] V. A. Kharlanov,[a] S. V. Borodaev,[a] and S. M. Aldoshin[b]*

[a]*Scientific Research Institute of Physical and Organic Chemistry at Rostov State University, 194/3 prosp. Stachki, 344038 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 28 5667*

[b]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (096) 515 3588*

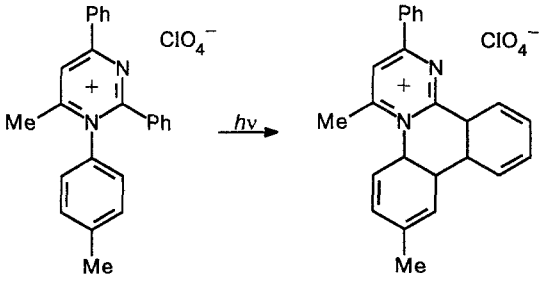
The structure and photochemical properties of 6-methyl-2,4-diphenyl-1-(*p*-tolyl)pyrimidinium perchlorate (**1**) and 4,8-dimethyl-2-phenylpyrimido[1,2-*f*]phenanthridinium (**2**) formed as a result of photocyclization of **1** have been studied. The crystal structure of compound **1** has been studied at −140 °C and 25 °C. In cation **1**, the *N*-tolyl substituent and α-Ph ring are noncoplanar with the pyrimidinium fragment (the angles are 67.9° and 41.1°, respectively), while the angle between the γ-Ph ring and the pyrimidinium moiety is only 7.1° (−140 °C). The photocyclization product **2** has a flattened structure.

Key words: 6-methyl-2,4-diphenyl-1-(*p*-tolyl)pyrimidinium perchlorate, photocyclization; 4,8-dimethyl-2-phenylpyrimido[1,2-*f*]phenanthridinium cation, molecular and crystal structure.

When studying photoinduced processes in the series of aryl-substituted pyridinium (Py) cations,[1,2] we found photocyclization of a new type and unusual fluorescence characterized by an anomalous Stokes shift. These processes occur with different efficiencies depending on the nature of substituents (in particular, at the N atom in the positively charged heterocycle) and the spatial structure of the cations, which are nonplanar in the ground electron state owing to deviations of the aryl rings from the plane of the charged heterocycle.[3–5] It was established that the initial stage of photoinduced processes in aryl-substituted Py cations is the barrierless rotation of aryl rings, which results in substantial flattening of the cation structure in the excited state. The character of excitation, which is caused by the charge transfer from aryl substituents to the heterocycle, and the mechanism of initial photoprocesses should essentially depend on the structure of the central charged nucleus and, in particular, on the number of heteroatoms in this cycle.

This work opens up a new cycle of studies of photoinduced processes in aryl-substituted nitrogen-containing heterocyclic cations with two N atoms in the heterocycle (pyrimidinium cations). We have studied the structures and photochemical properties of 6-methyl-2,4-diphenyl-1-(*p*-tolyl)pyrimidinium perchlorate (**1**). Differences in properties of the tetrasubstituted cation of **1** and the *N*-alkyl- and *N*-aryl-substituted cations of 2,4,6-triphenylpyridinium studied previously are primarily determined by the replacement of the Py fragment by the more electron-withdrawing pyrimidinium fragment and one of α-Ph substituents is replaced by the methyl group. The starting compound **1** exhibits no fluorescence in solutions at room temperature. However, irradiation of salt **1** at a long-wave absorption band (λ_{max} = 314 nm) causes irreversible modification of the absorption spectrum of the cation: new long-wave absorption bands (λ_{max} = 350 and 385 nm) and fluorescence band (λ_{max} = 475 nm) appear (Fig. 1). An analogous change in spectra is typical of photocyclization of 1,2,4,6-tetraaryl-substituted Py cations.[1,2]

The new photoproduct, 4,8-dimethyl-2-phenylpyrimido[1,2-*f*]phenanthridinium perchlorate (**2**), was isolated preparatively. Its structure was established by ^{1}H NMR, IR, and UV spectroscopy and confirmed by the data of elemental analysis and X-ray structural study.



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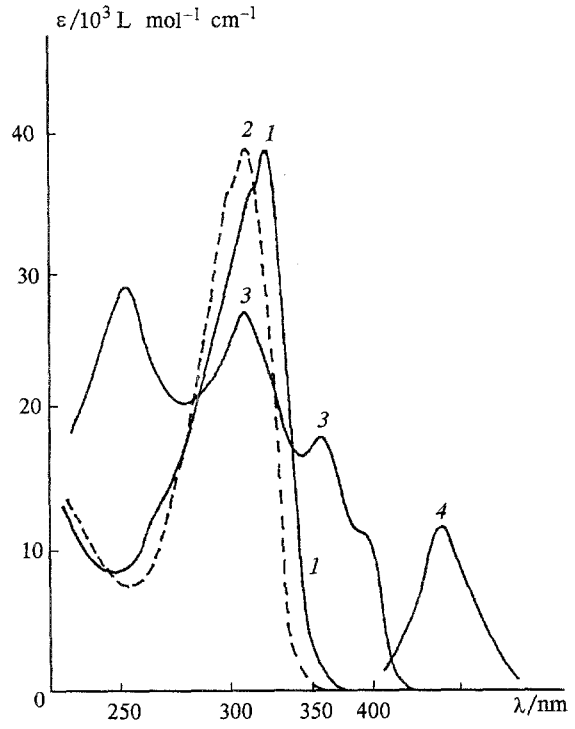

Fig. 1. Electronic absorption spectra (*1—3*) and the fluorescence spectrum (*4*) of the starting compound and the photocyclization product (MeCN, 293 K): *1*, 6-methyl-2,4-diphenyl-1-(*p*-tolyl)pyrimidinium perchlorate (**1**); *2*, 2-methyl-4,6-diphenyl-1-(*p*-tolyl)pyridinium perchlorate (**5**); *3* and *4*, 4,8-dimethyl-2-phenylpyrimido[1,2-*f*]phenanthridinium perchlorate (**2**).

In this work, the synthesis, structure, and photochemical properties of compound **1** and product **2**, which is formed as a result of photocyclization of **1**, are reported.

Experimental

Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer in ethanol and acetonitrile. The fluorescence spectra were obtained on an Elyumin-2M fluorimeter in acetonitrile. The IR spectra were recorded on a Specord IR-75 instrument in Vaseline oil. The ^{1}H NMR spectra were recorded on a UNITY-30 spectrometer (300 MHz) in acetonitrile-d_3.

6-Methyl-2,4-diphenyl-1-(*p*-tolyl)pyrimidinium perchlorate (1). *p*-Toluidine (0.556 g, 5.2 mmol) was added to a suspension of 6-methyl-2,4-diphenyl-3-azapyrilium (1.739 g, 5 mmol) in chloroform (50 mL), and the mixture was boiled for 3 min. The precipitate formed after cooling was filtered off, washed with ether, and recrystallized from nitromethane. The yield was 62 %, m.p. 280—281 °C. UV (MeCN), λ_{max}/nm: 314 (ε 37950). IR, ν/cm^{-1}: 1613, 1593, 1507, 1493, 1353, 1087 ([ClO$_4$]$^-$); 813, 767, 687. ^{1}H NMR, δ: 2.37 (s, 3 H, *p*-CH$_3$); 2.55 (s, 3 H, 6-CH$_3$); 7.34—8.47 (m, 14 H, H arom.); 8.56 (s, 1 H, H(5)). Found (%): C, 66.02; H, 4.70; Cl, 8.18; N, 6.32. $C_{24}H_{21}ClN_2O_4$. Calculated (%): C, 65.97; H, 4.87; Cl, 8.11; N, 6.41.

4,8-Dimethyl-2-phenylpyrimido[1,2-*f*]phenanthridinium perchlorate (2). A solution of salt **1** (0.437 g, 1 mmol) in ethanol (500 mL) with the addition of several drops of an alcohol solution of iodine as an oxidant was irradiated for 3 h in a quartz photoreactor with a DRT-230 mercury lamp. Air was bubbled through the solution. Photocyclization was monitored by UV spectroscopy. When the process was completed, the reaction mixture was concentrated to 15 mL under reduced pressure. The precipitate formed was filtered off, washed with ether, and recrystallized from ethanol. Yellow crystals were obtained. The yield was 58 %, m.p. 270—271 °C. UV (MeCN), λ_{max}/nm: 250 (ε 25604), 306 (ε 25329), 350 (ε 14045), 385 (ε 8427) — bend. IR, ν/cm^{-1}: 1613, 1596, 1520, 1087 ([ClO$_4$]$^-$); 707, 773, 727, 613. ^{1}H NMR, δ: 2.70 (s, 3 H, 8-CH$_3$); 3.23 (s, 3 H, 4-CH$_3$); 7.67—9.36 (m, 13 H, H arom.). Found (%): C, 66.20; H, 4.31; Cl, 8.26; N, 6.32. $C_{24}H_{19}ClN_2O_4$. Calculated (%): C, 66.28; H, 4.41; Cl, 8.15; N, 6.44.

X-ray structural analysis of crystals of 1 and 2. Crystals of **1** belong to the orthorhombic system; crystals of **2** belong to the triclinic system. The structure of **1** was studied at −140 °C and 25 °C (the first and second numbers in crystal-structural data, respectively). The principal crystallographic parameters of **1**: $C_{24}H_{21}ClN_2O_4$, a = 11.02(1) and 10.91(1) Å, b = 16.151(6) and 16.185(5) Å, c = 11.880(6) and 12.030(8) Å, V = 2114.45 and 2142.20 Å^3, Z = 4, d = 1.372 and 1.366 g cm^{-3}, space group $Pna2_1$; **2**: $C_{24}H_{19}ClN_2O_4$, a = 14.176(6) Å, b = 9.943(4) Å, c = 8.389(5) Å, α = 110.64(5)°, β = 103.11(4)°, γ = 103.34(4)°, V = 1013.2 Å^3, Z = 2, d = 1.426 g cm^{-3}, space group $P\bar{1}$.

Intensities of 1778 or 1850 (**1**) and 2167 (**2**) independent reflections with $I > 2\sigma(I)$ were measured on an automated DAR-UM diffractometer (**1**) and an automated four-circle RED-4 diffractometer (**2**) (in both cases, Cu-Kα radiation); absorption was ignored. The experimental diffraction data set at −140 °C was obtained with the use of a low-temperature device.[6] The largest relative change in unit-cell parameters of the crystal of **1** was observed upon cooling along the c axis; this change corresponds to the normal to close-packed layers of molecular cations. The structures were solved by direct methods using the RENTGEN-75 and SHELXS-86 programs and refined anisotropically by the full-matrix least-squares method using the SHELXS-76 program.[7] Atomic coordinates for hydrogen atoms were obtained from difference Fourier syntheses. The final refinement of atomic coordinates was carried out by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for H atoms to R = 0.046 and 0.068 (**1**) and R = 0.047 (**2**). Atomic coordinates for the structures of **1** and **2** are given in Tables 1 and 2, respectively.

Results and Discussion

The overall views of cations **1** and **2** are shown in Figs. 2 and 3, respectively. As is evident from the interplanar angles given below (the first and second values were obtained at −140 °C and 25 °C, respectively), no temperature dependence of geometric parameters is observed for cation **1**. The *N*-tolyl substituent in cation **1** is noncoplanar with the pyrimidinium fragment; the angle between these fragments is 67.9° (70.5°). This value is slightly smaller than that in the structure of 2,4,6-trimethyl-*N*-phenylpyridinium perchlorate (83.5°)[3] but is comparable with the values of the analogous

Table 1. Atomic coordinates for nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in the structure of **1**

Atom	−140 °C			25 °C		
	x	*y*	*z*	*x*	*y*	*z*
Cl	1978(1)	557(0)	318(0)	2092(0)	574(1)	318(0)
O(1)	2696(2)	208(2)	1177(3)	2684(5)	193(4)	1160(6)
O(2)	1497(3)	1346(2)	627(3)	1486(7)	1298(3)	617(6)
O(3)	2710(3)	648(2)	−689(3)	2766(4)	715(4)	−646(5)
O(4)	947(2)	20(2)	78(3)	1030(5)	66(4)	71(6)
N(1)	4898(3)	−5475(2)	−2342(3)	−4876(3)	−5487(2)	−2325(3)
N(2)	3887(3)	−4339(2)	−1506(3)	3907(3)	−4353(2)	−1482(3)
C(1)	3998(3)	−5148(2)	−1658(3)	4010(4)	−5161(2)	−1643(4)
C(2)	4739(3)	−3826(2)	−1959(3)	4737(4)	−3853(2)	−1950(3)
C(3)	5729(3)	−4145(2)	−2562(3)	5694(4)	−4170(3)	−2550(4)
C(4)	5799(3)	−4982(2)	−2775(3)	5759(4)	−4999(3)	−2764(4)
C(5)	3074(3)	−5686(2)	−1089(3)	3084(4)	−5689(2)	−1081(3)
C(6)	3412(3)	−6408(2)	−530(3)	3397(4)	−6416(2)	−531(4)
C(7)	2517(4)	−6859(2)	46(3)	2507(5)	−6843(3)	40(4)
C(8)	1301(4)	−6588(2)	79(4)	1301(5)	−6547(3)	84(4)
C(9)	958(3)	−5850(2)	−462(4)	1002(4)	−5821(3)	−459(5)
C(10)	1843(3)	−5403(2)	−1040(4)	1889(4)	−5386(3)	−1031(4)
C(11)	4879(3)	−6363(2)	−2649(3)	4858(4)	−6371(2)	−2630(4)
C(12)	5793(3)	−6873(2)	−2269(3)	5765(4)	−6887(3)	−2244(3)
C(13)	5788(3)	−7701(2)	−2624(4)	5749(4)	−7716(3)	−2589(5)
C(14)	4877(3)	−7999(2)	−3343(3)	4854(4)	−8000(3)	−3305(4)
C(15)	3959(3)	−7458(2)	−3702(4)	3951(4)	−7460(3)	−3674(4)
C(16)	3963(3)	−6625(2)	−3382(3)	3962(4)	−6632(3)	−3348(4)
C(17)	4879(6)	−8899(4)	−3701(7)	4851(5)	−8897(3)	−3660(6)
C(18)	6784(3)	−5340(2)	−3504(4)	6732(5)	−5350(3)	−3484(5)
C(19)	4524(3)	−2919(2)	−1818(3)	4524(4)	−2945(2)	−1802(4)
C(20)	5335(3)	−2346(2)	−2297(3)	5317(5)	−2371(3)	−2295(4)
C(21)	5100(4)	−1500(2)	−2197(4)	5068(6)	−1533(3)	−2178(5)
C(22)	4085(4)	−1225(2)	−1612(4)	4098(6)	−1268(3)	−1584(5)
C(23)	3268(4)	−1799(2)	−1110(4)	3326(6)	−1818(3)	−1104(6)
C(24)	3497(3)	−2643(2)	−1215(4)	3524(5)	−2679(2)	−1199(5)
H(3)	642(3)	−381(2)	−288(3)	659(4)	−378(3)	−279(4)
H(6)	436(3)	−659(2)	−58(4)	430(4)	−664(3)	−53(5)
H(7)	279(3)	−732(2)	48(3)	280(4)	−733(3)	46(4)
H(8)	70(3)	−686(2)	53(3)	67(4)	−684(3)	48(4)
H(9)	15(4)	561(2)	−37(4)	10(4)	−560(2)	−39(4)
H(10)	162(3)	−488(2)	−152(3)	175(4)	−486(2)	−145(4)
H(12)	636(2)	−669(2)	−175(3)	633(3)	−665(2)	−174(3)
H(13)	644(3)	−804(2)	−236(3)	650(4)	−802(3)	−228(4)
H(15)	330(3)	−763(2)	−417(3)	337(3)	−761(2)	−415(3)
H(16)	330(3)	−623(2)	−369(3)	332(5)	−615(3)	−368(5)
H(17)	425(3)	−897(2)	−430(3)	412(4)	−896(3)	−428(4)
H(17.1)	468(4)	−915(3)	−304(4)	474(4)	−910(3)	−309(4)
H(17.2)	576(3)	−914(2)	−397(4)	573(5)	−914(4)	−404(5)
H(18)	741(3)	−492(2)	−388(4)	735(6)	−491(4)	−383(7)
H(18.1)	643(3)	−564(2)	−418(4)	635(4)	−571(2)	−415(4)
H(18.2)	745(5)	−572(4)	−309(6)	744(4)	−579(3)	−314(4)
H(20)	611(3)	−252(2)	−285(3)	605(5)	−257(4)	−294(5)
H(21)	567(3)	−120(2)	−259(4)	576(5)	−128(4)	−294(5)
H(22)	389(4)	−67(3)	−156(5)	401(6)	−70(4)	−143(6)
H(23)	249(4)	−155(3)	−70(5)	251(4)	−156(3)	−78(4)
H(24)	291(3)	−304(2)	−81(3)	291(3)	−309(2)	−77(3)

angles in the structures of 1-(2-hydroxyphenyl)-2,4,6-triphenylpyridinium perchlorate (**3**) (71.1°) and 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium perchlorate (**4**) (72.3°).[4] The greatest conformational differences between cation **1** and Py are connected with the angles of rotation of the α- and γ-Ph rings with respect to the plane of the heterocycle. The angle between the planes of the α-Ph ring and the heterocycle is 41.1° (41.7°); the angle between the planes of the γ-Ph ring and the heterocycle is only 7.1° (7.0°). In the

Table 2. Atomic coordinates for nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in the structure of **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	2952(2)	3930(3)	1438(4)	C(18)	−3268(5)	6332(7)	3443(8)
O(1)*	2443(6)	4393(9)	289(8)	C(19)	−4663(5)	907(7)	2539(7)
O(1.1)*	3303(9)	2680(9)	190(9)	C(20)	−4610(5)	−572(7)	1896(8)
O(2)	3969(7)	4674(9)	2080(9)	C(21)	−5344(6)	−1756(7)	1920(8)
O(3)*	2582(8)	2881(9)	2218(9)	C(22)	−6109(6)	−1470(8)	2614(8)
O(3.1)*	2388(9)	255(10)	−310(9)	C(23)	−6153(6)	−34(7)	3257(8)
O(4)	2620(9)	5050(9)	2760(9)	C(24)	−5430(5)	1178(7)	3243(8)
N(1)	−2249(4)	4531(5)	3018(6)	H(3)	−455(4)	385(2)	294(3)
N(2)	−3085(4)	1889(6)	2052(7)	H(6)	−232(2)	23(4)	23(3)
C(1)	−2309(5)	3020(6)	2214(7)	H(7)	−113(3)	−28(3)	−123(2)
C(2)	−3890(5)	2177(7)	2534(7)	H(8)	27(3)	156(2)	−90(4)
C(3)	−3956(5)	3632(7)	2905(8)	H(9)	51(3)	417(2)	91(3)
C(4)	−3147(5)	4805(7)	3156(7)	H(13)	99(4)	635(3)	318(3)
C(5)	−1535(5)	2657(6)	1431(7)	H(15)	40(3)	931(4)	667(2)
C(6)	−1685(5)	1141(7)	367(7)	H(16)	−147(3)	738(4)	574(3)
C(7)	−1000(5)	786(7)	492(8)	H(17)	178(3)	1041(3)	686(2)
C(8)	−141(5)	1944(7)	−270(8)	H(17.1)	212(2)	901(3)	530(4)
C(9)	−12(5)	3434(7)	776(8)	H(17.2)	157(3)	988(2)	488(4)
C(10)	−675(5)	3842(7)	1681(7)	H(18)	−274(2)	703(3)	314(2)
C(11)	−1266(5)	−5714(6)	−3658(7)	H(18.1)	−392(3)	615(3)	270(3)
C(12)	−511(5)	5391(6)	2919(7)	H(20)	−410(4)	−81(3)	136(2)
C(13)	435(5)	6599(7)	3547(8)	H(21)	−531(3)	−280(3)	140(2)
C(14)	614(5)	8037(7)	4819(8)	H(22)	658(3)	−234(4)	269(3)
C(15)	−116(5)	8267(8)	5637(7)	H(23)	−664(4)	29(3)	379(4)
C(16)	−1035(5)	7138(7)	5099(7)	H(24)	−545(3)	239(2)	371(3)
C(17)	1619(5)	9330(7)	5384(8)				

* Atoms were disordered at two positions with occupancies of 0.5.

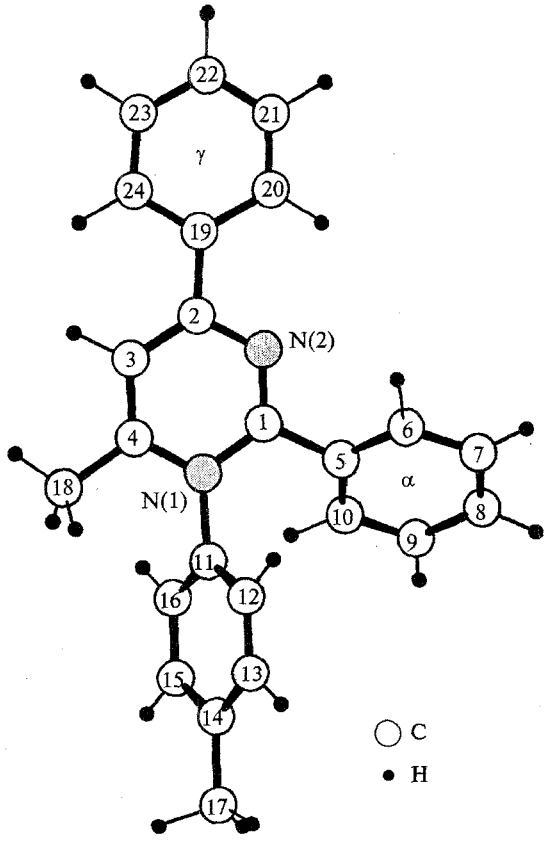

Fig. 2. Overall view of cation **1**.

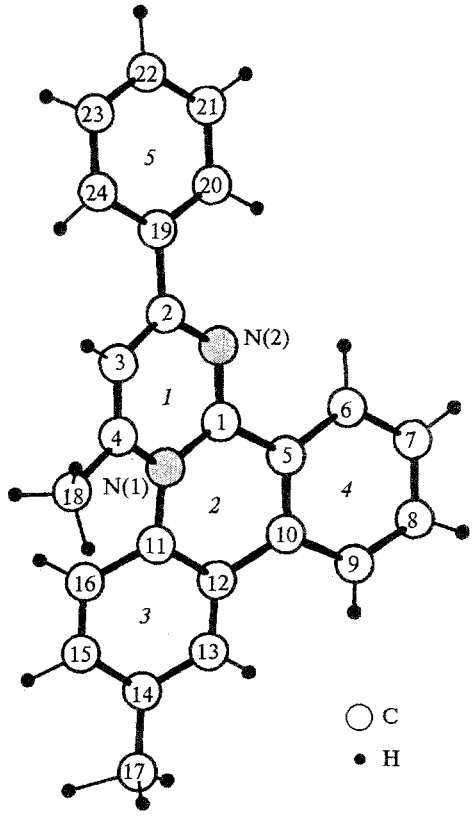

Fig. 3. Overall view of cation **2**.

Table 3. Principal bond lengths (*d*) in the structures of **1** and **2**

Bond	*d*/Å		
	1 (−140 °C)	**1** (25 °C)	**2**
N(1)—C(1)	1.387(4)	1.359(9)	1.385(8)
C(1)—N(2)	1.324(4)	1.327(4)	1.321(9)
N(2)—C(2)	1.362(4)	1.343(5)	1.351(9)
N(1)—C(4)	1.374(4)	1.353(5)	1.383(8)
N(1)—C(Ph)	1.479(4)	1.477(4)	1.440(9)
C(1)—C(5)	1.499(4)	1.486(8)	1.45(1)
C(2)—C(3)	1.404(5)	1.364(6)	1.40(1)
C(3)—C(4)	1.377(4)	1.368(6)	1.35(1)
C(2)—C(19)	1.493(4)	1.499(6)	1.47(1)

arylpyridinium cations, the α_1,α_2-Ph substituents are noncoplanar with the Py cycle; the angles between these substituents and the Py cycle are 50—71°; the angles of rotation of the γ-Ph substituents with respect to the plane of the heterocycle are 28—29°. Therefore, the conformation of the new cation **1** is characterized by a substantial flattening of the central fragment and α- and γ-Ph rings. The bond lengths and bond angles in the pyrimidinium fragment at two temperatures as well as the lengths of the bridge bonds (Table 3), which show the expected decrease as compared with the mean value (1.479 Å) for analogous bridge bonds in the structures of **3** and **4**, are identical within the experimental error.

Photocyclization product **2** has a tetracyclic structure (see Fig. 3). The tetracyclic fragment of molecular cation **2** is nonplanar. The dihedral angles between the plane of the pyrimidinium fragment *1* and the planes of Ph rings *2*, *3*, *4*, and *5* are 17.4°, 11.6°, 6.4°, and 12.8°, respectively. The principal bond lengths in the pyrimidinium cycle of cation **2** (see Table 3) are identical within the experimental error to the analogous bond lengths in the structure of **1**. Because of cyclization, the N(1)—C(Ph) bond length is decreased to 1.45 Å.

A comparative study of electronic absorption spectra of compound **1** (λ_{max} = 314 nm, ε 39200) (see Fig. 1) and 2-methyl-4,6-diphenyl-1-(*p*-tolyl)pyridinium **5** (λ_{max} = 301 nm, ε 39520) demonstrated that these compounds exhibit a long-wave absorption bands, which are similar in position, shape, and intensity, in the region of 300 nm; this band is typical of aryl-substituted Py salts.[1,2] This long-wave band is a superimposition of transitions with an intramolecular charge transfer from the α- and γ-Ph substituents to the heterocycle. A slight bathochromic shift (by 13 nm), which is typical of the band of an intramolecular charge transfer, in the spectrum of **1** compared to the spectrum of **5** can be determined by both a greater electron-withdrawing ability of the pyrimidinium nucleus and a substantial flattening of the α- and γ-Ph substituents and pyrimidinium fragment, which, as discussed above, agrees well with the structural data.

Therefore, as a result of studies performed, we established that the pyrimidinium cation **1** and Py cations **3**, **4**, and **5**, which we have studied previously, have similar structures in the ground electron state, which determines the similarity of their absorption spectra and photoinduced processes. In cations of both types, photocyclization occurs with formation of a nearly planar polycyclic fluorescent photoproduct as a result of excitation of the initial noncoplanar structure. The basic similarity in mechanisms of the initial stage of the photoprocess is determined by the necessity for mutual flattening of the α- and *N*-Ph rings as a result of their rotation about the C—C and C—N bonds when excitation of the nonplanar cation in the S^1 state of the intramolecular charge transfer type occurred. However, unlike the aryl-substituted Py cations **4** and **5**, pyrimidinium cation **1** is substantially less planar (see above), which leads to corresponding differences in the absorption spectra (bathochromic shift of the band of an intramolecular charge transfer), while the efficiency of photocyclization in cation **1** is substantially less than in the case of Py cation **5**. This may be a consequence of characteristic features of the electronic structure of pyrimidinium cations and calls for a more detailed study of the mechanism of photoconversions.

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