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Photochemical properties and structures of *N*-amino and *N*-azomethine derivatives of 2,4,6-triphenylpyridinium perchlorates

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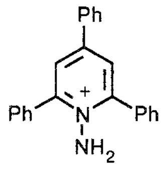
The molecular structures of the initial compounds and the products of photocyclization involving amino and azomethine groups in perchlorates of *N*-amino (**1**) and *N*-azomethine (**2**) derivatives of 2,4,6-triphenylpyridinium cations were studied. Cations **1** and **2** have an essentially non-coplanar arrangement of the α-Ph rings, and the product of photocyclization of **2**, cation **3**, is characterized by a flattened structure. It was found that the orientation of the lone electron pair of the N atom with respect to one of the planes of the α-Ph rings in molecule **1** is more favorable for monocyclization involving the amino group. The structure of molecule **2** allows two routes of the photoreaction, *viz.*, O → N proton transfer and monocyclization with an α-Ph ring. However, the structural features of molecule **2** are more favorable for photocyclization.

Key words: perchlorates of *N*-amino and *N*-azomethine derivatives of 2,4,6-triphenylpyridinium cations; molecular and crystal structure; photocyclization.

Owing to peculiarities of their electronic and molecular structures, aryl substituted pyridinium cations (APC) are convenient objects for the investigation of a wide range of photo processes: fluorescence with an anomalous Stoke's shift (ASS), intramolecular charge transfer, and photochemical reactions.[1,2] These processes are associated with adiabatic structural variations in the excited states, and, therefore, to study their mechanisms, it is important to know the structures of the molecules of the starting APC and the products of the photochemical reactions in the ground electronic state. For example, a study of spectral luminescent processes and the structure of 1,2,4,6-tetraaryl substituted pyridinium (Py) perchlorates made it possible to find out[3] that APC have nonplanar structures, and the barrier-free structural rearrangement from a nonplanar to a flattened conformation occurring in the excited state (through rotation of the aryl rings) results either in the emissive deactivation of the s_1-state with ASS fluorescence or in the cyclization of the 2,6-aryl rings with the *N*-aryl substituent. Fluorescence with ASS is observed for those cations in which rotation of the N-phenyl fragment is hindered due to steric factors or due to the interaction with the anion. If there are none of these restrictions, the whole *N*,α,α-triphenylpyridinium cation is flattened during photoexcitation, and photocyclization of these compounds occurs in competition with luminescence. In the present paper, in order to identify the structural factors that affect the mechanism of photoinitiated processes, we carried out an X-ray structural study of compounds containing novel tetrasubstituted APC, **1** and **2**, which differ from the previously studied *N*-alkyl and *N*-aryl substituted 2,4,6-triphenylpyridinium cations in that the former contain strong electron-donating groups (amino or azomethine) directly attached to the nitrogen atom of the pyridinium ring. The structure of photochemical product **3** was also studied (Scheme 1).



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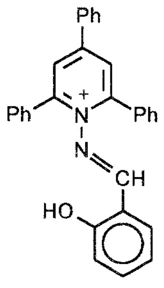

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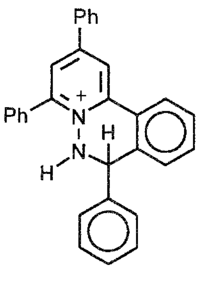

3

Cations **1** and **2** do not fluoresce, and on irradiation, unlike *N*-alkyl-2,4,6-triarylpyridinium salts, which are stable to irradiation, they are converted into polycyclic photochemical products. To the best of our knowledge, photocyclization reactions involving amino- and azomethine groups in ionic systems have been studied for the first time.[4–6]

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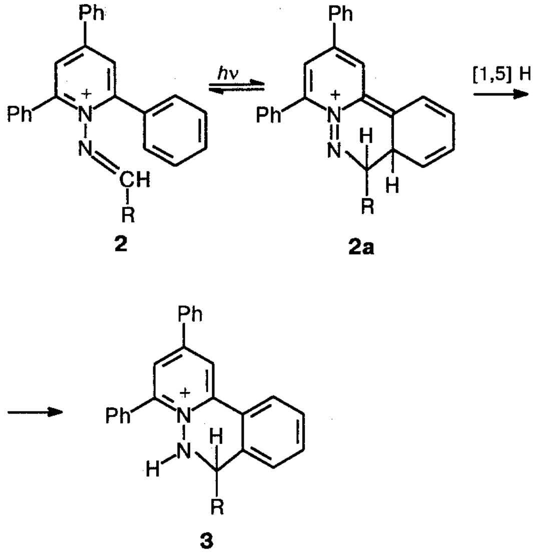
Scheme 1



R = Ph, *o*-C_6H_4OH, Me, *o*-$C_6H_4OCH_3$, *p*-$C_6H_4NO_2$

Photocyclization in *N*-azomethine APC derivatives **2** occurs according to Scheme 1 *via* dihydro intermediate **2a**, which undergoes a 1,5-sigmatropic proton shift to give the more stable photochemical product **3**, which can be isolated on a preparative scale. It should be noted that the choice of the objects for this study was restricted by the necessity of preparing samples suitable for X-ray diffraction analysis. For this reason, we did not carry out an X-ray structural study of the product of the phototransformation of compound **1**.

Crystals of **1** and **2** correspond to orthorhombic symmetry; those of **3** are monoclinic. The main crystallographic data are the following: **1** $C_{24}H_{19}N_2ClO_4$, a = 18.171 (9) Å, b = 14.674 (8) Å, c = 15.641 (8) Å, V = 4170.5 Å^3, Z = 8, d = 1.393 g cm^{-3}, space group *Pbca*; **2** $C_{30}H_{23}N_2OClO_4$, a = 16.322 (8), b = 15.169 (7), c = 21.657 (10) Å, V = 5362.0 Å^3, Z = 8, d = 1.313 g cm^{-3}, space group *Pcca*; **3** $C_{30}H_{23}N_2ClO_4 \cdot$ EtOH, a = 18.264 (8), b = 15.549 (7), c = 9.775 (6) Å, β = 89.45 (3)°, V = 2775.8 Å ^{3}, d = 1.333 g cm^{-3} Z = 4, space group $P2_1/a$. The intensities of 2179 (**1**), 2589 (**2**), and 3057 (**3**) independent reflections with $I > 2\sigma$ (I) were measured on a DAR-UM automatic diffractometer (**1**—**2**) (Cu-Kα radiation) and a RED-4 four-circle automatic diffractometer (**3**) (Cu-Kα radiation); absorption was not taken into account. The structures were solved by the direct method using RENTGEN-75 and SHELXS-86 programs and refined by the full-matrix least-squares method in the anisotropic approximation using the SHELXS-76 program. The presence of a solvating ethanol molecule in the crystal of **3** was shown by X-ray diffraction. The coordinates of the H atoms in the structure of **2** were calculated on the basis of geometric considerations. The H atoms in the structures of **1** and **3** were localized objectively from the Fourier differential syntheses. The final refinement of the coordinates was carried out by the full-matrix least-squares method in the anisotropic approximation for the

Table 1. Coordinates of nonhydrogen atoms (×10^4) and hydrogen atoms (×10^3) in structure **1**

Atom	*x*	*y*	*z*
Cl	1832(0)	926(0)	8485(0)
O(1)	1306(2)	522(2)	8830(2)
O(2)	2344(1)	628(2)	9091(2)
O(3)	2188(1)	1335(2)	7770(2)
O(4)	1462(2)	121(2)	8183(2)
N(1)	2167(1)	3455(1)	9046(1)
N(2)	2859(1)	3137(2)	8536(2)
C(2)	2373(1)	3885(2)	9913(2)
C(3)	1785(1)	3672(2)	10424(2)
C(4)	1081(1)	3833(2)	10097(2)
C(5)	1017(1)	3837(2)	9212(2)
C(6)	1607(1)	3651(2)	8690(2)
C(7)	439(1)	3973(2)	10658(2)
C(8)	519(2)	4321(2)	11477(2)
C(9)	−88(2)	4380(2)	12014(2)
C(10)	−770(2)	4110(2)	11740(2)
C(11)	−858(2)	3783(2)	10923(2)
C(12)	−258(1)	3725(2)	10388(2)
C(13)	3112(1)	3326(2)	10280(2)
C(14)	3171(2)	2729(2)	10965(2)
C(15)	3846(2)	2640(3)	11381(2)
C(16)	4442(2)	3139(3)	11116(2)
C(17)	4381(2)	3728(3)	10442(3)
C(18)	3721(2)	3818(2)	10021(2)
C(19)	1519(1)	3661(2)	7740(2)
C(20)	1962(2)	4195(2)	7231(2)
C(21)	1820(2)	4235(2)	6358(2)
C(22)	1231(2)	3770(3)	6006(2)
C(23)	788(2)	3247(2)	6520(2)
C(24)	932(2)	3195(2)	7391(2)
H(2)	323(3)	292(4)	901(4)
H(2.1)	268(3)	273(4)	814(3)
H(3)	190(2)	366(3)	1100(2)
H(5)	52(2)	399(2)	894(2)
H(8)	103(2)	459(2)	1161(2)
H(9)	3(2)	473(2)	1258(3)
H(10)	−120(2)	417(3)	1215(3)
H(11)	−140(3)	356(3)	1057(3)
H(12)	−32(2)	349(2)	977(2)
H(14)	277(2)	236(2)	1116(2)
H(15)	381(3)	216(3)	1178(3)
H(16)	494(2)	294(2)	1141(2)
H(17)	482(2)	410(3)	1023(3)
H(18)	368(2)	425(2)	954(2)
H(20)	243(2)	447(3)	738(3)
H(21)	218(2)	476(3)	601(3)
H(22)	114(2)	379(3)	531(3)
H(23)	35(2)	286(2)	635(2)
H(24)	59(2)	278(3)	775(2)

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	0(0)	3831(1)	7500(0)	C(13)	2766(4)	3374(4)	7706(3)	H(8)	227(2)	352(3)	740(3)
Cl(2)	2500(0)	0(0)	9246(1)	C(14)	3489(5)	3920(4)	7705(4)	H(9)	351(2)	446(4)	738(4)
O(1)	1752(3)	2866(3)	10295(2)	C(15)	4120(4)	3737(4)	8110(3)	H(10)	466(4)	416(3)	809(3)
O(2)	119(4)	4332(3)	6970(2)	C(16)	4082(3)	3043(4)	8504(3)	H(11)	458(4)	291(4)	882(3)
O(3)	616(5)	3280(6)	7624(3)	C(17)	3379(3)	2505(3)	8517(3)	H(12)	335(3)	196(2)	884(4)
O(4)	2124(3)	647(3)	9619(2)	C(18)	142(2)	1675(3)	9044(2)	H(14)	−54(4)	256(4)	845(3)
O(5)	1913(3)	−421(3)	8874(2)	C(19)	1495(3)	209(3)	6586(2)	H(15)	−169(3)	273(2)	918(3)
N(1)	1559(2)	2637(2)	9093(2)	C(20)	1426(3)	−508(5)	6160(3)	H(16)	−167(3)	192(3)	1018(4)
N(2)	1448(2)	2095(2)	8561(2)	C(21)	1152(4)	−1331(5)	6379(3)	H(17)	−50(3)	95(2)	1044(3)
C(1)	798(2)	1537(3)	8570(2)	C(22)	914(3)	−1448(4)	6981(3)	H(18)	65(2)	78(4)	970(3)
C(2)	738(2)	898(3)	8129(2)	C(23)	1007(3)	−742(3)	7417(2)	H(20)	170(3)	84(2)	644(4)
C(3)	1328(2)	814(3)	7659(2)	C(24)	1337(3)	3419(3)	9045(3)	H(21)	159(2)	−38(4)	569(4)
C(4)	1950(3)	1439(3)	7641(2)	C(25)	1360(4)	3995(4)	9588(3)	H(22)	110(4)	−185(2)	604(3)
C(5)	2026(2)	2063(3)	8103(2)	C(26)	1536(4)	3698(4)	10176(3)	H(23)	73(2)	−208(4)	713(3)
C(6)	2731(2)	2685(3)	8120(2)	C(27)	1460(5)	4268(6)	10707(4)	H(24)	84(3)	−86(2)	788(4)
C(7)	−522(3)	2214(3)	8881(3)	C(28)	1233(7)	5106(7)	10623(5)	H(25)	111(4)	366(3)	861(4)
C(8)	−1176(3)	2290(4)	9300(3)	C(29)	1076(11)	5434(7)	10013(6)	H(28)	157(3)	399(2)	1115(3)
C(9)	−1173(4)	1829(4)	9844(4)	C(30)	1164(7)	4873(5)	9477(4)	H(29)	116(2)	554(2)	1100(4)
C(10)	−518(4)	1306(5)	10013(3)	H(1)	159(2)	251(4)	999(3)	H(30)	89(2)	612(4)	995(4)
C(11)	139(3)	1204(4)	9578(3)	H(3)	23(2)	45(3)	814(4)	H(31)	104(2)	514(2)	905(4)
C(12)	1279(2)	89(3)	7205(2)	H(5)	238(2)	144(3)	726(4)				

nonhydrogen atoms and in the isotropic approximation for the H atoms to $R = 0.056$ (**1**), $R = 0.078$ (**2**), and $R = 0.050$ (**1**). The atomic coordinates in structures of **1**—**3** are given in Tables **1**—**3**.

Results and Discussion

The pyridinium fragment of cation **1** (Fig. 1) is distorted towards a boat conformation: the angles of bending along the C(2)—C(6) and C(3)—C(5) lines are 3.2 and 3.3°, respectively. The α_1,α_2-Ph substituents are non-coplanar with the Py ring and form similar angles of 50.4 and 50.8° with it. In the molecules of the other APC, *viz.*, 1-(2-hydroxyphenyl)-2,4,6-triphenylpyridinium (**4**) and 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium (**5**) perchlorates, these angles vary in the 54—71° range.[9] The angle of rotation of the γ-Ph fragment with respect to the Py ring in **1** (28.3°) does not differ from the corresponding values (27.6 and 29.1°) in structures **4** and **5**, and the lengths of the bridging C(4)—C(7), C(2)—C(13), and C(6)—C(19) bonds, equal to 1.474 (3), 1.479 (3), and 1.495 (3) Å, respectively, are comparable to the average value of 1.479 Å for the similar bridging bonds in structures **4** and **5**. The length of the N(1)—N(2) bond [1.418 (4) Å] indicates that the lone electron pair (LEP) of the N(2) atom is conjugated with the π-system of the Py ring where, in turn, the C(2)—C(3) and C(5)—C(6) bonds are shortened to 1.362 (3) and 1.375 (3) Å, respectively, which points to a certain contribution of the quinoid resonance form to the structure of the Py ring. The N(2) atom of the amino group in cation **1** has a pyramidal structure; its deviation from the coordination plane is 0.3 Å. The angle between the coordination plane of the N(2) atom and the plane of the Py ring is 26°.

The N(2)—N(1)—C(6) and N(2)—N(1)—C(2) bond angles are somewhat nonequivalent (117.4 and 120.7°), as are the intramolecular distances: N(2)...C(18) 2.974(3) Å and N(2)...C(20) 3.039 (3) Å. The orientation of the LEP of the N(2) atom (see Fig. 1) allows one to conclude that the interaction between the N(2) LEP and the π-electron system of the α_1-Ph ring is preferable in the excited state.

In the crystal structure of **1**, the ClO_4 anions interact with APC to form a N(2)—H(2)...O(3) hydrogen bond, 2.31 Å; the O(3)N(2) distance is 3.15 Å; the O(3)...H(2)—N(2) angle is 171°.

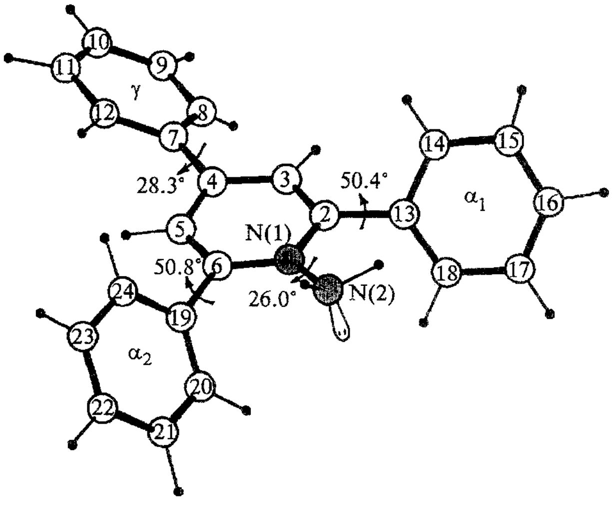


Fig. 1. General view of molecular cation **1**.

Table 3. Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in structure **3**

Atom	*x*	*y*	*z*
Cl	641(1)	7420(1)	8299(2)
O(1)	145(2)	6915(2)	9095(4)
O(2.1*)	111(1)	684(1)	762(2)
O(2.2)	−136(2)	280(3)	1193(5)
O(3)	230(3)	7780(5)	7185(7)
O(4.1)	−108(2)	214(2)	1082(2)
O(4.2)	67(1)	8231(7)	875(5)
O(5)	1227(3)	2208(3)	12052(5)
N(1)	978(2)	3235(2)	8533(4)
N(2)	1495(2)	2722(2)	9255(4)
C(1)	2197(3)	3158(3)	9408(5)
C(2)	506(3)	2808(3)	7692(5)
C(3)	−5(3)	3281(3)	6996(5)
C(4)	55(3)	4172(3)	7088(5)
C(5)	447(3)	4567(3)	7960(5)
C(6)	957(30	4106(3)	8690(5)
C(7)	1479(3)	4500(3)	9640(5)
C(8)	1362(3)	5323(3)	10145(5)
C(9)	1857(3)	5672(3)	11051(6)
C(10)	2461(3)	5214(4)	11461(6)
C(11)	2581(3)	4397(4)	10958(6)
C(12)	2093(33)	4038(3)	10016(5)
C(13)	3228(3)	3703(4)	7877(6)
C(14)	3636(3)	3683(4)	6669(8)
C(15)	3453(4)	3133(5)	5643(7)
C(16)	2879(4)	2579(4)	5809(6)
C(17)	2461(3)	2588(3)	7016(6)
C(18)	2635(3)	3155(3)	8060(5)
C(19)	563(2)	1865(3)	7499(5)
C(20)	485(3)	1279(3)	8449(5)
C(21)	508(3)	410(3)	8285(7)
C(22)	620(3)	113(3)	6981(7)
C(23)	695(3)	987(4)	5935(6)
C(24)	657(3)	1561(3)	6181(6)
C(25)	−601(3)	4661(3)	6331(3)
C(26)	−960(3)	4281(3)	5226(6)
C(27)	−1501(3)	4704(4)	4528(6)
C(28)	−1699(3)	5527(5)	4922(7)
C(29)	−1347(4)	5924(4)	5977(7)
C(30)	−795(3)	5495(3)	6678(6)
C*(31.1)	136(2)	117(2)	1203(4)
C*(31.2)	177(3)	165(4)	1262(2)
C(32)	196(1)	1038(9)	1210(2)
H(1)	249(2)	277(3)	1006(4)
H(2)	127(2)	255(33)	1007(4)
H(3)	−36(2)	295(2)	653(4)
H(5)	47(2)	518(3)	808(4)
H(8)	95(2)	564(3)	993(4)
H(9)	177(2)	622(2)	1134(4)
H(10)	281(2)	549(3)	1213(4)
H(11)	302(2)	406(3)	1122(4)
H(13)	339(2)	411(3)	865(4)
H(14)	407(2)	410(3)	661(4)
H(15)	373(2)	317(3)	485(4)
H(16)	273(2)	215(30	516(4)
H(17)	207(2)	206(3)	723(4)
H(20)	36(2)	149(3)	943(4)
H(21)	46(2)	2(3)	892(4)
H(22)	65(2)	−52(3)	683(4)
H(23)	73(2)	49(3)	504(4)
H(24)	71(2)	197(3)	549(4)
H(26)	−81(2)	371(2)	497(3)
H(27)	−176(2)	442(3)	369(4)
H(28)	−208(2)	580(3)	445(4)
H(29)	−146(2)	652(3)	627(4)
H(30)	−61(2)	576(3)	742(4)
H(31)	223(2)	52(3)	232(4)
H(31.2)	209(2)	152(3)	309(4)
H(31.3)	229(2)	151(3)	156(4)
H(32)	123(2)	58(3)	218(4)
H(32.2)	127(2)	140(3)	130(4)
H(32.3)	122(2)	153(3)	286(4)

* The atoms are disordered with a population of 0.5.

The pyridinium fragment in cation **2** (Fig. 2), like that in **1**, is somewhat distorted towards a boat conformation, the angles of bending along the C(2)—C(6) and C(3)—C(5) lines are equal to 1.8 and 4.3°, respectively. A distinctive feature of the conformation of APC **2** is the magnitudes of the angles between the α_1,α_2-Ph and γ-Ph substituents and the Py plane, which are substantially greater than those in the other cations. At the same time, the lengths of the bridging C(6)—C(7), C(2)—C(13), and C(4)—C(19) bonds, equal to 1.482 (9), 1.486 (8), and 1.492 (9) Å, respectively, are close to each other and coincide with the lengths of similar bonds in cation **1** within the experimental error.

The nearly orthogonal arrangement of the bridging azomethine fragment with respect to the Py ring (81°) is favorable for the conjugation of the LEP of the N(2) atom with the π-system of the Py fragment. On the other hand, this conformation prevents the π—π conjugation between the N(2)=C(25) bond and N(1)—Py fragment, which is manifested as a shortening of this bond to 1.23 Å, while the average N=C bond length in a series of molecules of aromatic azomethines is 1.27 Å. It is known that almost all of the arylimines of salicylic aldehyde are photochromic in solution due to the phototransfer of the proton from the O atom of the OH group in the benzoid form to the N atom along the hydrogen bond to give the quinoid NH form.[8,9] The characteristic features of the molecular structure of **2** do not rule out this route of the photoreaction. In the azomethinesalicyl moiety of cation **2**, as in all of the molecules of salicylideneanilines (SA),[10—23] an intramolecular hydrogen bond is formed; O(1)...N(2) is 2.63 Å, H(1)...N(2) is 1.70 Å, the O(1)—H(1)...N(2) angle is 130°. Unlike those SA in which the angle of rotation of the C ring varies from 49° in the molecule of the unsubstituted SA[10] to 0° in *N*-(chlorosalicylidene)aniline[11] and the role of the *n*-π interaction is small, in the structure of cation **2**, the role of this interaction increases due to the nearly orthogonal arrangement of the bridging azomethine fragment with respect to the Py ring (81°). The conjugation between the LEP of the N(2) atom and the Py fragment results in a decrease in the basicity of the N(2) atom, and this probably favors monocyclization. A certain structural nonequivalence of the reaction fragments of the molecular cation, namely the α_1,α_2-Ph rings and the methine group, in the monocyclization reaction was also found. The angle of rotation of the α_1-Ph ring is 12° greater than the corresponding angle of the α_2-Ph ring, and the C(18)...C(25) and C(8)...C(25) intramolecular distances equal to 3.75 and 3.58 Å, respectively, differ substantially from one another. One can assume that the α_1-Ph ring is preferred for cyclization in the phototransformation of cation **2**.

The Cl atoms in structure **2** occupy two independent crystallographic positions, and the O atoms of both perchlorate groups participate in shortened contacts with the α_2-Ph ring [O(3)...C(18) 3.25 Å, O(3)...H(18)

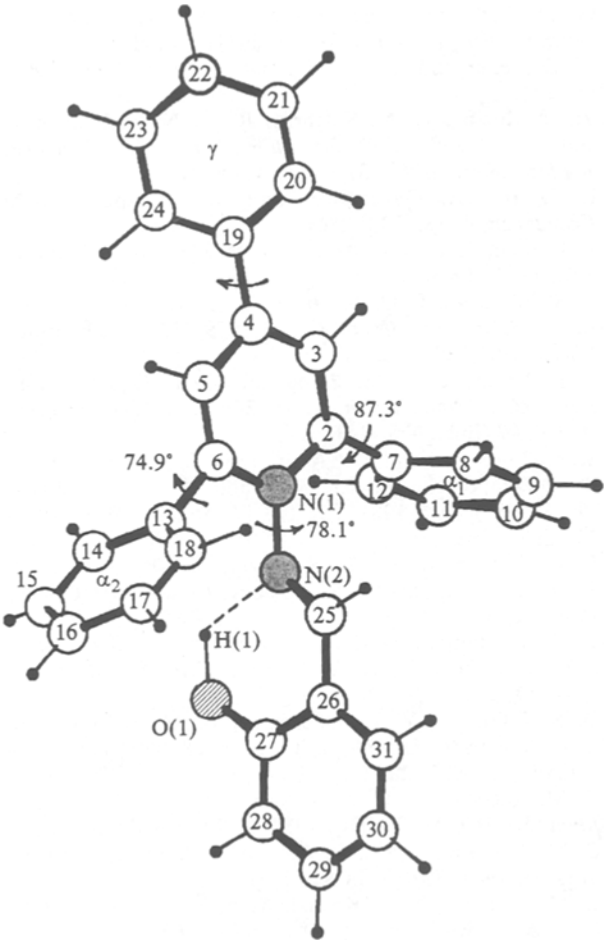


Fig. 2. General view of *N*-molecular cation **2**.

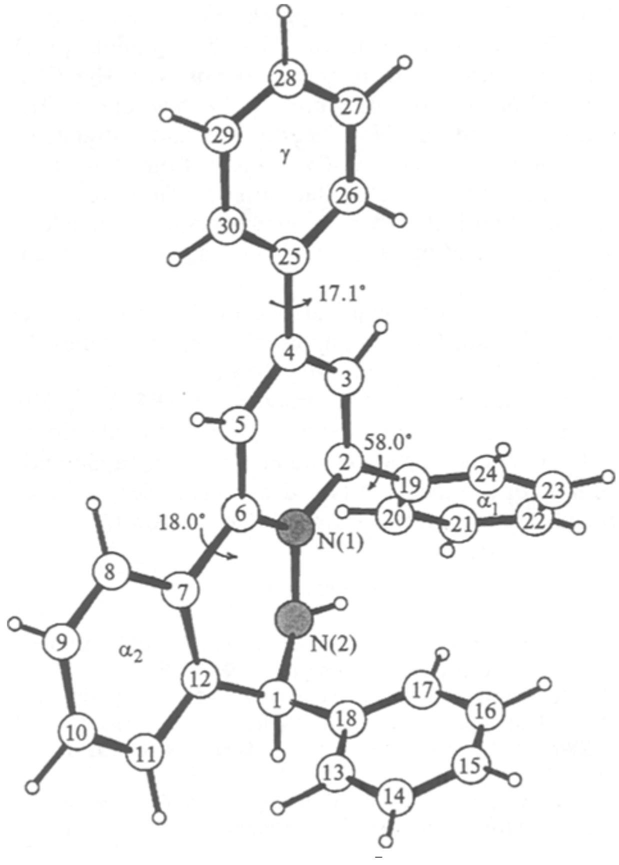


Fig. 3. General view of molecular cation **3**.

2.25 Å, O(4)...C(16) 3.36 Å, O(4)...H(16) 3.32 Å] and with the methylene group [O(5)...C(25) 3.31 Å, O(5)...H(25) 2.48 Å].

The tricyclic central unit in molecular cation **3** (Fig. 3) resulting from photocyclization of a type **2** APC consists of a planar Py fragment, a six-membered diazine heterocyclic ring, and the α_1-Ph ring, which is rotated with respect to the Py ring by only 18.0°. The N(2) atom has pyramidal coordination, its deflection from the plane of the pyramid base is equal to 0.43 Å, and the diazine ring has a "sofa" conformation. The N(1)—N(2) bond length of 1.428(7) Å is comparable to the length of the similar single bond in cation **1**, within the experimental error. The angle of rotation of the coordination plane of the N(2) atom with respect to the Py plane is 36°.

The structure of the crystals of **3** is formed by molecular cations **3**, ClO_4 anions, and ethanol molecules in a 1 : 1 ratio. The O(2) and O(4) atoms of the perchlorate anion and the methylene group of ethanol are disordered over two positions, O(2) and O(2′), O(4) and O(4′), and C(31) and C(31′) with identical populations of ~0.50 for each of them. The planar fragments of the cations in the structure overlap in a centrosymmetrical fashion, *i.e.*, head-to-tail, and thus form stacked packing along the short *c* direction. The perchlorate anions and ethanol molecules connected by hydrogen bonds, O(5)...O(3) 2.76 Å, O(3)...H(5) 1.76 Å, into dimeric associates are located between the cation stacks. This type of hydrogen bond is manifested as a lengthening of the Cl—O(3) distance to 1.442 Å with respect to a Cl—O(1) bond with the other non-disordered O(1) atom in the [ClO_4] tetrahedron equal to 1.424(4) Å. A weaker hydrogen bond is formed between the O(5) atom in ethanol and the N(2)H(2) group (O(5)...N(2) 2.89 Å, O(5)...H(2) 2.01 Å).

Thus, the photochemically active starting APC **1** and **2** possess a substantially non-coplanar arrangement of the α-Ph rings, whereas the products of cyclization, *viz.*, cations **3**, are characterized by a flattened structure. Thus, photoexcitation of **1** and **2**, like that of other APC,[1,3] results in flattening of the α-Ph rings followed by their cyclization with the N-amino (APC **1**) or the *N*-azomethine (APC **2**) substituent. However, one cannot draw the conclusion that this process in APC **1** and **2** is adiabatic, because of the absence of fluorescence with ASS typical of *N*-methyl substituted APC.[1]

The absence of strong hydrogen bonds in the crystals of **1** and **2** is in agreement with the data on the crystal structure of luminescent Py perchlorates containing *o*- and *p*-OH substituents in the N—Ph fragment, which form strong O—H...O hydrogen bonds with the ClO_4 anion and prevent the flattening of the *N*-*o*- and *p*-OH-Ph moieties and photocyclization. *m*-Cl substituents do not prevent the *m*-Cl-PhPy moiety from flattening, however, they obstruct the flattening of one of the α-Ph substituents with the Py ring, which made it possible to arrest the cyclization reaction at the stage of monocyclization.[29]

The structural nonequivalence of the reaction sites found in the starting APC apparently predetermines the most probable route of photocyclization.

The peculiarities of the structure of APC **2** are also unfavorable for intramolecular photoinitiated proton transfer in the salicylidene moiety, and this apparently accounts for the fact that type **2** cations undergo photoinduced photocyclization, rather than proton transfer.

References

1. M. I. Knyazhanskii, Ya. R. Tymyanskii, V. M. Feigelman, and A. R. Katritsky , *Heterocycles*, 1987, **26**, 969.
2. Ya. R. Tymyanskii, V. M. Feigel'man, M. I. Knyazhanskii, E. P. Ivakhnenko, and A. I. Pyshchev, *Dokl. Akad. Nauk SSSR,* 1988, **301**, 1435 [*Dokl. Chem.*, 1988, **301** (Engl. Transl.)].
3. S. M. Aldoshin, Ya. R. Tymyanskii, O. A. D'yachenko, L. O. Atovmyan, M. I. Knyazhanskii, and G. O. Dorofeenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2270 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, No 12 (Engl. Transl.)].
4. V. M. Feigel'man, Ya. R. Tymyanskii, N. I. Makarova, M. I. Knyazhanskii, M. P. Zhdanova, and E. A. Zvezdina, *Khim. Geterotsikl. Soedin.*, 1988, **3**, 424 [*Chem. Heterocycl. Compd.*, 1988, **3** (Engl. Transl.)].
5. V. M. Feigelman, Y. R. Tymyanskii, N. I. Makarova, M. I. Knyazhanskii, S. I. Druzhinin, and J. I. Uzhinov, *Phys. Org. Chem.*, 1990, 200.
6. Y. R. Tymyanskii, V. M. Feigelman, N. I. Makarova, M. I. Knyazhanskii, V. A. Kharlanov, V. S. Orekhovskii, M. P. Zhdanova, and E. A. Zvezdina, *J. Photochem. Photobiolog.*, A; Chemistry, 1990, **4**, 91.
7. G. M. Sheldrick, *Shelx-76. Program for Crystal Structure Determination*, University of Cambridge, England, 1976.
8. M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, 1962, **66**, 2442.
9. Yu. I. Kozlov, D. N. Shigorin, R. N. Nurmukhametov, and V. A. Puchkov, *Zh. Fiz. Khim.*, 1963, **37**, 2432 [*Russ. J. Phys. Chem.*, 1963, **37** (Engl. Transl.)].
10. P. Destro, A. Gavezzotti, and M. Simonetta, *Acta Crystallogr.*, 1978, **B34**, 2867.
11. J. Bregman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2068.
12. O. S. Filipenko, L. O. Atovmyan, B. L. Tarnopol'skii, and Z. Sh. Safina *Zh. Strukt. Khim.*, 1979, **20**, 80 [*J. Struct. Chem.*, 1979, **20** (Engl. Transl.)].
13. V. I. Ponomarev, O. S. Filipenko, and L. O. Atovmyan, *Dokl. Akad. Nauk SSSR,* 1979, **246**, 321 [*Dokl. Chem.*, 1979, **246** (Engl. Transl.)].
14. S. V. Lindeman, V. G. Andrianov, S. G. Kravcheni, V. P. Potapov, K. A. Potekhin, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1981, **22**, 123 [*J. Struct. Chem.*, 1981, **22** (Engl. Transl.)].
15. S. V. Lindeman, V. E. Shklover, Y. T. Struchkov, S. G. Kravcheni, and V. M. Potapov, *Cryst. Struct. Comm.*, 1982, **11**, 43.
16. S. V. Lindeman, V. E. Shklover, Y. T. Struchkov, S. G. Kravcheni, and V. M. Potapov, *Cryst. Struct. Comm.*, 1982, **11**, 149.
17. O. S. Filipenko, V. I. Ponomarev, B. M. Bolotin, and L. O. Atovmyan, *Kristallografiya,* 1983, **28**, 889 [*Sov. Phys.-Crystallogr.*, 1983, **28** (Engl. Transl.)].
18. C. M. Aldoshin, L. O. Atovmyan, and V. I. Ponomarev, *Khim. Fiz.* [*Chem. Physics*], 1984, **3**, 787 (in Russian).
19. C. M. Aldoshin, and L. O. Atovmyan, *Khim. Fiz.* [*Chem. Physics*], 1984, **3**, 915 (in Russian).
20. C. M. Aldoshin, M. I. Knyazhanskii, Ya. R. Tymyanskii, L. O. Atovmyan, and O. A. D'yachenko, *Khim. Fiz.* [*Chem. Physics*], 1982, **1**, 1015 (in Russian).
21. M. I. Knyazhanskii, L. M. Sitkina, C. M. Aldoshin, A. E. Lyubarskaya, A. D. Dubonosov, O. A. Kozina, and L. O. Atovmyan, *Khim. Fiz.* [*Chem. Physics*], 1987, **6**, 1199 (in Russian).
22. M. I. Knyazhanskii, C. M. Aldoshin, A. V. Metelitsa, A. Ya. Bushkov, O. S. Filipenko, and L. O. Atovmyan, *Khim. Fiz.* [*Chem. Physics*], 1991, **10**, 964 (in Russian).
23. C. M. Aldoshin, D. Sci. Chem. Thesis, Moscow, 1985, 342 pp (in Russian).

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