(dec., from acetic acid), was 4.5 g (61.5%). Found: C 63.2; H 4.6; N 12.7; S 9.9%. $C_{17}H_{15}N_3SO_2$. Calculated: C 62.8; H 4.6; N 12.9; S 9.9%.

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BASICITIES AND TRANSFORMATIONS OF PYRYLIUM AND PYRIDINIUM SALTS CONTAINING p-AMINOPHENYL SUBSTITUENTS

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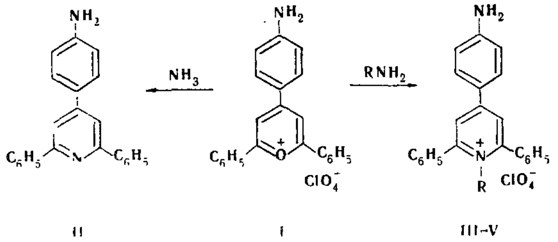
On the basis of the measured basicity constants of pyrylium and pyridinium salts containing p-aminophenyl substituents it is shown that the positive charge in the pyrylium cation is considerably higher than in the pyridinium cation. The σ constants of the pyrylium and pyridinium substituents, which show that the magnitude of the electronic effect of the pyrylium ring is considerably higher than that of the pyrydinium ring, were calculated. The reaction of the indicated pyrylium salts with some electrophilic and nucleophilic reagents was examined.

Pyrylium salts containing a p-aminophenyl group are interesting subjects for investigation because of the presence of two reactive centers (the amino group and the carbon atom in the α position of the pyrylium ring). The literature does not contain data on p-aminophenylpyrydinium perchlorates. We obtained 2,6-diphenyl-4-(p-aminophenyl)pyridine (II) and its N-substituted perchlorates (IV and V) from 2,6-diphenyl-4-(p-aminophenyl)pyrylium perchlorate (I) [1]:



II I III-V

III R = H; IV R = CH_3; V R = C_6H_5

The basicity constants in absolute acetonitrile were measured for these compounds and for 2,6-diphenyl-4-(p-aminophenyl)pyridinium (III) and 4-(p-aminophenyl)flavylium (VI) [2] perchlorates and 2,4,6-triphenylpyridine (VII) (see Table 1). It is apparent from a comparison of the pK_a values of VII and II that the amino group, as an electron-donor substituent, raises the basicity of 2,4,6-triphenylpyridine by 1.34 pK_a units; as one should have expected, the N-methyl substituent in pyridinium salt IV is a weak electron donor, and the N-phenyl residue in salt V displays weak acceptor properties.

These data also show that the positive charge in pyrylium cation I is considerably higher than in the corresponding pyridinium ion III, since the basicity of the NH_2 group in salt I is reduced by two orders of magnitude. If one of the two phenyl substituents is condensed with the pyrylium ring (salt VI), it partially compensates the charge of the latter, and this raises the basicity of the amino group by a whole order of magnitude.

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TABLE 1. Ionization Constants of the Amines and σ Values of the Pyrylium and Pyridinium Rings

Compound	pK_a (25 ± 0.1°C) in acetonitrile	σ
I	4,95	1,17
VI	5,84	0,98
VII	10,20	—
II	11,54(7,13)	—
III	7,13	0,72
IV	7,20	0,70
V	7,01	0,74

TABLE 2. Characteristics of the Compounds Obtained

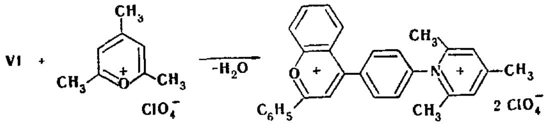
Compound	mp, °C (crystallization solvent)	Empirical formula	Found, %				Calculated, %				IR spectra, ν, cm⁻¹	Yield, %
			C	H	Cl	N	C	H	Cl	N		
Ia	298* (nitromethane)	$C_{25}H_{20}ClNO_6$	64,2	4,3	7,7	3,1	64,5	4,3	7,6	3,0	3340, 1710, 1632, 1585, 1630, 1585, 1100	96,5
Ib	>350 (ethanol)	$C_{30}H_{22}ClNO_5$	70,9	4,6	6,9	2,7	70,5	4,3	7,1	2,7		76
II	182—183 (butanol)	$C_{23}H_{18}N_2$	85,5	6,0	—	8,5	85,7	5,6	—	8,7	—	69
III	155 (butanol with ether)	$C_{23}H_{19}ClN_2O_4 \cdot H_2O$	62,2	5,3	8,1	6,0	62,7	4,8	8,0	6,4	3510, 3420, 1625, 1595,	71
IV	216—217 (ethanol with ether)	$C_{24}H_{23}ClN_2O_5 \cdot H_2O$	63,8	5,3	7,9	5,8	63,4	5,1	7,8	6,1	3480, 3390, 3250, 1620, 1590, 1100	95
IVa	187 (ethanol with ether)	$C_{26}H_{23}ClN_2O_5 \cdot H_2O$	63,1	5,3	7,5	5,4	62,8	5,1	7,1	5,6	3366, 1708, 1620, 1590, 1100	96
IVb	185—186 (ethanol)	$C_{23}H_{27}Cl_2N_2O_8$	59,8	4,7	10,7	4,4	60,2	4,4	11,1	4,5	—	79
V	326 (dec., ethanol)	$C_{29}H_{23}ClN_2O_4$	69,9	4,9	7,1	5,2	69,8	4,7	7,1	5,6	—	96
VIa	155 (three reprecipitations from glacial acetic acid by the addition of ether)	$C_{23}H_{18}ClNO_6$	62,4	4,4	7,6	3,2	62,8	4,1	8,1	3,2	3330, 1710, 1624, 1590, 1100	91
VIb	198—199 (butanol)	$C_{28}H_{20}ClNO_5$	69,0	4,5	7,7	3,2	69,2	4,2	7,3	2,9	—	71
VIII	169—170 (glacial acetic acid with ether)	$C_{29}H_{25}Cl_2NO_9$	58,2	4,7	11,2	2,1	57,8	4,2	11,8	2,3	—	70
IX	249 (acetone—alcohol)	$C_{23}H_{19}N_3$	82,2	5,9	—	—	81,9	5,7	—	—	3460, 3250, 3180, 1622, 1595, 1520, 1353, 1340, 1308, 1240, 777, 700†	100
IXa	131—132 (benzene with petroleum ether)	$C_{25}H_{21}N_3O \cdot 1/2H_2O$	77,2	5,8	—	—	77,3	5,7	—	—	—	87

*According to the data in [1], this compound had mp 220-225°.

† Compare with the IR spectrum of 3,5,7-triphenyl-4H-1,2-diazepine [5].

The calculated σ constants show the magnitude of the electron effect of the pyrylium and pyridinium rings as substituents in the para position of aniline. The calculations were made by means of the Hammett correlation equation for a series of substituted anilinium ions in acetonitrile [3] ($\log K = -10.59 + 4.838\sigma$). It is apparent from the data obtained that the magnitude of the electronic effect of the pyrylium ring is considerably higher than that of the pyridinium ring.

Pyrylium salts I and VI readily give acetyl derivatives at the amino group of Ia and VIa and react with benzaldehyde to give azomethines Ib and VIb. Perchlorate I does not react with p-nitrobenzaldehyde and dimethylformamide (DMF); in view of the reduced basicity of the amino group, it also does not react with 2,4,6-trimethylpyrylium perchlorate, whereas salt VI, the pK_a value of which lies above five units (the boundary of the basicity at which the amino group still reacts with pyrylium salts [4]) forms the corresponding VIII derivative:

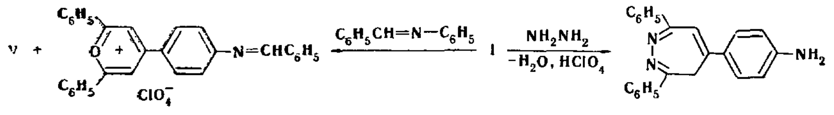


VIII

The amino group in perchlorate I is diazotized in sulfuric acid, and the diazo group is exchanged by a hydroxyl group.

Perchlorate I, like other pyrylium salts, reacts readily with ammonia to give the corresponding pyridine and with methylamine to give perchlorate IV. Its reaction with aniline proceeds only on refluxing in DMF. The resulting pyridinium perchlorate IV is also readily acylated at the amino group to give acyl derivative IVa, and it can be subjected to reaction with 2,4,6-trimethylpyrylium perchlorate to give 1-methyl-2,6-diphenyl-4-p-(N-collidinia)phenyl/pyridinium dipherchlorate IVb. Salts IV and V do not form Schiff bases with benzaldehyde and p-nitrobenzaldehyde.

Like 2,4,6-triphenylpyrylium perchlorate [5], salt I reacts with hydrazine at the α position to give diazepine IX:



Ib IX

The amino group of the latter is readily acetylated to give IXa. Compounds V and Ib form perchlorate I with benzalaniline. Benzalaniline evidently reacts preferably at the α position of salt I, as in the case of 2,4,6-triphenylpyrylium perchlorate [6], to give perchlorate V. Salt Ib is obtained by attack on the starting salt by the liberated benzaldehyde. As indicated above, perchlorate V does not react with benzaldehyde. If the initial reaction with benzalaniline were directed at the amino group, the liberated aniline would form not only perchlorate V but also 1,2,6-triphenyl-4-(p-benzalaminophenyl)pyridinium perchlorate, which was not isolated from the reaction products.

EXPERIMENTAL

The pK_a values in absolute acetonitrile [7] were measured at 25 ± 0.1° by potentiometric titration. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

All of the acetyl derivatives were obtained by refluxing the amines for 1 h in excess acetic anhydride. Reaction products Ia, VIa, IVa, and IXa, data on which are presented in Table 2, were precipitated by the addition of ether to the cooled reaction mixtures.

Reaction of Benzaldehyde with 2,4,6-Trimethylpyrylium Perchlorate. This reaction was carried out by refluxing in absolute DMF for 1 h (the reaction of perchlorate VI was carried out for 3 h). Compounds Ib, IVa, VIb, and VIII were precipitated by the addition of ether to the cooled reaction mixtures; VIII was purified preliminarily with a chromatographic column filled with silicic acid (elution with glacial acetic acid).

Diazotization of Perchlorate I. A saturated solution of 0.21 g (3.0 mmole) of sodium nitrite was added dropwise with stirring to a cooled (to 0-5°) suspension of 1 g (2.5 mmole) of salt I in 10 ml of 50% sulfuric acid, and the excess nitrous acid was removed with urea. The diazo solution was diluted with 100 ml of water, heated slowly to 50-60°, and allowed to stand overnight. The mixture was then filtered to give 0.4 g (40%) of the hydroxy derivative, which was washed with alcohol and reprecipitated from nitromethane by the addition of ether to give a product with mp 309° (dec.) (mp 312° [8]).

2,6-Diphenyl-4-(p-aminophenyl)pyridine (II). Ammonia was bubbled into a cold suspension of salt I in ethanol for 1 h, during which the salt gradually dissolved. The precipitated ammonium perchlorate was removed by filtration, and the filtrate was evaporated partially, diluted with ether, and washed thoroughly with water. The ether layer was separated, dried with potassium carbonate, and evaporated in a nitrogen atmosphere.

1-Methyl-2,6-diphenyl-4-(p-aminophenyl)pyridinium Perchlorate (IV). This compound was similarly obtained in nitromethane. 1,2,6-Triphenyl-4-(p-aminophenyl)pyridinium perchlorate (V) could be obtained only by refluxing in absolute DMF for 1 h. The reaction product was precipitated with ether.

3,7-Diphenyl-5-(p-aminophenyl)-4H-1,2-diazepine (IX). A solution of 0.2 ml (8 mmole) of 80% hydrazine hydrate in 2 ml of ethanol was added dropwise with stirring to a suspension of 0.85 g (2 mmole) of perchlorate I in 10 ml of ethanol, during which the color of the suspension changed to gray-brown. The mixture was allowed to stand at room temperature for 20 min, after which it was heated at 50° for 10 min. The color of the solution became red, and the color of the precipitate became lighter. The mixture was allowed to stand overnight in a refrigerator, after which it was filtered to give 0.67 g of a yellow precipitate of the diazepine.

Reaction of Perchlorate I with Benzalaniline. A solution of 0.21 g (0.5 mmole) of perchlorate I and 0.11 g (0.6 mmole) of benzalaniline in 2 ml of absolute DMF was refluxed for 1 h, after which it was cooled and treated successively with ether and water to give 0.23 g of light-brown crystals, which were washed thoroughly with chloroform to give 0.13 g (51%) of perchlorate V. The chloroform solution was evaporated to give 0.1 g (40%) of perchlorate Ib.

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