5,7-DIMETHYL-3-PHENYLFURAZANO- AND -FUROXANO[5,4-*a*]PYRIMIDINIUM PERCHLORATES: NEW TYPES OF CONDENSED SYSTEMS

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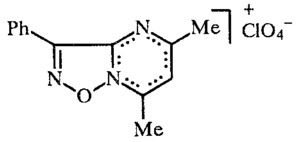
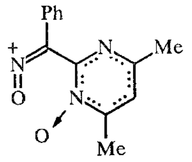
5,7-Dimethyl-3-phenylfuroxano[5,4-a]pyrimidinium perchlorate (II) was obtained by the reaction of 4-amino-3-phenylfuroxan with acetylacetone in the presence of $HClO_4$. The structures of II and its furazan analog I were proved by x-ray diffraction analysis, and their ^{13}C NMR spectra were studied. The cations of I and II (which contain a conjugated condensed system with delocalization of the positive charge) and their monocyclic analogs — phenylfurazan, 3-phenylfuroxan, and 4,6-dimethylpyrimidine — were subjected to quantum-chemical calculation by the CNDO/2 method.

A large number of aromatic condensed systems in which a furoxan [1] or furazan (1,2,5-oxadiazole) ring is condensed with another ring along the C—C bond are known. The condensation of a furazan ring along the C—N bond to give 5,7-dimethyl-3-phenylfurazano[2,3-*a*]pyrimidinium perchlorate (I) and its analogs (see the scheme) was first achieved in [2]. In the present research we have obtained for the first time (by the general method of condensation of amino-substituted heterocycles with β-diketones, as in the case of I) a similar furoxan derivative — 5,7-dimethyl-3-phenylfuroxano[5,4-*a*]pyrimidinium perchlorate or 5,7-dimethyl-3-phenyl-1,2,5-oxadiazolo[2,3-*a*]pyrimidinium perchlorate $N_{(2)}$-oxide (II).

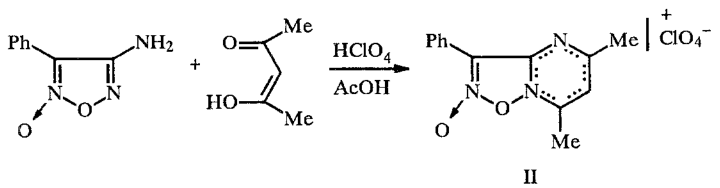
Salt II is a colorless crystalline substance that is stable in air. Analysis of it by x-ray diffraction showed that the cation has a condensed bicyclic structure rather than alternative structure IIa. To ascertain the electron structure of this new type of condensed system we also carried out the x-ray diffraction analysis of I and quantum-chemical calculations of the I and II cations by the CNDO/2 method.



I



IIa



II

The crystal structures of I and II are constructed from discrete cations (Fig. 1) and ClO_4^- anions. In the cations all of the nonhydrogen atoms lie in a single plane, except for the phenyl ring, which is tilted 5.3° with respect to this plane in I and 11° in II. On the whole, the geometries of the furazan and furoxan systems are the normal geometries [1, 3]. The anions

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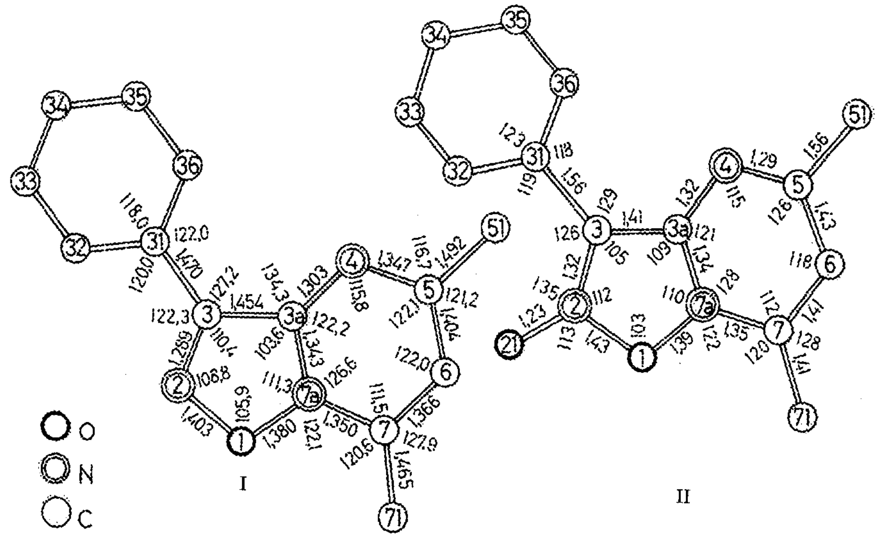

Fig. 1. Bond lengths and bond angles in the I and II cations (σ = 0.008-0.011 Å and 0.5-0.8° in I and 0.03-0.2 Å and 2° in II). The H atoms are not shown.

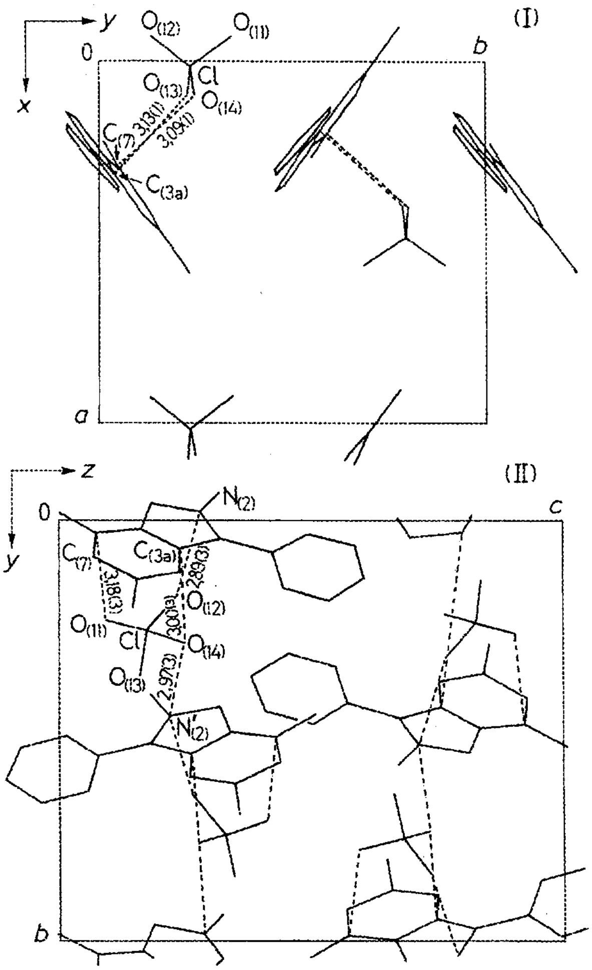

Fig. 2. Packing of the ions in structures I and II [projections on the (001) (I) and (100) (II) planes and short interionic contacts (dash lines)].

have a tetrahedral structure; the Cl—O bond lengths are 1.383(6)-1.417(6) Å in I and 1.29(3)-1.41(2) Å in II, while angles OClO are 107.3(4)-111.0(4)° and 100(2)-119(2)°, respectively.

A similar motif can be distinguished in the crystal packings of I and II: drawn-out (along the y axis) stacks of alternating cations and anions, which in I are connected by glancing-reflection plane b, whereas in II they are connected by helical axis 2_1 (Fig. 2). The planes of the condensed systems of adjacent cations form an acute angle (74° in I and 67° in II) within which the anion is located. The shortest cation—anion contacts (see Fig. 2) within the stacks are somewhat smaller than the sums of the van der Waals radii (O...N 3.07, O...C 3.22 Å [4]).

The charges on the atoms and the Wiberg bond orders calculated within the CNDO/2 approximation are presented in Fig. 3. In I the positive charge of the cation is distributed primarily between the $C_{(3a)}$, $C_{(5)}$, and $C_{(7)}$ atoms. Only the $N_{(4)}$, $O_{(1)}$, and $C_{(6)}$ atoms are negatively "charged" in the bicyclic system; half of the overall charge of these three atoms is concentrated on $N_{(4)}$. In the II cation a negative charge develops on the $C_{(3)}$ atom adjacent to the dipolar N-oxide grouping, which is characteristic for furoxan systems; the charge distribution in the remainder of the cation does not change fundamentally as compared with I.

Let us note that shortened contacts with the anion are formed precisely by those atoms [$C_{(3a)}$ and $C_{(7)}$, and also $N_{(2)}$ in II] that have, according to the calculations, large positive charges; this clearly indicates electrostatic attraction and indirectly confirms the results of calculation of the charge distribution that are presented in the molecular diagrams. The nonparticipation of the $C_{(5)}$ atom, which also has a large positive charge, in these contacts is possibly explained by packing effects.

We carried out the same calculations (see Fig. 3) for phenylfurazan (III), 3-phenylfuroxan (IV), and 4,6-dimethylpyrimidine (V) to ascertain which changes the neutral heterocycles undergo during construction of the bicyclic cations from them. The molecular geometry of IV was taken from [5], while x-ray diffraction data for diphenylfurazan [6] and pyrimidine [7] were used for III and V. Comparison shows that the electron density in the condensed I and II cations is decreased on most of the ring atoms, particularly at the sites of annelation of the rings — on the $C_{(3a)}$ (as compared with III or IV) and $N_{(7a)}$ (the charge of which changes sign) atoms. Though the negative charge on the $C_{(6)}$ atom remains virtually unchanged, it even increases on the $C_{(3)}$ atom (in II as compared with IV). Nevertheless, in its general features, the relative distribution of the electron density between the atoms is retained.

Significant delocalization of the π electrons in the pyrimidine rings and somewhat less delocalization in the five-membered furazan and furoxan rings, in which the bonds are close to single bonds, except for the $N_{(2)}$—$C_{(3)}$ bond, which has an order of 1.78 (I) or 1.40 (II), are observed in the I and II cations. The bond orders in bicyclic systems I and II are decreased by 0.02-0.12 as compared with monocyclic III-V and by 0.23-0.60 at the site of annelation of the $C_{(3a)}$—$N_{(7a)}$ bond. Let us note that the $N_{(4)}$—$C_{(5)}$ and $N_{(7a)}$—$C_{(7)}$ bonds, which are formed in the synthesis of the cations, have the lowest order in the six-membered rings of the cations after this bond. The weakness of these two bonds evidently implies the possibility of decomposition of the compounds to the starting components, i.e., reversibility of the synthesis, which should be realized when electron-acceptor substituents, which withdraw π electrons from these bonds and weaken them to an even greater extent, are introduced.

According to the quantum-chemical calculations, for the I cation $E_{HOMO} = -0.6128$ eV and $E_{LVMO} = 0.0590$ eV, as compared with -0.5431 eV and 0.0502 eV, respectively, for the II cation.

In the ^{13}C NMR spectra of I and II (Table 1) the assignment of the signals was made from their multiplicities (without suppression of the ^{13}C—^1H spin-spin coupling). The $C_{(5)}$ and $C_{(7)}$ signals are doubled quartets because of spin-spin coupling with the methyl protons and $H_{(6)}$; the $^2J_{[C(5)—H(6)]}$ (3.9 Hz) and $^2J_{[C(7)—H(6)]}$ (1.4 Hz) constants differ appreciably.

EXPERIMENTAL

Compound I was obtained by the method in [2]. The PMR spectra of solutions in CF_3COOH were obtained with a Tesla-60 spectrometer with hexamethyldisiloxane (HMDS) as the internal standard, while the ^{13}C NMR spectra of solutions in $CF_3COOH + D_2O$ were obtained with a Bruker AM-300 spectrometer (75.5 MHz) with tetramethylsilane (TMS) as the internal standard.

5,7-Dimethyl-3-phenylfuroxano[5,4-*a*]pyrimidinium Perchlorate (II, $C_{13}H_{12}ClN_3O_6$). A 0.5-ml (5 mmole) sample of acetylacetone was added to a warm (45°C) anhydrous solution of 0.71 g (4 mmole) of 4-amino-3-phenylfuroxan [8] and $HClO_4$. After 3-4 min, a crystalline precipitate began to form, and the entire mixture began to crystallize after another few minutes. It was diluted to two to three times its original volume with ether, and the precipitate was removed by filtration and washed with ether to give a product with mp 154-155°C (from acetic acid). PMR spectrum: 2.43 and 2.57 (3H each, s, 5-

TABLE 1. ^{13}C NMR Spectra of I and II

Atom	Chemical shift, δ, ppm		Atom	Chemical shift, δ, ppm	
	I	II		I	II
$C_{(3)}$	154,46	108,12	$C_{(32)}$, $C_{(36)}$	131,47	131,45
$C_{(3a)}$	146,41	150,16	$C_{(33)}$, $C_{(35)}$	130,26	129,22
$C_{(5)}$	152,44	151,24	$C_{(34)}$	136,00	135,10
$C_{(6)}$	123,26	122,34	$C_{(51)}$	26,11	25,86
$C_{(7)}$	180,37	177,14	$C_{(71)}$	16,51	16,62

TABLE 2. Coordinates of the Atoms in Structures I and II

Atom	I ($\times 10^4$)			II ($\times 10^3$, Cl$\times 10^4$)		
	x	*y*	*z*	*x*	*y*	*z*
			Cation			
$O_{(1)}$	1586(5)	-744(5)	962(2)	417(1)	-37(1)	185(1)
$O_{(21)}$	—	—	—	294(2)	-63(1)	318(1)
$N_{(2)}$	1444(7)	-872(6)	1461(2)	400(2)	-17(2)	285(1)
$N_{(4)}$	4260(6)	1106(5)	1339(2)	710(2)	129(1)	241(1)
$N_{(7a)}$	2670(5)	36(5)	894(2)	539(2)	23(1)	163(1)
$C_{(3)}$	2379(8)	-242(6)	1669(2)	503(2)	46(2)	321(1)
$C_{(3a)}$	3217(7)	377(6)	1315(2)	592(2)	70(1)	243(1)
$C_{(5)}$	4751(6)	1504(6)	915(3)	765(2)	143(2)	157(2)
$C_{(6)}$	4167(8)	1163(7)	476(2)	714(2)	95(2)	70(1)
$C_{(7)}$	3075(7)	394(7)	453(2)	587(2)	33(2)	73(2)
$C_{(31)}$	2512(9)	-187(7)	2194(2)	519(2)	82(2)	429(2)
$C_{(32)}$	1718(13)	-883(11)	2471(4)	431(3)	33(2)	497(2)
$C_{(33)}$	1808(15)	-852(13)	2959(4)	448(3)	60(3)	586(2)
$C_{(34)}$	2670(13)	-143(10)	3180(3)	547(3)	137(3)	613(2)
$C_{(35)}$	3477(13)	574(12)	2917(3)	631(3)	191(2)	540(2)
$C_{(36)}$	3404(12)	546(11)	2407(3)	614(3)	159(2)	451(2)
$C_{(51)}$	5963(7)	2318(8)	933(3)	903(2)	214(2)	150(2)
$C_{(71)}$	2376(9)	-50(9)	24(3)	516(2)	-19(2)	-4(2)
			Anion			
Cl	97(2)	2413(2)	838(1)	3079(7)	2637(6)	1761(6)
$O_{(11)}$	-712(6)	3497(5)	852(2)	366(5)	236(4)	92(2)
$O_{(12)}$	-677(7)	1338(6)	827(3)	239(2)	182(2)	227(2)
$O_{(13)}$	950(6)	2392(7)	1244(2)	229(2)	366(1)	162(1)
$O_{(14)}$	917(6)	2469(7)	429(2)	413(3)	281(2)	232(3)

and 7-CH_3), 7.45 [4H, m, $H_{(6)}$ and C_6H_5 meta and para protons], 8.10 ppm (2H, m, C_6H_5 ortho protons). The yield was 1.21 g (89%).

X-ray Diffraction Analysis. Single crystals of I and II were obtained by slowly cooling saturated (at 90°C) solutions in CH_3COOH until crystallization began (I at 80°C and II at 67-68°C), after which the solutions were maintained at these temperatures (5 h for I and 4 h for II); the crystals were washed with warm CH_3COOH and air dried. The diffraction experiments were carried out with Syntex $P2_1$ (I) and Hilger—Watts (II) four-circle diffractometers (Mo K_α emission, $\theta/2\theta$ scanning, $2\theta \leq 55°$ and 44°, 2341 and 1138 independent reflections, of which 1371 and 657 with $I \geq 2\sigma$ were used), while the calculations were made with an Eclipse S/200 computer by means of INEXTL programs [9]. The I and II crystals were rhombic and had the following parameters: I: a = 10.001 (2), b = 10.660(2), c = 27.873(5) Å, V = 2972(1) Å^3, Z = 8, d_{calc} = 1.452 g/cm^3, space group Pbca; II: a = 9.547(1), b = 11.638(1), c = 13.946(2) Å, V = 1549.6(3) Å^3, Z = 4,

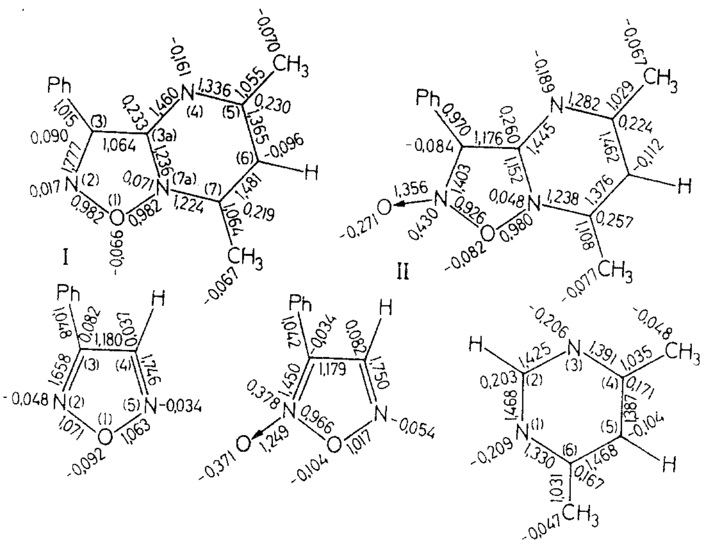

Fig. 3. Charges on the atoms and Wiberg bond orders in the I and II cations and in the III, IV, and V molecules.

d_{calc} = 1.465 g/cm^3, space group $P2_12_12_1$. The structures were decoded by the direct method and were refined by the method of least squares (I within the anisotropic approximation, II within the anisotropic approximation for the ClO_4 anion and within the isotropic approximation for the remaining atoms) taking into account the H atoms fixed in the calculated positions up to R = 0.068 and R_W = 0.063 (I) and R = 0.097 and R_W = 0.093 (II). The coordinates of the atoms are presented in Table 2.

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