2-(1-ISONICOTINOYLHYDRAZINOALKYLIDENE)-5,5-DIMETHYL-1,3-CYCLOHEXANEDIONES AND THEIR POLYCHROMISM. A NEW TYPE OF COMPOUND WITH INTRAMOLECULAR CHARGE TRANSFER THROUGH THE HYDRAZONOCARBONYL BRIDGE

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The product of condensation of 2-formyldimedone with the hydrazide of isonicotinic acid, namely 2-isonicotinoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione, has been obtained in three forms — red, colorless, and yellow — which with methyl iodide give one and the same iodide 2-[N-(1-methyl-4-pyridiniumcarbonyl)hydrazinomethylene]-5,5-dimethyl-1,3-cyclohexanedione. On the basis of UV spectra and x-ray structure analysis of this betaine and also the dark-red iodide of N-(4-diethylaminobenzal)-N'-(1-methyl-4-pyridiniumcarbonyl)hydrazine, it has been shown that intramolecular charge transfer in these linear molecules proceeds along the system of bonds D:—RC═N—NH—CO—A through the hydrazonocarbonyl bridge, which does not interrupt the conjugation chain. The existence of colored forms of the 2-isonicotinoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione can be explained by an admixture of the betaine form.

2-Isonicotinoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione (III) had been obtained previously [1] by reaction of 2-formyldimedone (Ia) with the hydrazide of isonicotinic acid (II). Here we are reporting on a more detailed study of this compound, which we have obtained in three forms. The experiment described in [1] — refluxing equimolar quantities of Ia and II in ethanol — yields a condensation product with a reddish orange color, which, upon heating in the 100-140°C interval, is converted to a colorless form with a melting point of 208-210°C, as indicated in [1].(See top of next page).

The colorless form of III is also obtained in the interaction of I with II in chloroform. Upon standing in air, the colorless form is converted to a red form. Both the red and colorless forms of compound III, upon refluxing in benzene with catalytic quantities of p-toluenesulfonic acid, are converted to a yellow form with a melting point of 192-194°C. These actions were undertaken in an attempt to cyclize III to the hypothetical 1-isonicotinoyl-5,5-dimethyl-4-oxo-4,5,6,7-tetrahydroindazole — a reaction that did not take place. Crystallization from ethanol converts both the colorless and the yellow forms of III to the red form.

None of the forms contains any nonconstitutional inclusions that could be responsible for distinctive coloration, as evidenced by their identical mass spectrometric characteristics.

PMR, IR, and UV spectra and chemical properties indicate that the three forms are one and the same compound. The PMR spectra of all three forms, taken in $CDCl_3$ solution (Table 1), are characterized by identical chemical shifts of the protons of $-CH_3$, $-CH_2-$, and $=CH-$ groups; and the spectra differ only very slightly in the signals of the NH-group protons, the shifts of which are close to those in 2-benzoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione (see Experimental section).

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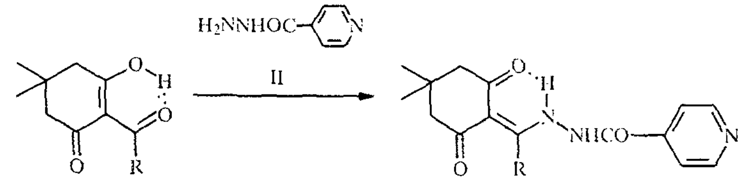
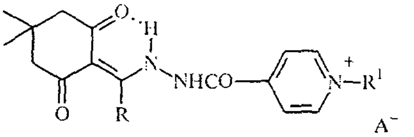
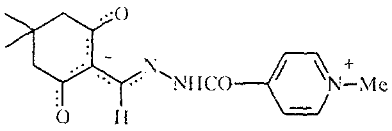


Ia, b

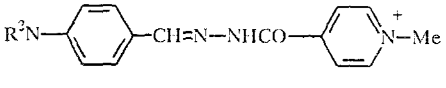
III, IV



V-VII



VIII



IX, X

Ia, III, V, VI) R=H; Ib, IV, VII, IX) R=Me; V) R^1 = H, A = Cl, VI, VII)·R^1 = Me, A = I, X) R^3 =Et.

From 2-acetyldimedone (Ib) and the hydrazide of isonicotinic acid in ethanol, we obtained 2-(1-isonicotinoylhydrazinoethylidene)-5,5-dimethyl-1,3-cyclohexanedione (IV) with an orange color, mp 159-161°C. Procedures analogous to those described above for the hydrazinomethylene derivative III (heating, performing the reaction in chloroform, or performing the reaction in benzene with p-toluenesulfonic acid) all gave colorless products that are characterized by the same melting point. The PMR spectra of all of the samples in $CDCl_3$ are essentially identical, and high magnetic equivalence of the $C_{(4)}$ and $C_{(6)}$ methylene groups is characteristic; the signal of the chelatized proton is shifted downfield. This is consistent with the known characteristics of PMR spectra of enamines and enhydrazines of 2-formyl- and 2-acetyldimedones [2, 3]. The PMR spectrum of 2-(1-benzoylhydrazinoethylidene)-5,5-dimethyl-1,3-cyclohexanedione (see Experimental section) is also characterized by the above-mentioned differences in comparison with the 2-benzoylhydrazinomethylene derivatives of dimedone. The IR spectra of compounds III and IV, taken on suspensions of the substances in white mineral oil or hexachlorobutadiene (see Experimental section for all IR spectra), do not provide any decisive information on the structures of the different forms. Slight differences are observed in the IR spectra of the yellow and colorless forms of III (practically identical) on the one hand, and the red form on the other hand. For the red form of III, above 3100 cm^{-1}, we observe two absorption maxima at 3260 and 3210 cm^{-1}, but the other two forms (yellow and colorless) have maxima at 3230 and 3180 cm^{-1}. Slight differences are also observed in the 1500-1800 cm^{-1} region. The highest-frequency maxima for the red form of III are observed at 1670 and 1635 cm^{-1}, and for the colorless and yellow forms at 1678-1680 and 1645-1650 cm^{-1}. The IR spectra of the orange and colorless forms of compound IV also differ only very slightly, and are similar in character to the IR spectra of enhydrazines of acetyldimedone that had been investigated previously [2].

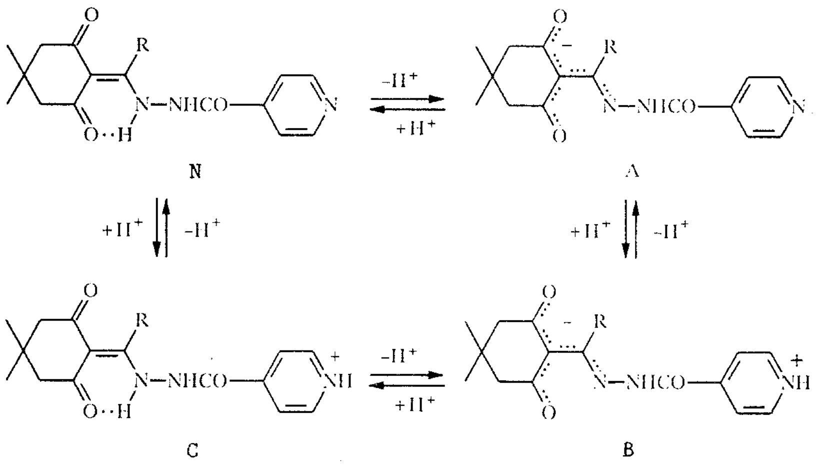
Upon passage of dry hydrogen chloride through solutions of the different forms of III in chloroform, the same bright-yellow hydrochloride V was obtained in all cases. In the PMR spectrum of the salt V, the proton shifts of the pyridine ring protons are different from those for III. This fact, and also the presence of an IR absorption band centered at 2600 cm^{-1}, due to stretching vibrations of $\equiv N^+-H$ bonds, indicate that the nitrogen atom of the pyridine ring has been protonated.

In order to determine the sources of polychromism of compounds III and IV and to confirm the hypothesis of possible formation of an internal salt form, i.e., betaines of III and IVB, fixed betaines were synthesized — the N-methylated compound VIII, and also dialkylaminobenzal derivatives of nicotinoylhydrazine: iodides of N-(4-dialkylaminobenzal)-N′-1-methyl-4-pyridiniumcarbonyl)hydrazines (IX, X).(See middle of next page.)

Methylation of compounds III and IV with excess methyl iodide in a metal ampul at 90-95°C gave the iodides VI and VII. In the PMR spectra, the chemical shifts of the protons of the N-methylated pyridine fragment are close to those for the salt V and are considerably different from those for III and IV; the signals of the protons of the methyl group $\equiv N^+-CH_3$ are

TABLE 1. PMR Spectra of Compounds III-VIII

Compound	$C(CH_3)_2$ (6H, s)	CH_2 CH_2 (2H, s)(2H, s)	CH_3 (3H, s)	$N-CH_3$ (3H, s)	C-H, pyridene =CH-	N-H (1 H) (1H)
III red	1,10	2,37; 2,47			7,87 (2H,d); 8,80 (3H)	12,17; 13,30
III colorless	1,10	2,37; 2,47			7,83 (2H,d); 8,77 (3H)	12,10; 13,76
III yellow	1,10	2,40; 2,47			7,83 (2H,d); 8,80 (3H)	11,90; 13,70
IV orange	1,03	2,33 (4H, bs)	2,57		7,76 (2Hd); 8,76 (2H, d)	11,20; 14,80
IV colorless	1,05	2,40 (4H, bs)	2,57		7,77 (2H,d); 8,77 (2H, d)	11,17; 14,83
V	1,07	2,33; 2,50			8,10 (1H) 8,33 (2H); 8,83 (2H)	11,2...11,9 (2H); 13,63
VI	1,00	2,33; 2,47		4,43	8,23 (1H); 8,47 (2H); 9,23 (2H)	11,5...13,0 (2H)
VII	1,07	2,40 (4H, bs)	2,63	4,57	8,50 (2H,d); 9,33 (2H, d)	11,5...12,5 (2H)
VIII	1,03	2,33(4H, bs)		4,27	8,10 (1H); 8,33 (2H,d); 8,83 (2H, d)	7,13



observed at δ 4.43-4.50 ppm. Upon treatment of an ethanol solution of the iodide VI with triethylamine, the dark-red betaine VIII was precipitated. Compounds IX and X were synthesized by the action of hydrazine on the iodomethylate of methyl isonicotinate, followed by treatment of the resulting hydrazide with 4-dialkylaminobenzaldehydes.

The electronic absorption spectra (EAS) of compounds VIII-X were taken in various solvents, and those of compounds III, IV, and VI, VII were also taken at various levels of pH.

The betaine VIII, which is dark-red in the crystalline form, changes color in solution: from yellow-orange in water to red-violet in acetone. In the EAS, an intense maximum is observed in the visible region (Table 2). The same sort of maximum is observed in the EAS of the iodides VI and VII in 50% alcohol at various pH levels (Table 3), indicating considerable acidity of these compounds (only at pH $\leq$ 3 does ionization begin to be suppressed). That is to say, in solutions at pH 3, ionization at the NH bond takes place, and the betaine form exists. Three bands are observed in the EAS, at 220-225, 265-280, and 400-500 nm. The positions of the first two absorption maxima are very little dependent on the nature of the solvent, but the position of the third maximum experiences significant solvatochromic shifts. For the betaine VIII, for example, the long-wave absorption band maximum shifts from 402 nm in water to 474 nm in acetone.

Such solvatochromic shifts of the long-wave absorption maximum are characteristic for compounds with an inner-ion (betaine) structure, having an electron-donor anionic part and an electron-acceptor cationic part, with a well-developed π-electron system. The long-wave absorption appears as a result of charge transfer from the donor part to the acceptor part upon excitation. As an example of such compounds we may cite N-pyridiniumphenolate betaine [4] and betaines of 2-N-pyridinium-

TABLE 2. Solvatochromism of Long-Wave Absorption Maximum in EAS of Compounds VI-VIII and X

Compound	Solvent, λ_{max} ($\varepsilon \times 10^{-3}$)				
	H_2O	50% ethanol	ethanol	CH_3CN	CH_3COCH_3
VI		408 (21,3)	430 (20,4)		
VIII	402 (21,3)		432 (20,5)	462 (15,6)	474 (15,3)
VII		416 (14,3)	436 (17,4)		
X	410 (15,9)		436 (12,1)		486 (10,9)*

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*In $CHCl_3$.

TABLE 3. EAS of Iodides VI and VII at Various pH in 50% Ethanol, and Iodides VI, VII, and X in Ethanol

Compound	Solvent, λ_{max} ($\varepsilon \times 10^{-3}$)				
	50% ethanol at indicated pH				Ethanol
	9,9	5,0	3,0	1,0	
VI	222 (28,4) 270 (14,9) 408 (21,3)	222 (28,0) 270 (14,8) 408 (21,4)	223 (28,1) 268 (14,9) 410 (20,7)		220 (29,3) 268 (15,3) 430 (20,4)
VII	223 (28,9) 268 (13,4) 416 (14,3)	222 (29,0) 267 (13,3) 416 (14,1)	223 (27,7) 267 (13,2) 416 (12,5)	221 (39,2) 255 (20,6) 285...290 (inflection)	220 (31,9) 269 (16,2) 436 (17,4)
X					219 (30,4) 271 (7,5) 341 (22,3) 436 (12,1)

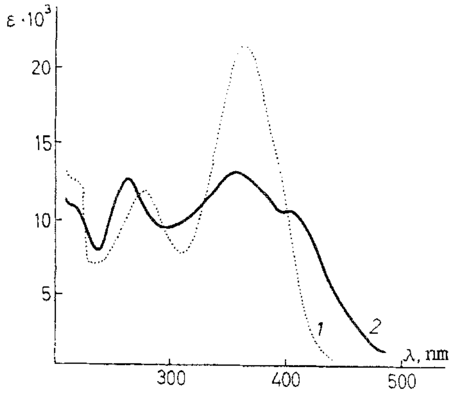

Fig. 1. EAS of compound III in 50% ethanol at pH 5.07 (1) or 2.98 (2).

1,3-diketones [5]. These compounds are characterized by intramolecular charge transfer (ICT), and they manifest distinct negative solvatochromism: With decreasing polarity of the solvent, there is a bathochromic shift of the long-wave absorption maximum. From this it follows that the red color of the betaine VIII and compounds IX and X is related to ICT from the anionic (dialkylaminophenyl) part to the cationic (pyridinium) part. The color of compounds III and IV is also due to transfer of a proton from the N−H bond to the nitrogen atom of the pyridine ring and the formation of the betaine species, the quantitative content of which is highly dependent on various external and structural factors. This is graphically illustrated in the EAS of compounds III and IV at different pH levels (Figs. 1 and 2). At pH ~ 3, i.e., under conditions for addition of a proton to the nitrogen atom of the pyridine fragment and possible ionization of the NH bond (compare the EAS of compounds

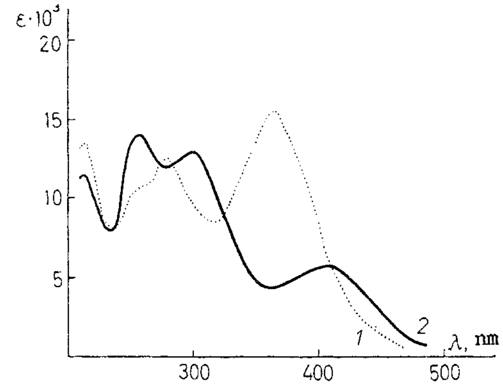

Fig. 2. EAS of compound IV in 50% ethanol at pH 5.1 (1) or 2.93 (2).

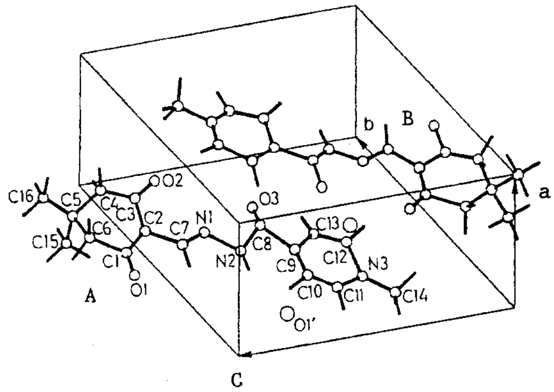

Fig. 3. Perspective view of molecules of betaine VIII in an elementary cell.

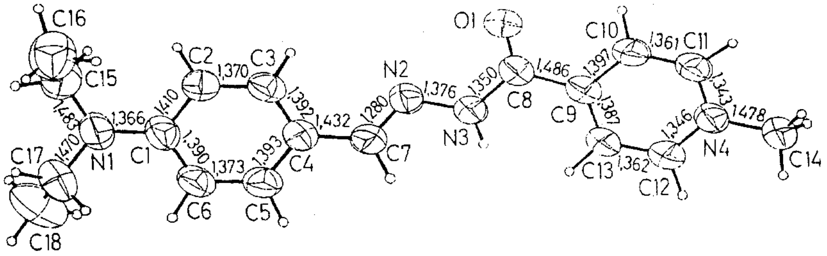

Fig. 4. Steric model of cation X, with bond lengths.

VI and VII at pH 5 and 3, Table 3), a new absorption maximum appears in the 400-410 nm region, determining the manifestation of an orange-red color and related to the formation of the betaine structure. The differences in the EAS of compounds III and IV at pH ~ 2.9-3.0 should apparently be attributed to a slight difference in their NH-acidities; i.e., there are differences in the content of forms of acid—base equilibrium.

The type of ICT depends on the steric structure of these molecules. In one instance, the molecules may be bent in the form of wings, resulting in intramolecular adjacency of the donor and acceptor parts, so that the ICT proceeds as in charge transfer complexes. In this case we may speak of a self-complex [6]. In another instance, the molecules may be stretched out, and the ICT will proceed through a system of conjugated bonds.

In order to resolve the question of the type of ICT, we carried out an x-ray structure analysis of crystals of the betaine VIII and 4-diethylaminobenzalhydrazone X. In Table 4 we have listed the coordinates of the nonhydrogen atoms of the elementary cell of the betaine VIII, and in Table 5 the mean bond lengths for the two molecules. In Fig. 3 we show a perspective view of the molecules in an elementary cell. The coordinates of the atoms of the hydrazone X are listed in Table 6; in Fig. 4 we show a steric model of the cation X with bond lengths, and in Table 7 we have listed the distances from the iodine atom to the nearest atoms.

TABLE 4. Coordinates of Nonhydrogen Atoms in Structure of Betaine VIII

Atom*	Molecule A			Molecule B		
	x	y	z	x	y	z
$C_{(1)}$	2582(23)	4495(64)	11474(14)	7643(29)	3317(10)	619(18)
$C_{(2)}$	3011(25)	5110(73)	10445(19)	7489(25)	2870(16)	1823(14)
$C_{(3)}$	3567(26)	6474(73)	10027(12)	6986(23)	1801(12)	2200(12)
$C_{(4)}$	3522(20)	7223(10)	10826(10)	7015(25)	844(17)	1301(15)
$C_{(5)}$	2399(28)	6933(69)	12003(17)	5987(20)	1789(10)	515(17)
$C_{(6)}$	2801(27)	5450(74)	12260(13)	7785(27)	2566(15)	-151(14)
$O_{(1)}$	2369(24)	3443(67)	11797(16)	7942(20)	4594(13)	301(12)
$O_{(2)}$	3829(25)	7258(71)	9102(11)	6866(26)	1297(17)	3064(14)
$C_{(15)}$	2985(27)	7719(77)	12615(13)	5117(20)	1055(17)	-226(19)
$C_{(16)}$	126(20)	7166(70)	12107(14)	4270(21)	2663(19)	1156(19)
$C_{(7)}$	2781(21)	4283(64)	9573(13)	7925(27)	3786(12)	2418(16)
$N_{(1)}$	2946(26)	4568(70)	8618(17)	7649(22)	3586(11)	3446(19)
$N_{(2)}$	2837(27)	3397(66)	7970(16)	7939(25)	4303(18)	4257(17)
$C_{(8)}$	3153(24)	4292(72)	6756(18)	7899(22)	3897(17)	5060(16)
$O_{(3)}$	3139(21)	5276(66)	6464(13)	7510(27)	2739(11)	5413(11)
$C_{(9)}$	2790(20)	3033(15)	6218(18)	8107(22)	4767(11)	5971(11)
$C_{(10)}$	2388(23)	1891(11)	6427(13)	8571(21)	6051(16)	5618(14)
$C_{(11)}$	2237(27)	1106(17)	5785(17)	8525(22)	6777(11)	6456(19)
$N_{(3)}$	2443(26)	1376(19)	4741(16)	8552(27)	6342(18)	7347(16)
$C_{(12)}$	2771(22)	2937(15)	4398(12)	8330(27)	5270(18)	7720(15)
$C_{(13)}$	2694(20)	3697(16)	5156(11)	7895(25)	4412(17)	6979(16)
$C_{(14)}$	1869(22)	579(19)	4006(17)	8895(20)	7216(19)	8063(18)
$O_{(1')}$	2603(24)	503(19)	8443(16)	7702(22)	411(18)	6780(18)

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*For numbering of atoms, see Fig. 3.

TABLE 5. Mean Values of Bond Lengths (Å) in Structure of Betaine VIII

Bond	Bond length	Bond	Bond length	Bond	Bond length
$C_{(2)}—C_{(1)}$	1,445	$C_{(5)}—C_{(4)}$	1.537	$O_{(3)}—C_{(8)}$	1.166
$C_{(6)}—C_{(1)}$	1,427	$C_{(6)}—C_{(5)}$	1.554	$C_{(10)}—C_{(9)}$	1,325
$O_{(1)}—C_{(1)}$	1,258	$C_{(15)}—C_{(5)}$	1,445	$C_{(13)}—C_{(9)}$	1.363
$C_{(3)}—C_{(2)}$	1,365	$C_{(16)}—C_{(5)}$	1,525	$C_{(11)}—C_{(10)}$	1,318
$C_{(7)}—C_{(2)}$	1,463	$N_{(1)}—C_{(7)}$	1,233	$N_{(3)}—C_{(11)}$	1,242
$C_{(4)}—C_{(3)}$	1,481	$N_{(2)}—N_{(1)}$	1,496	$C_{(14)}—N_{(3)}$	1,441
$O_{(2)}—C_{(3)}$	1.232	$C_{(8)}—N_{(2)}$	1,369	$C_{(13)}—C_{(12)}$	1,397

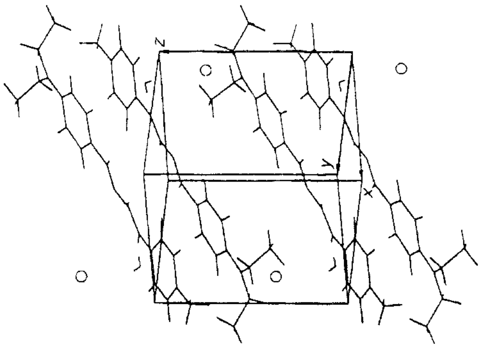

Fig. 5. Projection of crystal stacking of iodide X.

The structural maps show clearly that the molecules of the betaine VIII and the hydrazone X are linear and that we cannot speak of a self-complex. Hence, the ICT must proceed along the system of bonds :D–(R)C═N–NH–C(O)–A through the hydrazonocarbonyl bridge. From this it follows that the amide bond does not interrupt the conjugation chain and that the ICT proceeds with high efficiency: The intensity of the absorption maximum at 400-440 nm in water—ethanol solutions ε = 12,000 to 20,000.

TABLE 6. Coordinates of Nonhydrogen Atoms in Structure ($\times 10^4$) of Hydrazone X

Atom	x	y	z
I	-775 (1)	11896 (0)	-3926 (0)
$C_{(1)}$	4353 (9)	-4139 (5)	-1573 (5)
$C_{(2)}$	2319 (9)	-3971 (6)	-1325 (6)
$C_{(3)}$	1340 (8)	-3235 (6)	-628 (5)
$C_{(4)}$	2268 (8)	-2624 (5)	-121 (5)
$C_{(5)}$	4271 (8)	-2798 (6)	-361 (5)
$C_{(6)}$	5277 (8)	-3529 (6)	-1061 (5)
$C_{(7)}$	1310 (8)	-1845 (5)	615 (5)
$C_{(8)}$	-2992 (8)	-306 (5)	1691 (5)
$C_{(9)}$	-3526 (7)	410 (5)	2567 (4)
$C_{(10)}$	-5454 (8)	517 (6)	3134 (5)
$C_{(11)}$	-6015 (8)	1174 (6)	3932 (5)
$C_{(12)}$	-2874 (8)	1657 (6)	3662 (5)
$C_{(13)}$	-2242 (8)	997 (5)	2866 (5)
$C_{(14)}$	-5370 (9)	2480 (6)	5037 (5)
$C_{(15)}$	4358 (11)	-5389 (7)	-2927 (6)
$C_{(16)}$	3541 (14)	-6504 (8)	-2323 (8)
$C_{(17)}$	7383 (10)	-5220 (6)	-2365 (6)
$C_{(18)}$	8643 (12)	-4427 (9)	-3256 (8)
$N_{(1)}$	-5330 (8)	4850 (5)	2286 (5)
$N_{(2)}$	472 (7)	1482 (4)	-729 (4)
$N_{(3)}$	-1156 (6)	-777 (4)	1503 (4)
$N_{(4)}$	-4743 (7)	1748 (4)	4187 (4)
$O_{(1)}$	-4137 (6)	-442 (4)	1184 (4)
$O_{(1')}$	-7892 (6)	10848 (5)	1226 (4)

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*For numbering of atoms, see Fig. 4.

TABLE 7. Environment of I^- Ion in Compound X

Atom X	Distance I···X (Å)	Symmetry of atom X	Atom X	Distance I···X (Å)	Symmetry of atom X
$N_{(3)}$	3,656	-x, -1 - y, -z	$C_{(13)}$	3,927	-x, -1 - y, -z
$C_{(14)}$	3,823	x, 1 + y, -1 + z	$C_{(11)}$	3,939	1 + x, 1 + y, -1 + z
$C_{(12)}$	3,864	x, 1 + y, -1 + z	$C_{(10)}$	3,951	-1 - x, 1 - y, 1 - z
$C_{(14)}$	3,896	1 + x, 1 + y, -1 + z			

EXPERIMENTAL

The IR spectra were obtained in a Specord 75-IR spectrometer on suspensions of the substances in Nujol (1500-1800 cm^{-1}) or hexachlorocyclobutadiene (2000-3600 cm^{-1}), without indication of stretching vibration frequencies of C–H bonds. The PMR spectra were obtained in $CDCl_3$ or DMSO-d_6 in a Bruker WH-90/DS spectrometer (90 MHz), internal standard TMS. The electronic absorption spectra were taken in a Specord M-40 spectrometer at a solution concentration of 10^{-4} M. Molecular weights of the compounds III were determined in an MKh-1303 mass spectrometer.

The results of elemental analyses of compounds III-X for C, H, N, Cl, and I were in agreement with the calculated values.

2-Isonicotinoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione (III, $C_{15}H_{17}N_3O_3$). *Red-orange form of III* was obtained in accordance with [1] by refluxing equimolar quantities of Ia and II in ethanol; mp 210-212°C; literature data [1] mp 208-210°C. IR spectrum: 3260, 3210, 3290, 1670, 1635, 1600, 1560, 1540, 1510 cm^{-1}. M^+ 287.

Colorless form of III. A. To a solution of 0.84 g (5 mmoles) of Ia in 10 ml of chloroform, a solution of 0.69 g (5 mmoles) of II in 10 ml of chloroform was added, and the mixture was held for 1 h at 20°C. Then 15 ml of the chloroform was driven off, the remaining mixture was filtered, and the precipitate was washed on the filter with 2-3 ml of diethyl ether. Product mp 214-216°C. IR spectrum: 3230, 3180, 3090, 1680, 1645, 1570, 1530 cm^{-1}. M^+ 287. Yield 0.92 g (65%).

B. In a wide-necked flask in an oil bath, a thin layer of the red form of III was heated for 2 h at 130-140°C. Obtained the colorless form of III, mp 208-210°C.

Yellow form of III was obtained by 1-h refluxing of 3 mmoles of the red or colorless form of III in 20 ml of benzene in the presence of catalytic quantities of p-toluenesulfonic acid, and then driving off two-thirds of the volume of the solvent. Product mp 192-194°C. Did not give any melting point depression with samples of the red or colorless form of III. IR spectrum: 3230, 3180, 3070, 1678, 1650, 1530 cm^{-1}.

By recrystallization of the yellow or colorless form of III from ethanol, the red form was obtained, mp 210-212°C.

2-(1-Isonicotinoylhydrazinoethylidene)-5,5-dimethyl-1,3-cyclohexanedione (IV, $C_{16}H_{19}N_3O_3$). *Orange form.* To a solution of 0.91 g (5 mmoles) of acetyldimedone in 10 ml of ethanol, a solution of 0.69 g (5 mmoles) of II in 15 ml of ethanol was added, and the mixture was left for 24 h at 20°C. The precipitated orange needles of IV were filtered off; mp 159-161°C. IR spectrum: 3220, 3110, 1650, 1635, 1622, 1570, 1520, 1510 cm^{-1}. Yield 1.1 g (67%).

Colorless form of IV was obtained in the same manner as the colorless form of III, or by the interaction of Ib and II in chloroform, or by heating at 130-135°C, or by refluxing the orange form of IV in benzene in the presence of catalytic quantities of p-toluenesulfonic acid. Product mp 159-161°C. Did not give any melting point depression with a sample of the orange form. IR spectrum: 3210, 3110, 1650, 1640, 1620, 1565, 1520 cm^{-1}.

Crystallization of the colorless form from ethanol led to the formation of orange crystals with mp 159-161°C.

Hydrochloride of 2-Isonicotinoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione (V, $C_{15}H_{16}N_3O_3 \cdot HCl$) was obtained by passing dry hydrogen chloride through a solution of 0.57 g (2 mmoles) of III in 150 ml of dry chloroform. Yellow crystals, mp 250-251°C. From all forms of III, identical samples of V were obtained. IR spectrum: 3350, 3100, 2650-2550, 1695, 1620, 1585, 1545, 1505 cm^{-1}. Yield 0.42 g (70%).

2-Benzoylhydrazinomethylene-5,5-dimethyl-1,3-cyclohexanedione ($C_{16}H_{18}N_2O_3$). To a solution of 0.84 g (5 mmoles) of Ia in 10 ml of ethanol, a solution of 0.8 g (5 mmoles) of benzoylhydrazine in 10 ml of ethanol was added. The precipitate was recrystallized from ethanol; mp 220-222°C. IR spectrum: 3210-3190, 3110, 3060, 1670, 1650, 1575, 1535, 1500 cm^{-1}. PMR spectrum (DMSO-d_6): 1.06 (6H, s, $2CH_3$); 2.30 (2H, s, CH_2); 7.44-7.94 (5H, m, arom.); 8.72 (1H, s, $=CH-$); 11.70 (1H, NH); 13.60 ppm (1H, NH). Yield 1.47 g (98%).

2-(1-Benzoylhydrazinoethylidene)-5,5-dimethyl-1,3-cyclohexanedione ($C_{17}H_{20}N_2O_3$) was obtained by analogy with the previous preparation, from Ib and benzoylhydrazine. Product mp 132-134°C (from ethanol). IR spectrum: 3190, 1650, 1610, 1570, 1530, 1500 cm^{-1}. PMR spectrum ($CDCl_3$): 0.93 (6H, s, $2CH_3$); 2.33 (4H, bs, $2CH_2$); 2.57 (3H, s, CH_3); 7.40-7.83 (5H, m, arom); 9.90 (1H, NH); 15.0 ppm (1H, NH).

Iodide of 2[N-(1-Methyl-4-pyridiniumcarbonyl)hydrazinomethylene]-5,5-dimethyl-1,3-cyclohexanedione (VI, $C_{16}H_{20}IN_3O_3$). A 0.50-g quantity (2 mmoles) of III and 2 ml of methyl iodide were heated in a steel ampul for 1 h at 90-95°C. After cooling, the reaction mixture was treated with 10 ml of diethyl ether, the slurry was filtered, and the precipitate was recrystallized from ethanol; mp 230-232°C. IR spectrum: 3195, 3120, 3040, 1692, 1650, 1592, 1540, 1510 cm^{-1}. Yield 0.51 g (50%).

Iodide of 2-{1-[N-(1-Methyl-4-pyridiniumcarbonyl)hydrazino]ethylidene}-5,5-dimethyl-1,3-cyclohexanedione (VII, $C_{17}H_{22}IN_3O_3$) was obtained in the same manner as VI, from 2 mmoles of IV. Product mp 198-200°C. IR spectrum: 3170, 3120, 3040, 1685, 1635, 1580, 1550, 1510 cm^{-1}. Yield 62%.

2-[N-(1-Methyl-4-pyridiniumcarbonyl)hydrazinomethylene]-5,5-dimethyl-1,3-cyclohexanedionate (VIII, $C_{16}H_{19}N_3O_3$). To a solution of 0.50 g (1 mmole) of the iodide VI in 25 ml of ethanol, triethylamine was added dropwise until precipitation of the dark-red betaine VIII was completed; mp 310-313°C (from water). IR spectrum: 3120, 1660, 1650, 1592, 1580, 1560, 1540, 1530 cm^{-1}. Yield 0.20 g (66%).

X-Ray Structure Study of Betaine VIII. Single crystals of VIII belong to the triclinic system. The elementary cell parameters are: $a = 6.769(2)$, $b = 10.521(2)$, $c = 12.728(3)$ Å; $\alpha = 83.02(2)$, $\beta = 75.56(2)$, $\gamma = 84.58(2)°$; $V = 869.3$ $Å^3$, $d_{calc} = 1.22$ g/cm^3, $F(000) = 340$, $\mu(MoK\alpha) = 0.6$ cm^{-1}, Z = 2 (two independent molecules). Space group P1. In deciphering the structure, the intensities of 2278 independent reflections were measured in an automatic four-circle Syntex $P2_1$ diffractometer by the ω-scanning method up to $2\theta_{max} = 45°$. Molybdenum radiation was used (graphite monochromator) with $\lambda = 0.71069$ Å. In the calculations we used 1635 reflections with $I \geq 2\sigma_I$. The model of the structure was obtained by the direct method [7]; the initial value of the R-factor was 0.42. The structure was refined by the LSM in the full-matrix isotropic approximation. The positions of the hydrogen atoms were calculated geometrically. The final R-factor was 0.149. All calculations were performed by means of a set of programs given in [8].

Iodide of Hydrazide of 1-Methylisonicotinic Acid. A mixture of 2.06 g (15 mmoles) of methyl isonicotinate and 2.13 g (15 mmoles) of methyl iodide in 10 ml of ethanol was held for 48 h at 0-5°C. Obtained 3.98 g (98%) of the iodide of the methyl ester of 1-methylisonicotinic acid (mp 166-168°C); this substance was added to a solution of 1.00 g (20 mmoles) of hydrazine hydrate in 50 ml of ethanol and refluxed for 0.5 h, after which two-thirds of the solvent was driven off. After cooling, obtained 3.70 g (93%) of the desired substance, mp 208-210°C. According to [9], mp 211-213°C.

Iodides of N-(4-Dimethylaminobenzal)-N′-(1-methyl-4-pyridiniumcarbonyl)hydrazine (IX) and N-(4-Diethylaminobenzal)-N′-(1-methyl-4-pyridiniumcarbonyl)hydrazine (X, $C_{18}H_{23}IN_4O \cdot H_2O$) were obtained by 1-h refluxing of 1.31 g (5 mmoles) of the iodide of the hydrazide of 1-methylisonicotinic acid and an equimolar quantity of 4-dimethylaminobenzaldehyde or 4-diethylaminobenzaldehyde in 20 ml of ethanol. Dark-red crystals of IX and X precipitated from solution upon cooling. Iodide IX, mp 218-220°C (according to [10], mp 225°C). Yield 1.98 g (98%).

Iodide X, mp 194-196°C. IR spectrum: 3520, 3440, 3440, 3220, 1670, 1615, 1595, 1530, 1500 cm^{-1}. PMR spectrum (DMSO-d_6): 1.04 (6H, t, J = 7Hz, $2CH_3$); 3.33 (4H, q, J = 7Hz, $2CH_2$); 4.49 (3H, $N-CH_3$); 6.73 (2H, m, arom.); 7.49 (2H, m, arom.); 7.93 (2H, m, arom.); 8.8 (2H, m, arom.); 8.24 (1H, s, $=CH-$); 10.21 ppm (1H, NH). Yield 2.00 g (91%).

X-Ray Structure Study of Iodide of Hydrazone X. Single crystals of X belong to the triclinic system. The crystal lattice parameters are: $a = 7.2436(9)$, $b = 11.548(2)$, $c = 12.869(3)$ Å; $\alpha = 77.47(2)$, $\beta = 75.07(2)$, $\gamma = 82.41(1)°$; $V = 1011.8$ Å^3, $d_{calc} = 1.45 g/cm^3$, $F(000) = 446$, $\mu(MoK\alpha) = 8.4 cm^{-1}$, Z = 2, space group P1.

The intensities of 3617 independent nonzero reflections were measured in an automatic four-circle Syntex $P2_1$ diffractometer on molybdenum radiation (graphite monochromator, $\theta/2\theta$ scanning) up to $2\theta_{max} = 50°$. In the calculations, 3440 reflections with $I \geq 2\sigma_I$ were used.

The structure of X was deciphered by the heavy-atom method: The position of the iodine atom was found from a three-dimensional Patterson function; the subsequent Fourier synthesis defined all of the remaining nonhydrogen atoms (initial R-factor 0.25). The structure was refined by the full-matrix LSM with anisotropic temperature parameters, down to R = 0.058. Then a correction for absorption was applied ($\mu = 8.4 cm^{-1}$) by the method of [11], after which a difference synthesis was used to localize the positions of all hydrogen atoms, which were refined isotropically. The final divergence factor was 0.0359. All calculations were performed by a set of programs given in [8].

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