

mixture was determined from UV chromatograms according to the peak intensity of the band at  $\lambda$  224 nm with allowance for the fact that the extinction coefficient  $\epsilon_{224}$  was 18,200 for compounds IIa-e and 22,900 for compounds IIIa-e. Each experiment was run three times. The reproducibility of the results was  $\pm 2\%$ .

#### LITERATURE CITED

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#### CYCLIZATION REACTIONS OF NITRILES.

##### 50.\* REGIOSELECTIVITY IN THE REACTIONS OF QUATERNIZED PYRIDIN-3-YLIDENE MALONITRILE AND CYANOACETATE ESTER DERIVATIVES WITH 1,3-DICARBONYL COMPOUNDS. CRYSTAL STRUCTURE OF 2-AMINO-3,5-DICARBOETHOXY-6-METHYL-4-(1-METHYLPYRIDINIUM-3-YL)-4H-PYRAN IODIDE

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3'052.1'262:548.737

*The reaction of quaternized pyridin-3-ylidene malonitrile and cyanoacetate ester derivatives with 1,3-dicarbonyl compounds proceeds highly regioselectively to give substituted 2-amino-4-(1-methylpyridinium-3-yl)-4H-pyran iodides. The structure of 2-amino-3,5-dicarboethoxy-6-methyl-4-(1-methylpyridinium-3-yl)-4H-pyran iodide has been investigated by x-ray structural analysis.*

Reaction studies of arylmethylenemalononitriles and arylmethylenecyanoacetate esters with carbonyl and 1,3-dicarbonyl compounds are related to research into biologically active substances [2-9]. These reactions have been found to proceed highly regioselectively to give substituted 2-amino-4-aryl-4H-pyrans [3-6, 8, 9]. The reaction pathway is not altered when hetarylmethylenemalononitriles or heterocyclic carbonyl compounds, such as pyrazol-5-one, barbituric acid, or thiohydantoin derivatives are used as substrates [2, 4-6, 9]. The high regioselectivity observed in these reactions can be explained in terms of the formation of Michael adducts [4, 8], and their subsequent cyclization (thermally or upon treatment with base) to give substituted 2-amino-4H-pyrans. Electronic and steric factors appear to be the controlling or determining factors (in the observed regioselectivity) [2, 5]. However, the principal aspects of this problem have not yet been clarified, and elucidating the factors responsible for the regioselectivity in the reactions of unsaturated nitriles with carbonyl compounds remains an important problem with both practical and theoretical implications. For example, in [7] the authors erroneously attributed the reaction of arylmethylenemalononitriles with 3-methyl-4-phenylpyrazol-5-one to result from nucleophilic addition

\*See [1] for communication No. 49.

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TABLE 1. Physical Characteristics of Newly Synthesized Compounds

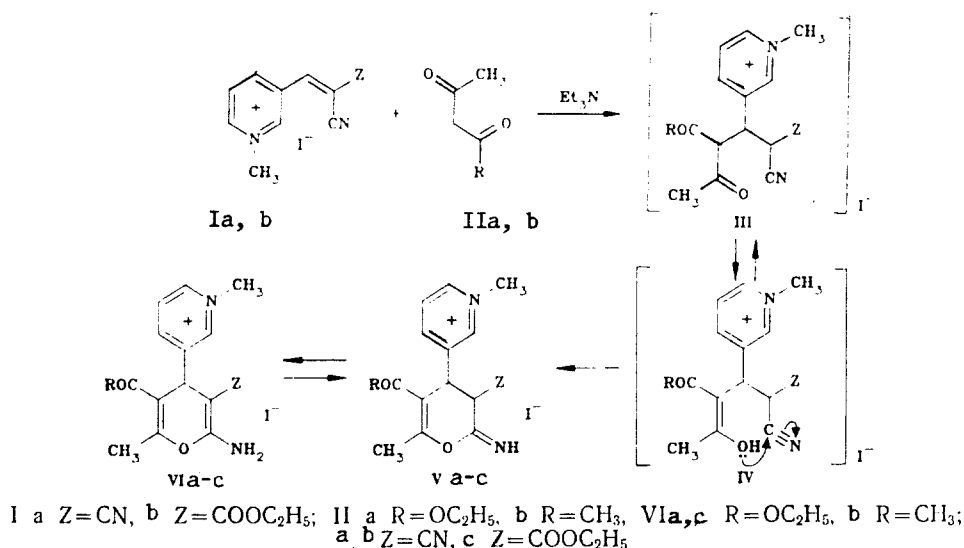
Com- pound	mp, °C <sup>±</sup>	IR spectrum, cm <sup>-1</sup>	PMR spectrum, δ, ppm (SSCC, J, Hz)	Yield, %
Ia	203 ... 205	1632 (C=C); 2232 (C≡N)	4.42 (3H, s, CH <sub>3</sub> ); 8.37 (1H, dd, C <sub>15</sub> H); 8.87 (1H, s, C≡C(CN) <sub>2</sub> ); 9.01 (1H, d, C <sub>14</sub> H, $\frac{3}{2}$ J=7.9); 9.18 (1H, d, C <sub>16</sub> H, $\frac{3}{2}$ J=6.2); 9.35 (1H, s, C <sub>12</sub> H) 1.34 (3H, t, CH <sub>3</sub> CH <sub>2</sub> , $\frac{3}{2}$ J=7.4); 4.36 (2H, q, CH <sub>2</sub> CH <sub>2</sub> , $\frac{3}{2}$ J=7.4); 4.41 (3H, s, CH <sub>3</sub> ); 8.35 (1H, s, C <sub>15</sub> H); 8.45 (1H, s, CH=CCN); 9.08 (1H, d, C <sub>14</sub> H, $\frac{3}{2}$ J=7.8); 9.15 (1H, d, C <sub>16</sub> H, $\frac{3}{2}$ J=6.1); 9.49 (1H, s, C <sub>12</sub> H)	93
Ib	195 ... 197	1636 (C=C); 1732 (C=O); 2228 (C≡N)	1.06 (3H, t, CH <sub>3</sub> CH <sub>2</sub> , $\frac{3}{2}$ J=7.5); 2.38 (3H, 6-CH <sub>2</sub> ); 3.98 (2H, q, CH <sub>2</sub> CH <sub>2</sub> , $\frac{3}{2}$ J=7.5); 4.38 (3H, s, CH <sub>3</sub> N); 4.62 (1H, s, C <sub>10</sub> H pyran); 7.26 (2H, br. s, NH <sub>2</sub> ); 8.10 (1H, dd, C <sub>15</sub> H); 8.48 (1H, d, C <sub>14</sub> H, $\frac{3}{2}$ J=8.1); 8.89 (1H, d, C <sub>16</sub> H, $\frac{3}{2}$ J=6.3); 8.98 (1H, s, C <sub>12</sub> H)	90
VIa	194 ... 196	1665 (δNH <sub>2</sub> ); 1712 (COOC <sub>2</sub> H <sub>5</sub> ); 2192 (C≡N); 3178, 3280, 3395 (NH <sub>2</sub> )	2.22 (3H, s, CH <sub>3</sub> CO); 2.37 (3H, s, 6-CH <sub>2</sub> ); 4.36 (3H, s, CH <sub>3</sub> N); 4.71 (1H, s, C <sub>10</sub> H pyran); 7.23 (2H, br. s, NH <sub>2</sub> ); 4.36 (3H, s, CH <sub>3</sub> N); 4.71 (1H, s, C <sub>14</sub> H, $\frac{3}{2}$ J=8.0); 8.87 (1H, d, C <sub>16</sub> H, $\frac{3}{2}$ J=6.2); 8.91 (1H, s, C <sub>12</sub> H)	95
VIb	215 ... 216	1668 (δNH <sub>2</sub> ); 1702 (C=O); 2198 (C≡N); 3176, 3298, 3376 (NH <sub>2</sub> )	1.11 (6H, t, (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> , $\frac{3}{2}$ J=7.3); 2.41 (3H, s, 6-CH <sub>2</sub> ); 4.05 (4H, q, (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> , $\frac{3}{2}$ J=7.3); 4.39 (3H, s, CH <sub>3</sub> N); 4.72 (1H, s, C <sub>10</sub> H pyran); 7.68 (2H, br. s, NH <sub>2</sub> ); 8.05 (1H, dd, C <sub>15</sub> H); 8.39 (1H, d, C <sub>14</sub> H, $\frac{3}{2}$ J=8.1); 8.83 (1H, d, C <sub>16</sub> H, $\frac{3}{2}$ J=6.1); 8.87 (1H, s, C <sub>12</sub> H)	93
VIc	192 ... 195	1642 (δNH <sub>2</sub> ); 1718 (COOC <sub>2</sub> H <sub>5</sub> ); 3165, 3272, 3380 (NH <sub>2</sub> )		92

\*The compounds were recrystallized from nitromethane.

at the two nitrile groups in the unsaturated nitrile to give 3-arylmethylene-2,4-diamino-5-methyl-7-phenylpyrano[2,3-c]pyrazoles.

In the present paper we have studied the reactions of quaternized pyridin-3-ylidene malononitrile Ia and cyanoacetate ester Ib derivatives with 1,3-dicarbonyl compounds IIa, b. Salts IIa, b were easily prepared by alkylation of the corresponding pyridines [10, 11] with methyl iodide. In contrast to arylmethylenemalononitriles compounds Ia, b not only contain an exocyclic double bond, capable of reacting with 1,3-dicarbonyl compounds via an addition-cyclization pathway, but also may undergo a hetarylation reaction characteristic of quaternized azines [12-15] (see scheme on page 167).

The structures of compounds Ia, b were confirmed by their IR and PMR spectral data (Table 1). The observed high-frequency shift of the C=C and C≡N bond stretching vibration bands in the IR spectra of these compounds relative to arylmethylene derivatives of other active methylene nitriles [16, 17] appears to be the result of the electron-withdrawing nature of the pyridinium cation. In the PMR spectra of salts Ia, b the signals for the pyridinium ring protons [18] also appear to be shifted downfield. The signal assignments for the methine proton and the C<sub>(2)</sub>H heteroring proton were made based on comparison of the spectra of compounds Ia, b. Thus, in compound Ia the methine proton signal is shifted downfield by  $\Delta\delta = 0.42$  ppm relative to that in compound Ib, due to the effect of the geminal nitrile groups. The chemical shift of the C<sub>(2)</sub>H heteroring proton is not significantly different (Table 1).



Reaction of compounds Ia, b with acetoacetate ester (IIa) and acetylacetone (IIb) in ethanol in the presence of triethylamine occurs highly regioselectively to give substituted 2-amino-4-pyrans VIa-c. The first stage in the reaction sequence involves nucleophilic addition of the 1,3-dicarbonyl compound to the unsaturated nitrile to form a Michael adduct III. Analogous addition products, but not incorporating quaternized compounds, have been isolated in previous studies [4-6, 19]. Subsequent intramolecular cyclization, via the enolization step III  $\rightleftharpoons$  IV, leads to the formation of imines Va-c, which are stabilized in the form of 2-amino-4H-pyrans VIa-c. The existence of the reaction products in the form of their amino derivatives VIa-c, and not their corresponding imino derivatives Va-c, has been verified by their IR and PMR spectral data (Table 1). Thus, the IR spectra of pyrans VIa-c contain absorption bands for the stretching and bending vibrations of the amino group at 3165-3395 and 1642-1665 cm<sup>-1</sup>, respectively. In the spectrum of compound VIc the second band is shifted 23-25 cm<sup>-1</sup> toward lower frequency compared to compounds VIa, b; this suggests the formation of intramolecular hydrogen bonding in the first case. This is supported by the observed 0.42-0.45 ppm shift of the amino group proton signal in the PMR spectrum of compound VIc relative to the corresponding signals for compounds VIa, b (Table 1).

Both the position of the cyano group vibrational band in the spectra of compounds VIa, b (2192-2198) and their strong intensity are indicative of efficient p- $\pi$ -conjugation in the H<sub>2</sub>N-C=C-C≡N fragment in these compounds. A similar conjugation effect in an enamionitrile fragment has been noted previously in other heterocyclic systems [20]. A characteristic feature of the PMR spectra of compounds VIa-c is the presence of the signal for the proton in the 4-position of the pyran ring in the form of a singlet at 4.62-4.72 ppm, suggesting a rigid orientation of this atom in space and, consequently, high stereoselectivity in the formation of these aminopyrans. Assignment of the amino-group proton signals in aminopyrans VIa-c was made based on the results of deuteration experiments on these compounds in solution during spectral acquisition.

TABLE 2. Bond Angles  $\omega$  in Cation VIc

Angle	$\omega$ ( $\sigma$ ) <sup>o</sup>
C <sub>(2)</sub> O <sub>(1)</sub> C <sub>(6)</sub>	120,2(3)
C <sub>(16)</sub> O <sub>(3)</sub> C <sub>(17)</sub>	119,0(4)
C <sub>(8)</sub> O <sub>(5)</sub> C <sub>(9)</sub>	116,4(3)
C <sub>(12)</sub> N <sub>(2)</sub> C <sub>(13)</sub>	120,9(3)
C <sub>(12)</sub> N <sub>(2)</sub> C <sub>(19)</sub>	119,5(3)
C <sub>(13)</sub> N <sub>(2)</sub> C <sub>(19)</sub>	119,5(3)
O <sub>(1)</sub> C <sub>(2)</sub> N <sub>(1)</sub>	110,1(4)
O <sub>(1)</sub> C <sub>(2)</sub> C <sub>(3)</sub>	122,0(4)
N <sub>(1)</sub> C <sub>(2)</sub> C <sub>(3)</sub>	127,9(4)
C <sub>(2)</sub> C <sub>(3)</sub> C <sub>(4)</sub>	121,3(3)
C <sub>(2)</sub> C <sub>(3)</sub> C <sub>(16)</sub>	120,5(4)
C <sub>(4)</sub> C <sub>(3)</sub> C <sub>(16)</sub>	118,2(3)
C <sub>(3)</sub> C <sub>(4)</sub> C <sub>(5)</sub>	110,4(3)
C <sub>(3)</sub> C <sub>(4)</sub> C <sub>(11)</sub>	110,7(3)
C <sub>(5)</sub> C <sub>(4)</sub> C <sub>(11)</sub>	111,0(3)
C <sub>(4)</sub> C <sub>(5)</sub> C <sub>(6)</sub>	121,6(3)
C <sub>(4)</sub> C <sub>(5)</sub> C <sub>(8)</sub>	119,1(3)
C <sub>(6)</sub> C <sub>(5)</sub> C <sub>(8)</sub>	119,2(3)
O <sub>(1)</sub> C <sub>(6)</sub> C <sub>(5)</sub>	122,3(4)
O <sub>(1)</sub> C <sub>(6)</sub> C <sub>(7)</sub>	110,0(4)
C <sub>(5)</sub> C <sub>(6)</sub> C <sub>(7)</sub>	127,7(4)
O <sub>(4)</sub> C <sub>(8)</sub> O <sub>(5)</sub>	121,7(4)
O <sub>(4)</sub> C <sub>(8)</sub> C <sub>(5)</sub>	126,7(4)
O <sub>(5)</sub> C <sub>(8)</sub> C <sub>(5)</sub>	111,6(3)
O <sub>(5)</sub> C <sub>(9)</sub> C <sub>(10)</sub>	108,1(4)
O <sub>(4)</sub> C <sub>(11)</sub> C <sub>(12)</sub>	119,8(3)
C <sub>(4)</sub> C <sub>(11)</sub> C <sub>(15)</sub>	121,8(3)
C <sub>(12)</sub> C <sub>(11)</sub> C <sub>(15)</sub>	118,4(3)
N <sub>(2)</sub> C <sub>(12)</sub> C <sub>(11)</sub>	121,0(3)
N <sub>(2)</sub> C <sub>(13)</sub> C <sub>(14)</sub>	120,3(3)
C <sub>(13)</sub> C <sub>(14)</sub> C <sub>(15)</sub>	119,6(3)
C <sub>(11)</sub> C <sub>(15)</sub> C <sub>(14)</sub>	119,9(3)
O <sub>(2)</sub> C <sub>(16)</sub> O <sub>(3)</sub>	122,3(4)
O <sub>(2)</sub> C <sub>(16)</sub> C <sub>(3)</sub>	127,2(4)
O <sub>(3)</sub> C <sub>(16)</sub> C <sub>(3)</sub>	110,5(3)
O <sub>(3)</sub> C <sub>(17)</sub> C <sub>(18)</sub>	110,6(5)

TABLE 3. Coordinates ( $\times 10^5$  for I;  $\times 10^4$  for O, N, C;  $\times 10^3$  for H) and Isotropic Equivalent Thermal Factors  $B_{\text{equiv}}^{\text{iso}}$  ( $\text{\AA}^2$ ) of Atoms

Atom	x	y	z	$B_{\text{equiv}}^{\text{iso}}$
I	17939(3)	7037(3)	69715(2)	5,54(1)
O <sub>(1)</sub>	4135(3)	8003(3)	694(3)	6,1(1)
O <sub>(2)</sub>	2832(3)	5074(4)	3783(3)	7,2(1)
O <sub>(3)</sub>	4962(3)	3374(3)	3484(2)	6,3(1)
O <sub>(4)</sub>	7708(4)	6233(4)	-1399(2)	6,7(1)
O <sub>(5)</sub>	8174(3)	4226(3)	66(2)	4,4(1)
N <sub>(1)</sub>	2397(4)	7899(5)	2211(4)	7,9(2)
N <sub>(2)</sub>	9678(3)	2917(3)	3344(2)	3,4(1)
C <sub>(2)</sub>	3712(4)	7104(4)	1717(4)	4,9(1)
C <sub>(3)</sub>	4517(3)	5676(4)	2150(3)	4,0(1)
C <sub>(4)</sub>	6011(3)	5025(3)	1584(3)	3,3(1)
C <sub>(5)</sub>	6193(4)	6057(4)	370(3)	4,1(1)
C <sub>(6)</sub>	5283(4)	7442(4)	8(4)	5,2(1)
C <sub>(7)</sub>	5323(6)	8522(6)	-1095(4)	7,7(2)
C <sub>(8)</sub>	7400(4)	5531(4)	-417(3)	4,5(1)
C <sub>(9)</sub>	9474(5)	3508(5)	-611(3)	5,3(1)
C <sub>(10)</sub>	10234(6)	1981(6)	98(4)	7,0(2)
C <sub>(11)</sub>	7399(3)	4646(3)	2365(2)	2,9(1)
C <sub>(12)</sub>	8416(3)	3270(3)	2681(2)	3,1(1)
C <sub>(13)</sub>	9939(4)	3898(4)	3731(3)	4,0(1)
C <sub>(14)</sub>	8949(4)	5278(4)	3452(3)	4,1(1)
C <sub>(15)</sub>	7665(3)	5664(3)	2760(3)	3,5(1)
C <sub>(16)</sub>	3991(4)	4737(5)	3209(3)	5,0(1)
C <sub>(17)</sub>	4680(6)	2287(6)	4543(5)	8,2(2)
C <sub>(18)</sub>	5819(6)	1896(7)	5403(5)	9,3(2)
C <sub>(19)</sub>	10813(4)	1446(4)	3601(3)	4,8(1)
H <sub>(1,1)</sub>	208(4)	726(4)	288(4)	
H <sub>(1,2)</sub>	166(4)	866(4)	165(4)	
H <sub>(4)</sub>	602(4)	411(4)	149(4)	
H <sub>(7,1)</sub>	454(4)	901(4)	-143(4)	
H <sub>(7,2)</sub>	608(4)	821(4)	-160(4)	
H <sub>(7,3)</sub>	554(4)	910(4)	-87(4)	
H <sub>(9,1)</sub>	1011(4)	415(4)	-86(4)	
H <sub>(9,2)</sub>	908(4)	352(4)	-136(4)	
H <sub>(10,1)</sub>	1112(4)	148(4)	-34(4)	
H <sub>(10,2)</sub>	1075(4)	189(4)	67(4)	
H <sub>(10,3)</sub>	961(4)	137(4)	40(4)	
H <sub>(12)</sub>	832(4)	255(4)	247(4)	
H <sub>(13)</sub>	1096(4)	361(4)	417(4)	
H <sub>(14)</sub>	915(4)	605(4)	365(4)	
H <sub>(15)</sub>	699(4)	665(4)	257(4)	
H <sub>(17,1)</sub>	505(4)	141(4)	443(4)	
H <sub>(17,2)</sub>	351(4)	241(4)	472(4)	
H <sub>(18,1)</sub>	566(4)	130(4)	608(4)	
H <sub>(18,2)</sub>	690(4)	181(4)	516(4)	
H <sub>(18,3)</sub>	495(4)	291(4)	520(4)	
H <sub>(19,1)</sub>	1107(4)	108(4)	434(4)	
H <sub>(19,2)</sub>	1038(4)	67(4)	363(4)	
H <sub>(19,3)</sub>	1165(4)	156(4)	314(3)	

In order to confirm our conclusions concerning the regio- and stereoselectivity of aminopyran VIa-c formation, which were derived on the basis of analysis of their spectral data, we have carried out an x-ray structural investigation of one of these products, namely iodide VIc (cf. Fig. 1 and Table 2). The pyran heterocycle adopts a tub conformation, with the O<sub>(1)</sub> and C<sub>(4)</sub> atoms deviating from the plane of the other four atoms in the "tub floor" by 0.088(3) and 0.171(3) Å, respectively. The pyran ring exists in an analogous conformation in other compounds we have studied, such as 2-amino-7,7-dimethyl-4-(3-fluorophenyl)-5-oxo-3-ethoxycarbonyl-5,6,7,8-tetrahydro-4H-benzo[b]pyran (VII) [8], and 2-amino-4-(2-fluorophenyl)-3-ethoxycarbonyl-4H-naphthol[2,1-b]pyran (VIII) [21] [the deviations of the opposite O and C atoms in the heterocycles are 0.097(2), 0.221(3) Å and 0.197(3), 0.303(3) Å, respectively].

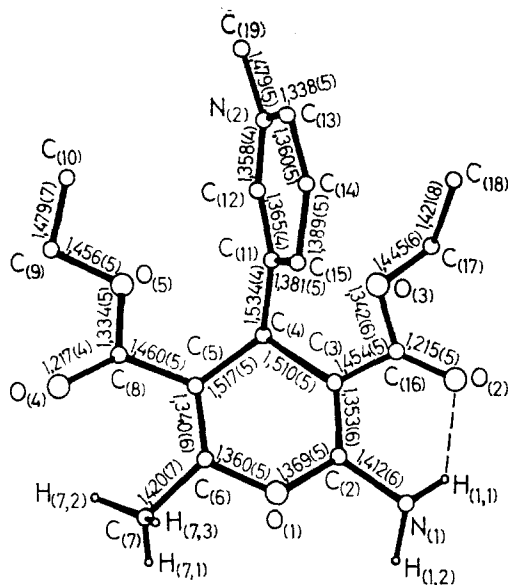


Fig. 1. Molecular structure of cation VIc and its bond lengths. The intramolecular NH...O hydrogen bond is indicated by a dashed line.

It is clear from Fig. 1 that the cation structure in VIc has approximate  $C_s$  symmetry; the mirror pseudoplane incorporates the pyridine ring and bisects the pyran ring, in which the planar fragment (the tub floor) is nearly perpendicular to the pyridine heterocycle (dihedral angle  $93.3^\circ$ ). The mutual orientation of the heterocycles is defined by short nonbonded intramolecular distances  $O(3) \cdots C(11)$  2.911(4),  $O(3) \cdots C(12)$  3.169(4),  $O(5) \cdots C(14)$  2.963(4),  $O(5) \cdots C(12)$  2.992(4),  $C(3) \cdots C(15)$  3.042(5),  $C(5) \cdots C(15)$  3.171(5),  $C(8) \cdots C(11)$  3.170(4), and  $C(11) \cdots C(16)$  3.142(5) Å (the sums of the van der Waals radii for O, C and C, C are 3.22 and 3.40 Å, respectively [22]).

The  $C_s$  symmetry of the cation is most markedly distorted by the ethoxycarbonyl substituents. Thus, although the  $C(3)C(16)O(3)C(17)$  and  $C(5)C(8)O(5)C(9)$  torsional angles are similar [ $177.1(8)$  and  $-176.1(7)^\circ$ , or nearly so,  $163.0(7)^\circ$ ], the  $C(16)O(3)C(17)C(18)$  and  $C(8)O(5)C(9)C(10)$  torsional angles differ significantly from one another [ $-109.5(9)$  and  $176.6(8)^\circ$ ], which suggests that the ethoxycarbonyl groups in cation VIc have different conformations.

The  $O(1)-C(2)$  and  $O(1)-C(6)$  bond lengths in the pyran heterocycle are normal for  $O-C_{sp^2}$  single bonds and similar to the corresponding values in compounds VII [1.372(3) and 1.376(3) Å] and VIII [1.370(4) and 1.389(5) Å]. Two conjugated fragments  $C(2), C(3), C(16), O(2)$  and  $C(6), C(5), C(8), O(4)$  can be identified in the structure of cation VIc. The  $N(1)-C(2)=C(3)-C(16)=O(2)$  fragment in compound VIc, as in the analogous fragments in compounds VII and VIII, is nearly planar [the  $N(1)C(2)C(3)C(16)$  and  $C(2)C(3)C(16)O(2)$  torsional angles are equal to  $4.5(7)$  and  $1.8(6)^\circ$ , respectively]. However, in contrast to the case in compounds VII and VIII, in which the nitrogen atom in this fragment exhibits trigonal planar coordination and is thus conjugated with the double bond, in cation VIc the  $N(1)$  atom exhibits pyramidal coordination (the sum of the bond angles is  $345^\circ$ ) and is not involved in conjugation. The  $N(1)-C(2)$  bond length, for instance, is consistent with the normal or standard  $C_{sp^2}-N_{sp^3}$  bond length of 1.416 Å [23]. The presence of conjugation in the  $C(2)=C(3)-C(16)=O(2)$  fragment manifests itself in elongation of the  $C(2)=C(3)$  and  $C(16)-O(2)$  bonds (their standard or reference values are 1.331 and 1.199 Å [23]), and in concomitant shortening of the  $C(3)-C(16)$  bond length (the standard value for a nonconjugated  $C_{sp^2}-C_{sp^2}$  bond length is 1.478 Å [23]), although this second effect is less pronounced in cation VIc than in compounds VII and VIII.

In analogy with the molecular structures of compounds VII and VIII, intramolecular hydrogen bonding of the type  $N(1)-H(1.1) \cdots O(2)$  [ $N(1) \cdots O(2)$  2.802(6),  $N(1)-H(1.1)$  0.94(4), and  $H(1.1) \cdots O(2)$  2.05(4) Å,  $N(1)-H(1.1) \cdots O(2)$  angle  $136(4)^\circ$ ] results in ring closure of the  $H(1.1)-N(1)-C(2)=C(3)-C(16)=O(2)$  fragment in cation VIc to form a six-membered pseudoring. The second hydrogen atom on the amino group  $H(1.2)$  does not engage in either intra- or intermolecular hydrogen bonding and does not form any short nonbonded distances.

The existence of conjugation can also be inferred for the nearly planar  $C(6)=C(5)-C(8)=O(4)$  fragment [ $C(6)C(5)C(8)O(4)$  torsional angle  $1.2(6)^\circ$ ]. The  $C(5)=C(6)$  and  $C(8)=O(4)$  bond lengths are somewhat elongated relative to their standard or reference values, which were cited earlier, and are in fact comparable to the  $C(2)=C(3)$

and  $C_{(16)}=O_{(2)}$  bond lengths in the analogous fragment discussed above in cation VIc. The  $C_{(5)}-C_{(8)}$  bond length, in contrast, is shortened slightly, and comparable to the  $C_{(3)}-C_{(16)}$  bond length. The planarity of the  $C_{(7)}-C_{(6)}=C_{(5)}-C_{(8)}=O_{(4)}$  functional group array leads to short nonbonded contact distances,  $O_{(4)} \cdots C_{(7)}$  2.734(7) Å and  $O_{(4)} \cdots H_{(7.2)}$  2.05(4) Å (the sums of the corresponding van der Waals radii are 3.22 and 2.90 Å [19], respectively). According to the data presented in [24], these short contact distances suggest the formation of C-H $\cdots$ O-type hydrogen bonding [ $C_{(7)}-H_{(7.2)}$  0.91(4) Å,  $C_{(7)}-H_{(7.2)} \cdots O_{(4)}$  angle 131(4)°]. Although the formation of intramolecular  $N_{(1)}-H_{(1.1)} \cdots O_{(2)}$  hydrogen bonding in the crystal has been verified by its IR spectral data, the existence of  $C_{(7)}-H_{(7.2)} \cdots O_{(4)}$  hydrogen bonding has not been detected spectrally. It would seem, apparently, that the structure of cation VIc, although exhibiting the characteristics of  $C_{(7)}-H_{(7.2)} \cdots O_{(4)}$  hydrogen bonding, is actually determined by the favorable or advantageous nature of the planar structure for the  $C_{(7)}C_{(6)}C_{(5)}C_{(8)}O_{(4)}$  array [conjugated in the  $C_{(6)}=C_{(5)}-C_{(8)}=O_{(4)}$  fragment] and by crystal packing forces, i.e., the structure is constrained by these factors and does not represent any supplementary nonbonded interaction between the  $O_{(4)}$  and  $H_{(7.2)}$  atoms.

There are no short intermolecular contact distances in the crystal structure of compound VIc. The only intermolecular contact distance which is comparable to the sum of the respective van der Waals radii is found for the  $C_{(14)}$  atom in the pyridinium ring and the I $^-$  anion [ $C_{(14)} \cdots I$  (I-x, I-y, I-z)] 3.816(4) Å, compared to the sum of the respective van der Waals radii 3.85 Å [22, 25].

## EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 557 spectrophotometer using KBr pellets. PMR spectra were measured on a Bruker WM-250 (250 MHz) spectrometer using solutions in DMSO- $D_6$  versus TMS as internal standard.

The results of C, H, N elemental analysis agreed with calculations.

**X-Ray Structure Analysis of 2-Amino-3,5-dicarboethoxy-6-methyl-4-(1-methylpyridinium-3-yl)-4H-pyran Iodide (VIc).** The crystals are triclinic, at 20°C:  $a = 9.1256(6)$ ,  $b = 10.262(1)$ ,  $c = 12.0845(6)$  Å,  $\alpha = 70.123(5)$ ,  $\beta = 83.384(5)$ ,  $\gamma = 71.059(6)^\circ$ ,  $V = 1006.6(2)$  Å<sup>3</sup>,  $d = 1.565$  g/cm<sup>3</sup>,  $Z = 2$  [ $C_{18}H_{23}N_2O_5$ ]<sup>+</sup>I<sup>-</sup>, space group  $P\bar{1}$ . The unit cell parameters and intensities of 3495 independent reflections were measured on a Hilger-Watts 4-circle automated diffractometer ( $\lambda_{MoK\alpha}$ , graphite monochromator,  $\theta/2\theta$ -scanning to  $\theta_{max} = 30^\circ$ ). The structure was solved by direct methods using the MULTAN program and was refined by full matrix least squares using anisotropic thermal approximations for all nonhydrogen atoms, based on 2985 reflections with  $I > 3\sigma$ . The hydrogen atoms were visualized (identified) using a difference synthesis, and were refined isotropically with a fixed value of  $B_{iso} = 6.0$  Å<sup>2</sup>. The final dispersion factors were  $R = 0.032$  and  $R_w = 0.040$ . All the calculations were carried out on an Eclipse S/200 computer using the INEXTL system of programs [26]. The atomic coordinates and their isotropic thermal parameters are summarized in Table 3.

**3-(1-Methylpyridinium)methylmalononitrile (Ia).** A suspension of 10 mmoles pyridin-3-ylmethylmalononitrile [27] and 40 ml methyl iodide was refluxed with stirring for 8 h. The reaction mixture was cooled, the precipitate removed by filtration and washed on the filter with acetone.

**Iodide Ib** was prepared in an analogous manner from pyridin-3-ylmethylacetoacetate ester [27] and methyl iodide.

**2-Amino-5-carboethoxy-6-methyl-4-(1-methylpyridinium-3-yl)-2-cyano-4H-pyran Iodide (VIa).** To a suspension of 10 mmoles iodide Ia and 10 mmoles acetoacetate ester IIa in 25 ml absolute ethanol was added 0.1 ml triethylamine. The reaction mixture was stirred at 20°C for 6 h, and the resulting precipitate was separated by filtration and washed sequentially with absolute ethanol and hexane.

Aminopyrans VIb, c were prepared in an analogous manner from iodides IIa, b and either acetylacetone or acetoacetate ester, respectively.

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