the filtrate was washed with water and worked up to give 0.6 g (72.3%) of colorless needles with mp 138-139°C (from C_2H_3OH). Found: C 49.2; H 7.6; N 10.0%. $C_{12}H_{22}N_2O_4S$. Calculated: C 49.6; H 7.6; N 10.0%.

<u>r-4-Ureido-t-3-hydroxy-c-2-(5'-ethoxycarbonylbutyl)thiophan (XIV)</u>. This compound was obtained from III under conditions similar to those described for X. Workup gave colorless plates (80%) with mp 157-158°C (from alcohol). Found: C 49.7; H 7.6; N 9.8%. $C_{12}H_{22}N_2O_4S$. Calculated: C 49.6 H 7.6; N 10.0%.

<u>r-4-Ureido-c-3-hydroxy-c-2-(5'-methoxycarbonylbutyl)thiophan (XI).</u> A solution of 0.7 g (2.6 mmole) of VIIa in 7 ml of pyridine was heated to 90-100°C, after which 2.5 g of potassium isocyanate was added in the course of an hour, and the mixture was stirred at the same temperature for 1 h. It was then cooled, and the precipitate was removed by filtration. The filtrate was evaporated, 3 ml of methanol was added to the residue, and the mixture was maintained at 0°C for 16-18 h. The resulting precipitate was removed by filtration to give 0.55 g (77%) of colorless needles with mp 147-149°C. Found: C 47.2; H 7.0; N 10.1%. $C_{11}H_{20}N_{2}O_{4}S$. Calculated: C 47.8; H 7.3; N 10.1%.

<u>r-4-Ureido-c-3-hydroxy-t-2-(5'-methoxycarbonylbutyl)thiophan (XIII)</u>. The reaction of 1 g (3.8 mmole) of IXa under similar conditions gave 0.7 g (94%) of XIII as colorless plates with mp 163-164°C (from CH₃OH). Found: C 47.3; H 7.3; N 10.0%. $C_{11}H_{20}N_2O_4S$. Calculated: C 47.8; H 7.3; N 10.1%.

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MESOIONIC COMPOUNDS WITH A BRIDGED NITROGEN ATOM.

4.* THIAZOLO[3,2-a]QUINOLINIUM 1-OXIDE DERIVATIVES

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It is shown that diverse 2-substituted thiazolo[3,2-a]quinolinium 1-oxides can be obtained from 2-quinolylmercaptoacetic acids. The structures of the synthesized compounds were confirmed by the PMR and mass spectra.

Up until recently it was assumed [2, 3] that thiazolo[3,2-a]quinolinium 1-oxides (IIa,b) are formed by the action of acetic anhydride on 2-quinolylmercaptoacetic acids (Ia,b). It was not until 1978 that it was observed [4] that the melting point of the product formed in the reaction of acid Ia and acetic anhydride depends on the conditions under which the reaction is carried out and ranges from 162 to 182°C (according to the data in [3], IIa melts at 194°C). Samples obtained under different conditions also differ with respect to the absorption frequency of the CO group in the IR spectra. On the basis of the data from the PMR spectrum, it was assumed that the isolated compound has the IIIa structure, although the ratio of the intensities of the signals of the protons of the methylene group and the heterorings (1:8) did not correspond to this structure.

*See [1] for communication 3.

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We have established that acetyl derivatives IVa, b are formed when solutions of 2quinolylmercaptoacetic acids Ia, b in purified acetic anhydride are heated to the boiling point, whereas compounds of the III type are formed when the reaction is carried out in a mixture of acetic anhydride and acetic acid [5].

The structures of the synthesized compounds are confirmed by the results of elementary analysis and the PMR and mass spectra. Thus a singlet of the protons of a methylene group with a chemical shift of 4.91 (2H), multiplets of aromatic protons at 7.66-8.16 (9H) and 9.83 (1H), and two doublets centered at 8.30 (1H) and 8.46 ppm (1H) with a spin-spin coupling constant of 10 Hz, one of which is related to the proton in the 5 position of the triazoloquinolinium ring, the other of which is related to the proton in the 4 position of the protonated quinoline ring, are observed in the PMR spectrum of a solution of 2-(2'quinolylmercaptoacetyl)thiazolo[3,2-a]quinolinium 1-oxide (IIIa) in trifluoroacetic acid. The signal at 9.83 ppm probably belongs to the proton in the 9 position of the mesoionic fragment. Its shift to weak field is due to the effect of the electron pair of the adjacent The PMR spectrum of a solution of IIIb differs from the preceding spectrum oxygen atom. with respect to the fact that a singlet of protons of two methyl groups with a chemical shift of 2.77 ppm is observed instead of two doublets at 8.30 and 8.46 ppm. The PMR spectrum of a solution of acetyl derivative IVa contains a singlet of the protons of a methyl group at 2.52 ppm (3H), a multiplet of aromatic protons at 7.69-8.20 ppm (4H), a doublet of a proton in the 5 position of the thiazoloquinolinium ring at 8.53 ppm (1H, J = 10 Hz), and a multiplet at 9.72 ppm, which belongs to the proton in the 9 position of the heteroring. As expected, a singlet of the protons of a methyl group at 2.82 ppm appears in the PMR spectrum of a solution of derivative IVb instead of a signal at 8.53 ppm.

The fragmentation of IIIa,b under the influence of electron impact is basically similar to the fragmentation of 2-(2'-pyridylmercaptoacetyl)thiazolo[3,2-a]pyridinium 3-oxide (V) [6]. The appearance of the principal fragment ions in the mass spectra is due to α cleavage relative to the carbonyl group, cleavage of the S-CH₂ bond, and elimination of a quinoline fragment. In contrast to thiazolopyridinium ion V, appreciable ejection of sulfur is observed in the fragmentation of IIIa,b. A diagram of the fragmentation of thiazolo[3,2-a]quinolinium 1-oxide IIIb is presented below:



The ions corresponding to the principal peaks in the mass spectra of IVa,b differ from one another by 14 amu, as expected for homologs. Their fragmentation is characterized by the successive splitting out of a methyl radical and a neutral CO fragment from the molecular ion. The subsequent fragmentation entails decomposition of the cyclic structure and is

TABLE 1. Data from the Mass Spectra of IIIa, b and IVa, b

Com- pound	m/e values (relative intensities of the ion peaks in percent of the maximum peak)
]]]a	38 (10,1), 42 (5,5), 43 (14,4), 44 (7,8), 49 (8,9), 51 (15,9), 52 (4,3), 58 (3,9), 60 (5,6), 62 (4,0), 63 (10,0), 64 (19,1), 67 (7,7), 69 (5,4), 74 (4,9), 75 (16,1), 76 (7,3), 77 (16,7), 80 (7,5), 81 (15,3), 89 (17,9), 90 (8,6), 96 (4,4), 101 (32,1), 102 (11,5), 114 (7,1), 115 (4,0), 116 (10,3), 117 (20,0), 127 (4,1), 128 (100,0), 129 (28,9), 130 (3,3), 133 (5,9), 140 (8,1), 141 (8,3), 142 (5,1), 160 (11,4), 161 (97,2), 162 (16,5), 163 (6,8), 169 (21,4), 170 (14,6), 171 (3,2), 172 (6,3), 173 (15,4), 174 (11,5), 192 (4,6), 201 (18,7), 202 (13,2), 228 (22,2), 229 (3,6), 243 (14,1), 256 (4,1), 311 (3,2), 339 (3,0), 370 (11,7), 402 (3,7)
IIIP	38 (48,0), 42 (6,4), 43 (19,7), 44 (18,8), 50 (11,5), 51 (24,0), 52 (8,4), 60 (40,0), 62 (8,0), 63 (28,9), 64 (15,2), 65 (4,5), 69 (8,5), 74 (7,9), 75 (13,0), 76 (19,1), 77 (31,5), 78 (7,9), 80 (4,8), 87 (16,5), 88 (18,1), 89 (32,5), 90 (9,2), 91 (5,6), 101 (16,2), 102 (15,9), 103 (15,1), 104 (4,6), 113 (10,9), 114 (16,4), 115 (89,6), 116 (66,8), 117 (10,7), 126 (4,1), 127 (19,0), 128 (25,6), 129 (12,7), 130 (55,7), 131 (18,6), 140 (69,1), 141 (30,8), 142 (92,4), 143 (56,2), 144 (7,9), 147 (5,9), 153 (4,3), 154 (45,3), 155 (13,8), 156 (14,7), 157 (14,8), 159 (6,3), 160 (4,9), 168 (7,1), 169 (11,7), 172 (4,3), 173 (7,8), 174 (15,8), 175 (100), 176 (44,7), 177 (19,8), 183 (93,5), 184 (75,4), 185 (16,4), 186 (10,8), 187 (52,0), 188 (46,4), 189 (9,4), 197 (4,4), 199 (7,7), 200 (4,8), 215 (38,5), 216 (14,4), 225 (7,4), 229 (5,2), 242 (24,8) 243 (4,1), 257 (61,7), 258 (10,1), 283 (4,5), 309 (6,5), 315 (4,3), 316 (4,4), 337 (6,1), 338 (19,9), 339 (5,4), 353 (13,3), 366 (19,2), 367 (5,0), 398 (87,1), 399 (24,7), 400 (7,4), 430 (4,9)
IVa	40 (5,1), 42 (3,2), 43 (100,0), 44 (73,4), 45 (8,0), 50 (9,8), 51 (24,2), 52 (9,9), 55 (3,7), 57 (8,9), 58 (4,0), 62 (2,4), 63 (5,9), 64 (2,3), 69 (3,7), 71 (5,2), 74 (5,6), 75 (26,2), 76 (8,2), 77 (23,8), 78 (3,6), 79 (7,9), 85 (3,2), 89 (7,7), 100 (5,1), 101 (49,8), 102 (16,9), 116 (7,3), 127 (5,8), 128 (80,9), 129 (61,8), 130 (5,9), 133 (4,6), 145 (4,4), 146 (4,0), 160 (9,5), 172 (28,2), 173 (47,4), 174 (6,4), 186 (4,4), 200 (5,3), 201 (6,7), 215 (3,2), 228 (96,2), 229 (21,0), 230 (7,9), 243 (95,8), 244 (20,7), 245 (7,7)
IVb	43 (51,3), 44 (12,8), 45 (3,1), 51 (4,9), 52 (1,9), 63 (5,5), 65 (3,4), 77 (3,4), 89 (9,7), 113 (3,6), 114 (4,5), 115 (35,6), 116 (21,5), 130 (3,2), 140 (14,2), 141 (4,0), 142 (3,4), 143 (27,9), 144 (3,1), 159 (3,3), 186 (21,5), 187 (21,8), 188 (3,9), 215 (4,1), 242 (100,0), 243 (15,5), 244 (5,7), 257 (96,4), 258 (14,6), 259 (5,5)

TABLE 2. Properties of Thiazolo[3,2-a]quinolinium 1-Oxide Derivatives

Com - pound	R	Rı	mp,* °C	Found,%	Empirical formula	Calc., %	Yield, %		
IIIa	н	-coch ₂ s	209—210	C 65,7 H 3,8 N 6,7	C ₂₂ H ₁₄ N ₂ O ₂ S ₂	C 65,7 H 3,5 N 7,0	60		
IIIp	CH₃	-COCH2S	205206	C 66,9 H 4,4 S 14,6	$C_{24}H_{18}N_2O_2S_2$	C 67,0 H 4,2 S 14,9	65		
IVa	н	-COCH3	255	C 64,0 H 3,5 N 5,8	C₁₃H₂NO₂S	C 64,2 H 3,7 N 5,8	66		
IAp	CH3	COCH3	250	N 5,4 S 12,4	C14H11NO2S	N 5,5 S 12,5	72		
VI	Н	$-N = N - C_6 H_4 NO_2$	257—258	N 16,2 S 9,1	C ₁₇ H ₁₀ N ₄ O ₃ S	N 16,0 S 9,2	75		
VII	CH₃	—CSNHC ₆ H₅	262—263	N 8,0 S 18,3	$C_{19}H_{14}N_2OS_2$	N 8,0 S 18,3	62		

*The compounds were recrystallized: IIIa from acetic anhydride; IIIb and IVa,b from pyridine; and VI and VII from dimethylformamide.



Fig. 1. π -Bond orders and effective charges of the thiazolo[3,2-a]quinolinium 1-oxide molecule (the charges for the thiazolo[3,2-a]pyridinium 3-oxide molecule are given in parentheses).

Fig. 2. Projection formula of the thiazolo[3,2-a]quinolinium 1-oxide molecule.

accompanied by the ejection of CO and HCN. The elimination of S or SH directly from the molecular ion is not observed (Table 1).

It should be noted that the melting points of derivatives IVa,b (255 and 250°C, respectively) are higher than for IIIa,b (209-210 and 205-206°C), and the melting points of IIIa and IVb are somewhat higher than the melting points (194 and 227°C) presented in [2] for thiazoloquinolinium 1-oxides IIa,b. It may be assumed that Duffin and Kendall [2] were not dealing with individual compounds but rather with mixtures consisting primarily of IIIa in the first case and primarily of IVb in the second case.

Further studies showed that the action of a mixture of acetic anhydride and pyridine on acids Ia,b at room temperature leads to the formation of different reaction products, whose absorption maxima in acetonitrile solutions (462 and 470 nm, respectively) differ from the absorption maxima of both IIIa,b (455 and 452 nm) and acetyl derivatives IVa,b (452 and 452 nm). The formation of IIIa,b in quantitative yields was observed when these substances were treated with organic acids, and their reaction with electrophilic agents (for example, p-nitrobenzenediazonium ion or phenyl isothiocyanate) leads to 2substituted thiazolo[3,2-a]quinolinium 1-oxides of the VI and VII types. These results indicate the formation from acids Ia,b of thiazolo[3,2-a]quinolinium 1-oxides (IIa,b), which, depending on the conditions, may either dimerize or react with electrophilic agents. Primarily thiazolo[3,2-a]quinolinium 1-oxide (IIa) was evidently obtained in [4], in which the cyclization of Ia was carried out in a mixture of acetic anhydride with triethylamine at room temperature, i.e., under conditions similar to those described above. However, in deuterochloroform, in which the PMR spectrum was recorded, dimerization under the influence of the HCl and DCl contained in the solvent may have occurred; as a result of partial exchange of the protons of the methylene group by deuterium, as in the case of thiazolopyridinium 3-oxide [7], the intensity of the corresponding signal decreased. The fact that thiazolo[3,2-a]quinolinium 1-oxides readily undergo dimerization under the influence of acids confirms the mechanism of the formation of compounds of the III type that was previously proposed [8] for its lower benzo homolog V.

However, the reason for the difference between thiazolo[3,2-a]pyridinium 3-oxide [8], which dimerizes extremely readily, and thiazolo[3,2-a]quinolinium 1-oxide, which is considerably more stable in that it can be isolated from solutions in the solid state and can subsequently be identified in the form of derivatives, remained unclear. This difference cannot be explained by the electronic structure of the thiazolo[3,2-a]quinolinium 1-oxide molecule. In fact, it is apparent from the molecular diagram calculated by the MO LCAO method within the Pariser-Parr-Pople approximation (Fig. 1) that the distribution of charges on the carbon atoms of the thiazolo[3,2-a]pyridinium 3-oxide molecule [8]. It is apparent from the distribution in the thiazolo[3,2-a]pyridinium 3-oxide molecule [8]. It is apparent from the projection of the IIa molecule on a plane (Fig. 2) constructed with allowance for the bond lengths, bond angles, and van der Waals radii [9] that steric hindrance exists

between the oxygen atom and the hydrogen atom in the 9 position. Data from the PMR spectra of derivatives III-VII also indicate the closeness of these atoms. The existence of steric hindrance in the thiazolo[3,2-a]quinolinium 1-oxide molecule should affect the electron density distribution in it and consequently its reactivity. In addition, annelation of the benzene ring leads not only to a decrease in solubility but also should present an obstacle to approach of the carbon atom in the 1 position. The latter also probably determines the lower tendency of this compound to undergo dimerization.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in CH₃CN were recorded with an SF-8 spectrophotometer. The PMR spectra of solutions in CF₃COOH were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the external standard. The mass spectra were obtained by direct introduction of the samples into the ion source with a Varian Mat-311A spectrometer at an ionizing voltage of 70 eV, and a cathode emission current of 1.5 mA under the standard operating conditions for the spectrometer. The quantum-chemical calculation was performed within the Pariser-Parr-Pople approximation with the following set of parameters [10]: $J_{\rm C} = -11.42$, $J_{\rm N} = -23.13$, $J_0 = -27.17$, $J_{\rm S} = -20.27$, $\gamma_{\rm CC} = 10.84$, $\gamma_{\rm NN} = 12.98$, $\gamma_{\rm OO} = 14.58$, $\gamma_{\rm SS} = 9.80$, $\beta_{\rm CC} = -2.32$, $\beta_{\rm CN} = -2.53$, $\beta_{\rm CO} = -2.53$, and $\beta_{\rm CS} = -1.65$ eV.

 $\frac{2-(2'-Quinolylmercaptoacetyl)thiazolo[3,2-a]quinolinium 1-Oxide (IIIa). A mixture of 0.22 g (1 mmole) of 2-quinolylmercaptoacetic acid, 1 ml of acetic anhydride, and 2 ml of acetic acid was heated to the boiling point, after which it was cooled, and the resulting precipitate was removed by filtration and washed with alcohol and ether (Table 2).$

<u>5-Methyl-2-(4'-methyl-2'-quinolinylmercaptoacetyl)thiazolo[3,2-a]quinolinium 1-Oxide</u> (IIIb). This compound was similarly obtained.

<u>2-Acetylthiazolo[3,2-a]quinolinium 1-Oxide (IVa).</u> A mixture of 0.22 g (1 mmole) of 2-quinolylmercaptoacetic acid and 5 ml of acetic anhydride was heated to the boiling point, after which it was cooled, and the resulting precipitate was removed by filtration and washed with alcohol and ether.

<u>5-Methyl-2-acetylthiazolo[3,2-a]quinolinium 1-Oxide (IVb)</u>. This compound was obtained from 4-methyl-2-quinolylmercaptoacetic acid under conditions similar to those in the preceding experiment.

2-(p-Nitrophenylazo)thiazolo[3,2-a]quinolinium 1-Oxide (VI). A 5-ml sample of acetic anhydride was added to a solution of 0.66 g (3 mmole) of 2-quinolylmercaptoacetic acid in 5 ml of pyridine, and the mixture was allowed to stand for 2 h. The precipitated thiazolo-[3,2-a]quinolinium 1-oxide was removed by filtration, washed with alcohol and ether, and mixed with 10 ml of acetonitrile. A 0.71-g (3 mmole) sample of p-nitrobenzenediazonium tetrafluoroborate and 0.3 g (3 mmole) of triethylamine were added to this mixture, and the resulting precipitate was removed by filtration and washed with acetonitrile, alcohol, and ether.

<u>2-Phenylmercaptocarbamoylthiazolo[3,2-a]quinolinium 1-Oxide (VII).</u> A mixture of 0.66 g (3 mmole) of 5-methylthiazolo[3,2-a]quinolinium 1-oxide, obtained by a method similar to the preceding method, 6 ml of phenyl isothiocyanate, and 0.01 g (0.1 mmole) of triethylamine was heated at 80°C for 25 min, after which the precipitate was removed by filtration and washed with alcohol and ether.

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PYRROLES FROM KETOXIMES AND ACETYLENE.

13.* STUDY OF SOME SUBSTITUTED PYRROLES BY ¹³C NMR

SPECTROSCOPY AND CALCULATIONS WITH THE CNDO/2 APPROXIMATION

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The ¹³C chemical shifts of six substituted pyrroles are compared with the calculated charges of the corresponding carbon atoms. The correlation is linear only when the charges of the immediate environment are taken into account. The sensitivity of the ¹³C chemical shift to a change in the charge is increased substantially in 1-vinylpyrroles as compared with their NH analogs. The energetically favorable conformations of the 2-methyl-1-vinyl molecule were established by the CNDO/2 method.

UDC 541.67:547.741:543.422.25

The interrelationship between the conformational and electronic factors in 1-vinylpyrrole molecules was examined qualitatively in [1] by ¹³C NMR spectroscopy. The electron distribution was discussed on the basis of known data [2-5] on the approximately linear interrelationship between the overall and π -charge densities on the carbon atoms and the chemical shifts of the corresponding nuclei. However, the results of many studies are contradictory. The parameters of the correlation equations always depend on the method by which the charges were calculated. In addition, pyrrole derivatives have not been studied independently in this respect but rather have been examined only in combination with other aromatic heterocycles.

In the present communication we present the results of a joint study of a number of 1-vinylpyrroles and model N-unsubstituted pyrroles by ¹³C NMR spectroscopy and the CNDO/2 method. The task of this study was to analyze the interrelationship between the ¹³C chemical shifts and the charge densities on the corresponding carbon atoms in order to quantitatively verify the model of steric inhibition of conjugation developed as applied to 2-substituted 1-vinylpyrroles in [1]. In addition, we set out to ascertain the effect of a vinyl group on the chemical shifts and charges of the ring carbon atoms.

To solve our problem we measured the ¹³C chemical shifts and calculated the charges of the atoms in pyrrole (I), 2-methylpyrrole (II), 2,3-dimethylpyrrole (III), and their 1-vinyl derivatives (IV-VI, respectively). In addition, we measured the ¹³C chemical shifts of 2-tert-butyl-1-vinylpyrrole (VII) and 2-methyl-5-phenyl-1-vinylpyrrole (VIII). The results are presented in Tables 1 and 2.

A comparison of the chemical shifts of the ring carbon atoms in I-III and IV-VI (Table 1) shows that C_3 and C_4 are deshielded under the influence of the N-vinyl group, in conformity with the effect of conjugation:



*See [18] for communication 12.

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