^{13}C NMR SPECTRA OF CYCLIC NITRONES.
2.* 1- AND 4-SUBSTITUTED 2,2,5,5-TETRAMETHYL-3-IMIDAZOLINE 3-OXIDES

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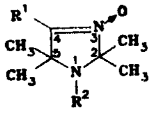
The chemical shift of the carbon atom of the nitrone group in the ^{13}C NMR spectra of 3-imidazoline 3-oxides lies in the region of 117-152 ppm and depends on the electronic effect of the substituents at positions 1, 4, and 5 of the heterocycle. Increase in the electron-withdrawing character of the substituent at these positions leads to an upfield shift of the signal for the nitrone carbon atom, and this corresponds to the increase in electron density on it.

As shown earlier [1], the introduction of the N-oxide oxygen atom into azomethines leads to an upfield shift of the signal for the carbon atom of the C=N group by 30-33 ppm in the ^{13}C NMR spectra. This is due to the increase in the electron density at this atom. In order to extend the discovered relationships and to establish more completely the range of chemical shifts (CS) of the carbon atoms of the nitrone group we compared the ^{13}C NMR spectra of a series of 4-substituted 3-imidazoline 3-oxides with the spectra of the corresponding 3-imidazolines. In connection with the fact that the substituent at position 1 of the heterocycle has a significant effect on the reactivity of the group at position 4 of the imidazoline ring [2-4] we studied the manifestation of the effect of this group in the ^{13}C NMR spectra of 1-substituted 3-imidazoline 3-oxides.

In the spectra of the 4-substituted 3-imidazoline 3-oxides (Table 1) the signal of the $C_{(4)}$ atom is observed 26-33 ppm upfield from the $C_{(4)}$ signals in the spectra of the corresponding 3-imidazolines. The signals of the $C_{(5)}$ atoms are also shifted upfield by 2-10 ppm. An effect smaller in magnitude and less well-defined in direction is observed for the signals of $C_{(2)}$, i.e., 1-2 ppm for the 1-hydroxy and 1-methyl derivatives, whereas the value for the 1-nitroso derivatives varies from −0.5 to −1.8 ppm.

The effect of the R^1 group on the ^{13}C NMR spectra of 4-R^1-1-R^2-2,2,5,5-tetramethyl-3-imidazoline 3-oxides (I–XXIV) was analyzed for compounds containing an identical substituent at position 1 (designated by the same letter). The R^1 and R^2 groups for the investigated compounds are given in Table 2.



I-XXIV

Variation of the substituents at the carbon atom of the nitrone group leads to changes in the chemical shifts of the nitrone carbon similar to the changes in the chemical shifts of the carbon of the carbonyl group in ketones [5]. Thus, the signal of the aldehyde nitrone carbon atom in the compounds is 8.0-8.7 ppm upfield compared with the chemical shift of the ketonitrone group (Table 2). We note that an upfield shift of the C=O signal by 5-10 ppm is observed for the aldehydes compared with the ketones [5]. As in the ketones, substitution of the hydrogen atoms by methyl groups at the α-carbon atom leads to a downfield shift: $\delta(\text{IIIa}) - \delta(\text{IIa}) = 5.4$; $\delta(\text{IIIe}) - \delta(\text{IIe}) = 3.9$; $\delta(\text{IVa}) - \delta(\text{IIIa}) = 1.5$ ppm. Successive substitution of the hydrogen atoms by methyl groups at the $C_{(5)}$ atom also has a similar effect. In the compounds given below each methyl group leads to a similar effect: 3.7, 4.3, and 2.8 ppm.

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*Communication 1 see [1].

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TABLE 1. The ^{13}C NMR spectra of 4-R^1-1-R^2-2,2,5,5-Tetramethyl-3-imidazolines^a

R^1	R^2	Solvent	C$_{(4)}$	C$_{(2)}$	C$_{(5)}$	C$_{R^1}$	2,5-CH$_3$	C$_{R^2}$	Reference
C_6H_5	NO	$CHCl_3$	169,3 (−30,6) 170,1 (−31,4)	89,8 (−0,5) 90,9 (−0,7)	70,9 (−2,2) 70,1 (−2,3)	131,1 (−5,1) (*i*), 128,4 (−0,3) (*o*), 127,7 (−0,7) (*м*), 130,8 (−0,5) (*n*)	28,5; 22,5 29,8; 22,2		—
p-$CH_3C_6H_4$	OH	$(CD_3)_2CO$	173,4 (−33,3)	88,7 (+1,4)	71,2 (−4,5)	131,8 (−7,0) (*i*), 128,1 (−0,9) (*o*), 129,2 (−0,2) (*м*), 141,8 (−2,9) (*n*), 20,8 (+0,4)	26,0; 24,1		[10]
tert-$C_4H_9N{=}CH$	CH_3	$CDCl_3$	172,4 (−28,9)	87,8 (+2,0)	69,3 (−6,0)	150,5 (−5,9) (=CH), 58,1 (−0,3) (—$\overset{\mid}{\underset{\mid}{C}}$—), 29,0 (−0,3) (3CH$_3$)	26,1; 23,9	26,6	[3]
tert-$C_4H_9N{=}CH$	NO	$CDCl_3$	169,5 (−29,8)	91,5 (−1,9)	71,2 (−2,2)	150,2 (−6,8) (=CH), 58,8 (−1,1) (—$\overset{\mid}{\underset{\mid}{C}}$—), 28,7 (0) (3CH$_3$)	27,9; 24,4		[3]
$CH_3ON{=}CH$	OH	$CDCl_3$	167,0 (−26,2)	91,3 (+0,6)	72,4 (−5,6)	145,5 (−7,2) (=CH), 63,4 (−0,3) (OCH$_3$)	26,3; 24,6		[11]
$C{\equiv}N$	CH_3	DMSO-D$_6$	152,6 (−32,8)	91,4 (+1,8)	71,6 (−9,7)	111,8 (−1,2) (CN)	25,7; 23,1	26,8	[3]

Note. a) The difference between the chemical shifts in the spectra of 3-imidazoline 3-oxides (Table 2) and the corresponding 3-imidazolines (R^1 and R^2 identical) is given in parentheses. The 1-nitroso derivatives exist as mixtures of two stereoisomers [12]. Here and subsequently (Table 2) the signals for each form are given according to their relative intensities.

TABLE 2. The ^{13}C NMR Spectra of 4-R^1-1-R^2-2,2,5,5-Tetramethyl-3-imidazoline 3-Oxides (I—XXIV) in Chloroform

Compound	R^1	R^2	$C_{(4)}$	$C_{(2)}$	$C_{(5)}$	C_{R^1}	C_{R^2}	2,5-CH_3	Reference
1	2	3	4	5	6	7	8	9	10
Ib	H	CH_3	136,4	90,6	61,0	—	26,6	23,8; 23,8	
Ie	H	NO	132,8	90,6	66,0	—	—	27,5; 23,2	
			131,8	91,5	65,1			28,2; 22,3	
If	H	NO_2	132,5	91,7	65,9	—	—	23,5; 23,1	
IIa	CH_3	H	143,6	89,9	60,5	8,2	—	26,8; 26,6	[13]
IIb	CH_3	CH_3	144,4	88,6	63,0	8,4	26,3	23,2; 22,7	[13]
IId	CH_3	OCH_3	143,9	90,7	67,2	8,9	64,4	—[a]	[14]
IIe	CH_3	NO	141,5	89,1	67,6	7,8	—	27,0; 22,1	[13]
			140,7	90,0	66,8	8,6		27,2; 21,6	
IIf	CH_3	NO_2	140,6	89,6	67,6	8,4		22,4; 21,7	[3]
IIg	CH_3	NH_2	144,6	89,1	64,9	8,9		22,6; 22,1	[13]
IIIa	C_2H_5	H	149,0	87,2	61,6	17,4; 9,0	—	27,7; 27,2	[13]
IIIe	C_2H_5	NO	145,4	88,7	67,9	17,9; 8,7	—	27,2; 22,1	[13]
			144,7	89,7	67,0	17,0		27,2; 21,8	
IVa	iso-C_3H_7	H	150,5	87,0	62,0	25,8; 17,0	—	28,1; 27,4	—
Vb	CH_2Cl	CH_3	140,8	89,7	62,6	32,0	26,3	23,5; 23,5	—
VIa	$CHCl_2$	H	141,7	88,6	62,3	61,1	—	29,4; 27,0	[2]
VIb	$CHCl_2$	CH_3	140,1	90,1	63,9	59,5	26,3	24,6; 23,6	[2]
VIc	$CHCl_2$	OH	141,7	92,0	67,8	59,9	—	24,3; 23,5	[15]
VIe	$CHCl_2$	NO	137,3	90,1	69,0	59,0	—	27,5; 23,1	[2]
				91,0	67,7	59,4		29,0; 22,3	
VIf	$CHCl_2$	NO_2	137,7	91,2	68,9	59,0	—	23,5; 23,3	—
VIIb	CH_2Br	CH_3	140,6	89,4	62,4	17,9	26,1	23,4; 23,2	[16]
VIIc	CH_2Br	OH	140,2	90,7	65,6	17,5	—	22,8; 22,8	[17]
VIIe	CH_2Br	NO	139,3	89,9	67,5	16,0	—	27,3; 22,6	[16]
			138,5	90,9	66,6	16,6		28,0; 22,2	
VIIf	CH_2Br	NO_2	138,4	90,7	67,6	16,7		22,8; 22,8	—
VIIIa	$CHBr_2$	H	141,9	88,7	62,6	25,2	—	29,1; 27,0	[13]
VIIIb	$CHBr_2$	CH_3	140,0	89,9	63,7	22,9	26,2	23,8; 23,4	[16]
VIIIc	$CHBr_2$	OH	138,6	90,8	66,2	23,2	—	22,5; 22,2	[17]
VIIId	$CHBr_2$	OCH_3	139,9	91,9	68,1	23,8	65,0	—[a]	[14]
VIIIe	$CHBr_2$	NO	137,4	90,3	68,5	21,1	—	27,5; 22,8	[13]
				91,2	67,7			28,7; 22,3	
VIIIf	$CHBr_2$	NO_2	137,5	91,6	68,0	21,0	—	23,3; 23,3	—
IXb	CH_3CHCl	CH_3	144,1	89,8	63,8	47,7; 20,8	26,6	23,9; 23,4	—
IXe	CH_3CHCl	NO	140,0	89,4	68,0	46,4; 20,0		27,2; 22,0	—
				90,2	67,0			27,8; 22,0	
Xb	CH_3CHBr	CH_3	143,5	89,4	63,3	36,4; 20,4	26,3	23,5; 23,1	—
Xe	CH_3CHBr	NO	140,8	89,9	68,0	34,2; 20,7	—	27,6; 22,3	[13]
			140,5	90,7	67,1	34,8; 20,9		28,3; 22,2	
Xf	CH_3CHBr	NO_2	140,7	91,0	68,1	34,5; 20,6	—	23,3; 22,8	—
XIb	$(CH_3O)_2CH$	CH_3	143,2	89,7	63,6	99,3; 56,1	26,6	23,8; 23,8	[2]
XId	$(CH_3O)_2CH$	OCH_3	142,5	91,6	67,8	99,1; 56,2	64,7	—[a]	
XIe	$(CH_3O)_2CH$	NO	140,8	89,7	69,3	99,2; 56,8	—	27,7; 22,5	[2]
				90,7	67,8	99,3; 56,8		28,7; 21,6	—
XIf	$(CH_3O)_2CH$	NO_2	140,5	90,5	69,0	99,0; 56,9	—	23,2; 23,2	
XIIb	CHO	CH_3	142,0	91,8	62,0	181,1	26,4	24,3; 23,8	[16]
XIIe	CHO	NO	138,9	91,7	67,6	180,9	—	27,9; 22,8	[12]
				93,0	66,3				
XIIf	CHO	NO_2	139,4	92,6	67,4	180,4	—	23,6; 22,8	—
XIIIa	*tret*-$C_4H_9N{=}CH$	H	143,9	88,2	61,7	145,2 (C=) 58,9 (—C—) 29,0 ($3CH_3$)	—	28,5; 27,4	[13]
XIIIb	*tret*-$C_4H_9N{=}CH$	CH_3	143,5	89,8	63,3	144,6 (C=) 58,8 (—C—) 28,9 ($3CH_3$)	26,4	23,8; 23,8	[16]
XIIIc	tert-$C_4H_9N{=}CH$	OH	143,4	91,3	67,0	144,1 (C=) 58,7 (—C—) 28,6 ($3CH_3$)	—	23,8; 23,5	[17]
XIIIe	tert-$C_4H_9N{=}CH$	NO	139,7	89,6	69,0	143,7 (C=)	—	27,7; 22,5	[16]
				90,7	67,4	143,5 (C=) 59,3 (—C—) 28,7 ($3CH_3$)		28,0; 22,3	

TABLE 2 (continued).

1	2	3	4	5	6	7	8	9	10
XIIIf	tert-$C_4H_9N=CH$	NO_2	140,4	90,7	69,0	143,7 (C=) 59,6 (—C—) 28,8 ($3CH_3$)	—	23,4; 22,9	—
XIVd	$CH=NOH$	OCH_3	143,0	92,5	68,3	138,5	64,9		[14]
XVb	$C(CH_3)=NOH$	CH_3	143,9	90,5	64,9	149,2; 11,8	26,9	24,1; 24,1	—
XVIb	$CH=NN(CH_3)_2$	CH_3	143,6	87,9	63,0	118,5; 41,8	26,3	23,9; 23,7	—
XVIIa	COOH	H	139,8	91,4	61,9	158,0	—	27,6; 27,1	[2]
XVIIb	COOH	CH_3	139,7	92,3	63,6	158,0	25,8	23,8; 23,3	[2]
XVIIc	COOH	OH	139,3	94,2	67,4	158,2	—	23,7; 23,7	[3]
XVIIe	COOH	NO	136,8	92,0	68,8	156,4	—	27,4; 22,3	[2]
			136,2	93,3	67,6	156,6		27,5; 21,9	
XVIIf	COOH	NO_2	136,9	93,0	69,1	156,3	—	23,5; 23,0	[3]
XVIIIb	$CONH_2$	CH_3	138,8	92,5	63,6	159,8	26,2	24,1; 23,7	[3]
XVIIIe	$CONH_2$	NO	136,7	91,8	69,5	158,4	—	28,0; 22,4	[3]
			136,1	93,0	68,1				
XIX^{b}	CN	CH_3	119,8	93,2	61,9	110,6	26,8	23,8; 23,8	[3]
		NO	118,3	92,6	66,3	108,2	—	27,7; 23,1	[3]
XIXe	CN		117,5	93,8	65,5	108,5		28,0; 22,6	
XIXf	CN	NO_2	117,4	93,7	66,2	108,1	—	23,5; 23,5	[3]
XXa	C_6H_5	H	142,2	87,7	62,0	127,5 (*i*) 127,2 (*o*) 127,9 (*m*) 129,3 (*n*)	—	29,1; 27,2	[13]
XXb	C_6H_5	CH_3	143,2	89,4	64,2	128,0 (*i*) 127,8 (*o*) 128,0 (*m*) 129,5 (*n*)	26,5	24,2; 23,8	[13]
XXd	C_6H_5	OCH_3	141,7	90,9	68,0	127,4 (*i*) 127,9 (*o*) 128,1 (*m*) 129,5 (*n*)	64,7	—^{a}	[14]
XXe	C_6H_5	NO	138,7	89,3 90,1	68,7 67,8	126,0 (*i*) 125,5 (*i*) 128,1 (*o*) 127,8 (*o*) 128,4 (*m*) 130,3 (*n*)	—	27,8; 23,0 29,0; 22,4	[13]
XXIc^{b}	p-$CH_3C_6H_4$	OH	140,1	90,1	66,7	124,8 (*i*) 127,2 (*o*) 129,0 (*m*) 138,9 (*n*) 21,2 (CH_3)	—	24,7; 23,9	[10]
XXIIc^{b}	p-ClC_6H_4	OH	139,2	90,7	66,8	127,3 (*i*) 129,2 (*o*) 127,8 (*m*) 134,2 (*n*)		24,9; 23,9	[10]
XXIIIc	p-$NO_2C_6H_4$	OH	141,1	91,8	67,4	133,5 (*i*) 123,4 (*o*) 128,7 (*m*) 147,5 (*n*)	—	24,6; 23,8	[18]
XXIVc	*o*-$NO_2C_6H_4$	OH	138,2	90,5	67,2	122,0 (*i*) 148,5 (*o*) 129,7 (*o'*) 124,0 (*m*) 132,3 (*m'*) 129,2 (*n*)	—	24,3; 23,2	[18]

Note. a) The signals of the gem-dimethyl groups are broadened at t > 0°C, and with decrease in temperature they appear in the form of four different signals. b) In DMSO.

For the ketones the average value of the relative shift during substitution of a hydrogen atom by one methyl group amounts to 2.4 ppm [5].

Increase in the withdrawing character of the R^1 substituent with the substitution of the hydrogen atoms in the α-methyl group (II) by Cl (V, VI) or Br (VII, VIII) leads to an upfield shift of the $C(_4)$ signal by 2-5 ppm, and a larger number of halogen atoms leads to a larger effect. The OCH_3 groups, which have weaker electron-withdrawing character (a −I effect), lead to a smaller effect: $\delta(XI) - \delta(II) \sim 1$ ppm. From the data from CNDO/2 quantum-chemical calculations (Table 3) it is seen that the substitutions of H by CH_3 in the transition from (Ib) to (IIb) and from (If) to (IIf) leads to a decrease in the total and π

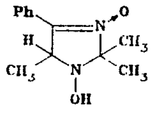
TABLE 3. The Total ($Q_{\sigma+\pi}\cdot 10^3$) and π Charges ($Q_{\pi}\cdot 10^3$)[a] Calculated by the CNDO/2 Method in Compounds (Ib, f, IIb, f, Vf)

Compound	R^1	R^2	$C_{(4)}$	$N_{(3)}$	O	$C_{(2)}$	$C_{(5)}$	$N_{(1)}$	R^1	R^2
Ib	H	CH_3	−10 (−94)	+200 (+837)	−468 (−815)	+210	+109	−204		+80[b]
If	H	NO_2	−67 (−160)	+249 (+809)	−433 (−778)	+213	+162	−187		+567[c]
IIb	CH_3	CH_3	+56 (−40)	+167 (+781)	−478 (−827)	+208	+99	−205	−34	+80[b]
IIf	CH_3	NO_2	+17 (−92)	+204 (+829)	−447 (−796)	+212	+149	−188	−30	+566[d]
Vf	CH_2Cl	NO_2	+10 (−110)	+208 (+842)	−441 (−787)	+211	+162	−191	+51[e]	+569[f]

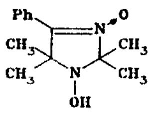
Note. a) The π charges for the C, N, and O atoms of the nitrone group are given in parentheses. b) $Q_{\sigma+\pi}\cdot 10^3$ at the carbon atom. c) The $Q_{\sigma+\pi}\cdot 10^3$ values at the oxygen atoms are −362 and −366. d) The $Q_{\sigma+\pi}\cdot 10^3$ values at the oxygen atoms are −364 and −366. e) The $Q_{\sigma+\pi}\cdot 10^3$ value at the chlorine atom is −145. f) The $Q_{\sigma+\pi}\cdot 10^3$ values at the oxygen atoms are −356 and −361.

charges, which corresponds to a downfield shift. Estimation of the change in the chemical shifts by means of the equation $\Delta\delta = f\Delta Q$, where f = 220 ppm/e for $Q_{\sigma+\pi}$ and 160 ppm/e for Q_{π} (cf. [1]), leads to the following values: $\Delta\delta = \delta(\text{IIb}) - \delta(\text{Ib}) = 14$ (for $Q_{\sigma+\pi}$) and 8.6 ppm (for Q_{π}); $\Delta\delta = \delta(\text{IIf}) - \delta(\text{If}) = 15$ (for $Q_{\sigma+\pi}$) and 11 ppm (for Q_{π}). The experimental value amounts to 8-9 ppm. According to the calculation, the introduction of the Cl atom into the α-methyl group should lead to upfield shift of the $C_{(4)}$ signal by 1.5 ppm, and this also agrees satisfactorily with the experimental data.

$\delta C_{(4)}$ (DMSO)

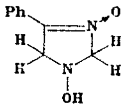


136.1 ppm

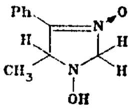


139.8 ppm

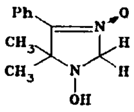
$\delta C_{(4)}$ (DMSO)



133.1 ppm



137.4 ppm



140.2 ppm

Substituents containing the π system of the C=O group (XII), the C≡N group (XIII–XVI), or the aromatic ring (XX) and capable of conjugation with the nitrone group have little effect on the position of the resonance signals for the nitrone carbon atom, leading to an upfield shift by 1-3 ppm (Table 3). A somewhat larger upfield shift (4-5 ppm) of the $C_{(4)}$ signal is observed for the 4-carboxy (XVII) and 4-carbamoyl (XVIII) derivatives. The nitrone carbon atom in the 4-cyano derivatives (XIX) undergoes the largest upfield shift [by 20 ppm, compared with (II)]. The chemical shift of the carbom atom of the nitrone group in the α-aryl nitrones (XX–XXIII) changes little with the introduction of substituents at the para position. The ortho-nitrophenyl group has a somewhat larger effect, leading to an upfield shift of the $C_{(4)}$ signal by about 4 ppm.

On the other hand, the strong π-electron-donating effect of the nitrone group shows up significantly in the position of the α-carbon atom of these groups, leading to their screening. Thus, the signal of the azomethine carbon atom of the imine (XIII), oxime (XIV, XV), and hydrazone (XVI) groups is 10-15 ppm upfield compared with the characteristic positions of these groups [5]. The carbon atoms of the carbonyl (XII) and carbozyl (XVII) groups undergo similar screening (−15 to −20 ppm) by the nitrone group.

The nature of the substituent R^2 at the nitrogen atom at position 1 of the heterocycle has a significant effect on the position of the $C_{(4)}$ signal. The $N_{(1)}$ nitrogen atom with the substituent added to it can be regarded as a substituent both at the $C_{(2)}$ atom and at the $C_{(5)}$ atom. As shown in [1], increase in the electron-withdrawing character of the substituent at the $C_{(2)}$ atom leads to a downfield shift of the $C_{(4)}$ signal. On the other hand, an electron-withdrawing substituent at the α-carbon atom (according to data from the present work) leads to the opposite effect, i.e., an upfield shift. The resultant effect coincides with the latter, i.e., increase in the electron-withdrawing character of the substituent in

TABLE 4. The Characteristics of the Synthesized Compounds

Compound	mp,[a] deg C	UV spectrum, λ_{max}, nm (log ε) (ethanol)	Found, %				Molecular formula	Calculated, %				Yield, %	Reference
			C	H	Hal	N		C	H	Hal	N		
Ib	93—94	233 (4,10)	60,9	10,0	—	18,0	$C_8H_{16}N_2O$	61,5	10,2	—	17,9	83	—
Ie	147—148	236 (4,11)	49,1	7,7	—	25,0	$C_7H_{13}N_3O_2$	49,1	7,6	—	24,6	83	—
If	172—174	238 (4,32)	44,8	7,1	—	22,1	$C_7H_{13}N_3O_3$	44,9	7,0	—	22,2	95	—
Vb	69—71	246 (3,91)	52,4	8,0	17,0	13,8	$C_9H_{17}ClN_2O$	52,8	8,3	17,4	13,7	20	[15]
VIf	156—157	248 (4,11)	35,3	4,8	26,0	15,1	$C_8H_{13}Cl_2N_3O_3$	35,6	4,8	26,3	15,6	75	[15]
VIIIf	189—190	244 (4,08), 265 (3,95)	27,1	3,7	43,9	11,7	$C_8H_{13}Br_2N_3O_3$	26,8	3,6	44,6	11,7	83	[16]
IXb	93—94	246 (3,87)	54,6	8,7	16,2	12,9	$C_{10}H_{19}ClN_2O$	54,9	8,7	16,2	12,8	30	[19]
IXe	125—127	245 (4,18)	46,2	7,1	15,1	17,9	$C_9H_{16}ClN_3O_2$	46,4	6,9	15,2	18,0	85	[19]
Xb	110—111	256 (3,90)	45,3	7,4	30,6	11,0	$C_{10}H_{19}BrN_2O$	45,6	7,2	30,4	10,6	70	[16]
Xe	126—129	250 (4,00)	38,6	5,5	28,5	15,2	$C_9H_{16}BrN_3O_3$	38,9	5,8	28,8	15,1	85	[16]
Xf	146—148	244 (4,00), 265 (3,86)	37,2	5,7	27,5	14,3	$C_9H_{16}BrN_3O_3$	36,8	5,4	27,2	14,3	70	[16]
XId	Oil	240 (3,92)	53,9	9,2	—	11,0	$C_{11}H_{22}N_2O_4$	53,7	8,9	—	11,4	52	[2]
XIf	88—89	241 (4,24)	46,0	7,2	—	15,9	$C_{10}H_{19}N_3O_5$	46,0	7,3	—	16,1	36	[2]
XIIf	173—175	240 (4,15), 301 (3,11)	44,9	6,3	—	19,4	$C_8H_{13}N_3O_4$	44,6	6,0	—	19,5	90	[16]
XIIIf	132—134	238 (3,96), 290 (4,06)	52,9	8,4	—	20,4	$C_{12}H_{22}N_4O_3$	53,3	8,1	—	20,7	80	[16]
XVIb	90—91	272 (3,58), 330 (4,45)	58,0	10,0	—	25,2	$C_{11}H_{22}N_4O$	58,4	9,7	—	24,8	90	[11]

Note. a) Compounds (Ib, e, f, Vb, XIIf, XVIb) were recrystallized from heptane; compounds (VIf, IXb, e, Xb, XIf, XIIf) from a 3:1 mixture of hexane and ethyl acetate; compounds (VIIIf, Xe, f) from ethanol.

the transition from the N—CH_3 to the N—NO_2 derivatives leads in each group of compounds to an upfield shift of the C(4) signal by 3-4 ppm. These results are consistent with data from quantum-chemical analysis of the effect of substitution of the CH_3 groups by the NO_2 group at the N(1) nitrogen atom in compounds (I, II). In both cases this substitution leads to an increase in the electron density at the nitrone carbon atom.

In their effect on the position of the signal for the nitrone carbon atom the hydroxy and methoxy groups occupy an intermediate position between the H and CH_3 groups, on the one hand, and the NO and NO_2 groups, on the other. Thus, the obtained data make it possible to arrange the substituents R^2 in the following order according to the electron-withdrawing effect on the nitrone group in the composition of the heterocycle; NO_2, NO$>$OH, $OCH_3$$>$H, CH_3 This agrees with the data from [4]. A similar order in the effect of the R^2 group is observed for the signals of the carbon atoms adjacent to C(4), i.e., the R^1 and C(5) groups. In the first case an upfield shift of 2-4 ppm is observed with increase in the withdrawing character of the R^2 group, whereas the C(5) signal is shifted downfield by 4-6 ppm. The position of the C(2) signal is less sensitive than that of C(5) to change in the nature of the substituent R^2, and this is reflected in the results from the quantum-chemical calculation (Table 3). In this case the maximum downfield shift is not greater than 3 ppm in (VI) and (VII) and in most cases amounts to approximately 1 ppm.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on an HX-90 spectrometer at 22.63 MHz by a pulsed technique. For the measurements we used 10-15% solutions of the compounds in chloroform or DMSO; to stabilize the resonance conditions at the deuterium nuclei we added ~10% of deuterochloroform and DMSO-D_6 respectively. The chemical shifts were measured with reference to the solvent signal (77.2 and 40.4 ppm from TMS). The accuracy of the measurements was ±0.05 ppm. The signals were assigned by comparison of the intensities in the spectra with full suppression of spin—spin coupling between the ^{13}C and ^1H nuclei.

The quantum-chemical calculations were made by the CNDO/2 method by the set of VIKING programs (at the NMR Laboratory, Moscow State University), realized on a BÉSM-6 computer. The geometry of the N—CH_3 in the derivatives (Ib) and (IIb) corresponded to the data from x-ray crystallographic analysis [6]. For the nitroamines (If, IIf, Vf) the geometric parameters of the N—NO_2 group agreed [7, 8], but the parameters of the heterocycle corresponded to the geometry of the nitroxyl radical 4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-3-oxyl 1-oxide [9], in which the N(1) nitrogen atom is in the same hybridization.

References to the methods for the production of the described compounds are given in Tables 1 and 2. The characteristics of the synthesized compounds and references to their preparation methods are given in Table 4.

1-Methyl-, 1-Nitroso-, and 1-Nitro-2,2,5,5-tetramethyl-3-imidazoline 3-Oxides (Ib, e, f). The compounds were obtained by the decarboxylation of the corresponding 4-carboxy derivatives (XVIIb, e, f). A 0.05-mole sample of the respective acid was boiled in 50 ml of heptane until completely dissolved. The precipitate which separated on cooling was filtered off, washed with heptane, and recrystallized from heptane.

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