3.61 (2H, narrow m, CH_2); 5.66 (1H, narrow m, $=CH_2$); 5.95 (1H, narrow m, $=CH_2$); and 7.79 ppm (5H, m, C_6H_5). ^{13}C NMR spectrum (d_6-DMSO): 11.73 (CH_3); 34.93 (CH_2); 36.65 ($N-CH_3$); 106.5 (3-C); 117.96 ($=CH_2$); 123.99, 126.62, 129.75, 132.40 (C_{arom}); 136.0 (BrC=); 156.0 ppm (C=O).

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VIBRATIONAL SPECTRA, STRUCTURES, AND CONFORMATIONS OF CONJUGATED AZOMETHINES — 3-IMIDAZOLINE DERIVATIVES

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UDC 547.77+548.737+543.424+543.422.2

The possibility of the use of the ratios of the intensities of the $\nu_{C=N}$ bands in the Raman spectra of the compounds to establish the conformations of the conjugated C=N bonds was demonstrated in the case of conjugated azomethines — derivatives of 2,2,5,5-tetramethyl-3-imidazoline and -3-imidazoline 3-oxide.

It was previously shown [1] in the case of imines and nitrones that are derivatives of 3-imidazoline and 3-imidazoline 3-oxide that the ratios of the intensities of the bands of the stretching vibrations of the multiple bonds in the Raman spectra can be used to establish the conformations of molecules with conjugated C=N bonds. However, a quantitative evaluation of the limits of the change in the ratios of the intensities of the $\nu_{C=N}$ bands in the Raman spectra on passing from s-trans to s-cis systems was not made. In addition, the conformations of the 4-acetyl-3-imidazoline derivatives were not established by independent methods, and this did not enable one to draw well-founded conclusions regarding the boundaries of the chang in the ratios of the intensities in the Raman spectra of s-trans and s-cis systems.

In the present research, to obtain a quantitative evaluation of the boundaries of the change in the ratios of the intensities of the $\nu_{C=N}$ bands in the Raman spectra of s-trans- and s-cis-conjugated azomethine systems we studied the Raman spectra in the region of the stretching vibrations of the C=N bonds of a number of derivatives of 4-formyl-2,2,5,5-tetramethyl-3-imidazolines (I-V, Table 1), 4-formyl-3-imidazoline 3-oxides (VI-XI), and 4-acetyl-3-imidazolines (XII-XV) (Table 1), as well as the Raman spectra of model compounds with con-

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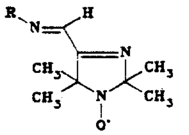
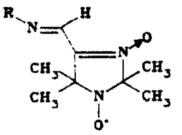
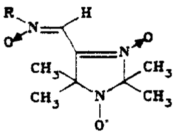
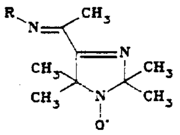
TABLE 1. Frequencies and Ratios of the Intensities of the $\nu_{C=N}$ Bands in the Raman spectra of Conjugated Derivatives of 3-Imidazoline


I-V


VI-X.


XI


XII-XV

Compound	R	$\nu_{C=N}{}^{h}$	$\nu_{C=N}{}^{l}$	$I^{\nu h}/I^{\nu l}$
I	tert-C_4H_9	1653	1613	2,5
II	*cyclo*-C_6H_{11}	1641	1602	3,6
III	OH	1637	1602	2,1
IV	$N(CH_3)_2$	1593	1562	4,5
V	OCH_3	1612	1586	10,0
VI	tert-C_4H_9	1612	1555	2,3
VII	*cyclo*-C_6H_{11}	1617	1559	2,7
VIII	OH	1585	1550	2,0
IX	OCH_3	1570	1543	13,1
X	$N(CH_3)_2$	1559	1533	10,0
XI	tert-C_4H_9	1543	1502	11,4
XII	tert-C_4H_9	1647	1604	0,6
XIII	*iso*-C_3H_7	1637	1607	0,7
XIV	OH	1632	1603	0,3
XV	OCH_3	1605	1598	1,0

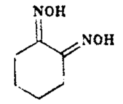
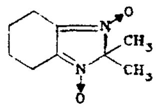
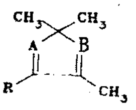
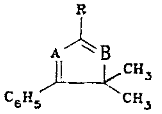
jugated C=N bonds that have fixed s-cis conformations (XVI-XXIII, Table 2). The structures of the 4-acetyl-3-imidazole derivatives — 4-(1-tert-butyliminoethyl)-2,2,5,5-tetramethyl-3-imidazoline 1-oxyl (XII) and 4-methoxyiminoethyl-2,2,5,5-tetramethyl-3-imidazoline 1-oxyl (XV) — were established by x-ray diffraction analysis. Independent confirmation of the s-trans conformation of 1-hydroxy-4-formyl-2,2,5,5-tetramethyl-3-imidazoline derivatives was previously obtained from an analysis of the PMR spectra of imines and nitrones that differ only with respect to the number and position of N-oxide oxygen atoms [1]. Data from vibrational spectro copy made it possible to extend this conclusion also to the corresponding nitroxyl radicals, since their vibrational spectra in the region of the stretching vibrations of the C=N bonds are virtually identical to the spectra of the diamagnetic analogs [1].

As a rule, two bands at 1500-1660 cm^{-1}, which correspond to stretching vibrations of multiple bonds, are observed in the IR spectra and Raman spectra of conjugated azomethines (I-XV, Table 1). For I-XI, which are derivatives of 4-formyl-3-imidazoline (I-V) and 4-formyl 3-imidazoline 3-oxide (VI-XI), it is characteristic that the band with a higher frequency (ν^{h}) in the Raman spectrum has a higher intensity than the band at lower frequency (ν^{l}) (Table 1). Quantitative measurements of the intensities of the $\nu_{C=N}$ bands show that the $I^{\nu h/\nu l}$ ratio ranges from 13.1 to 2.0.

To evaluate the effect of the conformation of the conjugated azomethine system on the $I^{\nu h}/I^{\nu l}$ ratio we examined the Raman spectra of a number of model compounds that contain conjugated —N=C—C=N— and —C=N—C=N— fragments in a fixed s-cis conformation (XVI-XXIII, Table 2). An analysis of the ratios of the intensities of the $\nu_{C=N}$ bands in the Raman spectra of the compounds with an s-cis conformation showed that they are, as a rule, less than 0.25. Thus the $I^{\nu h}/I^{\nu l}$ ratio is extremely sensitive to the conformation of the azomethine fragment. It should also be noted that the principles of the change in the ratios of the intensities in the Raman spectra of conjugated azomethines are similar to those that are known for dienes [2, 3] and α,β-unsaturated carbonyl compounds [4, 5].

The ratios of the $\nu_{C=N}$ bands in the Raman spectra of 4-acetyl-3-imidazoline derivatives XII-XV change substantially ($I^{\nu h}/I^{\nu l}$ = 0.5-1.0) as compared with the spectra of 4-formyl-3-imidazoline derivatives. If one follows the known analogy with α,β-unsaturated ketones [4], the observed change in the ratios of the intensities does not contradict the assumption of an s-trans structure of 4-acetyl-3-imidazoline derivatives. However, taking into account the fact that the interval of the change in the $I^{\nu h}/I^{\nu l}$ value for the $\nu_{C=N}$ bands in the Raman spectra of conjugated azomethines with a different conformation of the multiple bonds was not established, it is difficult to draw a well-founded conclusion regarding the conformation of 4-acetyl-3-imidazoline derivatives.

TABLE 2. Frequencies of the Stretching Vibrations of the C=N and C=C Bonds in the Raman Spectra and Ratios of the Intensities ($I^{\nu h}/I^{\nu l}$) of the Bands Corresponding to These Vibrations

Compound No.	Compound	$\nu_{C=N}$	$\nu_{C=N}$	$I^{\nu h}/I^{\nu l}$
XVI		1654	1586	0,10
XVII		1592	1555	0,15
				
XVIII	A=B=N→O, R=C_6H_5	1555	1531	0,20
XIX	A=N, B=N→O, R=CH_3	1612	1531	0,18
XX	A=N, B =N→O, R=$CBr(CH_3)_2$	1589	1511	0,17
				
XXI	A=N→O, B =N, R=CH_3	1592	1520	0,14
XXII	A=N→O, B =N, R=C_6H_5	1659	1512	0,23
XXIII	A=N→O, B =N→O, R=CH_3	1632	1510	0,10

To solve the problem regarding the conformation of these azomethines and to more reliably evaluate the limits of the change in the ratios of the intensities of the $\nu_{C=N}$ bands in the Raman spectra as a function of the conformation of the azomethine systems we subjected crystalline XII and XV to x-ray diffraction analysis.

TABLE 3. Coordinates of the Atoms ($\cdot 10^4$; $\cdot 10^3$ for H) of XII, XV

Atom	x/a	y/b	z/c
Compound XII			
$N_{(1)}$	3171(9)	2536(19)	2030(3)
$C_{(2)}$	5296(11)	2501(22)	2089(3)
$N_{(3)}$	5998(8)	2565(21)	1450(3)
$C_{(4)}$	4564(10)	2418(18)	1068(3)
$C_{(5)}$	2554(11)	2468(19)	1365(3)
$C_{(6)}$	5982(22)	3763(20)	2407(6)
$C_{(7)}$	5982(25)	1223(22)	2432(7)
$C_{(8)}$	1296(23)	3771(16)	1176(6)
$C_{(9)}$	1351(19)	1220(16)	1252(5)
$C_{(10)}$	4875(11)	2473(21)	377(4)
$N_{(11)}$	3403(8)	2585(16)	44(3)
$C_{(12)}$	7036(14)	2100(15)	197(5)
$C_{(13)}$	3382(10)	2467(16)	−650(4)
$C_{(14)}$A	4976(23)	3248(21)	−982(8)
$C_{(14)}$B	3652(33)	3950(21)	−900(11)
$C_{(15)}$A	4489(31)	1235(24)	−891(12)
$C_{(15)}$B	3442(35)	894(21)	−785(12)
$C_{(16)}$A	1416(28)	3165(31)	−796(16)
$C_{(16)}$B	1216(20)	2300(25)	−828(8)
O	2014(8)	2632(0)	2491(3)
Compound XV			
$N_{(1)}$	2547(4)	1410(4)	8417(4)
$C_{(2)}$	4033(5)	2188(5)	7846(5)
$N_{(3)}$	3098(4)	3677(4)	7231(3)
$C_{(4)}$	1387(5)	3801(5)	7417(4)
$C_{(5)}$	779(5)	2404(5)	8188(4)
$C_{(6)}$	5736(6)	1058(6)	6610(6)
$C_{(7)}$	4498(7)	2559(6)	9124(6)
$C_{(8)}$	−836(6)	2918(6)	9714(5)
$C_{(9)}$	381(6)	1407(6)	7213(6)
$C_{(10)}$	179(5)	5252(5)	6925(4)
$N_{(11)}$	−1481(4)	5191(4)	7105(4)
$C_{(12)}$	854(8)	6635(6)	6305(6)
$C_{(13)}$	−4402(6)	6529(7)	6951(6)
$O_{(1)}$	2762(4)	101(4)	9093(4)
$O_{(2)}$	−2524(4)	6619(3)	6629(3)
$H_{(61)}$	554(5)	81(5)	557(4)
$H_{(62)}$	638(6)	−13(5)	706(5)
$H_{(63)}$	651(6)	142(5)	627(5)
$H_{(71)}$	322(6)	340(6)	1010(5)
$H_{(72)}$	516(6)	311(6)	890(5)
$H_{(73)}$	507(5)	151(4)	964(4)
$H_{(81)}$	−82(5)	206(5)	1024(4)
$H_{(82)}$	−48(5)	365(4)	1044(4)
$H_{(83)}$	−186(5)	367(5)	956(4)
$H_{(91)}$	−64(6)	208(5)	694(4)
$H_{(92)}$	131(6)	122(5)	612(5)
$H_{(93)}$	43(4)	38(4)	770(4)
$H_{(121)}$	73(6)	686(5)	524(5)
$H_{(122)}$	−20(7)	780(6)	695(5)
$H_{(123)}$	166(6)	659(6)	647(5)
$H_{(131)}$	−512(6)	773(5)	661(5)
$H_{(132)}$	−494(6)	657(5)	809(5)
$H_{(133)}$	−411(6)	581(6)	610(5)

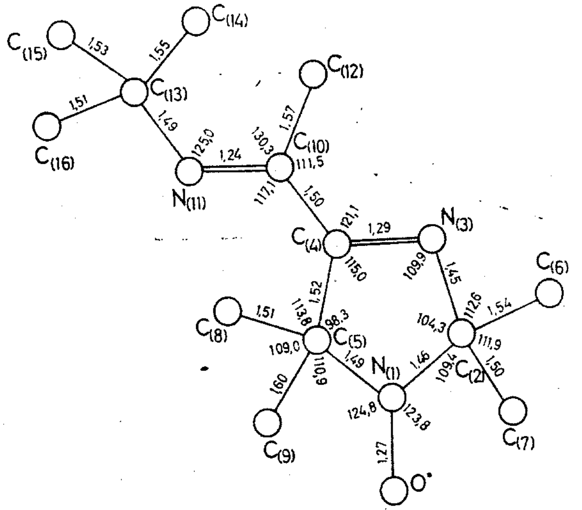
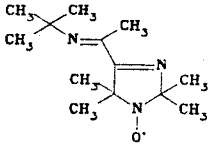
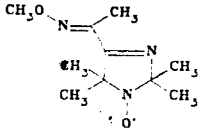


Fig. 1. Geometry of the XII molecule. The standard deviations for the bond lengths and bond angles were 0.01-0.02 Å and 1.3°, respectively.

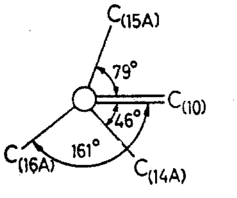


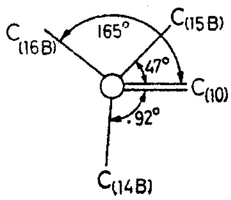
XII



XV

The geometries of the XII and XV molecules are presented in Figs. 1 and 2. The five-membered heterorings of the XII and XV molecules are planar within the limits ±0.05 Å and ±0.007 Å, respectively, and have close bond lengths and bond angles. The conformations of the XII and XV molecules are close to planar s-trans. The angle between the plane containing the $C_{(4)}$, $C_{(10)}$, $N_{(11)}$, $C_{(12)}$, $C_{(13)}$, and $O_{(2)}$ atoms in the XV molecule and the plane of the heteroring is 4° for the XV molecule, as compared with 11° for the XII molecule. Both molecules have an E configuration of the azomethine fragment of the side chain. The conformation of the $C_{(12)}H_3$ group in the XV molecule is such that one of the hydrogen atoms is anti-oriented with respect to $C_{(10)}{=}N_{(11)}$. The OCH_3 group is trans-oriented relative to the multiple bond. Two conformations, which are described by the following Newman projections [see the $N_{(11)}-C_{(13)}$ bond], are observed for the tert-butyl group in XII:





Considering the fact that the IR and Raman spectra of 4-(1-tert-butyliminoethyl)-2,2,5,5-tetramethyl-3-imidazoline 1-oxyl (XII) in the region of the stretching vibrations of the $C{=}N$ bonds are similar to the spectra of XIII and XIV and taking into account the data from x-ray diffraction analysis for XII and XV it may be assumed that conjugated azomethines XIII and XIV also have close-to-planar s-trans conformations of the multiple bonds. Thus the observed differences in the ratios of the intensities in the vibrational spectra of these compounds and 4-formyl-3-imidazoline derivatives are not associated with a change in the conformation of the conjugated azomethine fragment.

This investigation of the vibrational spectra of conjugated azomethines makes it possible to conclude that the ratios of the intensities of the bands of the stretching vibrations of the $C{=}N$ bonds in the Raman spectra are extremely sensitive to the conformation of the azometh-

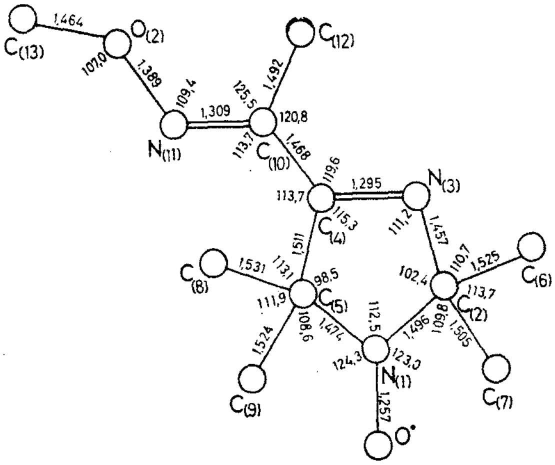


Fig. 2. Geometry of the XV molecule. The standard deviations for the bond lengths and bond angles were 0.006 Å and 0.6°, respectively.

ine system, and the $I^{\nu h}/I^{\nu l}$ value can be used as a criterion in solving the problem of the conformation of the conjugated system; however, for each series of compounds the boundaries of the change in the $I^{\nu h}/I^{\nu l}$ value require additional study. The $I^{\nu h}/I^{\nu l}$ value in the Raman spectra of the s-trans-conjugated azomethines that we studied is generally greater than 0.5, whereas it is less than 0.25 in s-cis systems (Tables 1 and 2).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds (c = 0.25%) were recorded with a Perkin-Elmer 180 spectrometer. The Raman spectra were obtained with a PH-1 spectrometer (Coderg). A Spectra-Physics 125 helium-neon laser (λ = 6328 Å) with a power of 50 mW served as the source of excitation. The spectra were recorded at an inlet and outlet slit width of 4-6 cm^{-1}. The relative intensities of the $\nu_{C=N}$ bands in the Raman spectra were measured for solid samples.

The set of experimental reflections was obtained with a Syntex P2$_1$ diffractometer with the use of MoK_α emission.

The XII crystals were grown from hexane, and the XV crystals were obtained by spontaneous sublimation of XV in a sealed weighing bottle at 20°C. The 4-(1-tert-butyliminoethyl)-2,2,5,5-tetramethyl-3-imidazoline 1-oxyl (XII) crystals had rhombic syngony with a = 6.856(2), b = 9.903(2), and c = 21.418(5) Å at −65°C, space group Pc2$_1$n, and Z = 4. The 4-(1-methoxyiminoethyl)-2,2,5,5-tetramethyl-3-imidazoline 3-oxide 1-oxyl (XV) crystals had triclinic syngony with a = 8.095(5), b = 8.773(5), c = 9.626(5) Å, α = 84.83(4)°, β = 68.18(4)°, and γ = 69.27(4)° at −96°C, space group P$\bar{1}$, and Z = 2. The intensities of the independent reflections (1529 for XII and 2087 for XV) were measured by the method of $2\theta/\omega$ scanning over the range $2\theta < 50°$. In the calculations we used reflections with $I > 2\sigma$ (821 for XII and 1473 for XV). The structures were decoded by the direct method with the MULTAN-XTL program. For the XII crystals selection of the Pc2$_1$n space group was made after observing the fact that the tert-butyl group occupies, with approximately equal mass, two positions that differ with respect to rotation about the corresponding C–N bond. The positions of the hydrogen atoms of XV were found from differential synthesis.

Refinement of the structures was accomplished by the method of least squares in the total-matrix anisotropic-isotropic (for the hydrogen atoms in XV) approximation up to R = 0.090 and 0.065, respectively, for XII and XV. The hydrogen atoms in XII, the positions of which were calculated geometrically, did not participate in the refinement. The coordinates of the atoms and the isotropic temperature factors of XII and XV are presented in Table 3.

The spectral curves, as well as the methods of preparation and physical constants of I-XV, are presented in [6].

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FORMATION OF 1,4- AND 1,5-REGIOISOMERS OF TRIAZOLINES IN REACTIONS OF 2-ETHOXYETHYL AZIDE WITH MONOSUBSTITUTED ETHYLENES

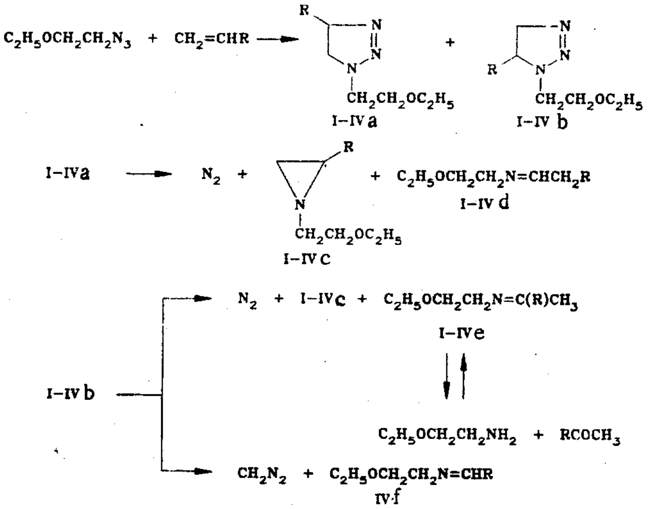
G. A. Lanovaya, V. F. Mishchenko, and E. D. Korniets

UDC 547.791.04:541.11'127'621.22:542.422.25

The structural specificity of the reactions of 2-ethoxyethyl azide with alkenes $RCH{=}CH_2$ [$R = CH_2C_6H_5$, $CH_2OC_6H_{13}$, $CH(OC_2H_5)_2$, C_6H_5] was studied. The formation of 1,4- and 1,5-substituted triazolines and the high stabilities of the latter were demonstrated by PMR spectroscopy, data from gas—liquid chromatography (GLC), and the kinetics of thermolysis.

The understanding of the structural possibilites of reactions involving the cycloaddition of azides to ethylene compounds $CH_2{=}CHR$ is far from complete. The formation of the 1,4- and 1,5-isomers that are possible in such reactions was demonstrated for the reactions of 4-nitrophenyl azide with styrene and 2-ethoxyethyl azide with alkenes [1, 2]. Only one isomer was described in the reactions of azides with vinyl ethers (1,5-isomers) and with methyl vinyl ketone, methyl acrylate, and acrylonitrile (1,4-isomers) (for example, see [3-5] and the liter ature cited therein).

In the present research we investigated the structural specificity of the reactions of 2-ethoxyethyl azide with four monosubstituted ethylenes with different polarities (see the scheme).



I $R=CH_2C_6H_5$; II $R=CH_2OC_6H_{13}$; III $R=CH(OC_2H_5)_2$; IV $R=C_6H_5$

In syntheses with the use of allylbenzene, allyl hexyl ether, and acrolein diethylacetal the elementary compositions of the isolated compounds corresponded to disubstituted 1,2,3-Δ^2-

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Siberian Technological Institute, Krasnoyarsk 660049. Institute of Chemistry and Chemical Technology, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk 660049. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 798-803, June, 1987. Original article submitted December 2, 1985; revision submitted August 11, 1986.

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