

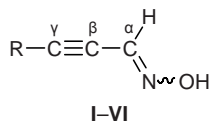
SHORT
COMMUNICATIONSStereospecificity of ^{13}C Shielding Constants
in the ^{13}C NMR Spectra of 3-Substituted Propynal OximesA. V. Afonin, M. M. Demina, T. V. Kon'kova, A. V. Mareev, D. E. Simonenko,
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It was shown previously that some NMR parameters of aldehyde and ketone oximes are stereospecific. Direct ^{13}C – ^1H [1] and ^{13}C – ^{13}C [2], geminal and vicinal ^{15}N – ^1H , and geminal ^{15}N – ^{13}C coupling constants [3, 4] change in going from their *E* isomers to *Z* isomers. In addition, aldehyde oximes are characterized by stereospecific shielding constant of the oxime proton [5], and the shielding constant of the ^{13}C nucleus in the α -position with respect to the $\text{C}=\text{N}$ bond in ketone oximes depends on their configuration [6].

We were the first to reveal that the shielding constants of the ^{13}C nuclei at both triple and double bonds of newly synthesized aldehyde oximes **I–VI** in which the triple bond is conjugated with the $\text{C}=\text{N}$ bond are considerably different for the *E* and *Z* isomers.



I, R = SiMe₃; **II**, R = SiEt₃; **III**, R = GeEt₃; **IV**, R = GePh₃;
V, R = *t*-Bu; **VI**, R = Ph.

The chemical shifts of the ^{13}C nuclei in the oxime fragment and at the triple bond in the spectra of compounds **I–VI** are as follows (C^α , C^β , and C^γ , respectively), δ_{C} , ppm: (*E*)-**I**: 134.40, 96.30, 101.55; (*Z*)-**I**: 130.34, 92.87, 108.49; (*E*)-**II**: 133.89, 97.36, 98.70; (*Z*)-**II**: 129.79, 94.29, 105.61; (*E*)-**III**: 134.31, 97.24, 100.34; (*Z*)-**III**: 130.21, 94.02, 107.55; (*E*)-**IV**: 134.50, 98.85, 96.60; (*Z*)-**IV**: 129.72, 95.17, 103.51; (*E*)-**V**: 135.49, 71.84, 104.57; (*Z*)-**V**: 131.16, 68.73, 111.45; (*E*)-**VI**: 134.06, 81.95, 94.00; (*Z*)-**VI**: 130.07, 79.00,

100.04. The signals were assigned to the *E* and *Z* isomers of aldehyde oximes **I–VI** on the basis of the following considerations. First, the oxime proton in the *E* isomers of **I–VI** appears in the ^1H NMR spectra in a much weaker field than the corresponding proton of the *Z* isomer [5]: its chemical shift ranges from δ 7.3 to 7.5 ppm for the *E* isomers and from δ 6.7 to 6.9 ppm for the *Z* isomers. Second, the direct coupling constant ^{13}C – ^1H for the oxime carbon nuclei increases by 10–15 Hz in going from *E* to *Z* configuration [1]: $^1J_{\text{C}^\alpha\text{H}} = 174$ – 175 and 188 – 189 Hz for (*E*)-**I**–(*E*)-**VI** and (*Z*)-**I**–(*Z*)-**VI**, respectively.

The above data show that the chemical shifts of the oxime carbon nucleus (C^α) and carbon nuclei at the triple bond (C^β , C^γ) change in a regular mode in going from the *E* isomers of aldehyde oximes **I–VI** to their *Z* isomers. The chemical shifts of C^α and C^β regularly decrease by 4–5 and 3–4 ppm, respectively, while the chemical shift of C^γ increases by ~ 7 ppm. Lower chemical shifts of the carbon nuclei in the α -position with respect to the $\text{C}=\text{N}$ bond (C^β in **I–VI**) in the *Z* isomers as compared to *E* isomers were observed previously for aldehyde and ketone oximes having alkyl or aryl groups [6, 7]. However, shielding constants of the oxime carbon nucleus (C^α) and C^γ (which is remote from the $\text{C}=\text{N}$ bond) are related to steric configuration only in the series of oximes having a triple bond. Unusually upfield position of the C^α signal (δ_{C} 130–135 ppm) in the spectra of aldehyde oximes **I–VI** relative to analogous oximes with an alkyl group (δ_{C^α} 145–160 ppm [6]) should be noted. Obviously, conjugation between the triple $\text{C}\equiv\text{C}$ bond and double

C=N bond enhances the shielding constant of C^α by 10–15 ppm [8].

Considerable differences in the chemical shifts of C^α , C^β , and C^γ in the *E* and *Z* isomers of aldehyde oximes **I–VI** are likely to result from different polarizations of the triple bond in those isomers. These differences may be used for both assignment of configuration of α,β -acetylenic aldehyde and ketone oximes and studying their electronic structure by ^{13}C NMR spectroscopy.

(*E,Z*)-3-Trimethylsilylprop-2-ynal oxime (I).

A mixture of 0.38 g (3 mmol) of 3-trimethylsilylprop-2-ynal, 0.21 g (3 mmol) of hydroxylamine hydrochloride, 0.25 g (3 mmol) of sodium hydrogen carbonate, and 9 ml of methanol was stirred for 8 h using a magnetic stirrer. The mixture was then diluted with water until it became homogeneous and extracted with diethyl ether. The extracts were combined and dried over MgSO_4 , the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel using acetonitrile–methanol (10:1) as eluent. Yield 0.27 g (63%), yellow viscous oily material. IR spectrum (film), ν , cm^{-1} : 3260 (OH); 2150, 2140 ($\text{C}\equiv\text{C}$); 1670 ($\text{C}=\text{N}$); 1235 (Me_3Si). Found, %: C 50.87; H 7.68; N 9.82; Si 19.94. $\text{C}_6\text{H}_{11}\text{NOSi}$. Calculated, %: C 51.02; H 7.85; N 9.91; Si 19.88.

Aldehyde oximes **II–VI** were synthesized in a similar way (yield 60–84%).

The IR spectra were recorded on a Specord 75IR spectrometer. The ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 100.61 MHz using CDCl_3 as solvent (*c* = 5–10 wt %) and HMDS as internal reference.

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