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Supporting Information for

Silylation of *N,O*-diacylhydroxylamines: NMR spectra and structure of the products

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Details of structure determination from NMR spectra

NMR data obtained from concentrated chloroform solutions and used for product identification are given in Table 1 (main text). In Table S1 are presented fully assigned ^{13}C and ^{29}Si chemical shifts in diluted solutions, as these are commonly used for compound identification and some shifts have different values than in the concentrated solutions. (Concentration dependent ^1H chemical shifts from the diluted solutions are given in the Experimental Part.)

All the NMR spectra recorded confirm the presence of two isomers in each silylation product. While the parent *N,O*-diacetylhydroxylamines (**5**) have ^{15}N chemical shifts around $\delta = -204$, similarly as the hydroxamic acids (acetohydroxamic acid $\delta = -209^1$, benzohydroxamic acid $\delta = -216^2$), all the ^{15}N shifts found in their silylation products studied here are in the range $\delta = -64$ - -84 , i.e. in the range of imidic acid derivatives.^{2,5} Thus the ^{15}N chemical shifts unambiguously confirm the presence of isomers with C=N double bond only (i.e., exclude the isomeric structure **6**).

Assignments of the *E/Z* isomer structures are based on the direct $^1\text{J}(^{13}\text{C}-^{13}\text{C})$ couplings between C=N carbon and α -carbon. This coupling is larger when the α -carbon is in the *cis* position than when it is in the *trans* arrangement relative to the nitrogen lone pair electrons.^{3, 4, 6-12} The four sp^2 carbon lines in the spectrum of each sample had to be assigned to C=N and C=O carbons of each isomer by $\{^1\text{H}\}-^{13}\text{C}$ experiments using selective decoupling of methyl protons (after the methyl proton lines were assigned by similar $\{^1\text{H}\}-^{15}\text{N}$ experiments, see further). Assignment of *E/Z* pairs of **7/8a,b** was straightforward since all the required couplings were measured (Table 1). For **7/8c** pair we could determine only one such coupling and, in the absence of any $\text{CH}_3\text{-C=N}$ or $\text{CH}_3\text{-C=O}$ methyl group, the method of C=N carbon assignment could not be applied to **7/8d** pair. Other methods were sought through the comparison of available results.

^{15}N chemical shift differences. In *N*-acetyl derivatives (**7/8a,b**) and in silylated acetohydroxamic acid **10/11** and its TMS analogue³, the *E*-isomers have ^{15}N signals shifted downfield from those of *Z*-isomers. The downfield shift depends on the nature of the substituents. Assuming general validity of this observation we assign the isomers in the *N*-benzoyl derivatives (**7/8c** and **7/8d**) as indicated in Table 1. However, one should be aware of that the ^{15}N chemical shift differences are smaller in *N*-benzoyl than in *N*-acetyl derivatives and that data on silylated benzhydroxamic acid for comparison are entirely missing as silylation of benzhydroxamic acid yields only *Z* isomers with the structure similar to that of **11** with ^{15}N chemical shifts around $\delta = -78$. Since in (*E*)- and (*Z*)-*O*'-ethylbenzhydroxamic acid derivatives the opposite orders of ^{15}N shieldings were found⁴ one should be careful in applying this rule and should rather seek an additional support for the assignment. Such support was found in the observations and overall consistency to be described further and so the assignment was accepted.

^{15}N - ^1H couplings. The ^{15}N NMR lines of *Z* derivatives **8a** and **8b** measured without proton decoupling ($\delta = -82$) are split into a 1:3:3:1 quartet with $J(^{15}\text{N}-^1\text{H}) = 3.5$ Hz while the shape of the lines of their *E* isomers **7a** and **7b** ($\delta = -65$) suggests similar splitting but with $J(^{15}\text{N}-^1\text{H}) < 0.5$ Hz. Since four-bond, $^4J(^{15}\text{N}-^1\text{H})$, couplings are observed only in π systems¹³ the observed splittings must be due to three-bond couplings, $^3J(^{15}\text{N}-^1\text{H})$, of nitrogen to protons of the CH_3 group of R unit. This observation provides additional support to our assignment of the isomers **7/8a** and **7/8b** as it agrees with a general observation that the three-bond couplings, $^3J(^{15}\text{N}-^1\text{H})$, in fragments $\text{H}-\text{C}-\text{C}=\text{N}$ are in absolute value larger (~ 4 Hz) when the HC group is *cis* to nitrogen lone electron pair than when it is in *trans* arrangement (~ 1 Hz).^{7, 13} A series of selective proton decoupling $\{^1\text{H}\}$ - ^{15}N experiments utilizing these $^3J(^{15}\text{N}-^1\text{H})$ couplings provided full assignment of all four CH_3 lines in ^1H NMR spectra of **7/8a**. Assignments of CH_3 proton lines in the spectra of **7/8b** and **7/8c** were obvious. Subsequent similar

selective $\{^1\text{H}\}$ - ^{13}C experiments identified CH_3 and sp^2 ($\text{C}=\text{O}$ and $\text{C}=\text{N}$) carbons (see above) of the two units R and R'. The sp^2 ($\text{C}=\text{O}$ and $\text{C}=\text{N}$) carbons in **7/8d** were differentiated according to their couplings with ^{29}Si nuclei ($^2\text{J}(^{29}\text{Si}-\text{O}-^{13}\text{C}=\text{N})$ was 3.3 Hz while $^5\text{J}(^{29}\text{Si}-\text{O}-\text{C}=\text{N}-\text{O}-^{13}\text{C}=\text{O})$ was not observable). The assignment is confirmed by couplings of C-1 aromatic carbons to silicon by $^3\text{J}(^{29}\text{Si}-\text{O}-\text{C}(\text{N})-^{13}\text{C}-1)$ and to the $\text{C}=\text{N}$ carbon. The C-1 aromatic carbons were assigned to different phenyl groups on the basis of their $^1\text{J}(^{13}\text{C}-^{13}\text{C})$ couplings to $\text{C}=\text{N}$ carbons.

^{13}C chemical shifts of α and $\text{C}=\text{N}$ carbons. The α -carbon *anti* to N-electron pair is shielded relative to the *syn* α -carbon in ketoximes¹⁴⁻¹⁶ or thiobenzimidates¹⁷. In the *Z* isomers of hydroxamic acid derivatives the $\text{C}=\text{N}$ carbon shifts are substantially and consistently smaller (by 9 - 10 ppm) than in the *E* isomers.^{3-5, 11, 18} The ^{13}C chemical shifts in **7d** and **8d** as assigned above are in line with these two observations. While no comparison is possible for the **8c** product, the numerical values of the chemical shifts as well as of the couplings in R unit and $\text{C}=\text{N}$ are so close to those of **8d** that these two compounds must have the same structure (**8**).

In an attempt to provide a general tool for assigning the structure to silylated products we measured long-range couplings of ^{29}Si nuclei with ^{13}C carbons. The measurements confirmed assignments of sp^2 - and α -carbon. The two-bond geminal couplings to $^{13}\text{C}=\text{N}$ carbon, $^2\text{J}(^{29}\text{Si}-\text{O}-^{13}\text{C})$, do not exhibit any obvious relationship with the isomer structure. The small three-bond vicinal couplings to α -carbons, $^3\text{J}(^{29}\text{Si}-\text{O}-\text{C}-^{13}\text{C})$, are consistently larger in the *E* than in the *Z* isomer. Though the difference is small (about 1 Hz), it is definitely larger than the experimental error (estimated ± 0.1 Hz). However, more data are needed before a general rule (that $^3\text{J}(^{29}\text{Si}-\text{O}-\text{C}-^{13}\text{C})$ couplings are larger when the nitrogen lone pair is *cis* to OSi group in $\text{Si}-\text{O}-\text{C}(=\text{N})-\text{C}$ moiety) can be put to use for stereochemical determinations.

Table S1. ^{13}C and ^{29}Si NMR chemical shifts (δ in ppm) in diluted chloroform-*d* solutions^a

| Compd. | unit R | | | | unit R' | | | | C=N-O-C=O | | $\text{Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$ | | | |
|--------|--|-----------------------------|-----------------------------|---------------------------|--|-----------------------------|-----------------------------|---------------------------|----------------------------------|----------------------------------|---|--|--|--|
| | $\delta(^{13}\text{C}-1)$ $\delta(^{13}\text{CH}_3)$ | $\delta(^{13}\text{C}-2,6)$ | $\delta(^{13}\text{C}-3,5)$ | $\delta(^{13}\text{C}-4)$ | $\delta(^{13}\text{C}-1)$ $\delta(^{13}\text{CH}_3)$ | $\delta(^{13}\text{C}-2,6)$ | $\delta(^{13}\text{C}-3,5)$ | $\delta(^{13}\text{C}-4)$ | $\delta(^{13}\text{C}=\text{N})$ | $\delta(^{13}\text{C}=\text{O})$ | $\delta(^{29}\text{Si})$ | $\delta(^{13}\text{CH}_3-\text{Si})$ | $\delta(^{13}\text{CH}_3-\text{C})$ | $\delta(^{13}\text{C}-\text{Si})$ |
| 7a | 15.90 | - | - | - | 19.77 | - | - | - | 168.87 | 167.49 | 26.18 | -4.84 | 25.54 | 17.79 |
| 8a | 18.92 | - | - | - | 19.65 | - | - | - | 168.02 | 158.26 | 24.94 | -4.08 | 25.26 | 18.27 |
| 7b | 16.13 | - | - | - | 129.36 ^b | 129.38 | 128.44 | 132.95, 132.96 | 168.61 | 163.73 | 26.75 | -4.81 | 25.61 | 17.84 |
| 8b | 19.07 | - | - | - | 129.36 ^b | 129.64 | 128.33 | 132.95, 132.96 | 159.17 | 164.27 | 24.89 | -3.91 | 25.28 | 18.18 |
| 8c | 131.32 | 127.43 | 128.26 | 131.01 | 19.99 | - | - | - | 156.57 | 168.25 | 26.86 | -3.72 | 25.60 | 18.75 |
| 7c | - | - | - | - | - | - | - | - | - | - | 27.21 | - | - | - |
| 8d | 131.55 | 127.77 | 128.28 | 131.09 | 129.38 | 129.77 | 128.41 | 133.11 | 158.62 | 164.39 | 27.08 | -3.81 | 25.50 | 18.53 |
| 7d | 130.45 | 128.87 | 128.07 | 130.83 | 129.13 | 129.47 | - | 132.92 | 164.94 | 163.65 | 27.78 | -4.76 | 25.74 | 18.06 |
| 10 | 14.33 | - | - | - | - | - | - | - | 163.72 | - | 25.04 ^c 22.26 ^c | -4.62 ^c -5.17 ^c | 26.16 ^c 25.68 ^c | 17.97 ^c 17.78 ^c |
| 11 | 18.82 | - | - | - | - | - | - | - | 154.80 | - | 25.48 ^c 21.69 ^c | -3.94 ^c 5.09 ^c | 26.36 ^c 25.61 ^c | 18.47 ^c 18.45 ^c |

Table S1. cont.

^aChemical shifts in δ scale relative to tetramethylsilane (^{13}C and ^{29}Si). ^bOne of the two lines is hidden under another line. ^cThe line is either not observed or not assigned due to low S/N. ^dTentative assignment: the first value is the shift in Si-O-C= fragment, the second one is in Si-O-N= fragment.

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