# Reconciling theory and experiment for SiH$_3$NCO: A comment to a recent article ☆

Tamás Veszprémi [a,*], Tibor Pasinszki [a], Miklós Fehér [b]

[a] *Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Hungary*
[b] *Chinoin Pharmaceutical and Chemical Works Co. Ltd., Research Analytical Laboratories, H-1045 Budapest, Tó u. 1-5, Hungary*

## Abstract

Contrary to a suggestion in a recent paper in this journal (S.S. Al-Juaid et al., *J. Organomet. Chem.*, **488** (1995) 155), there is no experimental evidence that casts doubt on our calculations that SiH$_3$NCO has a linear SiNCO framework.

Although the quasilinear structure of SiH$_3$NCO seemed to have been established beyond dispute, in a recent paper in this journal [1] the authors suggested that the X-ray data for a range of silicon cyanates cast doubt on the validity of our calculations (see below) that indicated an equilibrium value of 180° for the SiNC angle. To address this suggestion it is first necessary to outline the history of the elucidation of the structure of gaseous SiH$_3$NCO.

Silyl isocyanate was first synthesized in 1962 by Ebsworth and May [2], who observed an infrared spectrum in line with a molecule of C$_{3v}$ symmetry, i.e. with a linear SiNC chain. A similar conclusion on the linearity of the SiNC frame had been drawn from the infrared and Raman spectra of trimethylsilyl isocyanate [3]. In the 1960s, a popular explanation for the unique properties of organosilicon compounds involved the possible interaction between the empty d-orbitals of the silicon atom with the neighbouring groups (the so called d$_\pi$–p$_\pi$ interaction), and this provided a plausible explanation of the linearity of the silyl isocyanate frame, as opposed to the bent frame of methyl isocyanate. Thus an electron diffraction study by Kimura [4], pointing to the frame of trimethylsilyl isocyanate being bent at 150 ± 3 was at first surprising; though a microwave study in the same

year confirmed the linear frame of SiH$_3$NCO [5]. This obvious contradiction was partly resolved in 1972 by Glidewell et al. [6] when they concluded from the electron diffraction pattern that SiH$_3$NCO must possess a low frequency large amplitude bending mode and a considerable shrinkage effect. The results were shown to be interpreted almost equally well in terms of either a linear or a bent equilibrium frame. This was the first recognition of the quasilinearity of this molecule, although an unambiguous equilibrium structure could not be defined. This work was followed by a number of microwave investigations in which, a quasilinear frame was found to fit the observed spectra [7–11].

Ab initio quantum calculation yielded a different picture. It was shown that calculations at the MP2/6-31G* level of theory, a level that reproduced the equilibrium structures of a number of other pseudo-halides [12–14], failed to produce a bent frame for SiH$_3$NCO [15]. It was suggested that by including a number of further effects in the interpretation of higher resolution spectra, the discrepancies between theory and experiment might be resolved, and of these the inclusion of relaxation was shown to be important [16]. However, this work was still open to criticism; it was not clear how improving the level of theory would affect the results. Thus new calculations were performed with improved basis sets and at higher levels of theory (up to TZV2P/QCISD), still predicted a linear frame for SiH$_3$NCO [16]. Furthermore, by using the

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☆ See [1].
* Corresponding author.

linear bending potential function, the microwave spectra could be refitted with a similar standard deviation to that of the microwave work. An alternative assignment could also be given for the microwave spectra with a somewhat better fit. Hence it is clear that neither interpretation of the vapour phase spectra is unique, and that $SiH_3NCO$ is a 'strongly quasilinear molecule'. This statement is in line with the value of the 'correlation parameter', $\gamma_n$, which is defined using the ratio of energy differences between given rovibrational levels and may assume the values of 1 or $-1$ in the limiting cases of a bent or a linear molecule irrespectively [17], the value of $\gamma_n$ being $-0.24$ for $SiH_3NCO$ [17]. The lack of a unique interpretation for the microwave spectra may be due to the fact that the first vibrational level lies so far above the minimum of the potential that even if a small barrier to linearity exists, its presence might not be observable from the transitions involving the ground and excited vibrational levels.

This seems to settle the matter of the vapour phase structure but the authors of Ref. [1] suggested that X-ray data revealing SiNC angles of 158–163° in a range of silicon cyanates, when considered along with the reported angle of 159.8° derived for gaseous $SiH_3NCO$ from microwave studies [9], cast doubt on the equilibrium angle of 179.99° for $SiH_3NCO$ produced by our calculations [12]. We have shown [12,16] that the microwave data are equally consistent with the linear structure and so the only question to be considered is whether the X-ray data have any relevance for the vapour phase structure of $SiH_3NCO$. Athough in many cases there is good agreement between vapour and solid state structures this can only be regarded a coincidence. The interaction forces in the crystal are different, and the case of $SiH_3NCO$ has been commented on as follows: 'The linear ground state for this molecule in the vapour does not persist in the crystal where packing forces appear to constrain the low-frequency bending vibration of the free molecule' [18]. Thus, contrary to the suggestion in Ref. [1], there are no experimental data that cast doubt on the validity of our calculations. We understand that the authors of Ref. [1] have, indeed, already acknowledged that the X-ray data are not, in fact, inconsistent with those calculations [20].

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