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BARRIERS TO TORSION AROUND Si-N BONDS IN AMINOSILANES

EVIDENCE FOR A SMALL CONTRIBUTION FROM DIRECTIONAL p_π-d_π BONDING

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There has been much recent speculation regarding the contribution of p_π - d_π bonding to torsional barriers in formally single bonds.[1] Evidence for directional p_π - d_π bonding in N-S bonds has come from a recent study of acyclic sulphonamides.[2] We have examined a series of aminosilanes in an attempt to see if similar directional bonding exists in Si-N bonds. Spectra of diisopropylaminophenyldichlorosilane, $Pr_2^iNSiCl_2Ph$ at low temperatures showed a broadening of the isopropyl doublet which emerged and separated out below -105°, with $\Delta\nu$ 12.5Hz and $\Delta G^{\neq}$ 37kJ mol^{-1} at the coalescence temperature, -97 ± 3°.[3] The limiting spectrum of this compound had fairly broad lines even though the reference dichlorofluoromethane signal remained moderately sharp ($\Delta\nu$ half-height 3.2Hz at -106°). Spectra of diisopropylaminodiphenylchlorosilane $Pr_2^iNSiPh_2Cl$ and the fluorocarbon compounds $Pr_2^iNSiCl_2C_6F_5$ and $Pr_2^iNSiCl(C_6F_5)_2$ were examined . In all cases the signals broadened and apparently coalesced in the region -100 ± 5°. On further cooling, however, the spectra remained broad and did not split out into discrete absorptions. The formation of broad lines in spectra of compounds containing phenyl groups at temperatures below -100° has been noted previously.[4] Spectra of the aminosilanes Et_2NSiCl_2Ph, $Et_2NSiClPh_2$, and $Me_2NSiClMePh$ showed no broadening at temperatures above -100°. It thus appears probable that in compounds of the type $Pr_2^iNSiCl_2Ar$ and $Pr_2^iNSiClAr_2$ a barrier to torsion around the Si-N bond of <u>ca.</u> 37kJ mol^{-1} exists. The barrier is not sensitive to whether Ar = C_6H_5 or C_6F_5 but decreases rapidly when the Pr_2^iN moiety is replaced by Et_2N or Me_2N. Thus the barrier to torsion appears to be mainly steric in origin with only a minimal contribution from π-bonding. The conclusion is consistent with a broad line n.m.r. study of $(Me_3Si)_2N$ - $SiMe_2Cl$ which established a maximum value of <u>ca.</u> 30kJ mol^{-1} to torsion around the N-Si bond.[5] The possibility that the barriers were due to a rate limiting nitrogen inversion was discounted in view of the decrease in rate with increase in size of the substituent on nitrogen and the recent work which has shown that introduction of a silicon substituent on nitrogen usually leads to an accelerated inversion rate.[6]

Comparison of the above torsional barrier with the following published values for C-C, 44kJ mol^{-1} in Me_2ClC-CMe_3[7] and 28 kJ mol^{-1} in $PhMe_2C$-CMe_2H;[8] for N-C, 39kJ mol^{-1} in Me_3C-NCl_2;[9] and for P-C, 25 kJ mol^{-1} in $(Me_3C)_2$-PCl[9] again suggests that adverse steric effects predominate in the barrier. Thus the $p_\pi - d_\pi$ bond in Si-N compounds is either non-directional[10] or, as has been suggested recently,[11] non existent.

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