The proton spectrum is dominated by strong solvent peaks (monoglyme or dimethylformamide), but four groups of signals attributed to hydrogens associated with the boron atoms are observed. A quartet at τ 10.91 can be collapsed into a singlet (area 1) upon decoupling the highest field boron and, therefore, is assigned to the hydrogen attached to the apical boron. Decoupling experiments in which the basal borons were irradiated gave rise to two closely spaced signals of equal intensity (area 1 each) centered at τ 5.56, H–B(3), and at τ 5.77, H–B(6). Additionally, it was observed that selective double irradiation of only the τ 5.77 resonance noticeably sharpened a broad peak at τ 12.74 (area 1). This latter high-field resonance is located in the region associated with bridge hydrogens of molecules having pyramidal frameworks.[1,2] The double irradiation experiment indicates that the terminal hydrogen located at τ 5.77 is attached to one of the two borons sharing the bridge hydrogen.

Within a pentagonal-pyramidal framework having three borons and two carbons in the base, two isomers are feasible, one with carbons adjacent[3,4] and one with carbons separated by one boron. We propose the latter for the following reasons. (a) The chemical shift of the B–H doublet centered at δ −20.4 in the boron-11 nmr is low for a *nido*-carborane[2] and may reflect the combined field lowering effect of two neighboring carbons.[1] (b) Intuitively, any simple minimal-motion mechanism (*e.g.*, Figure 1) accounting for the formation of the $(CH_3)_3N^+$-$[C_2B_4H_6^-]$ from trimethylamine and 1,6-$C_2B_4H_6$ predicts that when one of the four equivalent borons in the latter compound move from an octahedral vertex to any position in the base of an incipient pyramid the carbons will remain separated by one boron. (c) An isomer with separated carbon atoms is expected to be favored thermodynamically over the one in which carbons are adjacent.[1,5–7]

The previously reported conversions of *nido*-carboranes to *closo*-carboranes usually are effected by high-energy processes[5] and reflect the greater thermodynamic stability of the "closed" polyhedra over their "open" relatives. The reaction of 1,6-$C_2B_4H_6$ with $(CH_3)_3N$, however, represents a reaction in which a *closo*-carborane is converted to a nido system which contains the same number of framework atoms. This behavior is consistent with the idea that the Lewis base introduces an extra electron pair onto the cage of the *closo*-1,6-$C_2B_4H_6$ carborane to form a product having the same number of cage electrons (and framework atoms) as in the nido family $C_nB_{6-n}H_{10-n}$.

Acknowledgment. This investigation was supported, in part, by the Office of Naval Research and by the Public Health Service. The authors wish to thank R. E. Williams and J. Ditter for the sample of 1,6-$C_2B_4H_6$.

(3) T. Onak, R. E. Williams, and H. G. Weiss, *J. Amer. Chem. Soc.*, 84, 2830 (1962).
(4) T. Onak and G. B. Dunks, *Inorg. Chem.*, 5, 439 (1966).
(5) Many pertinent references are cited in the recent review: R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.
(6) R. E. Williams, "Progress in Boron Chemistry," Vol. 2, Pergamon Press, Oxford, 1969, Chapter 2.
(7) We are presently seeking to verify this structural assignment by X-ray diffraction studies.

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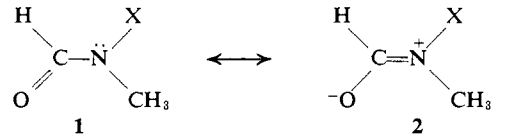
Influence of the Fluorine Atom on Conformational Behavior of Nitrogen in *N*-Fluoroamides and *N*-Fluoroamines

Sir:

The influence of electronegative substituents on the inversion barrier of nitrogen is now well known: if there is no strong conjugation, the electronegativity of the nitrogen substituents increases the height of the inversion barrier.[1]

On the other hand it is known that the rotation barrier along the N–C bond in amides is very high (21.5 kcal/mol for the dimethylformamide[2]) due to the conjugation between the electrons on nitrogen and the carbonyl group. This phenomenon has been studied mostly by varying the substituents on the carbonyl side, or by changing the alkyl groups substituted on nitrogen,[3] but the influence of electronegative groups on nitrogen in amides has not been studied, although a new and easily understandable effect can be expected: an electronegative atom X substituted on nitrogen, as it decreases the basicity of nitrogen, will increase the rate of rotation along the N–C bond in amides, for which free rotation is hindered by delocalization of the nitrogen lone pair toward the carbonyl group (the contribution of **1** in I_X must increase when X is a strong attractor).



1 **2**

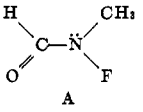
Therefore, to study this predicted effect and to be sure to have as strong an effect as possible we chose the most electronegative of the elements, *i.e.*, X = F, which moreover allows an observation of the phenomenon by ^{19}F nmr combined with the classical pmr.

The *N*-fluoro-*N*-methylformamide (I_F) has been prepared by reacting fluorine with *N*-methylformamide (I_H) according to a procedure already described,[4,5] and the pure compound obtained has been studied by nmr in two solvents of different polarities. Below coalescence temperature, one observes at −70° a pmr spectrum corresponding to two rotamers in unequal amounts (Figure 1): in $CFCl_3$ (low polarity solvent) the higher coupling constant between fluorine and the formyl proton ($^3J_{HCNF}$ = 20.2 Hz) corresponds to the less abundant rotamer (25%), whereas in CD_3COCD_3 (high polarity solvent), the high coupling constant corresponds to the most abundant rotamer (67%); as the most polar rotamer of I_F has to be more abundant in the most polar solvent, we can conclude that the high coupling constants correspond to the most polar rotamer A, and the low coupling constants correspond to the less polar rotamer B of the compound I_F.

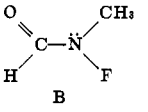
At room temperature these two rotamers are not any more distinguished and the complete shape of the spectra obtained between +30 and −70° leads to the calculation[6] of the mean lifetime τ and of the free

(1) J. M. Lehn, *Fortsch. Chem. Forsch.*, 15 (3), 311 (1970).
(2) M. S. Gutowsky and M. C. Holm, *J. Chem. Phys.*, 25, 1228 (1958).
(3) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 9, 219 (1970).
(4) V. Grakauskas and K. Baum, *J. Org. Chem.*, 35, 1545 (1970).
(5) The fluorination by elemental fluorine has been carried out in an apparatus previously described: C. Michaud, F. Dudragne, S. Bonjean, and J. Leroy, *Bull. Inform. Sci. Tech. C.E.A.*, 161, 51 (1971).
(6) J. J. Delpuech, J. Ducom, and V. Michon, *Bull. Soc. Chim. Fr.*, 1848 (1971).

Table I. Proportion of the Two Rotamers of the *N*-Fluoro-*N*-methylformamide (I_F) and Free Enthalpies of Activation for Rotation Processes in Different Solvents[a]



A



B

Solvent	$^3J_{HCNF}^{trans}$, Hz	Proportion at −70°, %	$\Delta G^{\ddagger}_{25°}$, kcal/mol	A/B	$^3J_{HCNF}^{cis}$, Hz	Proportion at −70°, %	$\Delta G^{\ddagger}_{25°}$, kcal/mol
$CFCl_3$	20.2	25	10.8	3	9.4	75	11.4
40% $CFCl_3$ + 60% CD_3COCD_3 (v/v)		50	11.05	1		50	11.05
CD_3COCD_3	21.5	67	11.2	0.5	9.8	33	10.7

[a] When the two rotamers are in equal amounts (A/B = 1) we have $\Delta G^{\ddagger}_{25°}$ = 11 kcal/mol which is taken as the mean value.

Table II. Free Enthalpy of Activation for the Nitrogen Inversion in N-Substituted Amines II_X of General Formula *t*-BuNXCH$_2$Ph

X	Compd	Solvent	T_c, °C, for CH_2	$\Delta G_c^{\ddagger}$, kcal/mol	Ref
CH_3	II_{CH_3}	CD_2=CDCl	−138	6.2	11
Cl	II_{Cl}	[CD_2Cl_2 + CF_2=CFCl]	−84	9.0	12
F	II_F	$CFCl_3$	25	14.7	This paper
		CD_3COCD_3	34	15.1	
		CD_3CN	35	15.2	

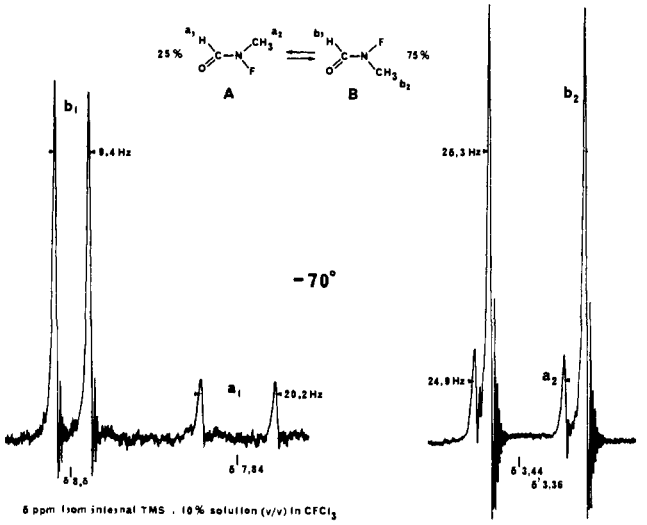


Figure 1. At low temperatures one can observe the different amounts of the two rotamers (most polar A and less polar B) of *N*-fluoro-*N*-methylformamide (I_F).

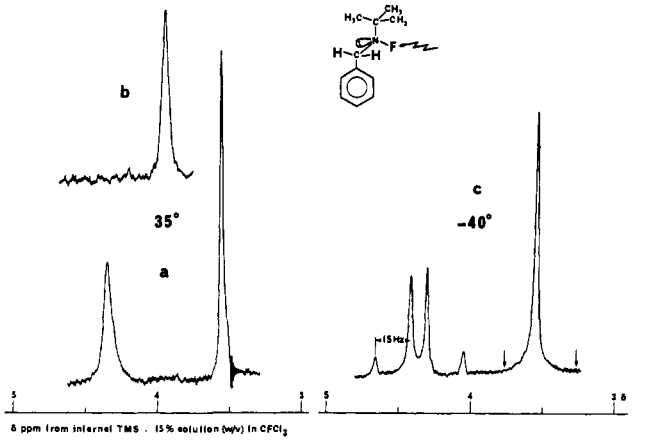


Figure 2. The pmr spectrum of the methylene group in *N*-fluoro-*N*-*tert*-butylbenzylamine (II_F): (a) the mean coupling constant of 49 Hz with fluorine (b) disappears by irradiation of fluorine nucleus, and (c) a quadruplet appears at low temperature indicating that nitrogen then becomes a chiral center. Two distinct values of $^3J_{HCNF}$ are obtained below coalescence: $^3J_{AX}$ = 42 Hz and $^3J_{BX}$ = 58 Hz.

enthalpy of activation $\Delta G^{\ddagger}_{25°}$ for the rotation process along the N–C bond (Table I). The comparison with the dimethylformamide I_{CH_3} is striking: *the N-substituted fluorine atom decreases the rotation barrier in amides by about 10.5 kcal/mol.*

We observe, therefore, that the influence of fluorine is rather large. In order to have a possibility of comparison for this effect of fluorine in amides, we wanted to compare it to the effect of the same N-substituted fluorine on the inversion process in amines. If it can be predicted that fluorine will increase strongly the inversion barrier of amines, a quantitative value cannot be given, since no experiments are reported which would allow calculation of the inversion barrier in *N*-fluoroamines. It has been possible, by coalescence experiments in pmr, to calculate barriers of inversion for amines which are substituted on nitrogen by different groups like alkyl,[7] bromine,[7] chlorine,[7,8] nitrogen,[7] and oxygen,[8] but in the few N-fluorinated amines which have been described, the inversion process is so slow that it is difficult to get the coalescence by heating the nmr sample. For instance, the *N*-fluoro-2,2-bis(trifluoromethyl)aziridine[9] shows an unchanged spectrum until +190° and in the *cis*-*N*-fluorodimethyl-2,6-piperidine the nitrogen appears as a rigid center[10] until the product decomposes (+60°). To obtain a value of the free enthalpy of activation for the inversion in *N*-fluoroamines we fluorinated a noncyclic amine in the series of benzyl-*tert*-butylamine where influence of the nitrogen substituents CH_3[11] and Cl,[12] on the inversion barrier, was already known (Table II).

(7) J. M. Lehn and J. Wagner, *Tetrahedron*, 26, 4227 (1970).
(8) D. L. Griffith, B. L. Olson, and J. D. Roberts, *J. Amer. Chem. Soc.*, 93, 1648 (1971).
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(10) J. Cantacuzène and J. Leroy, *J. Amer. Chem. Soc.*, 93, 5263 (1971).
(11) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, 93, 542 (1971).
(12) C. H. Bushweller and J. W. O'Neil, *Tetrahedron Lett.*, 3471 (1971).

The study of the temperature-dependent pmr spectrum of *N*-fluoro-*N*-*tert*-butylbenzylamine (II_F)[13] leads to the determination of the inversion barrier of nitrogen ($\Delta G_c^{\ddagger}$) at the coalescence temperature T_c (Table II). In the case of $PhCH_2NF$-*t*-Bu (II_F) the spectrum due to the CH_2 group should be, at low temperature, decomposed into two AB subspectra because of the coupling $^3J_{AX}$ and $^3J_{BX}$ with fluorine X ($^3J_{HCNF} \sim 50$ Hz[10]). In fact, one of the AB subspectra is a real quadruplet and gives an A_2 spectrum by increasing the temperature;[14] the other AB subspectrum is a singlet the shape of which is not changing with temperature (Figure 2). The whole pmr spectrum of the CH_2 group leads to a calculation of $^3J_{AX}$ and $^3J_{BX}$, and thus allows the discovery of the X part of the spectrum (F nmr), which is in agreement with what is expected. The effect of fluorine is therefore to increase the barrier of inversion in amines by about 9 kcal/mol, if we compare it to the *N*-methyl homolog (II_F compared to II_{CH_3}), and we can conclude that *the effect of fluorine on the inversion barrier of amines (+9 kcal/mol) is of the same order of magnitude as its effect on the rotation barrier in amides (−10.5 kcal/mol) but, of course, in the opposite sense.*

Acknowledgment. We thank Professor J. J. Delpuech from Nancy who did computations and one of us (J. Leroy) thanks the French Commissariat on Atomic Energy (C.E.A.) for a doctoral fellowship.

(13) The compound II_F has been prepared by the reaction of $FClO_3$ with *N*-*tert*-butylbenzylamine according to a previously described procedure.[10] The elemental analysis, the mass spectrum, and the pmr spectrum are in agreement with the assigned structure: mass m^+/e, M = 181 (0.13); M − CH_3 = 166 (0.47); M − HF = 161 (0.18); M − NF = 148 (1). *Anal.* Calcd for $C_{11}H_{16}NF$: C, 72.89; H, 8.89; N, 7.73; F, 10.48. Found: C, 73.16; H, 9.05; N, 7.75; F, 9.60.

(14) This allows the calculation of $\Delta G_c^{\ddagger}$, according to the formula[7]

$$\Delta G_c^{\ddagger} = 4.57 T_c \left[9.97 + \log \frac{T_c}{(\Delta\nu^2 + 6J^2)^{1/2}} \right]$$

(15) Centre National de la Recherche Scientifique.

(16) C. E. A., Etablissement T.

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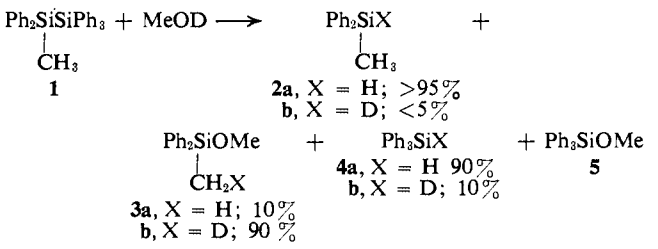
Photochemical Dehydrosilylation of Pentaphenylmethyldisilane. Generation and Trapping of an Unstable Intermediate Containing a Silicon–Carbon Double Bond or Its Equivalent

Sir:

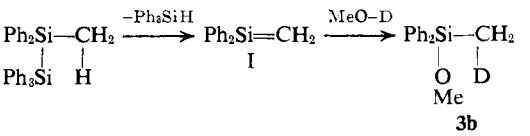
While there has been intense activity in the field of the photochemistry of carbon compounds, photochemical studies of organosilicon compounds have received comparatively little attention. We have initiated an investigation of the photochemistry of organodisilanes and we believe we have firmly established the formation of $Ph_2Si{=}CH_2$ or its close equivalent, the diradical $Ph_2\dot{S}i{-}\dot{C}H_2$.

Absorption of the Ph–Si–Si moiety in the accessible ultraviolet region[1] suggested that phenyl-substituted disilanes would be interesting subjects for photochemical investigations. We have found that when pentaphenylmethyldisilane[2] (**1**) is photolyzed at 2537 Å for 2 hr at 55° in methanol-d_1 and cyclohexane, $Ph_2(CH_2D)SiOMe$



(**3b**) and Ph_3SiH (**4a**) are obtained in approximately 60% yield.[3] **3b** was characterized using nmr and mass spectral techniques. The relative areas of the Si–C–H (m, τ 9.38) and O–C–H (s, τ 6.45) protons show that the isotopic purity is about 90%. An exact *m/e* measurement of the parent peak was carried out and a value of 229.1031 was obtained. This compares well with the calculated *m/e* of 229.1029. The structure and purity of **4a** were determined by comparison of its ir, nmr, and vpc spectra with those of a known sample.[4] It is important to note that the ir spectrum of this compound showed no band at 1550 cm^{-1} where the intense Si–D band is normally found.

These products are consistent with a dehydrosilylation mechanism[5] in which an intermediate like I must be important.[6,7] The overall yield is approximately 90% and the reaction is comparatively free of side reactions. The silanes **2a** and **5** occur in roughly equal amounts



and account for about 20% of the product mixture. These are probably formed from homolytic cleavage of the Si–Si bond in **1** followed by attack of the silyl radicals on the solvents. This process could also account for the presence of **3a** and some of **4a**. Nucleophilic attack on the Si–Si bond by methanol-d_1 is not occurring to a significant extent as shown by the small amounts of **2b** and **4b** in the products.

Further support for the intramolecular nature of this reaction comes from the photolysis of $Ph_2(CD_3)$-$SiSiPh_3$ (**6**) in methanol. The major products were $Ph_2(CD_2H)SiOMe$ (**7**) and Ph_3SiD (**4b**). An exact *m/e*

(1) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.*, **4**, 176 (1964).

(2) H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. Ind. (London)*, 1479 (1958).

(3) Vpc analysis of the product mixture showed six peaks, two of which were less than 2% of the sum of the peak areas and could not be isolated. The remaining four peaks were collected by vpc preparative methods.

(4) Pure samples of **2a**, **3a**, **4a**, and **5** were obtained by independent syntheses and their spectra used for comparison with the spectra of the reaction products.

(5) Intramolecular hydrogen transfer has been observed in the pyrolysis of disilane: P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

(6) Photolysis of I (2537 Å) in cyclohexane gave an insoluble yellow polymer resulting from polymerization of I in the absence of a methanol trap. Formation of dimer or trimer was not observed. The other major product was Ph_3SiH.

(7) It has been observed that the thermolysis of 1,1-dimethyl-1-silacyclobutane yields $Me_2Si{=}CH_2$ which dimerizes in the vapor phase and polymerizes in the liquid phase: M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968). These authors have also reported vapor-phase addition of water to give Me_3SiOH.