exhibited extensive scrambling of the label around the ring. From the ^{13}C spectrum, the enrichment at the ring carbons was estimated (±5%) as 15% (C-1, C-2), 12% (C-6), 8% (C-3), 5% (C-4, C-5). With shorter times or at slightly lower temperatures, the ^{13}C scrambling observed was also in agreement with the suggested mechanism. The excess ^{13}C initially entered C-2, but then began to appear at C-6 and to a lesser extent at C-3 while the ^{13}C content of C-2 and C-1 (ratio 1:5) was far from equivalent. This sequence of incorporation is that expected from the suggested mechanism if the rate of enolization has been drastically slowed in toluene,[7] thus making the rate of the combined enolization ($\rightarrow$ C-2)–interchange comparable with the rate of enolization ($\rightarrow$ C-6)–$\alpha \rightarrow \alpha'$ transfer. It is apparent that the $\alpha \rightarrow \alpha'$ transfer in toluene solutions of **1** is closely related to the thermal rearrangement of allylic esters,[8] and this transfer might be a source of side products in the preparation of unsaturated ketones by the pyrolysis (350–500°) of α-acetoxy ketones.

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by bubbling in nitrogen gas before sealing the tube is sufficient to prevent decomposition.

(7) Enolization is apparently occurring on the glass surface or as a result of collision. The possibility that enolization in the toluene reactions is mainly catalyzed by traces of HOAc formed by slight hydrolysis of **1** by traces of water is discounted because the ^{13}C scrambling results are reproducible, and the addition of 0.1 mol equiv of HOAc to one reaction gave no noticeable increase in the ^{13}C scrambling rate.

(8) E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Amer. Chem. Soc.*, **90**, 662 (1968).

(9) Holder of a National Research Council of Canada Scholarship, 1967–1970.

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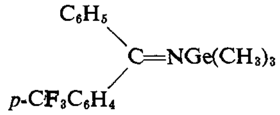
Barrier to Planar Inversion in an *N*-Germyl Imine[1]

Sir:

It has been shown that barriers to pyramidal inversion are significantly lowered when higher row atoms belonging to group IVa (silicon, germanium, tin) are attached to the inversion center.[2] This effect is correlated with the electronegativity of the group IVa element.[2] We now wish to report the first experimental demonstration of a similar effect on the barrier to planar nitrogen inversion.[3] This is also the first reported experimental barrier to inversion (planar *or* pyramidal) at nitrogen bonded to a group IVa element other than carbon.

N-(Trimethylgermyl)-*p*-trifluoromethylbenzophenone imine (**1**) was synthesized by the method of Chan and Rochow,[4] involving the addition of *p*-lithiobenzotrifluoride[5] to benzonitrile with subsequent addition of trimethylgermanium bromide. Distillation (bp 118–119° (0.1 mm)) yielded an analytically pure,[6] clear, yellow oil whose pmr spectrum (*ca.* 15 v/v % solution in $CDCl_3$ with *ca.* 1 v/v % tetramethylsilane) is consistent with the assigned structure: δ 7.60 (s, aromatic H), 7.41 (s, aromatic H), 0.17 (s, $GeCH_3$).



$$(C_6H_5)(p\text{-}CF_3C_6H_4)C{=}NGe(CH_3)_3$$

1

At temperatures below −110° the trimethylgermyl pmr absorption[7] of **1** consists of two overlapping singlets (limiting $\Delta\nu_{AB}$ = 1.1 Hz at 60 MHz) attributed to the syn and anti forms of the imine. These signals coalesce at −108°, and become a sharp singlet at higher temperatures (above −70°). Coalescence is between two uncoupled sites of apparently equal populations, and a first-order rate constant is readily calculated (k_{-108} = 2.4 sec^{-1}) using the Gutowsky–Holm equation.[8] Substitution of this rate constant into the Eyring equation (assuming a transmission coefficient of unity) leads to $\Delta G^{\ddagger}_{-108} = 9.2$ kcal/mol. This value is remarkably low when compared to typical inversion barriers of *N*-alkyl and *N*-aryl imines (similarly substituted at the imino carbon) which range from 17 to 27 kcal/mol.[3a]

Because a modified Pople–Santry–Segal CNDO/2 SCF-MO scheme has been successfully used[9] to calculate barriers to pyramidal inversion for first- and second-row elements, preliminary calculations were performed in the same manner to obtain planar nitrogen inversion barriers of simple imine systems. However, values obtained by this method proved to be appreciably lower than representative experimentally determined barriers.

Use of the standard CNDO/2 parameters,[10,11] with d orbitals deleted from the basis set,[12] afforded barriers to inversion for model imine systems which are in good agreement with the trend exhibited by experimentally measured values.[13] As shown in Figure 1 (solid line), the computed energy barriers correlate reasonably well with the Allred electronegativity[15] values of the N substituents, with the unexplained exceptions of hydrogen and chlorine. This correlation indicates that an *N*-

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[1] This work was supported by the National Science Foundation (GP-22542).

[2] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 773 (1971), and references cited therein.

[3] For a discussion of possible mechanisms of stereomutation at the carbon–nitrogen double bond, see, for example: (a) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); (b) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); (c) M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971). The lateral shift mechanism is assumed to account for the present results, even though the less likely alternatives (torsion or torsion–inversion) cannot be rigorously excluded.

[4] L.-H. Chan and E. G. Rochow, *J. Organometal. Chem.*, **9**, 231 (1967).

[5] Prepared from the metal–halogen exchange reaction of *n*-butyllithium and *p*-bromobenzotrifluoride.

[6] *Anal.* Calcd for $C_{17}H_{18}NF_3Ge$: C, 55.80; H, 4.96; N, 3.83. Found: C, 55.97; H, 4.88; N, 3.80.

[7] A *ca.* 20 v/v% sample of **1** in dimethyl ether with *ca.* 5 v/v% dichloromethane as internal reference was used for the variable temperature study.

[8] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[9] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6507 (1971).

[10] As contained in the program CNINDO (P. A. Dobosh) received from the Quantum Chemistry Program Exchange (QCPE), Bloomington, Ind.

[11] The CNDO/2 scheme has previously been used to study the effects of heteroatoms attached to the imino carbon upon both the inversional and the torsional mechanisms of isomerization: see M. Raban, *Chem. Commun.*, 1415 (1970).

[12] With d orbitals included, minima were not obtained in the potential curve for inversion for reasonable values of the out-of-line angle when the substituent on nitrogen was SiH_3 and Cl.

[13] The barriers for a majority of these systems appear to be too high to be experimentally accessible. However, the calculated values are consistent with the available data for imines of the type ArAr′C=NX[3a] (all numerical values in kilocalories per mole): X = CH_3, 25–27; OCH_3, >39; Cl, >31. When X is C_6H_5, the measured barrier range is 17–20, compared to a calculated value of 23.2. Inversion barriers for imines with X = OH, NR_2, and F are not available, and for X = H, bimolecular proton exchange interferes with a barrier determination.[14]

[14] J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5085 (1965).

[15] A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

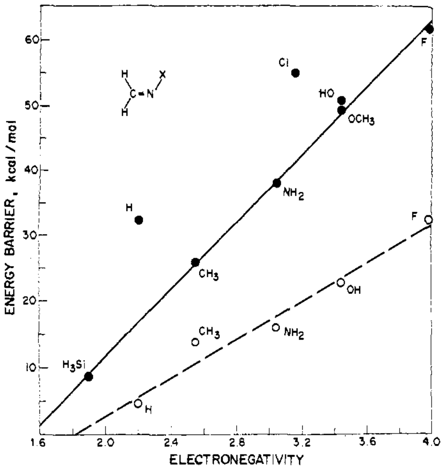

Figure 1. Calculated barriers of planar nitrogen inversion in $H_2C{=}NX$ *vs.* Allred electronegativity of the atom in group X bonded to the imino nitrogen: solid line and solid circles, values from CNDO/2 scheme (present work); dashed line and open circles, values from EHMO calculations.[16]

germyl imine should have a barrier to inversion of *ca.* 12 kcal/mol, based on an electronegativity of 2.01 for germanium,[15] in reasonable agreement with the barrier observed for **1**.

Previously reported[16] EHMO calculations on $H_2C{=}NX$ have indicated a similar trend of planar nitrogen inversion barriers *vs.* electronegativity of first-row elements (dashed line, Figure 1). However, barriers obtained by this method appear to be considerably lower than expected for comparable imine systems.[3a,13]

(16) F. Kerek, G. Ostrogovich, and Z. Simon, *J. Chem. Soc. B*, 541 (1971).

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Boron–Carbon Coupling Constants. I. 1-Methylpentaborane(9)

Sir:

Since the first direct determination of a $^{11}B-^{11}B$ coupling constant from our laboratories,[1] we have been interested in obtaining qualitative and semiquantitative information concerning the factors which influence boron–boron coupling constants. In connection with this study, it became of interest to examine the ^{13}C chemical shifts and possible carbon coupling constants to boron in some of the organoboron compounds used in this research. We wish to report here some preliminary data on the ^{13}C spectrum of 1-methylpentaborane(9). A more detailed presentation of $^{11}B-^{11}B$ and $^{11}B-^{13}C$ coupling constants will be the subject of future publications.[2]

The ^{13}C spectra were obtained on a Varian XL-100-15 nmr spectrometer operating in the Fourier transform mode at 25.2 MHz. The ^{13}C spectrum is shown in Figure 1. The chemical shift of the methyl carbon is 205 ppm more shielded than that of CS_2. The value of the boron–carbon coupling constant is 72.6 ± 0.5 Hz. Experimental work is currently in progress to determine the sign of J_{BC}.

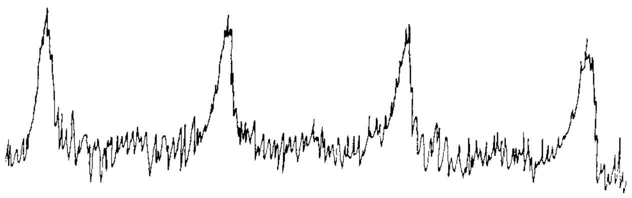

Figure 1. ^{13}C nmr spectrum (25.2 MHz) of neat $1\text{-}CH_3B_5H_8$ after 12,000 pulses, with an acquisition time of 4 sec per pulse, showing a J_{BC} of 72.6 Hz. The methyl carbon is shielded with respect to CS_2 by 205.0 ppm. A capillary of C_6F_6 furnished the ^{19}F lock signal.

Since this is the first reported $^{11}B-^{13}C$ coupling constant for a boron nucleus in a nonsymmetrical environment,[3] it is of interest to examine this coupling constant in terms of the nature of the carbon–boron bonding in this molecule. It can easily be shown from approximate molecular orbital and valence-bond theories of spin-coupling constants[4-6] that *if* the coupling constant is dominated by the Fermi contact mechanism, the coupling constant, J_{AB}, can be "related" to the fractional "s character" in the bond between atoms A and B; hence the hybridization of the atoms. Thus, if the Fermi contact mechanism dominates J_{BC} we can deduce a *crude* value for the hybridization of the apex boron in $1\text{-}CH_3B_5H_8$.

To accomplish this, one can compare boron–carbon couplings to carbon–carbon coupling constants by multiplying the value of J_{BC} by the ratio of the magnetogyric ratios, γ_C/γ_B. The calculated value of 57 Hz is reminiscent of J_{CC} values observed in $CH_3C({=}O)X$ compounds when X is an electronegative substituent,[7] *i.e.*, J_{CC} values between 54 and 59 Hz. From this comparison, one can conclude that the value obtained for J_{BC} in $1\text{-}CH_3B_5H_8$ is not unlike the values for J_{CC} found for sp^3-hybridized carbons bound to sp^2-hybridized carbons.

Recently, Blizzard and Santry have confirmed that the Fermi contact contribution to J_{CC} is the dominant mechanism.[8] Pople and Santry[9] and, more recently, Jameson and Gutowsky[10] have shown that the orbital-dipole contribution to the coupling constant (the second largest contributing mechanism[7]) would increase as one goes from lithium to fluorine in the periodic table. It would be expected that the orbital-dipole mechanism contributes even less to J_{BC} values than to J_{CC} values and, therefore, an approximate hybridization for the apex boron in $1\text{-}CH_3B_5H_8$ is sp^2. This hybridization

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(1) J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Amer. Chem. Soc.*, **93**, 3529 (1971).

(2) P. D. Ellis, J. D. Odom, and D. W. Lowman, manuscripts in preparation.

(3) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 4940 (1969), were the first to report a value of J_{BC}. They determined J_{BC} in the tetraphenylborate anion. However, there was not a discussion of this coupling constant in their communication. We wish to thank the referee who pointed out this reference to us.

(4) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768, 1471 (1959).

(5) H. S. Gutowsky and C. Juan, *ibid.*, 37, 2198 (1962).

(6) H. M. McConnell, *ibid.*, 24, 460 (1956).

(7) G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel, *J. Magn. Resonance*, **1**, 41 (1969).

(8) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).

(9) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1963).

(10) C. J. Jameson and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **91**, 6232 (1969).