be altered by solvent acid concentration. The absence of significant amounts of 4-nitro-*o*-xylene under any conditions of solvolysis of **4** rules out multistep rearrangements passing through ion **2**. In addition, this result implies that reversion of ion **1** to xylene (or encounter pair) is unimportant. Thus, addition–elimination products are required for a material balance.

One can estimate from the overall change in nitro-*o*-xylene isomer ratios that about 40% of the substitution proceeds *via* the $\sigma$ complex **1**.[6] For nitration at 60% $H_2SO_4$, this implies that about 66% of the products are nitro-*o*-xylenes; the remainder should be found as 3,4-dimethylphenol or products stemming from nitration and sulfonation of 3,4-dimethylphenol. When *o*-xylene was nitrated in 60% $H_2SO_4$, following the conditions reported by Coombes and Russell,[1] the following product distribution was obtained by gas chromatographic analysis: 3-nitro-*o*-xylene, 29%; 4-nitro-*o*-xylene, 38%; and mono- and dinitro-3,4-dimethylphenols, 33%.[7]

Perrin has discussed the potential importance of aromatic electrophilic attack at the substituent position (*ipso* attack).[8] Results reported here show how such processes can modify the yield and distribution of product in the superficially straightforward nitration of *o*-xylene. One can envision analogous situations arising in a number of polyalkylbenzene systems. The need to carefully consider *ipso* attack whenever one attempts to rationalize product or rate data in aromatic substitution reactions seems clear.

**Acknowledgment.** We thank Dr. John Penton for drawing our attention to this problem and for a number of valuable discussions. The interest, encouragement, and facilities made available by Professor H. Zollinger are gratefully acknowledged.

(6) This estimate is based on the assumption that the percentage of ion 3 formed is independent of acidity and that the nitration products formed in 70% $H_2SO_4$ represent a complete material balance.

(7) Coombes and Russell reported variable amounts of uncharacterized "highly polar oxidation product of *o*-xylene, particularly at lower acidities." [1]

(8) C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, **93**, 3389 (1971).

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## Synthesis of a Zwitterion *nido*-Carborane from 1,6-Dicarba-*closo*-hexaborane(6) and Trimethylamine

*Sir:*

We wish to report a new carborane obtained as a dipolar ion, 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$], from the reaction of 1,6-dicarba-*closo*-hexaborane(6) with trimethylamine. From available evidence a pyramidal structure is suggested with the nitrogen bonded to a boron atom in the pentagonal base, Figure 1.

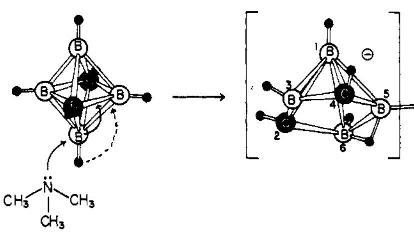

Figure 1. Reaction of 1,6-$C_2B_4H_6$ with trimethylamine to give 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$] (proposed overall mechanism).

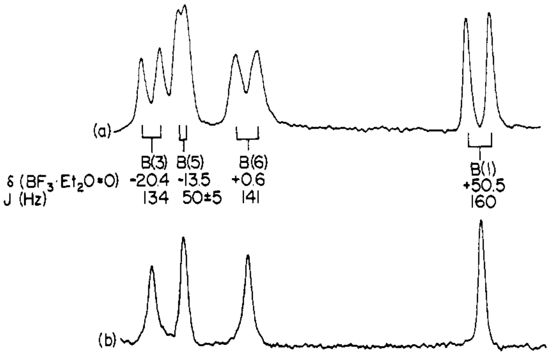

Figure 2. Boron-11 nmr of 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$] at 32.1 MHz: (a) undecoupled, (b) proton noise decoupled.

The reaction of 1,6-$C_2B_4H_6$ (5.98 mmol) with $(CH_3)_3N$ (15.20 mmol) was conducted in a sealed glass vessel. After 1 day at room temperature a white crystalline material began to form on the walls of the container. The contents of the vessel were allowed to stand with stirring for 10 additional days after which time any unreacted volatile starting materials were separated and measured. Both $(CH_3)_3N$ (10.52 mmol) and 1,6-$C_2B_4H_6$ (1.27 mmol) were recovered indicating that the reaction had proceeded to nearly 80% completion to give a compound with a 1:1 ratio of 1,6-$C_2B_1H_6$ and $(CH_3)_3N$. The new compound is a thermally stable white solid that does not appear to dissociate at ambient temperatures. It is soluble in polar solvents such as monoglyme and *N,N*-dimethylformamide but insoluble in carbon disulfide, chloroform, and trimethylamine. This suggests that the new product has ionic or partial ionic character, for every previously known parent carborane has reasonable solubility in a nonpolar solvent such as a carbon disulfide.

The boron-11 nmr of the new material is composed of four equal intensity doublets (Figure 2), three of which have coupling constants large enough to indicate B–$H_{terminal}$ groups.[1] The separation of peaks in the fourth doublet $\delta$ −13.5 ($J = 50 \pm 5$ Hz) is much too small for terminal-hydrogen coupling but is not unusual for bridge-hydrogen to boron splitting.[1] Since this boron has no terminal hydrogen, it is proposed that this atom is the site of attachment to the -$N(CH_3)_3$, a group which would not be expected to cause further observable splitting. One of the three B–$H_{terminal}$ doublets, $\delta$ +50.6, is located at very high field strongly suggesting an apical environment within the framework of a pyramid.[1,2] The other low-field resonances are in the region expected for borons located at the base of this pyramid.

(1) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(2) T. Onak and J. Spielman, *J. Magn. Resonance*, **3**, 122 (1970), and references cited therein.

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 $\tau$ 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 $\tau$ 5.56, H–B(3), and at $\tau$ 5.77, H–B(6). Additionally, it was observed that selective double irradiation of only the $\tau$ 5.77 resonance noticeably sharpened a broad peak at $\tau$ 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 $\tau$ 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 $\delta$ $-20.4$ 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-$C_2B_4H_6$.

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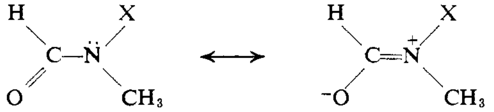
## Influence of the Fluorine Atom on Conformational Behavior of Nitrogen in *N*-Fluoroamides and *N*-Fluoroamines

*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 $\tau$ and of the free

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(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).