A Monomeric Aldiminoborane and Evidence for BN π-Bonding

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THE question of BN π-bonding has attracted much attention (*e.g.*, see ref. 1 for the most recent paper), but solely with respect to aminoboranes. We now report the results of a new approach.

Di-n-butyl-(t-butylaldimino)borane, b.p. 72—75°/0·3 mm., m.p. 74—76°, was prepared by the two reactions shown below. Although it is dimeric in benzene solution, it is monomeric in the vapour at $>\sim 70°$, as is evident from (i) the b.p. (*cf.*,[2] $\mathrm{Bu^n{}_2BNEt_2}$, b.p. 77°/0·3 mm., which has a similar molecular weight), (ii) the vapour density at $\sim 110°$ (we thank Dr. J. D. Smith for this result), and (iii) the mass spectrum. The infrared spectrum of the monomeric vapour has a strong band at 1840—1850 $\mathrm{cm.^{-1}}$, which is absent in the dimer; the latter has, instead, a strong band at $\sim 1670\ \mathrm{cm.^{-1}}$ The very-high-frequency band found in the spectrum of the monomer is consistent with the postulate of there being a significant degree of BN π-bonding. This is emphasized by the canonical form $>\overset{-}{B}=\overset{+}{N}=C<$; an implication is linearity at nitrogen. Thus, an iminoborane, like an allene (and other cumulative systems), is characterized by an asymmetric stretching vibration at high wavenumber.

The C=N stretching vibration in related monomeric silicon compounds (in which SiN π-bonding is not likely to be so significant) falls[3] at 1600—1700 $\mathrm{cm.^{-1}}$, and the BN stretching vibration in monomeric aminoboranes generally[4] lies at 1350—1500 $\mathrm{cm.^{-1}}$

Earlier attempts to make iminoboranes have invariably afforded dimers,[5,6] (but see Wade and his co-workers;[7] we thank Dr. Wade for exchange of information), although in one case evidence of a transiently stable monomeric intermediate was obtained.[5] The present result is attributed, in part, to a choice of substituents at boron and carbon which ensures some degree of steric hindrance towards dimerization.

$$\mathrm{Bu^n{}_3B} \xrightarrow[\text{or (ii)}]{\text{(i)}} (\mathrm{Bu^n{}_2B{\cdot}N{:}CHBu^t})_n$$

(i) $\mathrm{Bu^tCN}$; 150—160°

(ii) $\frac{1}{2}\mathrm{Et_3N,BH_3} + \frac{3}{2}\mathrm{Bu^tCN}$; 110—130°

(*Received, January 8th*, 1968; *Com.* 026.)

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