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Preliminary communication

RESTRICTED ROTATION ABOUT THE BORON–NITROGEN BOND IN DIALKYLAMINOFLUOROPHENYLBORANES

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Summary

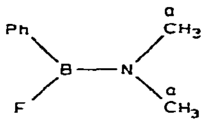
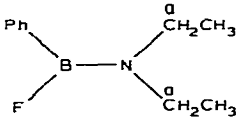
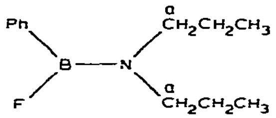
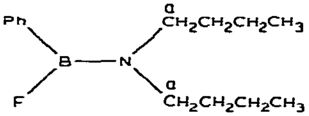
The application of variable temperature ^{13}C NMR to the study of dialkylaminofluorophenylborane has enabled $\Delta G^{\star}$ values for the rotational barrier about the boron–nitrogen bond to be determined.

The observation in the ^{1}H NMR spectrum of dimethylaminofluorophenylborane of a single methyl resonance at temperatures down to 223 K was assumed by Barfield [1] to indicate a low barrier to rotation arising from substantial backbonding from fluorine to boron. The results of our study of a series of dialkylaminofluorophenylboranes, by VT ^{13}C NMR, indicate that boron–nitrogen p_π–p_π-bonding in these compounds is significant. A value of $\Delta G^{\star}$ was obtained from each pair of resonances arising from isomer shifts, $\Delta\nu$, and coalescence temperature, Tc, using the relationship $\Delta G^{\star} = 4.57\ Tc\ [9.97 + \log_{10}(Tc/\Delta\nu)]$ derived by Pople [2]. Table 1 lists our results together with reported $\Delta G^{\star}$ values for the corresponding chlorodialkylaminophenylboranes for comparison.

The barrier to rotation is affected by a combination of the steric and electronic effects of substituents. It is well established that mesomeric back donation from halogen to boron in acyclic 3-coordinate boranes is F >> Cl which would lead to the expectation of substantially lower $\Delta G^{\star}$ values for the dialkylaminofluorophenylboranes when compared to their chlorodialkylaminophenylborane counterparts. Contrary to expectations, however, the $\Delta G^{\star}$ values for the dialkylaminofluorophenylboranes are not only significant but are of the same order as those reported for the corresponding chlorodialkylaminophenylboranes. The similarity in the results suggests that as the halogen size decreases in the order Cl > F, planarity of the *N,N*-dialkyl groups with the plane of the 3-coordinate boron would be achieved more easily in

TABLE 1

VT ^{13}C NMR RESULTS FOR DIALKYLAMINOFLUOROPHENYLBORANES
($\Delta G^{\star}$ values for analogous chlorodialkylaminophenylboranes ^{a})

Compound	Carbon	$\Delta\nu$(Hz)	Tc	$\Delta G^{\star}$ (kcal/mol)	$\Delta G^{\star a}$ (kcal/mol)
	a	54.2	386	19.1	20.3(3)
	a	43	362	18.0	19.2(3)
	a	43	369	18.4	19.2(3) 19.6(4)
	a	46	370	18.4	19.7(3) 19.7(4)

the less sterically hindered dialkylaminofluorophenylboranes thus permitting back bonding from nitrogen to occur in opposition to that from fluorine thus producing the observed rotational barriers.

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