Boron, Nitrogen, and Fluorine Nuclear Quadrupole Coupling and the Electronic Structure of the Boron–Nitrogen Single Bond *

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The ^{11}B and ^{19}F nuclear quadrupole couplings in $F_3BNH_x(CH_3)_{3-x}$ compounds are reported. The boron quadrupole couplings were measured by quadrupole perturbed NMR in the solid state. The fluorine quadrupole couplings were obtained by the time-differential observation of the angular distribution of the gamma radiation after excitation of the fluorine nuclei with accelerated protons (TDPAD). The results are discussed in connection with the nitrogen quadrupole couplings in $F_3BNH_xR_{3-x}$ compounds, and the nitrogen and boron quadrupole couplings in $H_3BNH_xR_{3-x}$ compounds which were previously determined by nuclear quadrupole double resonance. In the $F_3BNH_xR_{3-x}$ series of compounds, the donor-acceptor character of the B–N bond appears to be less important than in the $H_3BNH_xR_{3-x}$ compounds in favour of a more ionic character of the bond with a higher negative charge on nitrogen.

Introduction

Boron–nitrogen bonds are isoelectronic and isostructural with carbon–carbon bonds. The close analogy to carbon chemistry places much interest in boron–nitrogen compounds, and their chemistry, therefore, forms a very active field of current inorganic chemical research.

Nuclear quadrupole resonance is especially well suited to study the electronic structure of boron–nitrogen compounds, because both nuclei boron and nitrogen possess quadrupole moments. In a previous paper [1] we reported the quadrupole coupling of nitrogen in amine-boranes, $H_3BNH_xR_{3-x}$, and amine-trifluoroboranes $F_3BNH_xR_{3-x}$. In view of the large electronegativity difference between H and F, it was surprising to find similar nuclear quadrupole coupling constants of the nitrogen when the H_3BN- and F_3BN-compounds possess an equal number of organic substituents at N. Since the nitrogen nuclear quadrupole data were not sufficient for a more detailed interpretation of the electronic structure of these compounds, we have determined the quadrupole couplings of boron and fluorine as well.

Experimental

To do so, other experimental techniques than double resonance by level crossing used for nitrogen were applied. Boron quadrupole couplings can be obtained by double resonance, yet the very small boron couplings in the $F_3BNH_xR_{3-x}$ compounds renders their determination in this way unfeasible. The method of choice is the classical quadrupole splitting of nuclear magnetic resonance lines in the solid state [2]. The ^{11}B NMR spectra were recorded at room temperature on a Varian DP 60 CW-NMR spectrometer at 19.24 MHz. The boron quadrupole coupling is 80 ± 8 kHz in all compounds investigated (F_3BNH_3, $F_3BNH(CH_3)_2$, and $F_3BN(CH_3)_3$).

Fluorine does not possess a nuclear quadrupole moment in its nuclear ground state ($I = 1/2$). By bombardment with accelerated protons it can be excited to a state with $I = 5/2$, 197 keV above the ground state. The quadrupole coupling of this excited state causes an oscillating, non-isotropic distribution of the gamma-quants emitted on return of the nuclei to their ground state [3]. This oscillation is a superposition of the three transition frequencies in

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Table 1. Fluorine nuclear quadrupole coupling in $F_3BNH_x(CH_3)_{3-x}$ compounds.

	T (K)	A_{22} (%)	δ_L (%)	$eqeQ/h$ (MHz)	η
F_3BNH_3	23	10.5 (6)	3.6 (5)	30.3 (3)	0.20 (5)
	80	5.5 (4)	1.4 (6)	30.1 (3)	0.20 (5)
F_3BNH_2Me	23	4.3 (7)	6.6 (1.9)	29.4 (3)	0.24 (5)
	80	3.5 (5)	2.2 (1.2)	29.5 (3)	0.24 (5)
F_3BNHMe_2	23	6.4 (4)	2.7 (6)	30.0 (3)	0.24 (5)
	80	2.2 (2)	0	29.7 (3)	0.24 (5)
F_3BNMe_3	23	7.5 (3)	13.4 (4.2)	29.6 (5)	0.24 (5)
	80	3.6 (9)	4.4 (2.5)	29.8 (4)	0.24 (5)

the $I = 5/2$ nuclear quadrupole level system, and the coupling parameters can be determined by its observation. Table 1 summarizes the results of such measurements (TDPAD-time differential perturbed angular distribution) for $F_3BNH_x(CH_3)_{3-x}$ compounds.

Interpretation

The quadrupole couplings of boron, fluorine, and nitrogen can be used to obtain a picture of the electronic distribution in F_3BN- and H_3BN-compounds by means of the theory of Townes and Dailey [4]. Table 2 summarizes the results of such an analysis for F_3BNH_3 and H_3BNH_3.

Since no differences in the fluorine and boron coupling constants were found for the compounds with other substituents than H at nitrogen, Table 2 is approximately valid for all substituents attached to nitrogen, the only actual change being the electron distribution within the N–H or N–C bonds.

The charges q_I residing on the various atoms of H_3BNH_3 and F_3BNH_3 were calculated from the populations of their associated orbitals and their nuclear charge.

A remarkable fact is the increase of negative charge on nitrogen in F_3BN- compared to H_3BN-compounds. This is not only a result of a stronger polarisation of the N–H bond towards nitrogen in the former compounds but a stronger polarisation of the B–N bond towards nitrogen as well. A comparable result is obtained from both SCF [5, 6] and CNDO/2 [7] calculations according to which the increase in the charge on nitrogen in F_3BNH_3 compared to H_3BNH_3 is somewhat higher than the corresponding decrease on the hydrogens. In F_3BN-compounds, nitrogen should therefore be a less efficient donor than in H_3BN-compounds, in contrast to expectation according to which F_3B should be a better electron acceptor than H_3B on account of the high electronegativity of fluorine. It must be mentioned here that no difference in the B–N bond lengths in H_3BNH_3 and F_3BNH_3 was found within experimental error, the B–N distance being 1.60 ± 0.02 Å in F_3BNH_3 [8] and 1.56 + 0.05 Å [9] or 1.6 Å [10] in H_3BNH_3.

The equality of the coupling constant of nitrogen in corresponding members of the two series of compounds, H_3BN- and F_3BN-, appears to be due to two counterbalancing effects: the larger polarisation of the N–H(C) bonds towards nitrogen in F_3BN-compounds, and less donation of charge from nitrogen to boron. We think that the higher negative charge on nitrogen in F_3BN-compounds can be explained by energetic considerations. The high polarity of the F–B bond enforces a high positive

Table 2. Orbital populations (p_{IJ}) and atomic charges (q_I) in F_3BNH_3 and H_3BNH_3.

	X		B			N			H	
	q_X	p_{XB}	p_{BX}	q_B	p_{BN}	p_{NB}	q_N	p_{NH}	p_{HN}	q_H
X=F	−0.68	1.71	0.29	+1.86	0.27	1.73	−1.35	1.54	0.46	+0.54
X=H	−0.20	1.20	0.80	+0.17	0.43	1.56	−0.73	1.39	0.61	+0.39

charge on the boron atom so that a higher negative charge on nitrogen, i.e. a more ionic character of the B−N bond seems more favourable. In more polar bonds, the loss of covalent bond energy is made up by the incidence of ionic bond energy plus, according to VB theory, energy of ionic-covalent resonance.

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