Geometric and Electric Properties of the Donor–Acceptor Complex $H_3N–BF_3$

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Shrinkage corrections of the microwave structures of H_3NBF_3 isotopomers resolve an apparent discrepancy between experimental and theoretical values of the NB bond length; *ab initio* ^{10}B, ^{11}B and ^{14}N nuclear quadrupole coupling constants are in qualitative agreement with experiment, confirming the earlier microwave characterisation of this donor–acceptor adduct and providing a physical picture of dative bond formation.

In a recent communication,[1] Jonas and Frenking point out that the value of the bond length r(N–B) in the classical donor–acceptor complex $H_3N–BF_3$ determined from gas-phase spectroscopy[2] conflicts with those from various *ab initio* calculations. The central position of molecules such as $H_3N–BF_3$ (discovered as long ago as 1809 by Gay-Lussac[3]) in the theory of the dative bond[4,5] requires that the origin of this conflict should be examined. We show below that the discrepancy arises because the experimental principal axis coordinate z_B is significantly underestimated when determined by $^{10}B/^{11}B$ substitution and present a method of correcting z_B that brings the experimental and theoretical r(N–B) into satisfactory agreement.

The experimental distance r(N–B) resulted from an analysis of the $J = 1 \leftarrow 0$ transition of each of the four isotopomers $H_3{}^{14}N–{}^{11}BF_3$, $H_3{}^{14}N–{}^{10}BF_3$, $H_3{}^{15}N–{}^{11}BF_3$ and $H_3{}^{15}N–{}^{10}BF_3$. Although ^{15}N substitution in the $H_3{}^{14}N–{}^{11}BF_3$ parent gives the accurate value $z_N = 1.555$ Å (where z is the molecular symmetry axis and the origin of the axis system is at the molecular centre of mass), a proper determination of z_B is precluded. Normally, the change ΔI_b in the principal moment of inertia I_b on substitution of ^{11}B by ^{10}B would be used in Kraitchman's equation $z_i{}^2 = \Delta I_b/\mu$ to give z_B but in this case I_b *increases* on substitution of ^{10}B and the resulting z_B is imaginary. In ref. 2 the presented value $z_B = -0.03(3)$ Å was a crude estimate and the error placed on it should have been larger.

It is commonly observed that when isotopic substitution is made at an atom close to the centre of mass of a molecule, the resulting squared substitution coordinates (*e.g.* $z_B{}^2$ above) are grossly underestimated and the coordinates can become imaginary if the atom is within *ca.* 0.1–0.2 Å of the mass centre. The reason for this can be illustrated conveniently by reference to CO_2.

Although isotopic substitution of ^{12}C in CO_2 by ^{13}C must leave the equilibrium moment of inertia $I_b{}^e$ unchanged, it causes a *decrease* in the zero-point quantity $I_b{}^0$. The decrease arises because the heavier mass attenuates the zero-point motion and the averaged C=O bond lengths shrink. Laurie and Herschbach[6] showed that a shrinkage of 5×10^{-5} Å in each C=O bond could account for the observed decrease in $I_b{}^0$ of $^{13}CO_2$. Recently, shrinkages of 1.3×10^{-4} and 8×10^{-5} Å have been established in the C–F and C–C bonds of both $CF_3C{\equiv}CH$ and CF_3CN for ^{13}C substitution in the CF_3 group.[7] The fact that $H_3N–BF_3$ is isoelectronic with $H_3C–CF_3$ and that the dative bond is strong suggests that these shrinkages might also be applied to ^{11}B substitution for ^{10}B.

In ref. 2, $H_3{}^{14}N–{}^{11}BF_3$ was taken as the parent isotopomer and for convenience we adhere to this convention. We thus assume *expansions* of 1.3×10^{-4} and 8×10^{-5} Å in the B–F and B–N bonds when the ^{10}B substitution is made. By using the structure of $H_3N–BF_3$ in ref. 1 (Fig. 1), we find that such expansions would make $I_b{}^0$ of $H_3{}^{14}N–{}^{10}BF_3$ larger by 0.0156 μÅ^2 and hence the experimental value $I_b{}^0$ for this isotopomer can be corrected from 108.7171 μÅ^2 to 108.7015 μÅ^2. When used with $I_b{}^0 = 108.7156$ μÅ^2 for $H_3{}^{14}N–{}^{11}BF_3$ in Kraitchman's equation, the corrected z_B becomes ±0.118 Å and, if as argued in ref. 2 the minus sign holds, we find $r(N–B) = z_N - z_B = 1.673$ Å, a value now in satisfactory agreement with 1.678 Å from the MP2/TZ2P level calculation of Jonas and Frenking.[1]‡

It is difficult to estimate the error in z_B and therefore in r(N–B) but a value of ±0.01 Å for both seems reasonable. Interestingly, the MP2/TZ2P geometry in ref. 1 gives the principal axis coordinates $z_B = -0.128$ Å and $z_N = 1.550$ Å for $H_3{}^{14}N\cdots{}^{11}BF_3$, in excellent agreement with the revised experimental values.§ We also note that the MP2/TZ2P geometry predicts frequencies of 9343.6, 9345.3, 9143.8 and 9145.5 MHz for the $J = 1 \leftarrow 0$ transitions of $H_3{}^{14}N–{}^{11}BF_3$, $H_3{}^{14}N–{}^{10}BF_3$, $H_3{}^{15}N–{}^{11}BF_3$ and $H_3{}^{15}N–{}^{10}BF_3$, respectively, while the respective experimental values are 9297.3, 9297.1, 9097.9 and 9098.2 MHz. Experiment and theory are undoubtedly dealing with the same molecule.

A further important part of the experimental evidence for the $H_3N–BF_3$ complex is the set of nuclear quadrupole coupling constants $\chi(^{11}B)$, $\chi(^{10}B)$ and $\chi(^{14}N)$. Their low values were interpreted as indications that both nuclei were sitting in approximately tetrahedral environments.[2] As a check on this interpretation, the binding energy, dipole moment and electric field gradients at B and N nuclei were calculated as functions of the N–B distance. The optimal geometry is insensitive to both basis set and level of calculation,[1] and so the following strategy was adopted. For each distance r(N–B), all other internal coordinates were optimised using a self-consistent field wavefunction computed in the 6-31G** basis. At this partially optimised geometry the energy and electric properties were computed both in 6-31G** and the more flexible Sadlej[8,9] basis sets. Fig. 2 shows the resulting curves. Single-point values for a fully decontracted Sadlej basis are also shown in Fig. 2. Although there are minor differences in absolute values, the two sets of calculations give very similar pictures of the changes accompanying formation of the N–B bond. As the two molecules approach, the BF_3 moiety bends away from planarity and the BF bonds lengthen (F–B–F 114.5°, Δr(B–F) = 0.05 Å at equilibrium), but the geometry of the NH_3 fragment is little changed. (ΔH–N–H +1°, Δr(N–H) 0.003 Å at equilibrium). Comparison of the binding energies of 86 kJ mol^{-1} (6-31 G**) and 83 kJ mol^{-1} (Sadlej) with the MP2/TZ2P value of 84.9 kJ mol^{-1} suggests that the neglect of electron correlation in the present calculations will not have a major effect on computed properties. In the equilibrium geometry of the adduct the total

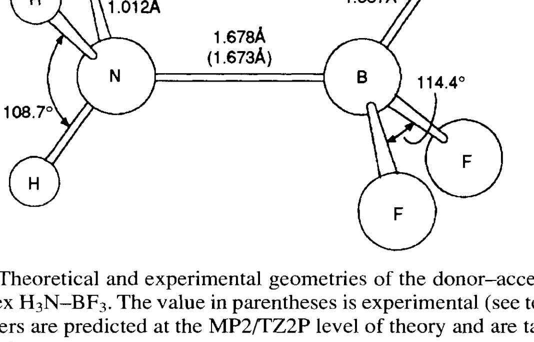

Fig. 1 Theoretical and experimental geometries of the donor–acceptor complex $H_3N–BF_3$. The value in parentheses is experimental (see text); the others are predicted at the MP2/TZ2P level of theory and are taken from ref. 1.

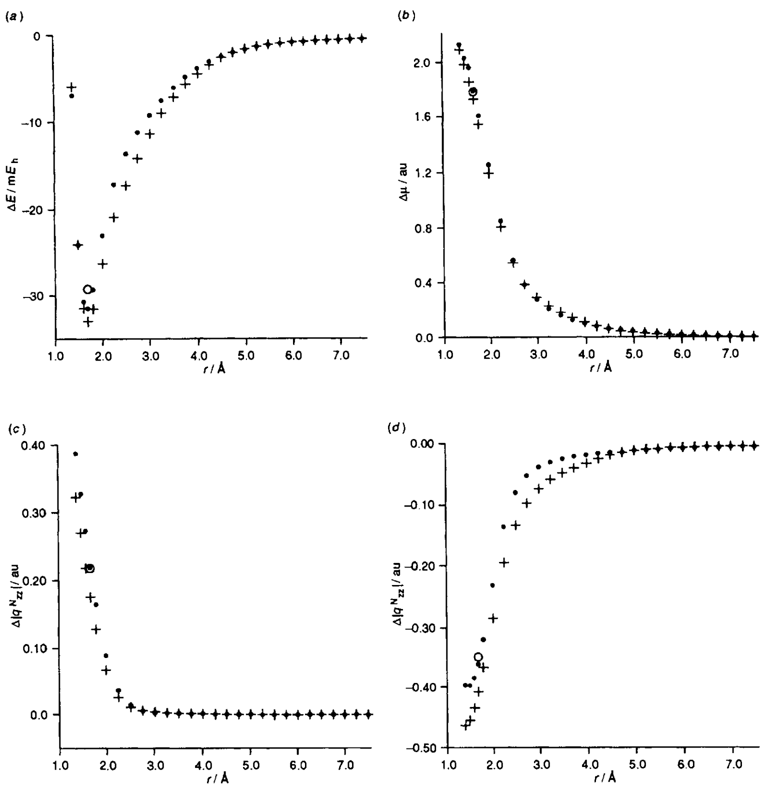

Fig. 2 Variation of properties of the H_3NBF_3 adduct with the N–B distance *r*. As described in the text, properties are calculated at the SCF level in the 6-31G** basis (+), the Sadlej basis (·) and a fully decontracted Sadlej basis (o) for structures in which all geometric parameters *except* *r*(N–B) have been optimised with the 6-31G** basis. The curves represent (*a*) the interaction energy (ΔE), (*b*) the interaction dipole ($\Delta\mu$), (*c*) the change in electric field gradient at B ($\Delta|q_{zz}{}^{B}|$) and (*d*) at N ($\Delta|q_{zz}{}^{N}|$).

dipole moment is computed to be 3.9 times the value for the isolated ammonia molecule, an enhancement of 4.6 D of which 40% is accounted for by the geometrical distortion of the BF_3 molecule in the complex. All the curves for geometric and electric properties, including those for polarisability (not shown here) show a marked change in slope in the region of *r*(N–B) ~2.5 Å as BF_3/NH_3 changes from a loose complex of slightly perturbed monomers to a chemically bound system. These features, especially that in Fig. 2(*c*), imply a sudden transfer of the electron pair at a well defined separation.

In the Sadlej basis the axial electric field gradient at B is −0.355 au for the isolated BF_3 molecule and −0.135 au for the complex. This reduction in magnitude by 62% is essentially electronic in origin; distortion of BF_3 contributes only 6% and the bare field gradient of an unperturbed NH_3 monomer a further 7%. The computed field gradient for the complex is equivalent to $\chi(^{10}B)$ = 2.69 MHz and $\chi(^{11}B)$ = 1.29 MHz if tabulated nuclear quadrupole moments[10] $Q(^{10}B)$ = 8.459(24) fm^2 and $Q(^{11}B)$ = 4.059(10) fm^2 are used. The 6-31G** basis gives slightly smaller field gradients and predicts $\chi(^{10}B)$ = 2.48 MHz, $\chi(^{11}B)$ = 1.19 MHz. These compare with the observed ranges of $\chi(^{10}B)$ = 2.33 to 2.47 MHz, $\chi(^{11}B)$ = 1.128 to 1.21 MHz for various states and isotopomers.[2]

The computed field gradient at N falls from 0.972 au in isolated NH_3 to 0.612 au in the complex using the Sadlej basis, a reduction of 37%. This is similar to the reduction factor of 44% implied by the measured value[2] of $\chi(^{14}N)$ = −2.301(6) MHz for $H_3{}^{14}N{-}^{11}BF_3$. The tabulated quadrupole moment[10] $Q(^{14}N)$ = 2.02(3) fm^2 converts the computed field gradient for the complex to −2.91 MHz (Sadlej), −2.74 MHz (6-31G**).

The calculated nuclear quadrupole coupling constants confirm the picture of the adduct H_3NBF_3 as an analogue of H_3CCF_3, comprising two approximately tetrahedral entities joined by a single bond. Taken together with the reinterpretation of the bond length data, the calculated properties present a satisfying picture of agreement between theory and experiment.

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Footnotes

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‡ When $H_3{}^{15}N{-}^{10}BF_3$ is the parent molecule, we find z_N = 1.537 Å, z_B (corr.) = −0.136 Å and *r* (N–B) = 1.673 Å. The values of z_N and z_B calculated from the MPZ/TZZP geometry are 1.530 and −0.148 Å for this isotopomer.

§ The value of z_B = −0.216 Å given in ref. 1 is referred to the centre of charge, not the centre of mass (G. Frenking, personal communication).

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