Studies on the Boron–Nitrogen Bond Length of the Classical Donor–Acceptor Complex $H_3N–BF_3$

Volker Jonas and Gernot Frenking*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Quantum mechanical calculations at correlated levels using different basis sets predict that the B–N bond length of $H_3N–BF_3$ is 1.68 ± 0.02 Å; the previously reported value of 1.59 ± 0.03 Å, which is based on microwave spectroscopic investigations, is probably too short.

Although the classical donor–acceptor complex $H_3N–BF_3$ **1** has already been prepared in 1809 by Gay-Lussac,[1] it has only recently been detected in the gas phase by Legon and Warner,[2] who report experimental results of **1** using microwave spectroscopy. The analysis of the observed $J = 1 \leftarrow 0$ transitions of the ^{14}N, ^{15}N, ^{10}B, and ^{11}B isotopomers of $H_3N–BF_3$ led them conclude that the B–N interatomic distance of **1** is 1.59 ± 0.03 Å,[2] which is practically the same value as in the solid state ($r_{B–N} = 1.60 \pm 0.02$ Å).[3] This is surprising, because the stronger base Me_3N has an observed B–N bond length between 1.664 ± 0.01 Å[4a] and 1.674 ± 0.004 Å[4b] in the related complex $Me_3N–BF_3$ **2** in the gas phase. Also, donor–acceptor complexes exhibit usually shorter donor–acceptor bonds in the solid state than in the gas phase.[5] The shortening between the gas phase and the solid state can be as much as 0.8 Å, which is observed for $HCN–BF_3$.[6] The B–N bond of **2** in the gas phase is 0.08 Å shorter than in the solid state.[7] Previous *ab initio* calculations predict[8] that the B–N bond of **1** should be 1.68 Å and not 1.59 Å as reported by Legon and Warner.[2]

In a systematic quantum mechanical investigation of the geometries, bond strengths and electronic structures of main group donor–acceptor complexes we found[9] that, the theoretically predicted geometries are in very good agreement with experimental gas-phase values. Because **1** as the 'archetypal'[2] donor–acceptor complex has been used by Lewis[10] as the first example to illustrate the concept of the dative bond,[11] the knowledge of the exact length of the donor–acceptor bond has particular importance. Therefore, we decided to study theoretically† the geometry of **1** using different basis sets and different methods for calculating the correlation energy. For comparison, we report also the optimized geometries of $Me_3N–BF_3$ **2** and $H_3N–BH_3$ **3**. The experimental gas-phase geometries of **2** and **3** are known.[4,12]

Fig. 1 shows the optimized structures of **1–3** at the MP2/TZ2P level of theory. The experimental gas-phase values are given in parentheses. The agreement between theory and experiment is very good, with the exception of the B–N bond length of **1**. The boron atom has a tetrahedral configuration in the complexes. The B–F bonds are significantly longer in **1** and **2** than in BF_3 (calculated 1.312 Å, experimental[13] 1.311 Å). The larger N–B–F angle and longer B–F bond of **2** than those of **1** indicate stronger donor–acceptor interactions in the former complex. Indeed, the bond strength has been calculated at the MP2/TZ2P level of theory to be significantly higher for **2** (D_e = 33.3 kcal mol^{-1}) than for **1** (D_e = 23.0 kcal mol^{-1}).[9]

Table 1 Experimental and calculated B–N bond lengths (Å) and dipole moments (Debye)

Method	$H_3N–BF_3$ **1** (C_{3v})	$Me_3N–BF_3$ 2 (C_{3v})	$H_3N–BH_3$ 3 (C_{3v})
Exp. (X-ray)	1.60 ± 0.02[a]	1.585 ± 0.03[c]	1.564 ± 0.006[f]
Exp. (Gas phase)	1.59 ± 0.03[b]	1.674 ± 0.004[d] 1.664 ± 0.011[e]	1.657 ± 0.02[g]
HF/6-31G(d,p)	1.688	1.674	1.687
HF/TZ2P	1.687	1.676	1.672
MP2/6-31G(d,p)	1.679	1.664	1.657
MP2/TZ2P	1.678	1.661	1.648
MP3/6-31G(d,p)	1.678		1.663
QCISD/6-31G(d,p)	1.679		1.667
D (MP2/TZ2P)	6.14	6.09	5.44
D (exp.)		5.63[h]	5.22[i]

[a] Ref. 3; [b] ref. 2; [c] ref. 7; [d] ref. 4*b*; [e] ref. 4*a*; [f] ref. 14; [g] ref. 12; [h] ref. 22; [i] ref. 12.

Table 1 shows the experimental and calculated B–N bond lengths of **1–3**. The theoretically predicted interatomic distances change very little at different levels of theory. The calculated bond lengths at the HF level are slightly longer than the MP2 values. The larger TZ2P basis set gives very similar results as the 6-31G(d,p) basis set at the HF and MP2 level, respectively. Also the bond lengths predicted at the QCISD/6-31G(d,p) level are practically the same as the MP2/6-31G(d,p) results. This means that the theoretical methods, which are used to calculate the B–N bond lengths of **1–3**, have nearly converged to a common value. The results in Table 1 show

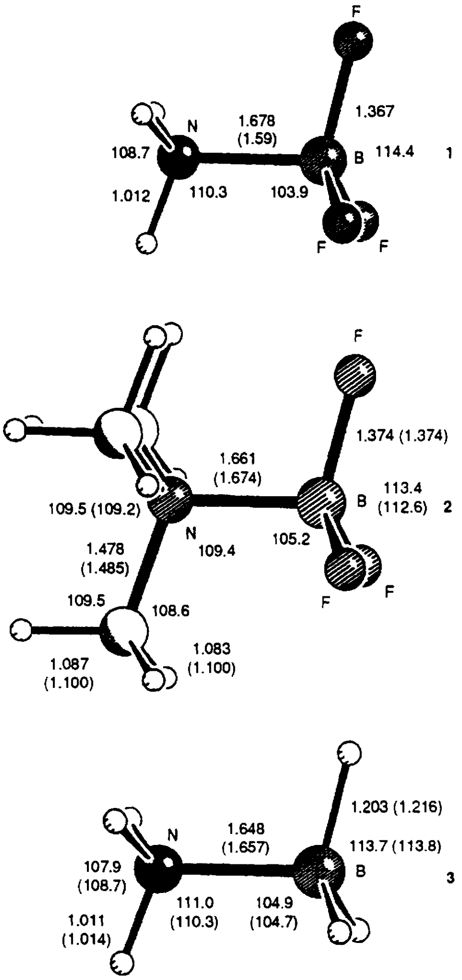

Fig. 1 Theoretically predicted geometries of the donor–acceptor complexes **1–3** at the MP2/TZ2P level of theory. Experimental gas-phase values[2,4b,12] are given in parentheses.

that the B–N bond lengths of **2** and **3** calculated at all levels of theory are essentially in agreement with the experimental gas-phase values. The calculated values for **1**, however, are clearly longer than the experimental value of 1.59 ± 0.03 Å.[2] The theoretical results suggest that the B–N bond length of **1** should be 1.68 ± 0.02 Å.

Table 1 shows that the B–N bond lengths of **2** and **3** are 0.08–0.10 Å shorter in the solid state than in the gas phase, which can be attributed to the intermolecular dipole–dipole interactions.[9,14] The calculated dipole moments of **2** (6.09 D) and **3** (5.44 D) at MP2/TZ2P are in reasonable agreement with the experimental values of 5.63 and 5.22 D respectively. The theoretical dipole moment of **1** is 6.14 D [MP2/TZ2P]. Because the calculated dipole moment of **1** has the same magnitude as those of **2** and **3**, the intermolecular dipole–dipole interactions in the solid state should be similar. The B–N bond length of **1** should therefore be 0.08–0.10 Å longer in the gas phase than in the solid state. This would agree with the calculated value of *ca.* 1.68 Å (Table 1). The experimental gas-phase value of 1.59 Å for $H_3N{-}BF_3$ **1** is also difficult to understand, because the bond length of $Me_3N{-}BF_3$ **2** (1.664 ± 0.01 Å; 1.674 ± 0.004 Å)[4] is clearly longer. Trimethylamine is a stronger base than ammonia. The experimentally reported B–N bond length of $Me_3N{-}BH_3$ (1.638 ± 0.01 Å; 1.656 ± 0.002 Å)[15] is similar or slightly shorter than that of $H_3N{-}BH_3$ (1.657 ± 0.02 Å).[12]

The experimental value of 1.59 ± 0.03 Å for the B–N bond length of **1** reported by Legon and Warner[2] is based on an estimate of the position of the boron atom on the axis of the symmetric top molecule. The position of the nitrogen atom of **1** was obtained from the change in B_0 on ^{15}N substitution in the $J = 1 \leftarrow 0$ transition as $z_N = 1.555$ Å. From the signals of the isotopomers it was concluded that the B atom lies very close to the centre of mass in $H_3{}^{14}N^{11}BF_3$, but probably on the opposite side from N. Based on experience, a value of $z_B = -0.03 \pm 0.03$ Å was chosen for the position of the boron atom, which gives a B–N interatomic distance of 1.59 ± 0.03 Å.[2] The calculations suggest that the boron atom is further away from the centre of mass. The theoretically predicted positions of the N and B atoms are (MP2/TZ2P) $z_N = 1.463$ and $z_B = -0.216$ Å.

Because the calculated B–N bond lengths of the related complexes **2** and **3** are in excellent agreement with the gas-phase values, and because it is difficult to understand why the weaker base NH_3 should have a much shorter bond with BF_3 than Me_3N, we think that the published value $r_{BN} = 1.59 \pm 0.03$ Å for the B–N bond length of **1** is too short. The calculations indicate, that the assumptions underlying the calculation of moments of inertia are deficient. The theoretical results presented here and in previous studies[8] suggest that the true value should be $r_{BN} = ca.$ 1.68 Å. The results predicted at different levels of theory allowed an error estimate of ± 0.02 Å.‡

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. Excellent service by the HRZ Marburg is gratefully acknowledged. Additional computer time was given by the HHLRZ Darmstadt.

Received, 11th March 1994; Com. 4/01462F

Footnotes

† The calculations have been carried out using the program packages Gaussian 92[16] and TURBOMOLE.[17] The geometries are optimized at the Hartree–Fock (HF) and MP2 (Møller–Plesset perturbation theory[18] terminated at second order) level of theory using a 6-31G(d,p)[19] and TZ2P basis set.[20] The structures are verified to be minima on the potential energy hypersurface by calculating the hessian matrix at the HF/6-31G(d,p) level, which has only positive eigenvalues. Further geometry optimizations have been carried out at the MP3/6-31G(d,p) and QCISD/6-31G(d,p) level (Quadratic CI with single and double excitations[21]).

‡ The coefficient of the leading configuration in the MP2/6-31G(d) calculations of **1** ($c_0 = 0.918$), **2** ($c_0 = 0.871$) and **3** ($c_0 = 0.960$) shows that the Hartree–Fock configuration is dominant in the correlated wave function.

References

1 J. L. Gay-Lussac and J. L. Thénard, *Mem. de Phys. et de Chim. de la Soc. d'Arcueil* 1809, **2**, 210.

2 A. C. Legon and H. E. Warner, *J. Chem. Soc., Chem. Commun.*, 1991, 1397.

3 J. L. Hoard, S. Geller and W. M. Cashin, *Acta Crystallogr.*, 1951, **4**, 396.

4 (*a*) M. Hargittai and I. Hargittai, *J. Mol. Struct.*, 1977, **39**, 79. (*b*) K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 711.

5 M. A. Dvorak, R. S. Ford, R. D. Suenram, F. J. Lovas and K. R. Leopold, *J. Am. Chem. Soc.*, 1992, **114**, 108.

6 W. A. Burns and K. R. Leopold, *J. Am. Chem. Soc.*, 1993, **115**, 11622.

7 (*a*) S. Geller and J. L. Hoard, *Acta Crystallogr.*, 1951, **4**, 399. (*b*) J. L. Hoard, S. Geller and T. B. Owen, *Acta Crystallogr.*, 1951, **4**, 405.

8 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley Interscience, NY, 1986, p. 217.

9 V. Jonas, G. Frenking and M. T. Reetz, *J. Am. Chem. Soc.*, in the press.

10 G. N. Lewis, *Valence and the Structures of Atoms and Molecules*, The Chemical Catalog Company Inc., New York, 1923, p. 98.

11 A. Haaland, *Angew. Chem.*, 1989, **101**, 1017; *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 992.

12 L. R. Thorne, R. D. Suenram and F. J. Lovas, *J. Chem. Phys.*, 1983, **78**, 167.

13 K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, 1966, **45**, 4342.

14 M. Bühl, T. Steinke, P.v.R. Schleyer and R. Boese, *Angew. Chem.*, 1991, **103**, 1179; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1160.

15 (*a*) P. Cassoux, R. L. Kuczkowski, P. S. Bryan, R. C. Taylor, *Inorg. Chem.*, 1975, **14**, 126; (*b*) K. Iijima, N. Adachi and S. Shibata, *Bull. Chem. Soc. Jpn*, 1984, **57**, 3269.

16 Gaussian 92, Revision A, M. J. Frisch, G. W. Trucks, M.Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, R. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1992.

17 M. Häser and R. Ahlrichs, *J. Comput. Chem.*, 1989, **10**, 104; R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165; H. Horn, H. Weiss, M. Häser, M. Ehrig and R. Ahlrichs, *J. Comput. Chem.*, 1991, **12**, 1058; M. Häser, J. Almlöf and M. W. Feyereisen, *Theoret. Chim. Acta*, 1991, **79**, 115; F. Haase and R. Ahlrichs, *J. Comput. Chem.*, 1993, **14**, 907.

18 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618; J. S. Binkley and J. A. Pople, *Intern. J. Quantum Chem.*, 1975, **9**, 229.

19 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta*, 1973, **28**, 213.

20 TZ2P for B, C, N: (9s5p2d)/[5s3p2d]. TZ2P for H: (5s2p)/[3s2p]. S. Huzinaga, *Approximate Atomic Wavefunctions*, Department of Chemistry Report, University of Alberta, Canada, 1971.

21 J. A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.*, 1987, **87**, 5968.

22 C. M. Bay, A. R. Katritzky and L. E. Sutton, *J. Chem. Soc.*, 1958, 1258.