Vibrational Spectra of the Boron Halides and Their Molecular Complexes. Part 11. Complexes of Boron Trifluoride with Phosphine and Its Methyl Derivatives. An ab Initio Study

Thomas A. Ford*

Centre for Theoretical and Computational Chemistry, School of Chemistry, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa

Received: March 21, 2008; Revised Manuscript Received: May 06, 2008

Ab initio calculations, at the second-order level of Møller−Plesset perturbation theory, using a triple-ζ Gaussian basis set with polarization and diffuse functions on all atoms, have been carried out on the donor−acceptor complexes of boron trifluoride with phosphine and its mono-, di-, and trimethyl derivatives. The structures, interaction energies, and vibrational spectra of the complexes were determined. The preferred conformer was found to be the staggered species in each case. The computed data were compared with those for some similar complexes containing boron trifluoride and a series of related oxygen, sulfur, and nitrogen bases, and the effect of successive methyl substitution in each series was investigated.

Introduction

In a recent series of articles, we reported ab initio studies of the structural, energetic and vibrational properties of the molecular complexes formed between boron trifluoride and water, hydrogen sulfide,[1] and ammonia[2] and their methyl derivatives.[2–5] In the case of the oxygen and sulfur bases, we established a good correlation between the interaction energies and the gas-phase basicities[6] of the bases. We also observed a number of other trends in the studied properties with increasing basicity of the electron donor, paralleling the increase in the degree of methylation. On extending these studies to nitrogen bases,[2] we confirmed that our results for the ammonia derivatives were consistent with our earlier findings on the water and hydrogen sulfide series.[1,3–5] We now turn our attention to the related series of bases phosphine and mono-, di-, and trimethyl phosphine.

Whereas the complexes of boron trifluoride with ammonia and its methylated analogues have received a great deal of theoretical attention (see ref 2 for a list of references), the methylated phosphines have enjoyed far less scrutiny. Hirota et al. reported the interaction energies, structures, and charge-transfer properties of $BF_3 \cdot PH_3$ and $BF_3 \cdot (CH_3)_3P$ at the SCF level,[7] and Ahlrichs et al. computed the structures, interaction energies, and vibrational spectra of the same two adducts at the SCF and MP2 levels.[8] Anane and co-workers also reported the structure, interaction energy, and degree of charge transfer of $BF_3 \cdot PH_3$ using G2/MP2 theory.[9] The related complexes of BH_3 with PH_3, PH_2F, PHF_2, and PF_3 have also been examined theoretically.[10–13] Experimental studies of the series of complexes considered here include the microwave spectrum of $BF_3 \cdot PH_3$;[14] the vibrational spectra of $BF_3 \cdot PH_3$[15] and $BF_3 \cdot (CH_3)_3P$;[16,17] and the NMR spectra of the complexes of BF_3 with PH_3, CH_3PH_2, $(CH_3)_2PH$,[18] and $(CH_3)_3P$.[17–20] The published infrared and Raman spectra of the related species $BCl_3 \cdot PH_3$,[21–23] $BBr_3 \cdot PH_3$, and $BI_3 \cdot PH_3$[15,23] and the NMR spectrum of $BF_3 \cdot (C_6H_5)_3P$[24] indicate a moderate amount of interest in these families of complexes. Only in the case of the NMR spectra of the BF_3 adducts with all four phosphines has a systematic study of the properties of the complexes and the influence on those properties of the degree of methylation been undertaken.[18] The field is therefore open for such a study of those properties of the complexes that are amenable to the application of ab initio methodology, comparable with our earlier work on the aggregates with H_2O, H_2S, and NH_3 and their derivatives.[1–5] In particular, the partially methylated species warrant special attention.

Computational Methods

The calculations were performed using the Gaussian 98 program[25] at the second-order level of Møller−Plesset perturbation theory (MP2),[26] using the 6-311++G(d,p) basis set,[27,28] which features polarization and diffuse functions on all atoms. Full optimizations were carried out, with the VERYTIGHT convergence criterion,[25] to ensure convergence to the correct minimum-energy structure, subject to the imposition of C_{3v} symmetry for the $BF_3 \cdot PH_3$ and $BF_3 \cdot (CH_3)_3P$ adducts and C_s symmetry for $BF_3 \cdot CH_3PH_2$ and $BF_3 \cdot (CH_3)_2PH$. Both staggered and eclipsed conformers were studied in each case. Interaction energies, computed from the energies of the complexes and the relaxed monomers, were corrected for basis set superposition error (BSSE),[29] using the full counterpoise method of Boys and Bernardi,[30] and for zero-point energy differences. The enthalpies of complexation were also calculated. The vibrational wavenumbers and infrared intensities of the complexes and monomers were computed using analytical derivatives, although the intensities are not reported here.

Results and Discussion

Molecular Structures. The optimized structures of the four complexes are illustrated in Figure 1. In each case, the preferred structure was found to be the staggered conformer, and the eclipsed isomer was a transition state. The computed values of the bond lengths and angles are presented in Table 1, along with their changes relative to those of the monomers. In the case of $BF_3 \cdot PH_3$, experimental data are available for comparison.[14] Odom et al. reported values of 137.2 pm for *r*(BF) and

---

* Telephone: +27-31-260-1096. Telefax: +27-31-260-3091. E-mail: ford@ukzn.ac.za.

10.1021/jp802493n CCC: $40.75

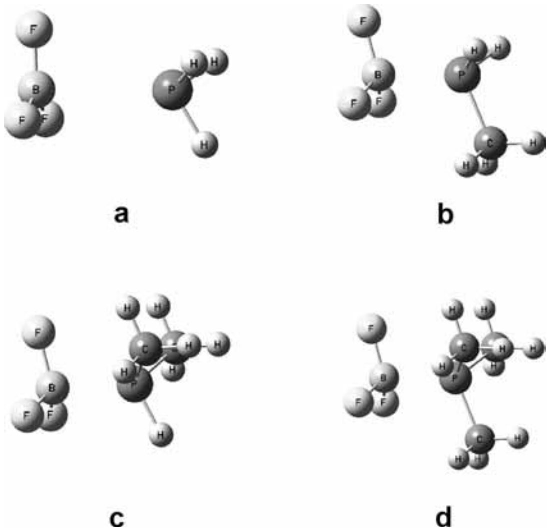

Figure 1. Optimized structures of the complexes of BF_3 with (a) PH_3, (b) CH_3PH_2, (c) $(CH_3)_2PH$, (d) $(CH_3)_3P$.

an intermonomer separation of 192.1 pm, with a FB···P angle of 106.69°.[14] Our intramolecular BF bond length is in rather poor agreement with the experimental value determined by Odom and co-workers.[14] However, our results are comparable with those of Ahlrichs et al.[8] and Anane et al.,[9] obtained under similar conditions, although, surprisingly, the work of Hirota et al.,[7] which was done with a small basis set, yields far better agreement with experiment.[14] For $BF_3\cdot(CH_3)_3P$, agreement with the other two sets of theoretical results[7,8] is much better than for $BF_3\cdot PH_3$. Apart from the very small perturbations of the bond lengths and angles predicted for $BF_3\cdot PH_3$, the remaining complex−monomer changes are similar in magnitude and increase steadily with increasing methylation. In general, the BF bond lengths and the HPH, CPH, and CPC bond angles increase, whereas the PH and PC bond lengths and the FBF angles decrease upon complexation.

Table 2 lists the calculated intermonomer separations and intermolecular bond angles. The B···P distance of $BF_3\cdot PH_3$ far exceeds that determined by Odom et al.[14] (192.1 pm), and the FB···P angle is far smaller than the 106.69° reported.[14] Again, our results are similar in magnitude to those of Ahlrichs et al.[8] and Anane et al.,[9] and again, the early value determined by Hirota et al.[7] agrees most closely with experiment.[14] This suggests that the later calculations severely underestimate the extent of interaction in $BF_3\cdot PH_3$. The B···P distance of $BF_3\cdot(CH_3)_3P$ is similar to those of Hirota et al. and Ahlrichs et al. Our values for the three methyl-substituted complexes appear to be more realistic and decrease regularly with increasing methylation, consistent with the greater perturbations of the intramolecular parameters, indicating increasingly stronger interaction.

Rotational Constants and Dipole Moments. The rotational constants and dipole moments are listed in Table 3. Comparison of our results for $BF_3\cdot PH_3$ with the experimental data of Odom et al.[14] reveals very poor agreement for the *B* rotational constant and a gross underestimation of the dipole moment. This observation is consistent with our findings regarding the molecular structures and points to a severe weakness in the methodology in the case of this particular complex, which has been traced to basis set deficiencies.[8] For the other three complexes, the trends in the values of these quantities are as expected.

Energetic Properties. The interaction energies of the four complexes, corrected for BSSE and zero-point energy differences, are given in Table 4. The interaction energies increase monotonically with increasing methylation, although the result for $BF_3\cdot PH_3$ indicates an anomalously low strength of interaction. The unique nature of the $BF_3\cdot PH_3$ complex, compared with the other three, bears out the observations mentioned above. In our parallel studies on the related oxygen, nitrogen, and sulfur bases,[1–5] we have noted a clear relationship between the computed interaction energies and the gas-phase basicities of the electron donors.[6] Such a relationship for the phosphorus bases is shown in Figure 2, which indicates that the same determinants of the extent of interaction in the oxygen, nitrogen, and sulfur families of complexes are also important for the phosphorus series. The results for the H_2S, CH_3SH, and $(CH_3)_2S$ complexes[3] are also included here, indicating that complexes with those bases containing donor atoms from the same period exhibit the same general relationship. This figure emphasizes the fact that, for $BF_3\cdot PH_3$, the interaction energy is severely underestimated, and this can now be explained by the high BSSE (50%) in the interaction energy of $BF_3\cdot PH_3$, compared with 14−19% for the three other phosphorus aggregates. The trend in the interaction energies is parallel to those in the structural

TABLE 1: Geometrical Parameters of the Complexes and Their Changes with Respect to Those of the Monomers

complex	parameter	value	difference	percentage difference
$BF_3\cdot PH_3$	*r*(BF) (pm)	132.2	0.4	0.27
	r(PH) (pm)	140.7	−0.2	−0.16
	∠FBF (deg)	119.8	−0.2	−0.14
	∠HPH (deg)	95.6	1.2	1.21
$BF_3\cdot CH_3PH_2$	*r*(BF) (pm)	136.8,137.5	5.6,4.9	4.27,3.74
	r(PC) (pm)	182.3	−3.3	−1.79
	r(PH) (pm)	140.0	−1.1	−0.78
	∠FBF (deg)	114.2,115.1	−5.8,−4.9	−4.80,−4.12
	∠CPH (deg)	104.5	7.0	7.12
	∠HPH (deg)	101.0	6.4	6.78
$BF_3\cdot(CH_3)_2PH$	*r*(BF) (pm)	137.8,138.6	6.8,6.0	5.12,4.51
	r(PC) (pm)	181.8	−3.3	−1.76
	r(PH) (pm)	140.1	−1.1	−0.81
	∠FBF (deg)	113.7,114.5	−6.3,−5.5	−5.26,−4.57
	∠CPH (deg)	104.3	7.3	7.51
	∠CPC (deg)	106.6	7.3	7.31
$BF_3\cdot(CH_3)_3P$	*r*(BF) (pm)	138.6	6.8	5.14
	r(PC) (pm)	181.6	−3.0	−1.64
	∠FBF (deg)	113.4	−6.6	−5.47
	∠CPC (deg)	105.9	7.3	7.43

TABLE 2: Intermolecular Geometrical Parameters of the Complexes

complex	R(B···P) (pm)	∠FB···P (deg)	mean ∠FB···P (deg)
$BF_3 \cdot PH_3$	307.5	92.4	92.4
$BF_3 \cdot CH_3PH_2$	213.3	105.6, 102.3	104.5
$BF_3 \cdot (CH_3)_2PH$	208.3	105.6, 102.2	104.5
$BF_3 \cdot (CH_3)_3P$	205.5	105.1	105.1

TABLE 3: Rotational Constants and Dipole Moments of the Complexes

complex	rotational constant (GHz) A	B	C	dipole moment (D[a])
$BF_3 \cdot PH_3$	4.869	1.783 (2.88932)[b]	1.783	1.728 (3.73)[b]
$BF_3 \cdot CH_3PH_2$	3.969	1.802	1.692	6.522
$BF_3 \cdot (CH_3)_2PH$	2.748	1.549	1.309	7.180
$BF_3 \cdot (CH_3)_3P$	2.061	1.209	1.209	7.633

[a] 1 D = 3.336×10^{-30} C m. [b] Experimental values from ref 14.

TABLE 4: Interaction Energies of the Complexes, Corrected for Basis Set Superposition Error and for Zero-Point Energy Differences, and Calculated Reaction Enthalpies

complex	interaction energy (kJ mol^{-1})	reaction enthalpy (kJ mol^{-1})
$BF_3 \cdot PH_3$	−6.90	−1.80
$BF_3 \cdot CH_3PH_2$	−104.08	−99.39
$BF_3 \cdot (CH_3)_2PH$	−143.66	−138.83
$BF_3 \cdot (CH_3)_3P$	−174.37	−169.36 (−190)[a]

[a] Experimental value from ref 32.

parameters and confirms the greater strength of interaction with increasing basicity. Other reported values for the interaction energy of $BF_3 \cdot PH_3$ vary from −9.8[8] to −41.4[7] kJ mol^{-1}, whereas for $BF_3 \cdot (CH_3)_3P$, values of −57.3[8] and −95.8[7] kJ mol^{-1} have been recorded, although it is not always clear to what extent the computed values have been corrected. Table 4 also presents the enthalpies of complexation, determined from the tabulated interaction energies according to the prescription of Del Bene.[31] The experimental reaction enthalpy determined by Mente et al.[32] is also included here, and agreement between our calculated value and the experimental result is quite reasonable.

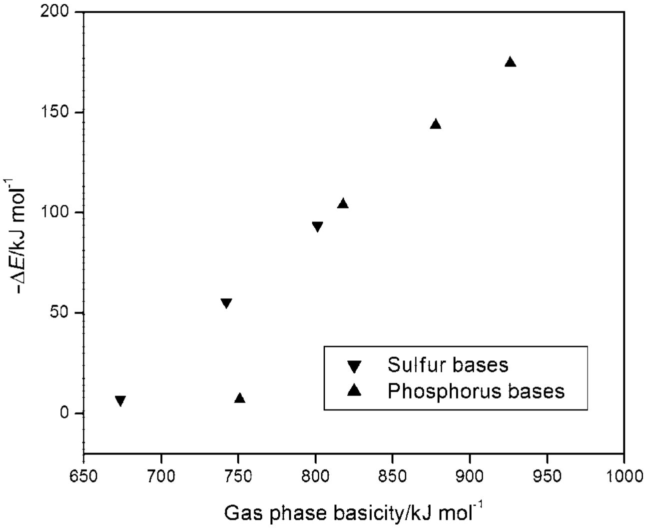

Figure 2. Plot of the interaction energies of the complexes versus the gas-phase basicities of the bases.

Vibrational Properties. The computed wavenumbers of the four complexes are collected in Tables 5–8, along with the approximate descriptions of the normal modes. These descriptions appear reasonable when the complex modes are compared with those of the respective isolated monomers. The calculated spectra of Ahlrichs et al.[8] and the experimental spectra of Durig,[15] Beg,[16] and Mente[17] and their colleagues are also presented here. For $BF_3 \cdot PH_3$ (Table 5), our computed intramolecular wavenumbers overestimate the experimental values of Durig et al.[15] by the standard 3−10%, with the exception of the symmetric BF_3 bending and antisymmetric BF_3 stretching modes, where we feel that Durig et al.'s[15] wavenumbers are substantially too low. Coupled with the overestimation of the B···P stretching wavenumber by Durig et al.,[15] we suggest a misassignment of these vibrations. We also propose that Durig et al.'s assignments of the intermolecular vibrations ν_{11} and ν_{12} are considerably too high, although they should have been observed within the range of their instrumentation.[15] This interpretation of the spectrum finds support in the fairly good agreement between Ahlrich et al.'s[8] and our computed wavenumbers, although where the assignments are not in dispute, our wavenumbers are in better agreement with those of Durig et al.[15] than are Ahlrich et al.'s.[8] Durig et al.'s assignments of ν_{11} and ν_{12} to the PH_3 and BF_3 rocking vibrations[15] simply reflect a difference in terminology from that used here.

In Table 8, the experimental wavenumbers of $BF_3 \cdot (CH_3)_3P$ reported by Beg and Clark[16] and Mente et al.[17] and the computed

TABLE 5: Wavenumbers and Approximate Descriptions of the Modes of the $BF_3 \cdot PH_3$ Complex

symmetry species	mode	wavenumber (cm^{-1}) calculated this work	calculated ref 8	experimental ref 15	approximate description
a_1	ν_1	2527	2553	2441	$\nu_s(PH_3)$
	ν_2	1055	1100	1021	$\delta_s(PH_3)$
	ν_3	861	945	797	$\nu_s(BF_3)$
	ν_4	627	718	331	$\delta_s(BF_3)$
	ν_5	75	53	607	ν(B···P)
a_2	ν_6	21	25	—[a]	τ(B···P)
e	ν_7	2538	2553	2468	$\nu_a(PH_3)$
	ν_8	1416	1562	1120	$\nu_a(BF_3)$
	ν_9	1161	1234	1085	$\delta_a(PH_3)$
	ν_{10}	471	510	430	$\delta_a(BF_3)$
	ν_{11}	190	159	570	geared libration
	ν_{12}	72	55	225	antigeared libration

[a] Not observed.

TABLE 6: Wavenumbers and Approximate Descriptions of the Modes of the $BF_3 \cdot CH_3PH_2$ Complex

symmetry species	mode	wavenumber (cm^{-1})	approximate description
a′	ν_1	3208	$\nu_a(CH_3)$
	ν_2	3099	$\nu_s(CH_3)$
	ν_3	2570	$\nu_s(PH_2)$
	ν_4	1483	$\delta_a(CH_3)$
	ν_5	1367	$\delta_s(CH_3)$
	ν_6	1214	$\nu_a(BF_3)$
	ν_7	1150	$\delta(PH_2)$
	ν_8	1037	$\rho(CH_3)$
	ν_9	832	$\nu_s(BF_3)$
	ν_{10}	768	$\omega(PH_2)$
	ν_{11}	759	$\nu(PC)$
	ν_{12}	609	$\delta_s(BF_3)$
	ν_{13}	455	$\delta_a(BF_3)$
	ν_{14}	286	geared libration
	ν_{15}	229	$\nu(B\cdots P)$
	ν_{16}	88	antigeared libration
a″	ν_{17}	3200	$\nu_a(CH_3)$
	ν_{18}	2585	$\nu_a(PH_2)$
	ν_{19}	1482	$\delta_a(CH_3)$
	ν_{20}	1191	$\nu_a(BF_3)$
	ν_{21}	1047	$\tau(PH_2)$
	ν_{22}	721	$\rho(CH_3)$
	ν_{23}	497	$\delta_a(BF_3)$
	ν_{24}	404	$\tau(CH_3)$
	ν_{25}	209	geared libration
	ν_{26}	131	antigeared libration
	ν_{27}	43	$\tau(B\cdots P)$

values of Ahlrichs et al.[8] are also included. Ahlrich et al.'s[8] data set contains some unassigned modes [667 cm^{-1} (a_1) and 798 and 299 cm^{-1} (e)], whereas in the cases of the experimental assignments,[16,17] the observed bands were not allocated to the possible symmetry species. Two modes (705 and 675 cm^{-1}) were also left unassigned by Beg and Clark.[16] Moreover, the assignments of Mente and Mills' spectrum[17] are not readily accessible, and we attempted to match the observed bands to the group vibrations by inspection. Our predicted spectrum is in fairly good accord with that of Ahlrichs et al.,[8] although we challenge the high value of 719 cm^{-1} assigned[8] to the intermonomer stretching mode.

TABLE 7: Wavenumbers and Approximate Descriptions of the Modes of the $BF_3 \cdot (CH_3)_2PH$ Complex

symmetry species	mode	wavenumber (cm^{-1})	approximate description
a′	ν_1	3195	$\nu_a(CH_3)$
	ν_2	3192	$\nu_a(CH_3)$
	ν_3	3088	$\nu_s(CH_3)$
	ν_4	2562	$\nu(PH)$
	ν_5	1488	$\delta_a(CH_3)$
	ν_6	1483	$\delta_a(CH_3)$
	ν_7	1369	$\delta_s(CH_3)$
	ν_8	1160	$\nu_a(BF_3)$
	ν_9	1044	$\delta_s(CPH)$
	ν_{10}	1002	$\rho(CH_3)$
	ν_{11}	844	$\nu_s(BF_3)$
	ν_{12}	758	$\rho(CH_3)$
	ν_{13}	729	$\nu_s(CPC)$
	ν_{14}	631	$\delta_s(BF_3)$
	ν_{15}	451	$\delta_a(BF_3)$
	ν_{16}	329	$\nu(B\cdots P)$
	ν_{17}	285	$\delta(CPC)$
	ν_{18}	200	geared libration
	ν_{19}	184	$\tau(CH_3)$
	ν_{20}	102	antigeared libration
a″	ν_{21}	3196	$\nu_a(CH_3)$
	ν_{22}	3192	$\nu_a(CH_3)$
	ν_{23}	3089	$\nu_s(CH_3)$
	ν_{24}	1474	$\delta_a(CH_3)$
	ν_{25}	1473	$\delta_a(CH_3)$
	ν_{26}	1354	$\delta_s(CH_3)$
	ν_{27}	1181	$\nu_a(BF_3)$
	ν_{28}	1055	$\delta_a(CPH)$
	ν_{29}	880	$\rho(CH_3)$
	ν_{30}	793	$\nu_a(CPC)$
	ν_{31}	743	$\rho(CH_3)$
	ν_{32}	454	$\delta_a(BF_3)$
	ν_{33}	264	geared libration
	ν_{34}	163	$\tau(CH_3)$
	ν_{35}	84	antigeared libration
	ν_{36}	35	$\tau(B\cdots P)$

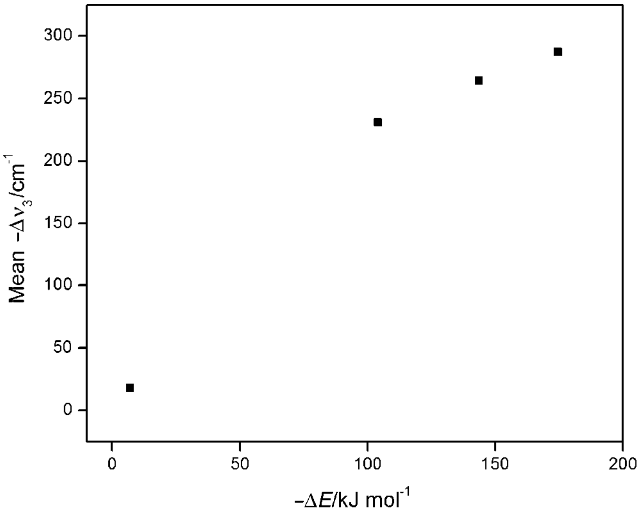

Figure 3. Plot of the mean wavenumber shifts of the ν_3 mode of the BF_3 fragments versus the interaction energies of the complexes.

In our earlier studies of the vibrational spectra of complexes of BF_3,[1–5] we used the complex−monomer wavenumber shifts of the modes of the BF_3 submolecule as probes of the strength of interaction with the bases. These wavenumber shifts are reported in Table 9. Discounting the shifts of the $BF_3 \cdot PH_3$ complex, which are questionable in view of the basis set errors discussed above, the shifts of the remaining complexes should be expected to vary in a monotonic fashion with the energy of interaction. Inspection of Table 9 reveals that, for the symmetric BF_3 stretching and bending modes, the shifts are indeed monotonic but are in the reverse direction to that expected. The explanation for this is to be found in the fact that the modes assigned in Tables 5–8 to BF_3 fragment modes imply that those vibrations are highly localized in the BF_3 fragments. However, the approximate potential energy distributions (PEDs) for the BF_3 ν_1 mode, for example, indicate that the percentage contribution of the BF_3 fragment to the normal mode varies considerably, as shown in Table 10, and the BF_3 contributions for the methylated species are all less than 45%. For the ν_2 mode, with the exception of $BF_3 \cdot PH_3$, the percentage BF_3 contributions are all less than 60%, showing that these modes are not characteristic of the BF_3 fragment. Thus, the shifts of the BF_3 ν_1 and ν_2 modes are not good indicators of the strength of interaction. For the ν_3 mode, the percentage BF_3 contributions are all greater than 64%, so the shifts of this mode, for all four complexes, are expected to be more characteristic of the BF_3 moiety and, therefore, to vary monotonically with the degree of methylation. A plot of the mean ν_3 shift versus the interaction energy is shown in Figure 3. The fact that the datum for $BF_3 \cdot PH_3$ is not wildly out of line with the other three points is simply due to

TABLE 8: Wavenumbers and Approximate Descriptions of the Modes of the $BF_3\cdot(CH_3)_3P$ Complex

		wavenumber (cm^{-1})				
		calculated		experimental		
symmetry species	mode	this work	ref 8	ref 16 [a]	ref 17 [a]	approximate description
a_1	ν_1	3176	3252	3000	2960−2890	$\nu_a(CH_3)$
	ν_2	3079	3172	2900		$\nu_s(CH_3)$
	ν_3	1490	1596	1425	1470−1450	$\delta_a(CH_3)$
	ν_4	1372	1475	1300	1375, 1365	$\delta_s(CH_3)$
	ν_5	1028	890	970	955	$\rho(CH_3)$
	ν_6	854		785	787, 766	$\nu_s(BF_3)$
	ν_7	710	667[b]		530	$\nu_s(PC_3)$
	ν_8	639		675[b]	680, 639	$\delta_s(BF_3)$
	ν_9	359			269	$\delta_s(PC_3)$
	ν_{10}	187	719		242	$\nu(B\cdots P)$
a_2	ν_{11}	3196				$\nu_a(CH_3)$
	ν_{12}	1467				$\delta_a(CH_3)$
	ν_{13}	822				$\rho(CH_3)$
	ν_{14}	147				$\tau(CH_3)$
	ν_{15}	35	31			$\tau(B\cdots P)$
e	ν_{16}	3196	3259			$\nu_a(CH_3)$
	ν_{17}	3176				$\nu_a(CH_3)$
	ν_{18}	3080	3171			$\nu_s(CH_3)$
	ν_{19}	1483	1585		1438	$\delta_a(CH_3)$
	ν_{20}	1470				$\delta_a(CH_3)$
	ν_{21}	1349	1455		1301	$\delta_s(CH_3)$
	ν_{22}	1147	1280	1090−1030		$\nu_a(BF_3)$
	ν_{23}	993	1053		875	$\rho(CH_3)$
	ν_{24}	880	936			$\rho(CH_3)$
	ν_{25}	784	798[b]	705[b]	720, 697	$\nu_a(PC_3)$
	ν_{26}	453			315	$\delta_a(BF_3)$
	ν_{27}	285	299[b]		298, 293	$\delta_a(PC_3)$
	ν_{28}	225				geared libration
	ν_{29}	191				$\tau(CH_3)$
	ν_{30}	85				antigeared libration

[a] Symmetries not specified. [b] Not assigned.

TABLE 9: Complex−Monomer Wavenumber Shifts of the BF_3 Modes of the Complexes

	complex			
BF_3 monomer mode	$BF_3\cdot PH_3$	$BF_3\cdot CH_3PH_2$	$BF_3\cdot(CH_3)_2PH$	$BF_3\cdot(CH_3)_3P$
$\nu_s(BF_3)$	−13	−42	−30	−20
$\delta_s(BF_3)$	−68	−86	−65	−56
$\nu_a(BF_3)$	−18	−220 (a′)	−274 (a′)	−287
		−243 (a″)	−254 (a″)	
$\delta_a(BF_3)$	−3	−20 (a′)	−24 (a′)	−22
		22 (a″)	−20 (a″)	

the underestimation of both the interaction energy and the wavenumber shift, as a result of the basis set problem for this complex. For the ν_4 mode, the shifts of the two components for the $BF_3\cdot CH_3PH_2$ complex are in opposite directions. This is because the BF_3 contribution for the ν_{23} (a″) mode of the complex is only 8% [compared with 79% for the ν_{13} (a′) mode], which causes the ν_{23} mode to appear at a higher wavenumber than in the BF_3 monomer. Thus, ν_4 is not a good probe of interaction strength.

The wavenumbers of the intermolecular vibrations do not appear to follow a pattern. The intermonomer stretching mode of $BF_3\cdot PH_3$ appears at a very low wavenumber, consistent with the anomalous behaviour of this complex discussed above. The wavenumbers of this mode for the remaining complexes reach a maximum at $BF_3\cdot(CH_3)_2PH$ and then decrease. The values of the $B\cdots P$ torsional wavenumber are particularly insensitive to the nature of the base. Apart from the low wavenumbers of the geared and antigeared librational vibrations of $BF_3\cdot PH_3$, those of the remaining three complexes are fairly constant. Because of the intermolecular nature of these modes, however, the vibrational motion is delocalized throughout the whole complex, and the distribution between the BF_3 fragment and the base varies widely, as shown in Table 11. The intermolecular stretching and torsional force constants could potentially be useful as indicators of the strength of binding. These are listed in Table 12. The experimental stretching force constants of $BF_3\cdot PH_3$[15] and $BF_3\cdot(CH_3)_3P$[17] are also included. The stretching force constant of $BF_3\cdot PH_3$ severely underestimates that reported

TABLE 10: Approximate Percentage Potential Energy Distributions of the Complex Modes Nominally Described As Intramolecular BF_3 Vibrations

	percentage distribution (BF_3/base)			
BF_3 monomer mode	$BF_3\cdot PH_3$	$BF_3\cdot CH_3PH_2$	$BF_3\cdot(CH_3)_2PH$	$BF_3\cdot(CH_3)_3P$
$\nu_s(BF_3)$	97/3	10/90	20/80	45/56
$\delta_s(BF_3)$	95/5	60/40	59/41	55/45
$\nu_a(BF_3)$	99/1	64/35 (a′)	76/24 (a′)	95/5
		82/19 (a″)	94/6 (a″)	
$\delta_a(BF_3)$	97/3	79/21 (a′)	64/37 (a′)	82/18
		8/92 (a″)	84/16 (a″)	

TABLE 11: Approximate Percentage Potential Energy Distributions of the Intermolecular Vibrations of the Complexes

intermolecular mode	percentage distribution (BF_3/base)			
	$BF_3 \cdot PH_3$	$BF_3 \cdot CH_3PH_2$	$BF_3 \cdot (CH_3)_2PH$	$BF_3 \cdot (CH_3)_3P$
$\nu(B \cdots P)$	21/79	25/74	10/88	8/92
$\tau(B \cdots P)$	0/100	6/95	11/89	17/82
geared libration	1/98	18/82 (a′) 4/97 (a″)	6/93 (a′) 32/67 (a″)	0/100
antigeared libration	13/87	9/92 (a′) 2/97 (a″)	8/90 (a′) 7/93 (a″)	7/91

TABLE 12: Intermolecular Stretching and Torsional Force Constants of the Complexes

	force constant (N m^{-1})		
complex	stretching, calculated	stretching, experimental	torsional, calculated
$BF_3 \cdot PH_3$	10.1	204[a]	5.5
$BF_3 \cdot CH_3PH_2$	104.5		8.7
$BF_3 \cdot (CH_3)_2PH$	133.1		6.5
$BF_3 \cdot (CH_3)_3P$	155.7	123[b]	10.4

[a] Reference 15. [b] Reference 17.

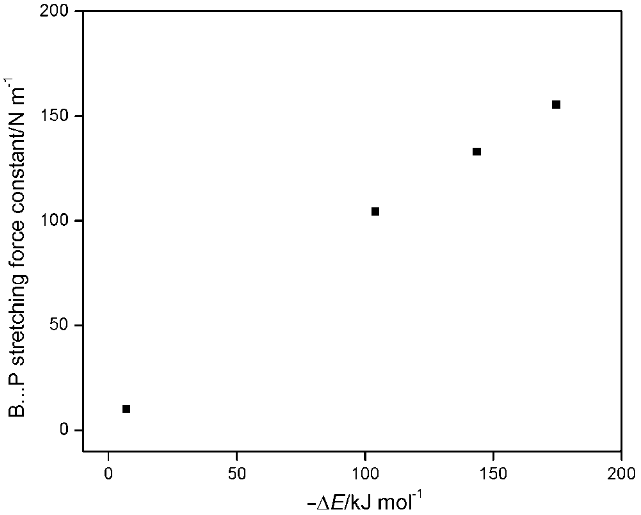

Figure 4. Plot of the intermonomer stretching force constants of the complexes versus the interaction energies.

by Durig et al.,[15] as a result of a combination of the poor theoretical representation of the properties of this complex, mentioned earlier, and the exaggeration of the experimental $B \cdots P$ stretching wavenumber, also discussed above. Our force constant for $BF_3 \cdot (CH_3)_3P$, however, is in acceptable agreement with that reported by Mente and Mills.[17] The stretching force constants are plotted against the interaction energies in Figure 4. The torsional force constants are fairly independent of the base, mirroring the observation regarding the torsional wavenumbers (Tables 5–8).

Conclusions

The structural and vibrational properties of the four related bases reported here show some correlations with the gas-phase basicity of the base fragments, but our argument is weakened by the questionable results for the $BF_3 \cdot PH_3$ complex, which are due to deficiencies in the basis set used for this series of calculations. This complex is characterized by the underestimation of the strength of interaction, coupled with the small perturbations of the intramolecular geometrical parameters, the exaggerated intermonomer separation, the minimal distortion of the angles around the boron atom, and the small intramolecular wavenumber shifts on complexation. Notwithstanding this disappointing feature, the results for the methylated derivatives show a satisfactory series of trends, rationalized by an increase in the strength of interaction with increasing basicity and degree of methylation, leading to successively greater perturbation of the structural and vibrational properties throughout the series. The results are entirely consistent with those for the analogous families of complexes containing the methyl derivatives of water, hydrogen sulfide, and ammonia.[1–5]

Acknowledgment. This material is based on work supported by the National Research Foundation under Grant 2053648. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the National Research Foundation. The author also acknowledges the financial assistance of the University of KwaZulu-Natal Research Fund, through its support of the Centre for Theoretical and Computational Chemistry, and the invaluable technical assistance of Mr. Kishore Singh.

References and Notes

(1) Yeo, G. A.; Ford, T. A. *S. Afr. J. Chem.* **2006**, *59*, 129.
(2) Gaffoor, F.; Ford, T. A. *Spectrochim. Acta A*, in press. DOI: 10.1016/j.saa.2008.01.014.
(3) Ford, T. A. *J. Mol. Struct.* **2007**, *834–836*, 30.
(4) Nxumalo, L. M.; Ford, T. A. *J. Mol. Struct. (THEOCHEM)* **1996**, *369*, 115.
(5) Nxumalo, L. M.; Ford, T. A. *J. Mol. Struct.* **2003**, *656*, 303.
(6) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
(7) Hirota, F.; Miyata, K.; Shibata, S. *J. Mol. Struct. (THEOCHEM)* **1989**, *201*, 99.
(8) Ahlrichs, R.; Bär, M. B.; Häser, M.; Sattler, E. *Chem. Phys. Lett.* **1991**, *184*, 353.
(9) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *J. Phys. Chem. A* **1998**, *102*, 7070.
(10) Durig, J. R.; Shen, Z. *J. Mol. Struct. (THEOCHEM)* **1997**, *397*, 179.
(11) Anane, H.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *Chem. Phys. Lett.* **2000**, *324*, 156.
(12) Jensen, J. O. *J. Mol. Struct. (THEOCHEM)* **2004**, *673*, 165.
(13) Anane, H.; El Houssame, S.; El Guerraze, A.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *J. Mol. Struct. (THEOCHEM)* **2004**, *709*, 103.
(14) Odom, J. D.; Kalasinsky, V. F.; Durig, J. R. *Inorg. Chem.* **1975**, *14*, 2837.
(15) Durig, J. R.; Riethmiller, S.; Kalasinsky, V. F.; Odom, J. D. *Inorg. Chem.* **1974**, *13*, 2729.
(16) Beg, M. A. A.; Clark, H. C. *Can. J. Chem.* **1962**, *40*, 393.
(17) Mente, D. C.; Mills, J. L. *Inorg. Chem.* **1975**, *14*, 1862.
(18) Rapp, B.; Drake, J. E. *Inorg. Chem.* **1973**, *12*, 2868.
(19) Heitsch, C. W. *Inorg. Chem.* **1965**, *4*, 1019.
(20) Markham, R. T.; Dietz, E. A., Jr.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 503.
(21) Tierney, P. A.; Lewis, D. W.; Berg, D. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1163.
(22) Odom, J. D.; Riethmiller, S.; Witt, J. D.; Durig, J. R. *Inorg. Chem.* **1973**, *12*, 1123.
(23) Drake, J. E.; Hencher, J. L.; Rapp, B. *J. Chem. Soc., Dalton Trans.* **1974**, 595.
(24) Muylle, E.; van der Kelen, G. P.; Claeys, E. G. *Spectrochim. Acta A* **1976**, *32*, 1149.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(27) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(28) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. *J. Comput. Chem.* **1983**, *4*, 294.

(29) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1973**, *59*, 4557.

(30) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(31) Del Bene, J. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 1, pp 319−349.

(32) Mente, D. C.; Mills, J. L.; Mitchell, R. E. *Inorg. Chem.* **1975**, *14*, 123.

JP802493N