THE "CYCLOHEXANE-LIKE" STRUCTURE OF $(MeOBF_2)_3$ AND OTHER SPECIES ARISING FROM MIXING $(MeO)_3B$ AND BF_3. AN *ab initio*/IGLO/NMR INVESTIGATION

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Received January 19, 1999
Accepted April 6, 1999

Dedicated to Dr Stanislav Heřmánek, a very Special Friend, a "Grey Eminence" of Borane and Carborane Chemistry and the Father of the International IMEBORON Conferences on the occasion of his 70th birthday.

An *ab initio*/IGLO/NMR investigation shows that $(MeOBF_2)_3$, **3**, is the thermodynamically most stable product when $(MeO)_3B$ and BF_3 are mixed in a 1 : 2 ratio. Compound **3** has a symmetrical, "cyclohexane-like", structure with C_{3v} symmetry. The *ab initio* calculated structures of less stable intermediates, *i.e.* the monomeric $MeOBF_2$, **1**, the dimeric $(MeOBF_2)_2$, **2**, the "diadduct" $MeOB(O(BF_3)Me)O(BF_3)Me$, **4**, and the "monoadduct" $(MeO)_2BO(BF_3)Me$, **5**, are also discussed.

Key words: IGLO/NMR calculations; Structure of $(MeOBF_2)_3$; *Ab initio* calculations; Boron trifluoride; Trimethyl borate.

In 1894 Gasselin[1] reported that alcohols, ROH, and boron trifluoride, BF_3, reacted to form what he called alkoxyboron difluorides $ROBF_2$, **1**, (Eq. (*1*)). The same or similar compounds were later found to arise from the "mixing" of one part trialkoxyboron $(RO)_3B$, with two parts boron trifluoride BF_3. Various candidate structures were proposed, including the monomeric $ROBF_2$, **1**, the dimeric $(ROBF_2)_2$, **2**, and the trimer $(ROBF_2)_3$, **3** (see Eqs (*1a*)–(*3*)) as well as a diadduct $ROB(O(BF_3)R)_2$, **4**, wherein two of the three "alkoxy-oxygens" donate a lone electron pair of to two BF_3 groups (Eq. (*4*)).

$$ROH + BF_3 \longrightarrow ROBF_2\ (\mathbf{1}) + HF \qquad (1)$$

$$(RO)_3B + 2\ BF_3 \longrightarrow 3\ ROBF_2\ (\mathbf{1}) \qquad (1a)$$

$$2\ (RO)_3B + 4\ BF_3 \longrightarrow 3\ (ROBF_2)_2\ (\mathbf{2}) \qquad (2)$$

$$(RO)_3B + 2\ BF_3 \longrightarrow (ROBF_2)_3\ (\mathbf{3}) \qquad (3)$$

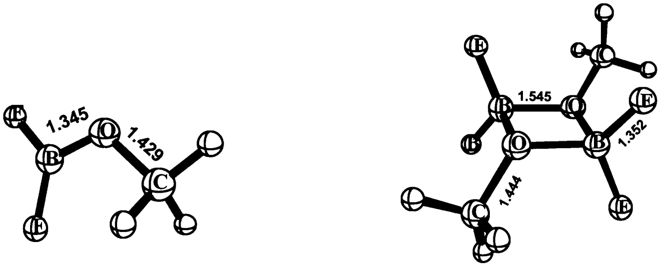
$$(RO)_3B + 2\ BF_3 \longrightarrow ROB(O(BF_3)R)_2\ (\mathbf{4}) \qquad (4)$$

Based on elemental analysis and the molecular weight, determined in the vapor phase, Gasselin[1] supported the monomer **1** as the correct gas phase structure. In 1932 Allen and Sugden[2] favored the dimer structure **2** based on parachor determinations in the liquid state. In 1952 Gobeau and Lucke[3] also favored the dimer structure **2** based on “over sized” values for the Trouten constant.

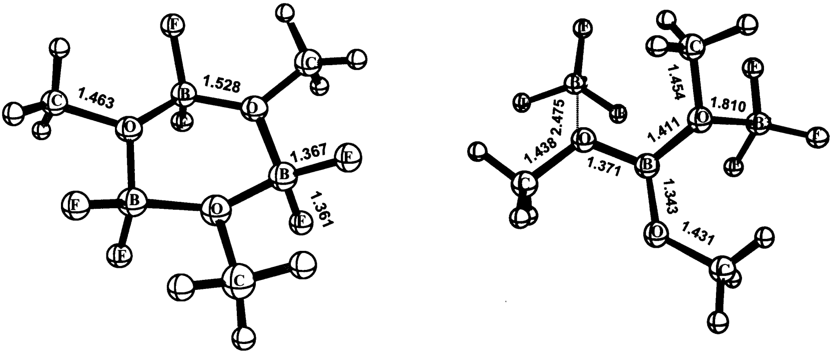
In 1960, utilizing more modern cryoscopic data, McKusker and Kilzer determined that the molecular weight was three times that of **1**, in both benzene and cyclohexane[4]. This result suggested that either (i) the trimer **3** or (ii) the diadduct **4** (with the same empirical composition) was the correct structure in solution. Of the two configurations, the consideration of various physical measurements, as well as comparisons with the well-characterized ether–BF_3 coordination compounds, persuaded McKusker and Kilzer[4] to favor the diadduct **4** structure rather than the trimer **3**.

A new instrument had become accesible by 1957 that was felt could “probably” tell the difference between **3** and **4** with some confidence. This new tool, first used at Varian Associates in 1955, yielded, the now primitive, ^{11}B NMR spectra at 12.8 MHz for ^{11}B (40 MHz for ^{1}H). Based on patterns observed in a previous investigation[5], one of the current authors (R. E. W.) favored the symmetrical trimer structure **3**.

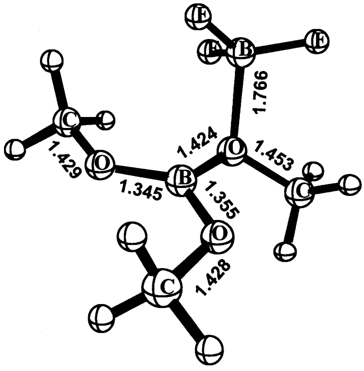
It was noted that there were “at least” two kinds of boron in diadduct **4** but only one kind of boron in trimer **3**. In 1960 it was assumed[4,6] (inaccurately, see Fig. 1) that the two BF_3 groups in the diadduct **4** would be structurally identical and thus ^{11}B NMR equivalent. At the time it was also presumed that the one trigonal sp^2 boron, in diadduct **4** which is surrounded by three oxygens, would produce a one-boron ^{11}B NMR resonance at about +18 ppm. All comparable sp^2 borons (from boric acid to trialkylborates) resonate around +18 ppm. Secondly, it was felt that the two tetrahedral sp^3 borons surrounded by three fluorines and one oxygen would produce an ^{11}B NMR resonance, reflecting two borons at about zero. The sp^3 borons in both $B(OH)_4^-$ and BF_4^- resonate at about zero. In fact, all comparable tetrahedral boron atoms surrounded by four fluorines or four



Monomeric $MeOBF_2$ (**1**) (C_S) Dimeric $(MeOBF_2)_2$ (**2**) (C_2)



Trimeric $(MeOBF_2)_3$ (**3**) (C_{3V}) and diadduct $MeOB(O(BF_3)Me)(O(BF_3)Me)$ (**4**) (C_1)



Monoadduct $(MeO)_2B(O(BF_3)Me)$ (**5**) (C_1)

FIG. 1
B3LYP/6-31G* optimized structures of **1–5**

oxygens (or any mixed combination) as is the case in trimer **3** were all known to resonate at about zero.

Assuming there might be some convoluted mechanism by which the diadduct **4** could rapidly scramble the three borons (of two kinds on an NMR time scale), then all three borons would have been expected to yield a single three-boron resonance at +6 ppm, *i.e.* the average of 18 ppm. In contrast, the three identical tetrahedral sp^3 borons in trimer **3** should result in a single three-boron resonance at zero, not +6 ppm.

A mixture **X** consisting of $(MeO)_3B$ and BF_3 in a 1 : 2 ratio was prepared and allowed to react. The ^{11}B NMR spectrum revealed only one boron resonance (not two) at zero (not +6 ppm). Both results supported[6] the trimer structure **3** over the diadduct structure **4**. On the other hand, an exchange reaction of the "product" (the trimer structure **3** or the diadduct structure **4**) with excess ^{10}B-enriched BF_3 showed that the ^{10}B did mix with the ^{11}B borons in the product so the system was rearrangement prone[6]. Such reversibility (regenerating BF_3 units available for exchange) indicated that a compound like **4** was probably involved.

Since 1961 (ref.[6]) to date, one of the authors (R. E. W.) has intermittently felt apprehension about selecting structure **3** over structure **4**. After all, the preference 38 years ago, had been based on (i) a single ^{11}B resonance, and (ii) a chemical shift difference of only 6 ppm. Moreover, it involved the study of (iii) a system that was known to be rearrangement prone and was based upon (iv) a ^{11}B spectrum obtained from the first (and most primitive) NMR spectrometer that had ever produced useful ^{11}B NMR spectra. Thus, even though there was only a small chance that the ^{11}B NMR spectrum was misleading, the circumstantial evidence was not felt to be "ironclad". In any event, there was no obvious, easy way to investigate further.

COMPUTATIONAL

The ab Initio/IGLO/^{11}B NMR Procedure

Much has changed during the intervening years. Dramatic increases in computer power have allowed fundamental improvements in *ab initio* structural calculations and in the capacity to handle larger molecules. Kutzelnigg and Schindler[7] have made possible the IGLO method of calculating accurate NMR chemical shift values dependent upon the accuracy of the various input geometries. Schleyer[8] has fused the two techniques into the "*ab initio*/IGLO/NMR procedure". Now *ab initio* optimized structures, their relative stabilities and the chemical shift values of their various atoms may be calculated and subsequently compared with experimentally observed chemical shift values obtained either today or several decades ago.

Method

Calculations were carried out with the Gaussian 98 program system[9]. The geometry optimizations and frequency calculations were performed at the density functional theory[10] (DFT) B3LYP/6-31G* level. From calculated frequencies, the optimized structures were characterized as minima (number of imiganary frequencies, NIMAG = 0). Zero point vibrational energies (ZPE) were calculated at the B3LYP/6-31G* level and scaled by a factor of 0.96. Relative energies were calculated at the B3LYP/6-31G*//B3LYP/6-31G* + ZPE level. NMR chemical shifts were calculated by IGLO methods[7] at the basis II (ref.[11]) using B3LYP/6-31G* geometries.

As a part of this study, detailed DFT calculations have been carried out on the candidate structures **1**, **2**, **3**, **4**, and **5**, illustrated in Fig. 1. By far the most stable structure is trimer **3** (see Table I) which reassuringly supports our previous conclusion[6]. At the B3LYP/6-31G* level, a minimum was also found for the diadduct **4**, wherein one of the two BF_3 groups is associated with the oxygen of one of the OMe groups, –O(BF_3)Me. The calculated O–BF_3 distance is 1.810 Å. The length of an O–B bond of order 1 (a single bond) is estimated to be 1.54 Å. The other BF_3 moiety is involved at very long range with the oxygen of a second OMe group, identified as an –O(BF_3)Me group. The boron in the latter BF_3 group is only 5° from being

TABLE I
Calculated and experimental ^{11}B NMR chemical shift values[a]

Structure	Atom	IGLO DZ//B3LYP/6-31G*	IGLO II//B3LYP/6-31G*	Experimentally observed[a]
1	^{11}B	15.1		≠ 0.0
2	^{11}B	–1.4		1.6 ← ≈ → 0.0
3	^{11}B	–2.1		1.8 ← ≈ → 0.0
4	^{11}B(B1)	17.1	20.8	
	^{11}B(B2)	4.1	5.3	} 12.6 ≠ 0.0
	^{11}B(B3)	13.4	11.7	

[a] ^{11}B NMR chemical shifts (in ppm) referenced to BF_3OEt_2.

coplanar with the three fluorine atoms. The O–BF_3 distance is 2.475 Å which implies a bond order of <0.5.

RESULTS AND DISCUSSION

Calculated ^{11}B NMR Chemical Shift Values and Relative Stabilities

The calculated ^{11}B chemical shift values of compounds **1**, **2**, **3**, and **4** (at the IGLO II//B3LYP/6-31G* level) are illustrated in Table I and compared to the experimentally observed value of zero. It is apparent that both the trimer **3**, and dimer **2**, having ^{11}B values of 1.8 and 1.6 ppm, respectively, are both acceptably close to the experimentally observed ^{11}B value of zero. The monomer **1** (15.1 ppm) and the diadduct **4** (12.6 ppm) are not in agreement.

A relative energy comparison (at the B3LYP/6-31G*//B3LYP/6-31G* + ZPE level) was made between diadduct **4** and trimer **3**, and (to keep the molecular weight constant) 1.5 mol of dimer **2** and 3 mol of the monomer **1**. By this contrived measure, 1.5 mol of the dimer **2** is 12.2 kcal mol^{-1} less stable than trimer **3** while 3 mol of the monomer **1** is 21.7 kcal mol^{-1} less stable than trimer **3**. Table I reveals that both **2** and **3** had acceptable ^{11}B chemical shift values but that **3** was much more stable than **2**.

In order to relate the various structural species to each other, the relative energies of the initial mixture **X** as well as the monoadduct **5** (illustrated in Fig. 1) and compounds **4**, **3**, **2**, and **1** are compared in Table II and Fig. 2. Following this procedure the relative energies of the various combinations,

TABLE II
Calculated relative energies

Structure	$(MeO)_3B_3F_6$ Optional composition	ΔE, kcal mol^{-1}
1	3 $MeOBF_2$	21.7
2	1.5 $(MeOBF_2)_2$	12.2
3	1 $(MeOBF_2)_3$	0.0
4	$MeOB(O(BF_3)Me)(O(BF_3)Me)$	13.6
5	$(MeO)_2B(O(BF_3)Me)$ + 1 BF_3	13.8
X	1 $(MeO)_3B$ + 2 BF_3	26.2

all having the total composition of $(MeO)_3B_3F_6$, can be compared with each other.

The initial 1 : 2 mixture of $(MeO)_3B$ and BF_3, **X**, is calculated to be 26.2 kcal mol^{-1} less stable than the final most stable product, the trimer $(MeOBF_2)_3$, **3**, to which is assigned 0.0 kcal mol^{-1}. Along the most probable reaction pathway is the monoadduct **5** which is found to be 13.8 kcal mol^{-1} less stable than **3** (a second "noncomplexed" BF_3 moiety is necessarily included in the calculation). The driving force that causes the monoadduct **5** to complex a second BF_3 group, producing diadduct **4** (0.2 kcal mol^{-1}) is trifling, but accounts for the uniquely weak complexation of this second BF_3 group. Diadduct **4** is found to be 13.6 kcal mol^{-1} less stable than **3**. Indeed the O–BF_3 bond length in the monoadduct **5** is 1.766 Å which stretches slightly, to 1.810 Å, in the diadduct **4**, but the second O–BF_3 bond length in the diadduct **4** is 2.475 Å ("almost nonbonding"). The subsequent rearrangement (of the diadduct **4** into the trimer **3**) results in the gain of an additional 13.6 kcal mol^{-1} in stability. The possibility that monoadduct **5** could somehow dissociate into $MeOBF_2$, **1**, (leading to trimer **3**) and $(MeO)_2BF$, **6**, was considered but no transition state could be found.

The energetic relationships illustrated in Fig. 2 are such that it is not unreasonable that trimer **3** at elevated temperatures could dissociate into dimer **2** (12.2 kcal mol^{-1} less stable than **3**) and/or perhaps even monomer[1] **1** (21.7 kcal mol^{-1} less stable than **3**) in the gas phase.

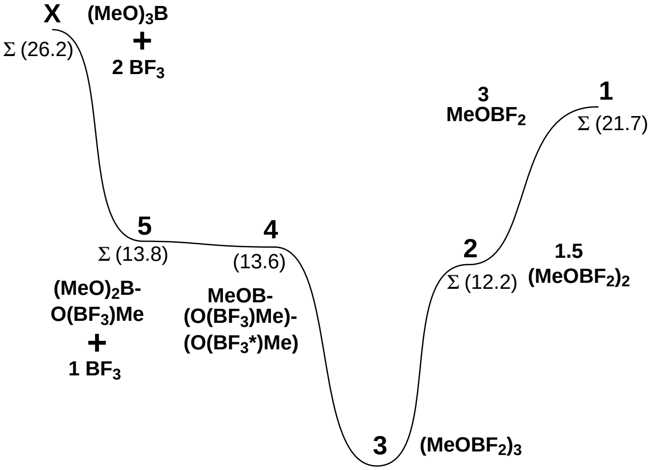


FIG. 2
Relative energies of $(MeO)_3B_3F_6$ compositions in kcal mol^{-1}

*Structural Details of Trimer **3** and Dimer **2***

Returning to Fig. 1, the trimer **3** has a cyclohexane-chair-like configuration. All three equatorial methyl groups are coplanar. The carbon and two borons surrounding each positively charged oxygen, *i.e.* the COB_2 units, are flattened from tetrahedral symmetry while the negatively charged borons, BF_2O_2 units, are much more tetrahedral. One fluorine on each boron is equatorial, the other fluorine is axial and might be capable of differentiation by ^{19}F NMR spectroscopy. In contrast, dimer **2** incorporates a four-membered $(BO)_2$ planar ring with the two methyl groups pointing in opposite directions. The COB_2 units are also flattened in this case.

CONCLUSIONS

An *ab initio*/IGLO/NMR investigation shows that the trimer $(MeOBF_2)_3$, **3**, is the thermodynamically most stable product when $(MeO)_3B$ and BF_3 are mixed in a 1 : 2 ratio. Compound **3** has a symmetrical, cyclohexane-like, structure with C_{3v} symmetry. The DFT calculated structures of less stable intermediates are also illustrated. They are the monomer $MeOBF_2$, **1**, the dimer $(MeOBF_2)_2$, **2**, the diadduct $MeOB(O(BF_3)Me)O(BF_3)Me$, **4**, and the monoadduct $(MeO)_2BO(BF_3)Me$, **5**. The boron in the marginally associated BF_3 group in the diadduct $MeOB(O(BF_3)Me)O(BF_3)Me$, **4**, is calculated to be 2.475 Å from the oxygen.

We thank Professors G. K. S. Prakash and G. A. Olah for helpful discussions and the U. S. National Science Foundation (GR) and the Loker Hydrocarbon Research Institute (REW) for financial support.

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