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Experimental and Calculational Studies of the Interactions of BF$_3$ With Fluoroethers

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EXPERIMENTAL AND CALCULATIONAL STUDIES OF THE INTERACTIONS OF BF$_3$ WITH FLUOROETHERS

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ABSTRACT

BF$_3$ was co-condensed with $(C_2H_5)_2O$, $(CF_3CH_2)_2O$, and $(C_2F_5)_2O$ in excess argon at 15 K. Infrared spectra of the matrices showed a definite Lewis acid-base interaction between BF$_3$ and diethyl ether; a weak but definite interaction with bis(2,2,2,-trifluorodiethyl)ether, and no observable interaction with perfluorodiethyl ether. Molecular orbital (MO) calculations complemented the experimental observations by revealing that fluorine atoms on the ethers decreased electron localization about the oxygen atom. Thus, the experimental data and MO calculations indicated a clear trend between strength of interaction with BF$_3$ and the degree of ether F substitution. The implications of the results for commercial perfluoro ether lubricant/metal oxide surface interactions are discussed.

KEY WORDS: Infrared spectroscopy, chemical attack, fluorocarbons

INTRODUCTION

The chemistry of perfluoroalkyl ethers has come under increasing study recently because of their application to lubrication of computer magnetic media and spacecraft devices (Refs. 1 and 2). The behavior of commercial fluids, and model compounds that mimic their chemistry, has been studied both theoretically (Refs. 3 and 4) and experimentally for exposure to the influence of electrons (Ref. 5), Lewis acids (Refs. 6 to 9), metal oxides (Refs. 9 and 10), and bare metal surfaces (Refs. 11 and 12). Much attention has been given to the catalytic decomposition of perfluoroalkyl ethers which occurs when they are heated in the presence of metal oxides or halides. The effectiveness of the surfaces in catalyzing the decomposition is a strong function of the fluoroether's structure. A number of workers have observed that the presence of an -O-CF$_2$-O- (acetal) linkage greatly enhances their reactivity towards catalyzed breakdown by metal oxides (Refs. 8 and 13).

The postulated mechanisms for this catalyzed breakdown usually involve an initial acid-base interaction between the surface metal ions and the lone electron pairs on the fluoroether oxygen atoms followed by chain scission. Kasai et al. (Refs. 7 and 10) used ^{19}F NMR and mass spectrometry to study the Lewis acid-catalyzed breakdown of several perfluoroethers of different structures. The initial step in the mechanism they proposed, as well as that of most other mechanisms advanced, is the donation of electron density from oxygen atoms in the chain to one or more acidic metal atoms on the Lewis acid surface. Although this mechanism is a well-established process for hydrocarbon ethers, one expects that for perfluoroethers the oxygen atoms will exhibit a much lower basicity and therefore vulnerability to attack.

Alternate mechanisms which do not involve Lewis acid attack on the oxygen atoms have been proposed. Zehe and Faut (Ref. 8) studied the catalyzed breakdown of commercial fluids by α-Fe$_2$O$_3$ and proposed a mechanism involving acidic attack on the nonbonding electrons on the fluorine atoms. Basu et al. (Refs. 14 to 16) studied decomposition of hydrocarbon ethers and $(CF_2H)_2O$ on planar and powdered Al$_2$O$_3$. They observed decomposition to occur for $(CF_2H)_2O$ in contact with powdered Al$_2$O$_3$, even after pre-adsorbing pyridine to block Lewis acid sites. They concluded that Lewis sites were not involved in the reaction, and postulated that the first step in the decomposition was a nucleophilic attack by surface oxygen on a carbon atom in the ether.

Infrared matrix-isolation spectroscopy has been used successfully for producing and studying reaction complexes, including Lewis acid-base adducts. This technique has been applied by Ault (Refs. 17 and 18) to the study of a large number of Lewis acid-base complexes, both strongly and weakly bound. Strong Lewis acids such as BF$_3$ and SO$_3$ have been co-condensed at high dilution with weak Lewis bases, and complexation observed through shifts in the measured vibrational frequencies. With a given base, rough correlations have been observed between the strength of the acidity or basicity and the measured spectral shifts.

In this paper, an infrared matrix-isolation apparatus was used to investigate the interaction between the strong Lewis acid BF$_3$ with

diethyl ether, bis(2,2,2-trifluorodiethyl)ether and perfluorodiethyl ether. The results were used to assess the Lewis acid-base hypothesis for the postulated decomposition mechanism of commercial perfluoroether lubricants by metal oxides. Molecular orbital (MO) calculations were performed on the interaction between BF_3 and the three ethers to aid the analysis of the experimental data.

EXPERIMENTAL

The matrix isolation apparatus used in this study has been previously described (Ref. 19). Briefly, sample vapors were co-condensed, inside a vacuum chamber, onto the polished surface of a gold-plated copper block which was kept at 15 K. Sample vapors were introduced into the vacuum chamber via stainless steel tubing and were regulated with high precision needle valves. Deposition rates were measured manometrically. Deposition onto the gold-plated surface typically lasted 30 min to 2 hr. After deposition, the Fourier transform infrared spectrum was measured by reflection off the gold-plated surface through ZnSe windows using a Fourier transform infrared spectrometer at 2 cm^{-1} resolution. Five hundred scans were measured and averaged.

BF_3 (99.5+%), $(C_2H_5)_2O$ (reagent grade), $(CF_3CH_2)_2O$ (97+%), $(C_2F_5)_2O$ (97%), and Ar (99.9995%) were used without further purification. CAUTION: BF_3 is a highly toxic, moisture-sensitive gas; only small quantities should be used at a time, under a fume hood. $(CF_3CH_2)_2O$ is a convulsant and should be used only in adequate ventilation or in a fume hood.

CALCULATIONAL

The AM1 self-consistent field molecular orbital procedure developed by Dewar and co-workers (Ref. 20) was used in this study. Computations were performed using a commercial software package, utilizing the RHF option, on a Pentium based, 166 MHz, desktop computer. Complete geometric optimization during energy minimization was performed on all single molecules and for all interacting pairs of molecules. The convergence criterion for energy minimization was selected so that the change in total energy on successive iterations was less than 0.01 kJ/mol Å. Configuration interaction was not used.

RESULTS

Experimental

When BF_3 was co-condensed with diethyl ether in excess Ar at 15 K, new absorptions were measured in the infrared spectrum. Figure 1(a) shows the wavelength region 1300 to 600 cm^{-1} for BF_3 in Ar, illustrating the BF_3 bending mode (Ref. 21) (split into two absorptions following the natural 20%/80% $^{10}B/^{11}B$ isotopic abundance of boron). Several new absorptions appeared, indicated by the features in Fig. 1(c) marked with an asterisk. The absorptions appearing at 1241.1 and 1207.6 cm^{-1} are very close to the

positions reported by Hunt and Ault (Ref. 18) for the antisymmetric B-F stretches of the $BF_3/(CH_3)_2O$ complex. A broad absorption appearing at 875.8 cm^{-1} corresponds to the symmetric C-O stretch of the ether moiety. A new absorption at 762.0 cm^{-1} can be assigned to a symmetric B-F stretch; a very weak feature at 796.8 cm^{-1} could be the ^{10}B counterpart.

When BF_3 was co-condensed with $(CF_3CH_2)_2O$, new absorptions appeared. These new absorptions are illustrated in Figs. 2 and 3. All of the new absorptions shown in Fig. 2, occurring at 1229.6, 1220.0, and 1161.1 cm^{-1}, appeared very close to the infrared absorptions of the parent molecules. Another absorption, not shown in the figures and occurring at 1330.0 cm^{-1}, appeared to be a shift of a parent fluoroether absorption. Figure 3(a) shows the infrared spectrum of BF_3 between 740 and 600 cm^{-1}, where the out-of-plane bending vibration of the planar BF_3 molecule absorbs. $^{10}BF_3$ absorbs at 705 cm^{-1}, and $^{11}BF_3$ at 678 cm^{-1}. These absorptions show an approximate intensity ratio expected for naturally occurring boron. Figure 3(c) shows the same region for the co-deposited $BF_3/(CF_3CH_2)_2O$ sample and indicates two broad absorptions at 694.9 and 668.0 cm^{-1} that are present only upon co-condensation.

When BF_3 was co-condensed with $(C_2F_5)_2O$ in excess Ar, no new absorptions were observed. In a subsequent test, BF_3 and $(C_2F_5)_2O$ were co-condensed at 15 K without Ar. No new absorptions appeared upon condensation.

Calculational

Before computational runs were performed on the interaction between the ether molecules and the BF_3 molecule, a preliminary test of the AM1 program was made. This test involved the analysis of the computational results between the interaction of NH_3 and BF_3. NH_3 is a molecule that interacts strongly with surface Lewis acid sites and is widely used as a poison to block the effect of these sites. Select optimized geometries of the BF_3-NH_3 complex are shown in Fig. 4 and total energy values are listed in Table I.

The B-N distance was 1.782 Å and the net charges on the BF_3 and NH_3 groups were ±0.326 respectively. The calculated dihedral angle of the BF_3 group, -130.7°, showed that this molecule was distorted from its normal planar trigonal geometry. The total energy of the BF_3-NH_3 system was 51 kJ/mol lower than the added total energy of the isolated molecules. The HOMO orbital plot (a two dimensional contour) for the this system is shown in Fig. 5. A strong electron withdrawal of the nitrogen 2p orbital toward the boron atom was observed. These MO calculations on the BF_3/NH_3 system confirmed that the AM1 method was able to reproduce computationally the formation of a well-known Lewis acid-base adduct.

The optimized structure and total energy for the BF_3-$(C_2H_5)_2O$ system are shown in Fig. 6 and Table I. The B—O distance was 1.908 Å. The net charges on BF_3 and the ether were ±0.119. The BF_3 molecule had a dihedral angle of -158.2°. The total energy of the BF_3-$(C_2H_5)_2O$ system was 19 kJ/mol lower than the added total energy of the isolated molecules. The HOMO orbital plot (Fig. 7) showed substantial withdrawal of the orbital, around the oxygen atom, toward the boron atom.

The optimized structure and total energy for the BF_3—$(CF_3CH_2)_2O$ system are shown in Fig. 8 and Table I. The B—O distance was 2.007 Å, and net charges on the BF_3 and ether molecules were ±0.057. The BF_3 dihedral angle was −167.0°. The total energy of the BF_3—$(CF_3CH_2)_2O$ system was 8 kJ/mol lower than the added total energy of the isolated molecules. The HOMO orbital plot (Fig. 9) showed a slight withdrawal of the orbital, around the oxygen atom, toward the BF_3 molecule.

The optimized structure and total energy for the BF_3—$(C_2F_5)_2O$ system are shown in Fig. 10 and Table I. The B—O distance was 5.182 Å, and the net charges on the BF_3 molecule and ether molecule were both zero. The BF_3 dihedral angle was −180.0°. The total energy of this system equaled the added total energy of the isolated molecules. The HOMO orbital plot (Fig. 11) showed no orbital withdrawal toward the BF_3 molecule.

DISCUSSION

New absorptions found when diethyl ether was co-condensed with BF_3 indicated a Lewis acid-base complex was formed. Several of the new absorptions appeared in spectral regions that were similar to new vibrations in BF_3/dimethyl ether samples reported by Hunt and Ault (Ref. 18). The new absorptions at 1241.1 and 1207.6 cm^{-1} are assigned to the antisymmetric B-F stretching vibration of the BF_3 moiety. The 875.8 cm^{-1} peak appears in the expected region for the symmetric C-O stretching vibration, and the absorptions at 796.8 and 762.0 cm^{-1} coincide with the symmetric B-F stretch. These two absorptions have the correct approximate 1:3 intensity ratio, suggesting assignment to a vibration involving a boron atom. No boron isotopic splitting was seen for either the 1241.7 or the 1207.6 cm^{-1} absorption. The assignments to BF_3—$(C_2H_5)_2O$ are similar to those of the BF_3/dimethyl ether matrix spectra (Ref. 18). The absorptions of BF_3—$(C_2H_5)_2O$ and their approximate assignments are listed in Table II.

When BF_3 was co-condensed with bis(2,2,2 trifluoroethyl)ether, new absorptions were again detected. These new absorptions are listed in Table III. However, instead of appearing in spectral regions characteristic of a Lewis acid-base interaction, the new absorptions appeared to be only slightly shifted from the absorptions of the parent molecules; they are assigned as such in Table III. This suggests that the interaction between BF_3 and $(CF_3CH_2)_2O$, while apparent, is weak. This weak interaction is best illustrated by the 10 cm^{-1} shifts in the out-of-plane bending vibrations of $^{10}BF_3$ and $^{11}BF_3$ shown in Fig. 7. The same red shift in energy as well as the proper intensity ratio of the absorptions at 694.9 and 668.0 cm^{-1} supports the idea of a mutually perturbing influence of the dopant molecules, not the formation of a new bona fide molecular complex.

When BF_3 was co-condensed with perfluorodiethyl ether in excess argon, no new infrared absorptions were detected. While it is certainly possible that new infrared-active vibrations were too weak to be detected, it is more probable that there is no interaction between BF_3 and $(C_2F_5)_2O$ under these conditions. The increased electron-withdrawing capacity of more fluorine substituents on the ether seems to prevent any sort of detectable interaction in these circumstances. This lack of reactivity is not unique; Ault (Ref. 17) reported no Lewis acid/base adducts forming between SiF_4 and any oxygen-containing bases. Neat co-condensation

of BF_3 with $(C_2F_5)_2O$ also failed to yield any new absorptions: the infrared spectrum was simply the sum of the two neat components.

MO calculations supported the experimental observation that a true Lewis acid-base adduct was formed between $(C_2H_5)_2O$ and BF_3. The orbital displacement toward the BF_3 molecule was very similar to the NH_3 orbital displacement toward BF_3. MO calculations for the $(CF_3CH_2)_2O$—BF_3 system, like the experimental results, revealed a slight interaction but not a true Lewis acid-base complexation. The calculations for the $(C_2F_5)_2O$—BF_3 showed no interaction between the two molecules, in accord with the experimental results. A comparison of all three HOMO plots revealed that fluorine substitution resulted in decreased electron localization about the oxygen atom.

CONCLUSIONS

The catalytic degradation of commercial fluororether lubricants by metal halides and metal oxides is of continuing interest to tribologists and engineers in the development of advanced lubrication systems. With very few exceptions, the proposed catalysis mechanisms involve an initial acidic attack of the ether's oxygen lone-pair electrons by surface acid sites. The results reported in this study confirmed the greatly lowered reactivity of highly fluorinated ethers towards Lewis acid-base complexation. They suggest that initiation of the catalyzed degradation by metal oxides involves a more complicated process than mere electron transfer from ether oxygen to surface sites. The experiments and MO calculations conducted in this study indicated that classic complex formation between the Lewis acid BF_3 and fluoroether's oxygen atoms did not occur, thus suggesting that decomposition of commercial poly(perfluroroether) lubricants by metal oxide surfaces is necessarily assisted by some other process. Future studies will focus on elucidating this process.

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Table I.—Total Energy Calculations

Molecule	Total energy/kJ mol⁻¹	System	Total energy/kJ mol⁻¹
BF_3	−147,694	BF_3/NH_3	−171,731
NH_3	−23,986	$BF_3/(C_2H_5)_2O$	−241,395
$(C_2H_5)_2O$	−93,682	----------	----------
$(CF_3CH_2)_2O$	−366,713	$BF_3/(CF_3CH_2)_2O$	−514,415
$(C_2F_5)_2O$	−548,705	$BF_3/(C_2F_5)_2O$	−696,398

Table II.—Infrared Absorptions of the BF_3–$(C_2H_5)_2O$ Complex In Ar Matrices

Frequency	Approximate assignment
1241.1	antisym B-F str
1207.6	antisym B-F str
875.8	sym C-O str
796.8	sym ¹⁰B-F str
762.0	sym ¹¹B-F str

Table III.—Infrared Absorptions of the BF_3–$(CF_3CH_2)_2O$ Complex In Ar Matrices

| Frequency	Approximate assignment
1330.0	perturb. of $(CF_3CH_2)_2O$
1229.6	perturb. of $(CF_3CH_2)_2O$
1220.1	perturb. of $(CF_3CH_2)_2O$
1116.1	perturb. of $(CF_3CH_2)_2O$
694.9	perturb. of v_2, ¹⁰BF_3
668.0	perturb. of v_2, ¹⁰BF_3
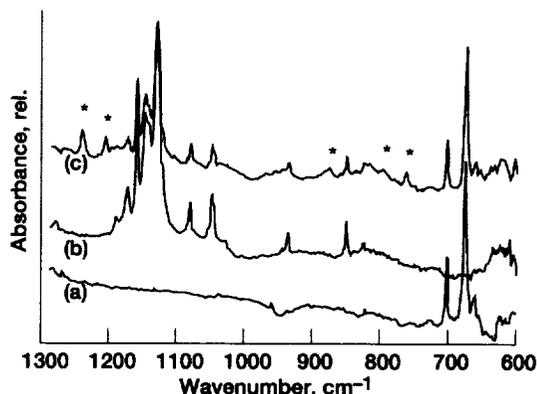
Figure 1.—Infrared spectra of BF₃ and diethyl ether in excess argon at 15K. New absorptions are marked with an *. (a) BF₃:Ar = 3:1000. (b) (C₂H₅)₂O: Ar = 8:1000. (c) BF₃:(C₂H₅)₂O:Ar = 4:7:1000.
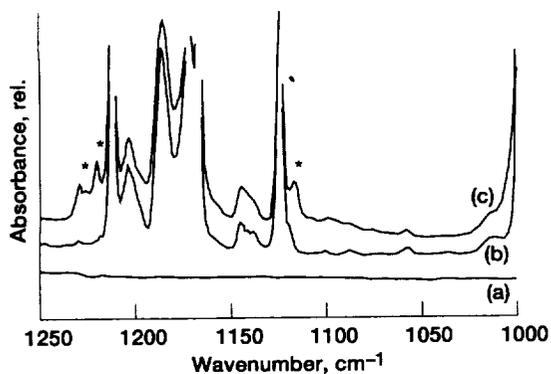
Figure 2.—Infrared spectra of BF_3 and bis(2,2,2-trifluorodiethyl)ether in excess argon at 15K. New absorptions are marked with an *. (a) BF_3:Ar = 3:1000. (b) $(CF_3CH_2)_2O$:Ar = 2:1000. (c) BF_3:$(CF_3CH_2)_2O$: Ar = 3:2:1000.
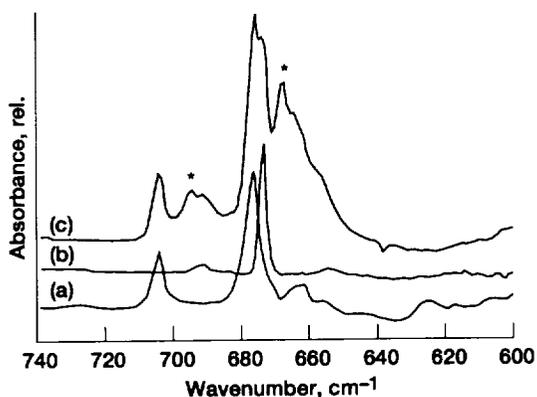

Figure 3.—Infrared spectra showing the perturbation of the BF_3 modes by $(CF_3CH_2)_2O$ in excess Ar at 15K. Sample concentrations are same as in Figure 2. Note that the new absorptions marked with * are separated by almost the same amount as the unperturbed [10,11]BF_3.
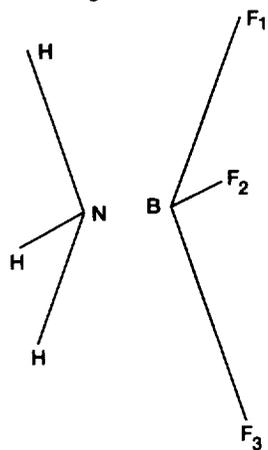
Net atomic charge on BF_3: –0.326
B–N distance: 1.782 Å
∡ $F_1BF_2F_3$: –130.7°

Figure 4.—Optimized molecular interaction between BF_3 and NH_3.
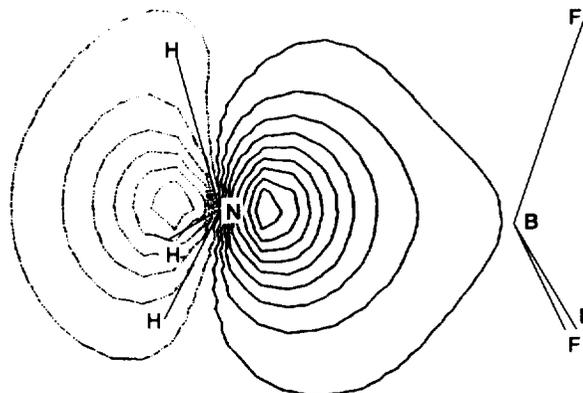
Figure 5.—HOMO orbital plot for BF_3–NH_3 interaction.
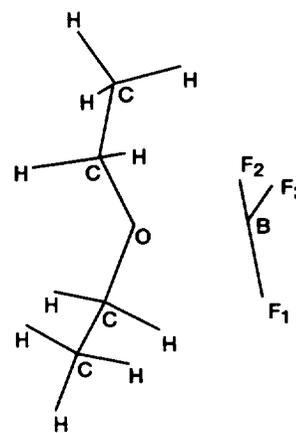
Net atomic charge on BF_3: –0.119
B–O distance: 1.908 Å
∡ $F_1BF_2F_3$: –158.2°

Figure 6.—Optimized molecular interaction between BF_3 and $(C_2H_5)_2O$.
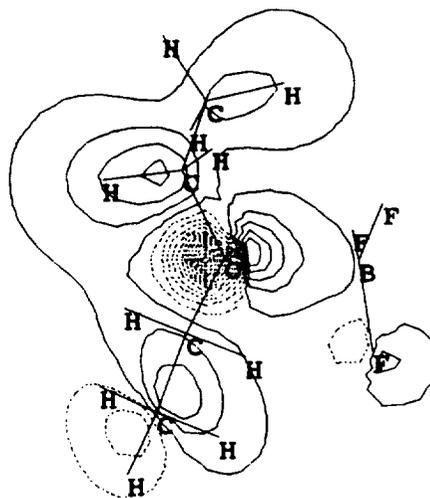
Figure 7.—HOMO orbital plot for BF_3–$(C_2H_5)_2O$ interaction.
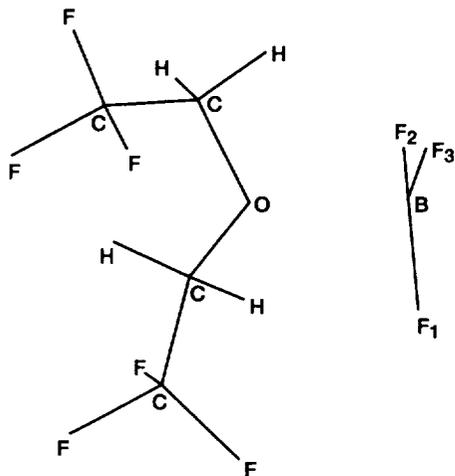
Net atomic charge on BF$_3$: –0.057
B–O distance: 2.007 Å
∡ F$_1$BF$_2$F$_3$: –167.0°

Figure 8.—Optimized molecular interaction
between BF$_3$ and (CF$_3$CH$_2$)$_2$O.
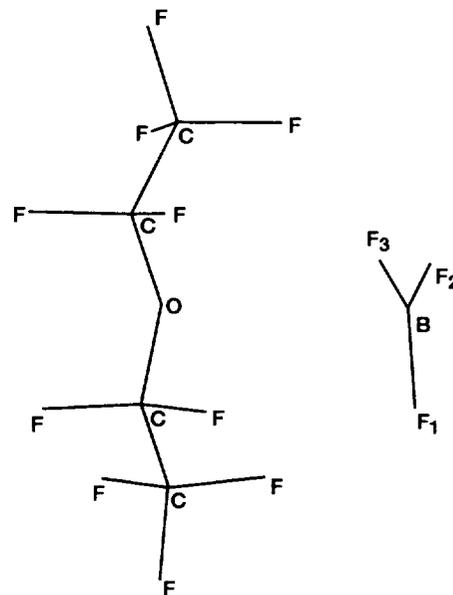
Net atomic charge on BF$_3$: 0
B–O distance: 5.182 Å
∡ F$_1$BF$_2$F$_3$: –180°

Figure 10.—Optimized molecular interaction
between BF$_3$ and (C$_2$F$_5$)$_2$O.
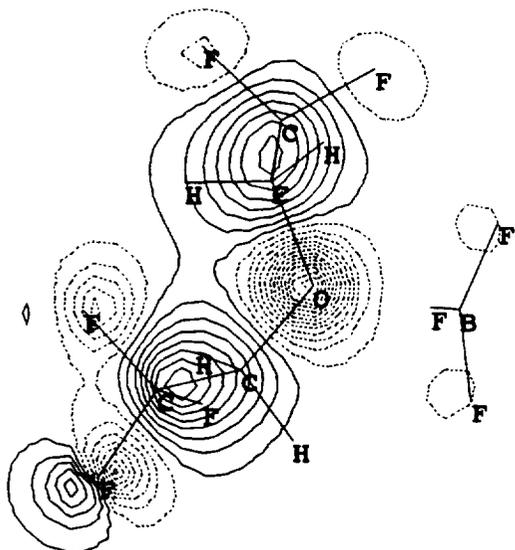
Figure 9.—HOMO orbital plot for BF$_3$–(CF$_3$CH$_2$)$_2$O
interaction.
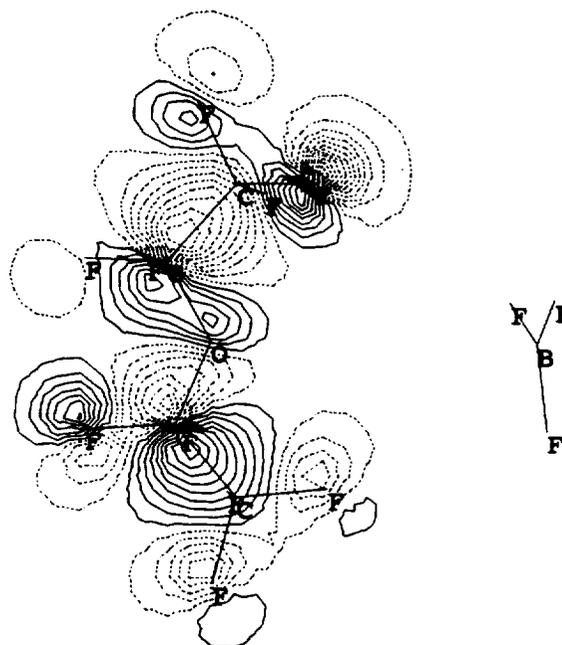
Figure 11.—HOMO orbital plot for BF$_3$–(C$_2$F$_5$)$_2$O
interaction.

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