Vibrational Analysis of the van der Waals Complex between Cyclopropane and Boron Trifluoride in Liquefied Inert Gases

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Abstract: The mid-infrared (4000 – 400 cm^{-1}) spectra of mixtures of cyclopropane and boron trifluoride, dissolved in liquid argon (93 – 125 K) or in liquid nitrogen (80 – 118 K), are discussed. In all the spectra, the formation of a 1:1 van der Waals complex, $c\text{-}C_3H_6 \cdot BF_3$, was observed. From spectra recorded between 95 and 125 K, the complexation enthalpy in liquid argon was determined to be $-7.8(6)$ kJ mol^{-1}. Using an SCRF/SCIPCM scheme to correct for the solvent influences and applying statistical thermodynamics to account for the zero-point vibrational and thermal influences, we calculated the gas-phase complexation energy ΔE_c^{exp} from the liquid-phase ΔH° to be $-12.0(6)$ kJ mol^{-1}. The analysis was completed by carrying out ab initio calculations at the MP2/6-31+G(d) level.

Keywords: ab initio calculations • IR spectroscopy • Lewis acids • van der Waals molecules • vibrational analysis

Introduction

Strong Lewis acids such as HX and BX_3 (X = F, Cl, Br, I) are effective catalysts for a variety of inorganic and organic reactions.[1–3] One system which has received considerable attention in this regard is the isomerization of cyclopropane, $c\text{-}C_3H_6$, to propene.[4–11] Stimson[6] originally postulated that the catalysis proceeds through a polar transition state with a 1 →2 internal shift of a hydrogen atom. Recent studies[12–18] using high-resolution molecular-beam and matrix-isolation spectroscopy have demonstrated the stability of hydrogen-bonded complexes of cyclopropane, denoted here as $c\text{-}C_3H_6 \cdot HX$, with the same Brønsted acids that are effective as catalysts. These results suggest that complex formation may be the first step in the acid-catalyzed reaction, and that the reaction proceeds through a stable intermediate rather than through a polar transition state.

Molecular complexes of the boron trihalides with a variety of Lewis bases have been known for many years[19–43] and have been well characterized in different media. In the spectra of solid argon matrices containing both cyclopropane and BF_3, BCl_3, or BBr_3,[44] however, no indications of the occurrence of such species were found. In contrast, various $c\text{-}C_3H_6 \cdot HX$ complexes have been identified[16–18] in solid Ar. This result is surprising since BCl_3 and BBr_3 are more effective than the hydrogen halides at catalyzing the isomerization of cyclopropane, and the stabilization of a 1:1 complex is known to correlate with the catalytic activity. Moreover, the boron halides are relatively strong Lewis acids, and have been shown to form stable complexes with both stronger and weaker bases than cyclopropane. Furthermore, cyclopropane and its methyl derivatives readily form 1:1 complexes[45] with the molecular halogens, particularly Cl_2, Br_2, and ClF, all of which are Lewis acids of moderate strength. It is, therefore, difficult to imagine that complex formation between $c\text{-}C_3H_6$ and BF_3 could not occur under an appropriate set of conditions; rather, the solid matrices may not be the ideal medium for formation of such adducts.

Over the last few years, spectroscopy in cryosolutions has emerged as a powerful tool for the study of weak molecular complexes.[46,47] As for the solid matrices, the observation of weak molecular complexes in these solutions is strongly facilitated by the low temperatures and by the great inertness of the surrounding noble gas atoms. In contrast to the matrices, however, the liquid cryogenic systems are characterized by a thermodynamic equilibrium.

In the course of a study of the weak interactions between unsaturated hydrocarbons and electron-acceptor molecules, we have recently reported[43] the infrared spectra of ethene/BF_3 and propene/BF_3 mixtures dissolved in liquid argon (LAr) and in liquid nitrogen (LN_2). In all spectra, evidence

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was found for the occurrence of a 1:1 bonded species, in which BF_3 binds to the π-system of the Lewis base. The complexation enthalpies ΔH° were determined to be $-10.0(2)$ kJ mol^{-1} for ethene · BF_3 and $-11.8(2)$ kJ mol^{-1} for propene · BF_3. These results clearly demonstrate that for Lewis bases involving a π-system, relatively strong adducts with BF_3 can be formed.

For cyclopropane a substantial electron density is predicted beyond the immediate vicinity of the lines connecting the carbon nuclei. Therefore, the c-C_3H_6 moiety is regarded as a pseudo-π system. In analogy to ethene/BF_3 mixtures, the formation of a complex species may be expected for cyclopropane/BF_3 mixtures in cryosolutions also. Because of the considerable interest in van der Waals molecules, we have embarked upon an investigation of the complexes between these two compounds. In this paper, the mid-infrared spectra of cyclopropane/BF_3 mixtures dissolved in LAr and in LN_2 are reported. To complete the analysis, structural and spectral information on the complex was obtained from ab initio calculations at the MP2/6-31+G(d) level.

Results and Discussion

Vibrational spectra:

Monomers: The vibrational spectra of boron trifluoride dissolved in liquefied inert gases have been described in detail elsewhere.[41,48] For the infrared region, active fundamentals appear between 0 cm^{-1} (ν_{11}, E') and 6 cm^{-1} (ν_8, E') below their gas-phase value, and between 0 cm^{-1} (ν_{10}, E') and 11 cm^{-1} (ν_1, A_1') above their matrix value. Hence, from literature data[16,49] on gas-phase and matrix-isolation infrared spectra of cyclopropane, the bands in cryosolution are easily assigned and need not be discussed here.

c-C_3H_6/BF_3 mixtures: The solubility of BF_3 in liquid argon is limited to about 2×10^{-3} mol L^{-1}.[41] In solutions containing such concentrations of BF_3 and c-C_3H_6, complex bands can hardly be detected. Therefore, a large excess of c-C_3H_6 was used, leading to a concentration typically higher than that of BF_3 by a factor of 20. In the spectra of these solutions, new bands indicating the presence of a complex were observed for both the BF_3 antisymmetric stretching ($\nu_3^{BF_3}$) and the BF_3 out-of-plane deformation ($\nu_2^{BF_3}$).

In Figure 1, the 1500 – 1400 cm^{-1} region of a solution containing 0.8×10^{-3} mol L^{-1} BF_3 and 16×10^{-3} mol L^{-1} c-C_3H_6, and that of a solution containing only c-C_3H_6 or BF_3, are compared. Next to the $\nu_3^{BF_3}$ bands at 1494 and 1444 cm^{-1} and the c-C_3H_6 band at 1435 cm^{-1}, new bands are observed at 1489 and 1439 cm^{-1} for the mixture, proving the presence of a complex between c-C_3H_6 and BF_3. These bands are assigned to the ^{10}B and ^{11}B antisymmetric BF_3 stretches of the complex. No direct information relating to the stoichiometry of the complex was obtained in this study. However, on statistical grounds, the 1:1 complex c-C_3H_6 · BF_3 is the most probable candidate, and we have therefore assigned the complex bands described above, and all the others observed, to this species.

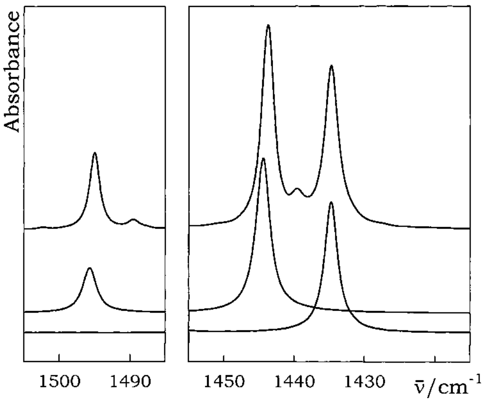

Figure 1. The $\nu_3^{BF_3}$ region of the IR spectrum of a c-C_3H_6/BF_3 mixture dissolved in liquid argon (top), of a solution containing only BF_3 (middle), and of a solution containing only c-C_3H_6 (bottom).

The $\nu_2^{BF_3}$ region of a solution in LAr containing both BF_3 and c-C_3H_6 at different temperatures between 103 and 119 K is shown in Figure 2. The bands at 709 and 681 cm^{-1} are assigned[41] to $\nu_2^{^{10}BF_3}$ and $\nu_2^{^{11}BF_3}$, and the new band at 661 cm^{-1} is attributed to the corresponding mode in c-C_3H_6 · $^{11}BF_3$. Thus, upon complexation with cyclopropane, the $^{11}BF_3$ out-of-plane deformation redshifts by approximately 20 cm^{-1}. A similar band should be observed for the ^{10}B isotopomer at approximately $709-20=689$ cm^{-1}. However, no such band was observed, because of the presence of an intense monomer band at 681 cm^{-1}.

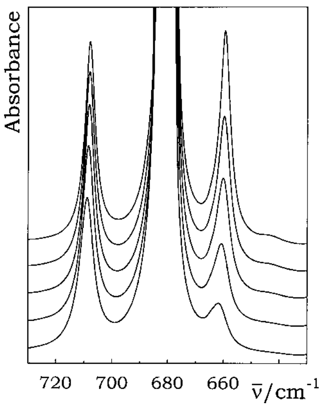

Figure 2. The BF_3 out-of-plane bending mode ($\nu_2^{BF_3}$) of a c-C_3H_6/BF_3 mixture dissolved in liquid argon. From top to bottom, the temperature of the solution increases from 103 to 119 K.

Splittings indicating the presence of a complex were also observed for some of the combination bands and overtones involving $\nu_2^{BF_3}$ or $\nu_3^{BF_3}$. On the low-frequency side of the bands at 2375 and 2325 cm^{-1} assigned to the $\nu_1^{BF_3}+\nu_3^{BF_3}$ combination in $^{10}BF_3$ and $^{11}BF_3$, as shown in Figure 3, new bands due to the corresponding modes in the complex are observed at 2367 and 2318 cm^{-1}, respectively. For the $\nu_1^{BF_3}+\nu_4^{BF_3}$ mode as well, a small red shift, from 1358 to 1353 cm^{-1}, is observed upon complexation with cyclopropane.

The complexation shifts of $\nu_2^{BF_3}$ and $\nu_3^{BF_3}$, -20 and -5 cm^{-1}, respectively, take place in the same direction as in ethene · BF_3, but the shifts for the latter, -30 and -7 cm^{-1}, respectively, are substantially larger. Hence, it seems likely that the interaction energy of c-C_3H_6 · BF_3 will be smaller than that of C_2H_4 · BF_3.

The relative intensity of the complex bands in Figures 1 and 2 suggest that only a minor fraction of the BF_3 is complexed. As c-C_3H_6 was used in a 20-fold excess, complex bands

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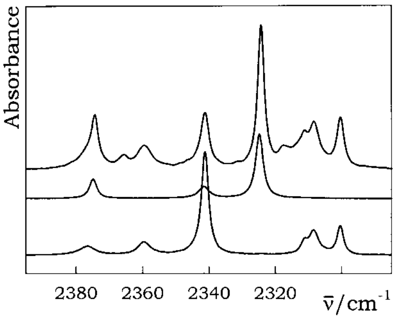

Figure 3. The $\nu_1^{BF_3} + \nu_3^{BF_3}$ region of a c-C_3H_6/BF_3 mixture dissolved in liquid argon (top), of a solution containing only BF_3 (middle), and of a solution containing only c-C_3H_6 (bottom).

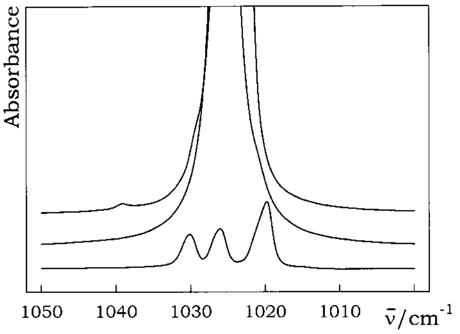

Figure 4. The $\nu_{11}^{c\text{-}C_3H_6}$ region of a c-C_3H_6/BF_3 mixture in liquid argon (top), an argon solution containing only c-C_3H_6 (middle), and crystalline c-C_3H_6, recorded at 10 K (bottom).

localized in the c-C_3H_6 moiety are necessarily very weak compared with the corresponding monomer bands. Also, ab initio results (discussed below) show that the complexation shifts for the allowed fundamentals are mostly quite small. Moreover, for the more intense fundamentals, because of the high concentrations used, the absorption near the band maximum is saturated over a significant frequency range. The combination of these facts explains why most of the complex bands localized in the c-C_3H_6 moiety escape detection. The exception is $\nu_{10}^{c\text{-}C_3H_6}$, one of whose components in the complex is predicted to blue-shift by 15.6 cm^{-1} (see below). The spectral region involved is displayed in Figure 4. Lowering the temperature of the solution increases the fraction of the complex present and narrows the bands in the spectrum, increasing the detectability of complex bands. However, with the concentrations of c-C_3H_6 used, at the lowest temperatures precipitation of the c-C_3H_6 starts, giving rise to bands in the spectrum due to crystalline solid. Therefore, in Figure 4 the spectrum of crystalline c-C_3H_6, obtained at 10 K, is also given. Comparison shows that the shoulders at 1029.5 and 1021.5 cm^{-1} in the spectrum of the mixed solution, recorded at 90 K, are due to precipitated c-C_3H_6. The fact that the frequencies of these shoulders do not precisely match those of the crystalline spectrum is attributed to the temperature difference between the two spectra. The spectrum of crystalline c-C_3H_6 shows no absorption band near 1040 cm^{-1}, and no bands can be detected in this region for a solution containing only c-C_3H_6. This proves that the weak band at 1039 cm^{-1} in the spectrum of the mixture must be due to the complex. Its shift, +14 cm^{-1}, is in very good agreement with the predicted value, +15.6 cm^{-1}. The assignment is further confirmed by the fact that similar complex bands have been assigned in matrix spectra of c-C_3H_6 complexes with halogens, hydrogen halides, and water.[16–18] In the latter studies a complexation shift of approximately 10 cm^{-1} for the $\nu_{11}^{C_3H_6}$ out-of-plane deformation mode at 864 cm^{-1} was also reported. In the spectra of the LAr solutions, no indication of the presence of this band was found, probably because it is strongly overlapped by both the $\nu_{11}^{c\text{-}C_3H_6}$ and $\nu_7^{c\text{-}C_3H_6}$ monomer bands.

In the spectra of ethene/BF_3 mixtures in LAr, a weak band due to the BF_3 symmetric stretch, $\nu_1^{BF_3}$, was observed near 878 cm^{-1}, and a weak band due to the C$\sim$C stretch, $\nu_2^{C_2H_4}$, in the complex was observed at 1621 cm^{-1}. These bands are IR-inactive in the monomers and appear in the complex because the symmetry decreases during the complexation. For c-$C_3H_6 \cdot BF_3$, similar bands may be expected. However, no band due to $\nu_1^{BF_3}$ in c-$C_3H_6 \cdot BF_3$ was observed, maybe because it is overlapped by the intense c-C_3H_6 band at 866 cm^{-1}. Also, no complex bands due to modes that are symmetry-forbidden in the c-C_3H_6 monomer were observed.

To complete the analysis of the c-$C_3H_6 \cdot BF_3$ complex, we also investigated the mid-infrared spectra of c-C_3H_6/BF_3 mixtures dissolved in liquid nitrogen. The occurrence of a 1:1 complex was again deduced from the appearance of new bands close to the BF_3 or the c-C_3H_6 monomer bands. Because of the similarity with the argon solutions, no detailed description of these bands is given here. In LN_2, the BF_3 molecules are linked by van der Waals bonds to N_2 solvent molecules,[48] that is, they occur as $N_2 \cdot BF_3 \cdot N_2$ or $N_2 \cdot BF_3$. This interaction strongly stabilizes monomeric BF_3, and consequently causes a substantial destabilization of the complex in the solution. When equal concentrations of c-C_3H_6 and BF_3 are used, the intensities of the c-$C_3H_6 \cdot BF_3$ bands observed in LN_2 solutions are indeed much weaker than those observed in LAr.

Relative stability of c-$C_3H_6 \cdot BF_3$: The complexation enthalpy ΔH° for the complex was derived from a van't Hoff curve[50] constructed by plotting the logarithm of the intensity ratio $I_{c\text{-}C_3H_6 \cdot BF_3}/(I_{c\text{-}C_3H_6} \times I_{BF_3})$, measured at different temperatures, versus $1/T$. The slope of the curve, corrected for the thermal expansion of the solution,[50] equals $-\Delta H^\circ/R$. For the present study, solutions containing c-C_3H_6 (16.0×10^{-3} mol L^{-1}) and BF_3 (0.8×10^{-3} mol L^{-1}) were recorded at 14 different temperatures between 93 and 125 K. The intensities for the complex, $I_{c\text{-}C_3H_6 \cdot BF_3}$, and for monomeric BF_3, I_{BF_3}, were taken from a least-squares band fitting, by means of Gauss/Lorentz sum functions, of the $\nu_2^{BF_3}$ region. Because the bands of c-C_3H_6 strongly overlap with the corresponding modes in c-$C_3H_6 \cdot BF_3$, an accurate determination of $I_{c\text{-}C_3H_6}$ is rather difficult. However, it was argued above that only a very minor proportion of the c-C_3H_6 molecules are involved in complexation. Therefore, as $I_{c\text{-}C_3H_6}$ we have used the integrated intensity of a monomeric c-C_3H_6 band, without correcting for the presence of a complex band. To avoid problems with saturation in the fundamentals, the integrated intensities of the overtones at 2863 and 1765 cm^{-1} have been used. Both result in very similar van't Hoff plots, one of which is shown in Figure 5. From these plots the complexation enthalpy of c-$C_3H_6 \cdot BF_3$ was then calculated to be $-7.8(6)$ kJ mol^{-1}, which, as expected from the vibrational spectra, is smaller than that of $C_2H_4 \cdot BF_3$ ($-10.0(2)$ kJ mol^{-1}).

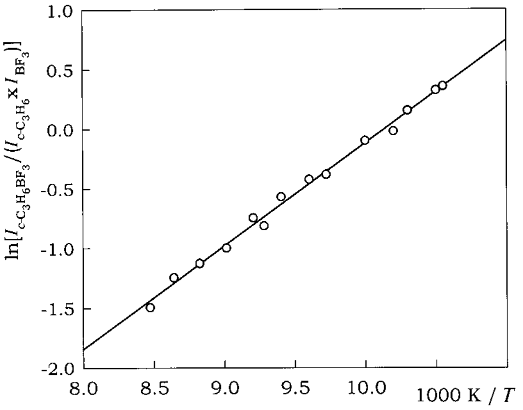

Figure 5. The van't Hoff plot for c-$C_3H_6 \cdot BF_3$ in liquid argon.

For ethene and propene, the BF_3 complex has a complexation enthalpy 2–3 kJ mol^{-1} higher than that of the corresponding HCl complex. Analogous results are obtained for complexes involving the Lewis bases CO,[41] CH_3F,[42] ethyne, and propyne.[51] Therefore, a similar increase might be expected for the complexes with cyclopropane. The ΔH° for c-$C_3H_6 \cdot BF_3$, however, is almost identical to that obtained for the c-$C_3H_6 \cdot HCl$ complex, $-7.5(3)$ kJ mol^{-1}.[52] This is thought to be due to the steric hindrance exerted on the BF_3 moiety by the C–H bonds of the cyclopropane ring.

The complexation enthalpy obtained in LAr is not a measure of the stability of the isolated complex, because of solvent influences.[53] These were estimated for both the monomeric and complex species from ab initio reaction field calculations, by a procedure outlined previously.[43] In a first step, the liquid-phase ΔH° is transformed into a gas-phase ΔH° by applying solvation corrections obtained from SCRF/SCIPCM calculations. In the second step, straightforward statistical thermodynamics[54] is applied to transform the gas-phase ΔH° into a complexation energy, so that comparisons can be made with the ab initio results. The solvation energies were calculated at the RHF/6-31+G(d) level, and were found to be 0.59, 4.13, and 2.91 kJ mol^{-1} for c-C_3H_6, BF_3, and the 1:1 complex, respectively. Equating these energies to solvent enthalpies, as before,[43] it follows that in liquid argon the complex is destabilized by 1.83 kJ mol^{-1}. Conversely, the gas-phase ΔH° is calculated to be $-9.6(6)$ kJ mol^{-1}. The translational and rotational thermal contributions to ΔH°_{gas} were calculated in the classical limit, and the thermal and zero-point vibrations were calculated from the harmonic MP2/6-31+G(d) ab initio frequencies discussed below. The resultant gas-phase complexation energy, ΔE_c^{gas}, was then found to be $-12.0(6)$ kJ mol^{-1}.

Ab initio calculations: Information on the geometry of the complex was obtained from ab initio calculations at the MP2/6-31+G(d) level. In Figure 6, the resulting equilibrium geometry for c-$C_3H_6 \cdot BF_3$ is shown. The structure of the complex was described with reference to the threefold symmetry axis of monomeric c-C_3H_6. This axis was defined by dummy atoms X_1 and X_2, with X_2 situated in the plane of the ring. The dummy atoms have also been indicated in Figure 6. In addition, the structural parameters for c-$C_3H_6 \cdot BF_3$ and those for the constituent molecules are collected in Table 1.

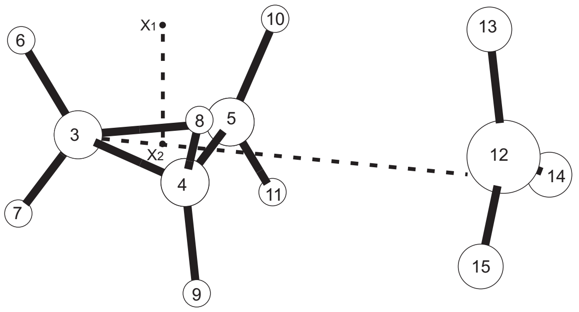

Figure 6. The MP2/6-31+G(d) equilibrium structure for c-$C_3H_6 \cdot BF_3$.

In the complex a van der Waals bond is formed between the boron atom and the center of a C–C bond, with the boron atom slightly above the plane of the cyclopropane ring. As BF_3 interacts with electron-rich regions, this structure is in agreement with the pseudo-π description of the C–C bonds;[55,56] it is also analogous to the structure of the HX complexes of cyclopropane.[12–15] The small shift of the boron atom out of the plane of the carbon atoms is attributed to the higher steric hindrance on the opposite side of the plane.

As can be seen in Table 1, the complexation slightly weakens the C–C bond involved in the van der Waals bond, increasing its length from 1.505 to 1.514 Å. In contrast, the other C–C bond lengths show a small decrease, from 1.505 to 1.503 Å, that is, they are slightly strengthened by complexation. The complexation leads to small deviations from planarity for the BF_3 molecule in the complex: the B–F bonds make an angle of 1.26° with the plane perpendicular to the symmetry axis of the BF_3 moiety. The BF_3 moiety shows a positive tilt of 3.49° with respect to the van der Waals bond, R_{vdW}, defined as the distance between the boron atom and the midpoint of the C4–C5 bond. This tilt is also attributed to the steric hindrance between the fluorine atoms out of the symmetry plane and the opposing hydrogen atoms.

The B–F bonds in the complex are slightly longer than those in the monomer. However, the average B–F bond length in c-$C_3H_6 \cdot BF_3$ is slightly smaller than that in $C_2H_4 \cdot BF_3$. This suggests that the c-C_3H_6 complex is the weaker one, which is confirmed by the MP2/6-31+G(d) complexation energies, $\Delta E_c^{ab\ initio}$, obtained before and after the correction for basis set superposition error (BSSE). The values are summarized in Table 2; for instance, the uncorrected values decrease from -17.32 kJ mol^{-1} for $C_2H_4 \cdot BF_3$ to -15.76 kJ mol^{-1} for c-$C_3H_6 \cdot BF_3$. It is clear that, for each complex, the experimental gas-phase complexation energy obtained as described above agrees better with the uncor-

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Table 1. MP2/6-31+G(d) structural parameters (bond lengths in Å, bond angles in degrees) for c-$C_3H_6 \cdot BF_3$, for c-C_3H_6 and for BF_3.

	c-$C_3H_6 \cdot BF_3$	c-C_3H_6	BF_3
r ($X_1 \cdots X_2$)	1.0000	1.0000	
r ($X_2 \cdots C_3$)	0.8617	0.8691	
r ($X_2 \cdots C_4$)	0.8739	0.8691	
r ($X_2 \cdots C_5$)	0.8739	0.8691	
r (C_3–C_4)	1.5030	1.5053	
r (C_3–C_5)	1.5030	1.5053	
r (C_4–C_5)	1.5136	1.5053	
r (C_3–H_6)	1.0849	1.0851	
r (C_3–H_7)	1.0849	1.0851	
r (C_4–H_8)	1.0854	1.0851	
r (C_4–H_9)	1.0851	1.0851	
r (C_5–H_{10})	1.0854	1.0851	
r (C_5–H_{11})	1.0851	1.0851	
r ($X_2 \cdots B_{12}$)	3.4148		
r (B_{12}–F_{13})	1.3294		1.3278
r (B_{12}–F_{14})	1.3292		1.3278
r (B_{12}–F_{15})	1.3292		1.3278
RvdW [a]	2.9790		
$\sphericalangle$ ($X_1 \cdots X_2 \cdots C_3$)	90.000		
$\sphericalangle$ ($X_1 \cdots X_2 \cdots C_4$)	90.000		
$\sphericalangle$ ($X_1 \cdots X_2 \cdots C_5$)	90.000		
$\sphericalangle$ (C_3-C_4-C_5)	59.766	60.000	
$\sphericalangle$ (C_3-C_5-C_4)	59.766	60.000	
$\sphericalangle$ (C_4-C_3-C_5)	60.467	60.000	
$\sphericalangle$ (H_6-$C_3 \cdots X_2$)	122.722	122.797	
$\sphericalangle$ (H_7-$C_3 \cdots X_2$)	122.705	122.797	
$\sphericalangle$ (H_8-$C_4 \cdots X_2$)	122.656	122.797	
$\sphericalangle$ (H_9-$C_4 \cdots X_2$)	122.765	122.797	
$\sphericalangle$ (H_{10}-$C_5 \cdots X_2$)	122.656	122.797	
$\sphericalangle$ (H_{11}-$C_5 \cdots X_2$)	122.765	122.797	
$\sphericalangle$ ($B_{12} \cdots X_2 \cdots X_1$)	85.775		
$\sphericalangle$ (F_{13}-$B_{12} \cdots X_2$)	87.154		
$\sphericalangle$ (F_{14}-$B_{12} \cdots X_2$)	93.318		
$\sphericalangle$ (F_{15}-$B_{12} \cdots X_2$)	93.318		
τ ($C_4 \cdots X_2 \cdots X_1 \cdots C_3$)	120.00	120.00	
τ ($C_5 \cdots X_2 \cdots X_1 \cdots C_3$)	– 120.00	– 120.00	
τ (H_6-$C_3 \cdots X_2 \cdots X_1$)	0.00	0.00	
τ (H_7-$C_3 \cdots X_2 \cdots X_1$)	180.00	180.00	
τ (H_8-$C_4 \cdots X_2 \cdots X_1$)	– 0.65	0.00	
τ (H_9-$C_4 \cdots X_2 \cdots X_1$)	180.53	180.00	
τ (H_{10}-$C_5 \cdots X_2 \cdots X_1$)	0.65	0.00	
τ (H_{11}-C5 $\cdots X_2 \cdots X_1$)	179.47	180.00	
τ ($B_{12} \cdots X_2 \cdots X_1 \cdots C_3$)	180.00		
τ (F_{13}-$B_{12} \cdots X_2 \cdots X_1$)	0.00		
τ (F_{14}-$B_{12} \cdots X_2 \cdots X_1$)	119.88		
τ (F_{15}-$B_{12} \cdots X_2 \cdots X_1$)	– 119.88		
dipole moment /Debye	0.56	0.00	0.00
energy /Hartree	– 441.268823	– 117.458671	– 323.804151

Table 2. Complexation energies (kJ mol^{-1}) for $C_2H_4 \cdot BF_3$ and c-$C_3H_6 \cdot BF_3$.

	$C_2H_4 \cdot BF_3$[a]	c-$C_3H_6 \cdot BF_3$
MP2/6-31+G(d)		
ΔE	– 17.32	– 15.76
E_{BSSE}[b]	– 9.85	– 8.48
ΔE_{corr}	– 7.47	– 7.28
MP2/6-311++G(2d, 2p)		
ΔE	– 17.89	– 18.86
E_{BSSE}[b]	– 8.25	– 9.31
ΔE_{corr}	– 9.64	– 9.58
MP2/6-311++G(3df, 2p)		
ΔE	– 17.61	– 17.69
E_{BSSE}[b]	– 6.61	– 6.77
ΔE_{corr}	– 11.00	– 10.92
experimental values		
ΔH°_{LAr}	– 10.0 ± 0.2	– 7.8 ± 0.6
ΔH°_{gas}[c]	– 11.8 ± 0.2	– 9.6 ± 0.6
ΔE_c^{gas}[d]	– 14.3 ± 0.2	– 12.0 ± 0.6

[a] Taken from ref. [43]. [b] Obtained by means of the full counterpoise correction described by Boys and Bernardi (ref. [61]). [c] Including the solvent destabilization calculated with SCRF/SCIPCM calculations at the RHF/6-31+G(d) level. [d] Including both zero-point vibrational and thermal influences.

rected ab initio complexation energy than with the BSSE-corrected value. The poorer agreement with the BSSE-corrected values was noted previously and was attributed to the counterbalancing effect of the basis set incompleteness error (BSIE) when a small, truncated basis set such as 6-31+G(d) is used.[43,57] As the BSIE is not accounted for during the counterpoise correction, the results obtained above again confirm that, for a comparison with experimental data, the uncorrected $\Delta E_c^{\text{ab initio}}$ must be preferred.

Both the BSSE and the BSIE should decrease when the basis set is saturated. In this study, for both $C_2H_4 \cdot BF_3$ and c-$C_3H_6 \cdot BF_3$ the complexation energies $\Delta E_c^{\text{ab initio}}$ were calculated by carrying out MP2/6-311++G(2d, 2p) single-point computations with the MP2/6-31+G(d) geometries described above. Moreover, to obtain information on the influence of basis functions of higher angular momentum, the MP2/6-311++G(3df, 2p) interaction energies were also calculated. The results of these calculations are collected in Table 2. It can be seen that, for both $C_2H_4 \cdot BF_3$ and c-$C_3H_6 \cdot BF_3$, enlargement of the basis set decreases the BSSE. However, the data clearly suggest that in order to suppress the BSSE fully for species of this kind, unreasonably large basis sets would be required. No such calculations have been attempted. Inspection of the calculated energies indicates that the slow convergence of the BSSE seen in Table 2 is almost completely due to the BF_3 moiety, its contribution varying between 66 and 79%. The data in Table 2 further show that enlargement of the basis set improves the agreement of the experimental values with the BSSE-corrected ones, while the agreement with the uncorrected value deteriorates. However, even for the largest basis set used, the BSSE-corrected complexation energies are still underestimates of the experimental values. Also, the difference in complexation energy between $C_2H_4 \cdot BF_3$ and c-$C_3H_6 \cdot BF_3$ remains very small. This contrasts with the experimental data, where from $C_2H_4 \cdot BF_3$ to c-$C_3H_6 \cdot BF_3$ the complexation energy ΔE_c^{gas} decreases from – 14.3(2) to – 12.0(6) kJ mol^{-1}.

The equilibrium geometry of c-$C_3H_6 \cdot BF_3$ includes a dihedral angle τ, $\sphericalangle(F_{13}-B_{12} \cdots X_2 \cdots X_1)$, equal to 0°. Calculations in which τ was systematically varied yielded a sixfold barrier to internal rotation of a mere 0.2 kJ mol^{-1}. Thus, the BF_3 internal rotation must be regarded as quasi-free.

To complete the theoretical analysis, the vibrational frequencies and infrared intensities were also calculated by means of harmonic ab initio force fields. The results of these calculations are summarized in Table 3. Upon complexation, the BF_3 out-of-plane deformation ($\nu_2^{BF_3}$) and the BF_3 antisymmetric stretches ($\nu_3^{BF_3}$) red-shift by – 5.0 and – 34.7 cm^{-1} respectively. These shifts compare favorably with the experimental results described above. The overall symmetry of the complex is C_s. Hence, it is expected that the BF_3 antisym-

Table 3. MP2/6-31+G(d) vibrational frequencies (cm^{-1}), infrared intensities ($km\,mol^{-1}$) and complexation shifts for c-$C_3H_6 \cdot BF_3$, c-C_3H_6 and BF_3.

Assignment[a]			c-$C_3H_6 \cdot {}^{11}BF_3$			c-$C_3H_6 \cdot {}^{10}BF_3$			c-C_3H_6		${}^{11}BF_3$		${}^{10}BF_3$	
			$\tilde{\nu}$	Int.	$\Delta\tilde{\nu}$	$\tilde{\nu}$	Int.	$\Delta\tilde{\nu}$	$\tilde{\nu}$	Int.	$\tilde{\nu}$	Int.	$\tilde{\nu}$	Int.
cyclopropane submolecule														
A_1'	$\nu_1^{c\text{-}C_3H_6}$	CH_2 sym. stretch	3211.7	0.9	0.7	3211.7	1.0	0.7	3211.0	–				
	$\nu_2^{c\text{-}C_3H_6}$	CH_2 scissoring	1573.3	0.2	– 3.1	1573.4	0.5	– 3.0	1576.4	–				
	$\nu_3^{c\text{-}C_3H_6}$	sym. ring deformation	1256.5	0.1	– 2.1	1256.5	0.1	– 2.1	1258.6	–				
A_1''	$\nu_4^{c\text{-}C_3H_6}$	CH_2 twist	1201.5	0.0	9.4	1201.5	0.0	9.4	1192.1	–				
A_2'	$\nu_5^{c\text{-}C_3H_6}$	CH_2 wagging	1126.3	0.0	8.7	1126.3	0.0	8.7	1117.6	–				
A_2''	$\nu_6^{c\text{-}C_3H_6}$	CH_2 asym. stretch	3310.3	12.2	2.6	3310.4	12.3	2.7	3307.7	21.9				
	$\nu_7^{c\text{-}C_3H_6}$	CH_2 rocking	892.8	0.9	2.9	892.8	0.9	2.9	889.9	0.8				
E'	$\nu_8^{c\text{-}C_3H_6}$	CH_2 sym. stretch	3203.7	12.1	1.6	3203.7	12.1	1.6	3202.1	16.9				
			3203.2	8.6	1.1	3203.2	8.7	1.1						
	$\nu_9^{c\text{-}C_3H_6}$	CH_2 scissoring	1519.6	1.7	– 1.7	1519.7	3.9	– 1.6	1521.3	1.0				
			1518.8	3.3	– 2.5	1519.1	12.3	– 2.2						
	$\nu_{10}^{c\text{-}C_3H_6}$	CH_2 wagging	1120.9	20.9	15.6	1120.9	20.5	15.6	1105.3	15.5				
			1100.8	26.2	– 4.5	1100.8	25.6	– 4.5						
	$\nu_{11}^{c\text{-}C_3H_6}$	asym. ring deformation	928.3	21.5	5.4	928.3	21.5	5.4	922.9	25.2				
			916.3	16.3	– 6.3	916.6	14.3	– 6.3						
E''	$\nu_{12}^{c\text{-}C_3H_6}$	CH_2 asym. stretch	3293.1	0.0	3.6	3293.1	0.0	3.6	3289.5	–				
			3293.0	0.1	3.5	3293.1	0.2	3.6						
	$\nu_{13}^{c\text{-}C_3H_6}$	CH_2 rocking	1251.5	3.5	4.7	1251.6	2.8	4.8	1246.8	–				
			1245.9	0.0	– 0.9	1245.9	0.0	– 0.9						
	$\nu_{14}^{c\text{-}C_3H_6}$	CH_2 twist	789.6	0.2	14.4	789.6	0.21	4.4	775.2	–				
			787.6	0.0	12.4	787.6	0.0	12.4						
BF_3 submolecule														
A_1'	$\nu_1^{BF_3}$	BF_3 sym. stretch	867.3	2.9	– 5.1	867.4	3.3	– 5.0			872.4	–	872.4	–
A_2''	$\nu_2^{BF_3}$	BF_3 out-of-plane bend	663.0	225.3	– 32.6	689.4	245.3	– 34.7			695.6	118.0	724.1	127.8
E'	$\nu_3^{BF_3}$	BF_3 asym. stretch	1436.3	395.1	– 6.3	1488.9	426.8	– 6.7			1442.6	483.1	1495.6	524.0
			1435.5	373.8	– 7.1	1487.9	– 7.7	397.3						
E'	$\nu_4^{BF_3}$	BF_3 in-plane bend	471.3	11.7	– 0.6	473.2	11.4	– 0.6			472.0	15.2	473.8	14.8
			470.6	10.9	– 1.4	472.4	10.6	– 1.4						
low-energy deformation modes														
				106.8	0.0		106.8	0.0						
				101.6	0.2		101.7	0.2						
				89.4	0.8		89.7	0.8						
				78.7	0.2		78.8	0.2						
				73.3	0.0		73.3	0.0						
				21.6	0.0		21.6	0.0						

[a] Symmetry species and mode numbers belonging to the respective monomer species.

metric stretch in the complex will give rise to two nondegenerate vibrational modes. Indeed, a splitting of approximately 1 cm^{-1} was calculated. However, as described above, it was found that the barrier hindering internal rotation is extremely low. In such a potential, the majority of the molecules contributing to the observed contour of the antisymmetric stretches are thermally excited to levels above the barrier. As a consequence, and taking into account the relatively small splitting calculated in the harmonic approximation, a single band must be expected for the BF_3 antisymmetric stretches. This is observed experimentally.

Finally, the results in Table 3 show that, as stated above, the fundamentals localized in the c-C_3H_6 moiety, with the exception of $\nu_{10}^{c\text{-}C_3H_6}$, are only marginally disturbed by the complexation.

Experimental Section

Cyclopropane (>99% pure) and boron trifluoride (CP grade) were purchased from Aldrich and Union Carbide, respectively, and were used without further purification. The solvent gases, argon and nitrogen, were supplied by L'Air Liquide and have a stated purity of 99.9999%.

The infrared spectra were recorded on Bruker IFS 66v and Bruker 113v Fourier Transform spectrometers using a Globar source in combination with a Ge/KBr beamsplitter and a broadband MCT detector. The interferograms were averaged over 200 scans, Happ–Genzel apodized, and Fourier transformed with a zero filling factor of 4, to yield spectra at a resolution of 0.5 cm^{-1}. A detailed description of the liquid-noble-gas setup was given previously.[47]

Solid-state spectra of c-C_3H_6 and BF_3 were obtained by condensing a small amount of the compound onto a CsI window cooled to 10 K with a Leybold Heraeus ROK 10-300 cooling system, then annealing the sample until no further changes were observed in its IR spectrum.

Ab initio calculations were performed with the Gaussian 94 package.[58] For all calculations, the second-order perturbation theory (MP2), including all electrons, was used. A 6-31+G(d) basis set was used, as this computationally economical basis set has been regarded as a flexible and powerful approach for intermolecular interactions.[59,60]

The interaction energies of the weak complexes were calculated by subtracting the calculated energies of the monomers from that of the complex in the dimer-centered basis set. This corresponds to the counterpoise correction method described by Boys and Bernardi,[61] accounting for the BSSE. For all equilibrium geometries, the vibrational frequencies and the corresponding infrared intensities were calculated with standard harmonic force fields.

The calculations were carried out on a Cray C94 supercomputer at the CSC Center for Scientific Computing Ltd., Espoo (Finland), and on an IBM RS/6000 RISC workstation.

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