

with

$$y = 1 + (2r/3^{1/2}R) \quad (7b)$$

as obtained from eq 5 by zeroing the variation in I_0 . The assumption about r could be eliminated altogether in future work on isotopic variants of cubane. C_8D_8 would be an obvious possibility, but a symmetric top species such as C_8H_7D , C_8HD_7 , or $^{13}C^{12}C_7H_8$ might in practice prove easier. The ^{13}C species could be examined in natural abundance if a suitable band could be found.

It should also be mentioned that our present uncertainty in B_0 from the perturbation theory fit to ν_{11} and ν_{12} of C_8H_8 might be reduced by an analysis of the present spectrum of the ν_{10} band. This band is so extensively perturbed that the usual concepts of "allowed" and "forbidden" transitions become meaningless, and so assignment of this band should yield numerous ground-state combination differences leading to a higher precision B_0 value as well as ground-state octahedral splitting and centrifugal distortion parameters.

Registry No. Cubane, 277-10-1.

Rotational Spectroscopy of Molecular Complexes of BF_3 with $NCCN$, CO_2 , and N_2O [†]

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Abstract: The microwave spectrum of the van der Waals complex $NCCN \cdot BF_3$ has been obtained by molecular beam electric resonance spectroscopy. This molecule is shown to be a symmetric rotor. The rotational constants for the ^{11}B and ^{10}B species are $B_0 = 672.2$ (2) and 675.6 (2) MHz, respectively. These values are consistent with a B-N bond length of 2.647 (3) Å. Radio-frequency and microwave transitions of the complex $CO_2 \cdot BF_3$ have been observed and establish that this molecule is an asymmetric rotor. One radio-frequency transition observed for $N_2O \cdot BF_3$ suggests an asymmetric structure for this complex as well.

Introduction

Addition complexes of the strong Lewis acid- BF_3 are fundamental in classical donor-acceptor chemistry. Recently the van der Waals complexes of BF_3 with Ar, CO, and N_2 have been formed in an adiabatic expansion and structurally characterized by their microwave spectra.¹ The van der Waals bonds form along the C_3 axis of the BF_3 in a manner analogous to the binding in the "classical complexes". This behavior seems chemically reasonable and suggests that the van der Waals interaction may also be viewed in terms of a Lewis acid-base model. Such a picture has successfully provided an intuitive understanding of van der Waals interactions in a variety of weakly bound systems.

In view of the chemical character of weakly bound systems it seems reasonable to consider whether, in fact, there is a smooth transition between van der Waals and covalent bonding. Despite structural similarities between the covalent and van der Waals complexes of BF_3 , for example, dramatic differences exist. The B-N bond length in BF_3 -amines is 1.6 Å while that in $N_2 \cdot BF_3$ is 2.9 Å. Such a large variation in bond length with nitrogen donor may permit, at least in principle, the observation of a smooth transition between "covalent" and "van der Waals" binding, provided the nature of the nitrogen donor were properly chosen. Two classes of nitrogen donors which may be used for this purpose are the amines and the cyanides. Microwave data for a number of the gas-phase amines are available, but the analogous data for the cyanides are lacking. With the simplest of these, HCN and CH_3CN , BF_3 forms solid compounds. Cyanogen, on the other hand, does not form a solid with BF_3 , and so was chosen as an interesting system to study.

The structure of $NCCN \cdot BF_3$ is also of interest for comparison with a number of other previously studied "van der Waals" molecules. Recent rotational spectroscopic studies of $CO_2 \cdot HF$ ² and $NCCN \cdot HF$,³ as well as $SCO \cdot HF$ ² and $CO_2 \cdot HCl$,⁴ have shown these complexes to have linear, hydrogen bonded structures. The linear structures of the $CO_2 \cdot HX$ complexes are not readily un-

derstandable from consideration of oxygen lone pairs on CO_2 , as might be expected if chemical reasoning were applicable. Moreover, the geometry of the closely related, isoelectronic species $N_2O \cdot HF$ is quite different, having a bent, hydrogen bonded structure. In view of the similarities between CO_2 and N_2O and the dissimilarities in their complexes with HF, a simple HOMO-LUMO approach does not appear applicable to these systems, since any argument based on lone pairs would have to predict the same structure for $N_2O \cdot HF$ and $CO_2 \cdot HF$. In contrast, HF and BF_3 appear quite similar in their weak interactions. For example, studies of the complexes of CO and N_2 with HF and BF_3 show that HF and BF_3 behave similarly as simple Lewis acids. Specifically, viewed as electron-pair acceptors, both HF and BF_3 accept electrons along their symmetry axes. Thus, given the observed behavior of CO_2 with HF, the complex $CO_2 \cdot BF_3$ is expected to be a symmetric top in which the CO_2 axis is coincident with the symmetry axis of the BF_3 . Likewise, the linear structure of $NCCN \cdot HF$ suggests a similar geometry for $NCCN \cdot BF_3$.

We have studied the complexes $NCCN \cdot BF_3$, $CO_2 \cdot BF_3$, and $N_2O \cdot BF_3$ by rotational spectroscopy using the molecular beam electric resonance technique. The spectra show that the complex $NCCN \cdot BF_3$ does indeed have the anticipated C_{3v} structure, while $CO_2 \cdot BF_3$ and $N_2O \cdot BF_3$ do not. This result further emphasizes the complexity of the binding in CO_2 and N_2O systems.

Experimental

A beam of $NCCN \cdot BF_3$ was formed by expanding a mixture of 1% BF_3 and 25% $NCCN$ in Ar through a $25\text{-}\mu\text{m}$ nozzle at room temperature. The stagnation pressure was typically 2.5 atm. Under these conditions,

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Table I. Observed Zero-Field Transitions of NCCNBF₃^a

<i>J</i>	<i>J'</i>	¹¹ BF ₃ ·NCCN	¹⁰ BF ₃ ·NCCN
4	5	6722 (2)	
5	6	8068 (2)	
6	7	9412 (2)	9459 (3)
7	8	10752 (3)	
8	9	12095 (5)	12158 (5)

^a All frequencies given in MHz.

prominent mass spectral features included BF₂⁺ and NCCNBF₂⁺, but ArBF₂⁺ and B₂F₃⁺ were conspicuously absent. At lower NCCN concentrations (e.g., ~12%) both ArBF₂⁺ and NCCNBF₂⁺ were observed, while B₂F₃⁺ still was not. Both the NCCNBF₂⁺ and BF₂⁺ mass peaks were observed to be polar, but about four times more focussed beam could be obtained on the latter. Therefore, as with previously studied complexes of BF₃, spectroscopy was performed monitoring *m/e* 49 (or 48 for ¹⁰BF₂⁺). Interestingly, in the absence of any NCCN, B₂F₃⁺ was formed in abundance and was found to be nonpolar in agreement with a previous observation. From the nonpolarity of (BF₃)₂ and the lack of ArBF₂⁺ in the mass spectrum it can be concluded that most if not all of the focussed beam on the BF₂⁺ peak was due to NCCNBF₃. In experiments with CO₂BF₃ and N₂OBF₃, 25% CO₂ or N₂O with 1% BF₃ (in Ar) was also used, and no ArBF₂⁺ was formed. Mass spectral and focussing data in these systems indicate that the observed resonances must arise from the 1:1 complexes of BF₃ with CO₂ or N₂O. All spectra were taken by using the molecular beam electric resonance technique with the spectrometer operated in the flop-out mode.

A quick, and therefore useful, way to test whether a molecule is a symmetric rotor may be applied to these BF₃ systems. The quadrupole coupling constant of ¹¹B (*I* = 3/2) in ArBF₃ and COBF₃ has been determined¹ to be 2.75 MHz. This value, identical with that in solid BF₃,^{5,6} is seen to be unchanged upon van der Waals complexation. If no additional quadrupolar nuclei are present, any axially symmetric complex of ¹¹BF₃ will have the *J* = 2, *K* = 2, *F* = 1/2 → 3/2, and *F* = 5/2 → 7/2 transitions at 1/4(*eqQ*) = 680 kHz. This transition, which is electric dipole allowed since *K* ≠ 0, will occur at this frequency regardless of the rotational constants of the complex. Thus, direct observation of these transitions affords a method of determining if a molecule is a symmetric rotor. Indeed a strong resonance is observed at 680 kHz with COBF₃, but despite extensive effort, no such resonance could be observed for CO₂BF₃. Instead, four radio-frequency frequency transitions between 2 and 7 MHz and seven microwave transitions which do not fit a symmetric rotor pattern were observed. We note that considering only states which are expected to be populated in our beam, the largest pure quadrupole splitting produced by a spin 3/2 nucleus on the axis of a symmetric top occurs between the *F* = 1/2 and *F* = 3/2 levels of *J* = 1 and *K* = 0 and corresponds to 0.45*eqQ* (= 1.24 MHz for ¹¹BF₃). Direct transition between these levels, however, is electric dipole forbidden since *K* = 0. Thus, the observed radio-frequency transitions are too high in frequency to be pure quadrupole transitions. No radiofrequency transitions other than the pure quadrupole transitions are possible at zero electric field if this is a rigid symmetric rotor, and inversion of a symmetric CO₂BF₃ does not appear to be sensible motion. The radio-frequency transitions are those of an asymmetric rotor which are, perhaps, complicated by internal rotation. The inability to fit the microwave lines to a symmetric top spectrum lends further support to this interpretation. The possibility of internal rotation in CO₂BF₃ makes this molecule especially interesting, but no further discussion of its structure other than the fact that it is an asymmetric rotor will be given here.

A transition at 2.6 MHz was also observed for N₂OBF₃. The zero-field pure quadrupole spectrum (calculated for a symmetric top structure) contains no transitions above ~1.5 MHz. Thus, it seems likely that this molecule is also an asymmetric rotor. In experiments with OCS·BF₃, no "1/4*eqQ*" transition could be observed.

The quadrupole coupling constants in NCCN·HF have previously been determined³ to be -4.28 and -4.56 MHz for the bonded and non-bonded nitrogens, respectively. Due to the complex hyperfine structure expected for NCCN·BF₃, no attempt was made to observe a "1/4*eqQ*" transition, but a low-resolution microwave spectrum characteristic of a symmetric top was quickly found by using an oscillator broadened to 3 MHz with white noise.

Results

The observed transitions of NCCN·BF₃ are given in Table I. Figure 1 shows the *J* = 6 ← 7 transition of NCCN·¹¹BF₃. The

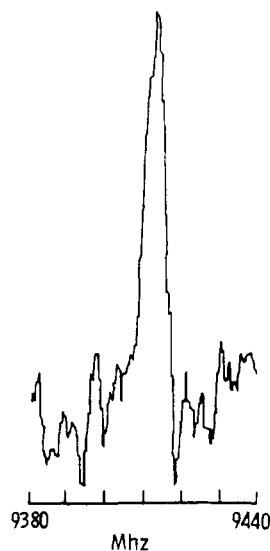


Figure 1. The *J* = 6 ← 7 transition of ¹¹BF₃·NCCN. This is a single sweep, using a 10s time constant.

data clearly show that NCCNBF₃ is a symmetric rotor. Note that the observed line widths are too broad to be accounted for by quadrupole hyperfine structure or oscillator line width and are likely due to a *D*_{JK} term in the energy expression. A small "*D*_J" value of 3 kHz can be fit to the frequencies given in Table I. While this value is quite reasonable, lack of knowledge of *D*_{JK} as well as uncertainty concerning the distribution of *K* levels being focussed in the spectrometer preclude a meaningful interpretation of this number. Thus, the *B* value used for calculation of the weak bond length was just that obtained from the lowest frequency transition (where the centrifugal distortion would be the least) and computed assuming a nondistortable rotor. The values obtained are 672.2 (2) and 675.6 (2) MHz for the ¹¹B and ¹⁰B isotopes, respectively. If the 3-kHz *D*_J were considered, the corrected *B* values would be 672.5 and 676.0 MHz for the ¹¹B and ¹⁰B species, respectively. With use of the known rotational constant⁷ of NCCN and known bond lengths^{8,9} and the assumption that the NCCN is along the BF₃ axis, a boron-nitrogen bond length of 2.647 (3) Å is obtained. If the rotational constants obtained by including the *D*_J term were used, the boron-nitrogen bond length would be only 0.002 Å lower than the above stated value. A more detailed treatment of the internal motions in this complex is not justified with the resolution of these data.

The signal-to-noise ratio of the observed transitions was not adequate to resolve the complex structure arising from nuclear quadrupole and *D*_{JK} centrifugal distortion effects. Consequently, no Stark measurements were performed. Transitions involving lower *J*, where this structure would be simpler, were at best difficult to observe, even at low resolution.

The two rotational constants obtained for the isotopically substituted species permit, in principle, the determination of the degree of out-of-plane deformation of the BF₃. The data obtained are consistent with a FBN angle of 90°, but due to the relatively low resolution of the spectra, the data cannot preclude angles less than about 100°. We feel, however, that comparison with other similar systems indicates that the out-of-plane distortion of BF₃ in NCCNBF₃ is negligible. This was found to be the case in the weakly bound complexes BF₃CO and BF₃N₂ where the higher resolution spectra set the out-of-plane bending angle at less than 1°. Since the nitrogen-boron bond length in the cyanogen system is quite comparable to the van der Waals bond length in other weakly bound systems, and since under the scrutiny of higher

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Table II. Comparison of van der Waals Bond Lengths to Nitrogen

	BF ₃ (B-N)	HF (F-N)
N ₂	2.88 ^a	3.08 ^d
NCCN	2.65 ^b	2.86 ^e
CH ₃ CN	1.64 ^{c,h}	2.759 ^f
HCN	?	2.796 ^g

^a Reference 1. ^b This work. ^c Reference 12. ^d Reference 10.
^e Reference 3. ^f Reference 13. ^g Reference 14. ^h Solid-state value.

resolution these other systems show little or no deformation of the BF₃ upon complexation, we shall assume that the BF₃ moiety is planar in NCCN·BF₃ as well.

Discussion

The nitrogen-boron bond length in NCCN·BF₃ may be compared with the van der Waals bond length in several other complexes containing van der Waals bonds to nitrogen. These data are summarized in Table II. It is seen that with both HF and BF₃, NCCN forms bonds which are about 0.22–0.23 Å shorter than those formed with N₂. In this context, the B–N bond length in NCCN·BF₃ is not surprising. Interestingly, BF₃ forms solids¹¹ with HCN and CH₃CN, and an X-ray crystallographically study¹² of the latter compound has shown it to consist of individual BF₃·NCCN units with a B–N distance of 1.64 Å. Clearly, the substitution of CN with CH₃ produces a tremendous change in the radial potential between BF₃ and NC–R. With HF, however, this is not the case, the N–H bond lengths in CH₃CN·HF and NCCN·HF being 1.833 and 1.936 Å, respectively. This difference between HF and BF₃ undoubtedly occurs because it is possible to form a covalent bond to BF₃ without violating the octet rule, while such bonding is not possible for HF. In this sense, it would seem that the BF₃ systems provide a rare opportunity for examining the transition between van der Waals and covalent bonding if the nature of the substituent were properly varied. The relationship between the stability of the adduct and electron-withdrawing capabilities of the donor substituent is well known for the classical addition complexes of BF₃. Interestingly, the B–N lengths in H₃N·BF₃, CH₃H₂N·BF₃, and (CH₃)₃N·BF₃ are 1.60, 1.57, and 1.59 Å, respectively. The contraction relative to CH₃CN·BF₃ has been interpreted in terms of greater stability of the amines. The relative similarity of these distances, however, compared with the 2.64-Å length in NCCN·BF₃ underscores the dramatic nature of the increase in bond length with NCCN·BF₃.

It would appear that at least in principle there is not reason to expect an abrupt transition between “covalent” and “van der Waals” binding as the donor molecule is varied, though the adducts of BF₃ with CH₃CN and NCCN are apparently two extreme

cases. The complex between BF₃ and CH₃CN shows significant electronic reorganization within the BF₃ moiety: The FBN angle in the solid is 103°, indicating a 13° distortion of the initially planar BF₃, and the boron atom may be thought of as approaching an sp³ configuration. Whether this process can occur on its own in an isolated pair of molecules or must be concomitant with the appearance of the long-range stabilizing forces present in the solid is an open question. Clearly, it would be interesting to prepare a “van der Waals” complex of CH₃CN·BF₃. The vapor phase of this material is completely dissociated above 50° C,¹⁵ so that adiabatic expansion in an argon carrier above this temperature should provide a gas-phase sample of CH₃CN·BF₃. It will be interesting to see if under these conditions this adduct more closely resembles NCCN·BF₃ (long bond length, planar BF₃), or if it remains essentially unchanged from its configuration in the crystal. The structural characterization of the other BF₃·NC–R complexes with a variety of substituents may also be useful in trying to observe a continuous transition from covalent to van der Waals bonding.

While both HF and BF₃ show some degree of regularity in their binding to N₂ and NCCN, it is of interest to observe that there is a striking dissimilarity between the binding of HF and BF₃ to CO₂. CO₂·HF is axially symmetric, while CO₂·BF₃ is not. One might have naively expected an asymmetric structure for CO₂·BF₃ from consideration of lone sp² electron pairs of CO₂, but such a description would fail to account for the linear structure of CO₂·HF. One frequently tends to think of van der Waals binding in terms of donor-acceptor picture, and HF and BF₃ are two simple Lewis acids which accept electrons along their axes of symmetry. The difference in structure between their CO₂ complexes illustrates the complexity of the behavior of CO₂ as a Lewis base. The contrast between the structures of HF with CO₂ (linear complex) and isoelectronic N₂O (nonlinear complex) has already been discussed^{2,16,17} and further emphasizes that the binding of CO₂ complexes is probably rather subtle. Further work in our laboratory^{18,19} shows still other binding patterns of CO₂ when bound to simple Lewis bases, and the structural chemistry of CO₂ van der Waals complexes appears quite rich. Clearly a more complete structural characterization of CO₂·BF₃ as well as complexes of CO₂ with other Lewis acids in desirable in order to better understand binding in this system.

Registry No. BF₃, 7637-07-2; ¹⁰BF₃, 15875-25-9; ¹¹BF₃, 20654-88-0; NCCN, 460-19-5; CO₂, 124-38-9; N₂O, 10024-97-2.

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