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HeI Photoelectron, Mid-Infrared, and ab Initio Studies of the Unstable Fluoroisocyanatoboranes F_2BNCO and $FB(NCO)_2$

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Abstract: HeI photoelectron and Fourier transform infrared spectra are reported for the new unstable boron isocyanate molecules F_2BNCO and $FB(NCO)_2$ obtained in a low-pressure flow system from the reaction of a gaseous BCl_3/BF_3 mixture with solid AgNCO at moderate temperatures. Structural information from ab initio calculations at the 6-31G* level indicates that these molecules have planar structures with trans-bent BNCO chains, although inversion at nitrogen is a relatively low energy process. For $FB(NCO)_2$ the C_s sickle structure is predicted to be the most energetically favorable over linear (two negative frequencies), U (transition state), or W (minimum) structures. The observed ionization potentials and vibrational frequencies compare favorably to the results of the ab initio calculations, supporting the identification and assisting with the assignments.

Introduction

We have demonstrated previously that unstable chloroisocyanatoboranes $Cl_xB(NCO)_{3-x}$ can be prepared and investigated in the gas phase by ultraviolet photoelectron spectroscopy (UPS)[1] and infrared spectroscopy.[2] Together with semiempirical MNDO calculations, the UPS work indicated that these molecules are planar with bent BNCO chains. A priori it is not always clear whether isocyanates of main group elements attached through nitrogen as X–NCO would have bent (at nitrogen), linear, or quasilinear (e.g. H_3SiNCO) structures.[3-5] (In general, the NCO group is found to be nonlinear with the CO moiety trans-bent by 5–10°.) Off-axis substitution on an isocyanate, or indeed, a thiocyanate or azide group, is generally the norm, leading to interesting spectroscopic properties caused by splitting of the π degeneracies. UPS of several XNCO molecules (X = H, halogen, Me, CN) have been obtained and interpreted on this basis.[6-9] However, for isocyanates of boron there is a lack of data, since the discrete species may polymerize or, as with many trigonal boron compounds, disproportionate.[10,11] Some synthetic and spectroscopic studies have however been reported for comparable isothiocyanates $X_xB(NCS)_{3-x}$, usually in solution mixtures, with X = Me, SMe, Cl, Br, and I.[12-14]

More recently we have performed high-level ab initio calculations on the molecules H_2BNCO and F_2BNCO,[15] both at the Hartree–Fock (HF) level with double (6-31G*) and triple (6-311G* and 6-311G**) split valence basis sets and at the post-HF level using Møller-Plessett theory to second order (MP2/6-31G*). Calculations on the parent H-substituted molecule indicated essentially no difference in energy between the bent and linear forms; basis sets employing a triple split valence or correlation were required to make the molecule bend, whereas a commonly used level of theory, 6-31G*, predicted the molecule to have a linear BNCO chain. The bent structure was favored by a mere 0.53 kJ mol^{-1} at the HF 6-311G* level and by 1.12 kJ mol^{-1} with MP2/6-31G*. The introduction of correlation in order to bring theory and experiment into accord has been noted for the isoelectronic propadienone molecule H_2CCCO.[16]

As discussed previously,[1] a deciding structural feature of halo-substituted boron isocyanates is the extent of interaction of the ligand X in, say, X_2BNCO with B through pπ donation. Competition between Xpπ and NCOpπ donation is the determining factor for either bent or linear configurations. When a relatively good π donor like F is placed on B, e.g. F_2BNCO, the energy difference between the bent (minimum) and linear (transition state (TS)) structures increases to 3.85 kJ mol^{-1} (HF 6-311G*) and 3.58 kJ mol^{-1} (MP2/6-31G*), and the molecule is already bent at the 6-31G* level, albeit by only 1.47 kJ mol^{-1}. The corresponding isoelectronic difluoropropadienone, F_2CCCO, also exhibits similar basis set effects.[17,18]

Information based mainly on derived force constants had favored linear BNCO chains for Cl_2BNCO[10] and Me_2BNCO,[19] whereas our recent computational results[1,15] have indicated a strong preference for bent structures. This has been substantiated by a recent electron diffraction study of Me_2BNCO, which has now been determined to be bent with a BNC angle of 153.8°.[20]

As a synthetic target the propadienone analog H_2BNCO is difficult; monosubstituted trigonal boranes are notoriously unstable, and so it was decided to attempt to generate the fluoro analog F_2BNCO plus the bisisocyanato species $FB(NCO)_2$. This has some advantages; for UPS work the F-based ionization potentials (IPs) would not overlap with the high-lying π nonbonding orbitals of the NCO moiety, unlike the Cl case where there was considerable overlap in the 11–13-eV range.[1] In the

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infrared (IR), bands attributable to BF stretches (typically 1500–1200 cm^{-1}) should not obscure the BN stretching region, as observed for the Cl analogs.[2] Finally, the F-substituted species would be more computationally tractable than the Cl species and could be handled by ab initio methods. If bent structures are favored, attention must also be given to the conformations and relative energies of the bisisocyanato species FB(NCO)$_2$ with U or W C_{2v} structures or a sickle C_s structure (see below, Figure 4).

Experimental Section

A perusal of the literature reveals that F$_2$BNCO has been suggested as an intermediate in the reaction of silyl isocyanate with boron trifluoride.[21] Previous work[13] has also indicated no exchange between BF$_3$ and solid AgNCO in solution, unlike facile Cl replacement;[1] we can confirm that this holds also for the gas–solid reaction even up to 160° C. This is not surprising given the strength of the BF bond (613 kJ mol^{-1}) compared to the BCl bond (456 kJ mol^{-1}).[22] The logical step is, therefore, to use F$_2$BCl to produce F$_2$BNCO, and FBCl$_2$ to produce FB(NCO)$_2$. Unfortunately, these starting materials do not exist as stable compounds, and so instead, mixtures of BF$_3$ and BCl$_3$ (Matheson) were used. These molecules undergo exchange producing BF$_2$Cl and BFCl$_2$, with all four species coexisting with each other in thermodynamic equilibrium.[23,24] Since the individual species cannot be separated, the two desired starting materials for the isocyanation reaction, F$_2$BCl and FBCl$_2$, were used from the equilibrated mixture.

In the simplest configuration the BF$_3$/BCl$_3$/BF$_2$Cl/BFCl$_2$ gas mixture was passed through loosely packed and heated AgNCO contained inside a Pyrex tube (8-mm i.d. × 20 cm) which was attached directly to the ionization chamber of a home-built fast-pumping photoelectron spectrometer.[25] AgNCO was prepared[26] by precipitation from aqueous solutions of KNCO and AgNO$_3$ and dried under vacuum at ca. 100 °C for a few hours. HeI photoelectron (PE) spectra were obtained with data acquisition via a PC/XT. Resolution was 40 meV during the course of the experiments, and spectra were calibrated with the known IPs of Ar, CO$_2$, and BF$_3$.

A similar setup was used for the IR measurements. FTIR spectra were collected on a Nicolet 20SXC interferometer equipped with either a variable path length White cell or a 20-cm single-pass cell. Both cells had KBr windows, giving a spectral range down to 400 cm^{-1}. The path length of the White cell was kept at 16 m. In either case the effluent from the reaction train was slowly pumped through the cell using a rotary pump whilst maintaining the pressure between 50 and 500 mTorr. Spectra were collected at 2- or 0.5-cm^{-1} resolution, with 32 scans coadded.

The overall yields of the desired compounds were improved in practice by adopting a more complicated inlet pathway. Potentially ten products can contribute to the final spectra, since each of the chloro-containing species can yield partially or fully isocyanated products. Spectroscopically, such a mix is impossible to handle, and so, to reduce the number of products, the AgNCO was maintained at 110 °C to ensure that every chloro-containing species was converted to the corresponding isocyanate. This leads to only four products, viz. unreacted BF$_3$, F$_2$BNCO, FB(NCO)$_2$, and B(NCO)$_3$. To further maximize the yield of the desired F$_2$BNCO and FB(NCO)$_2$ species and minimize BCl$_3$ (which forms interfering B(NCO)$_3$), the reaction mixture was passed through a following trap at −132 °C (*n*-pentane/liquid N$_2$) to select preferentially the more volatile components. The final products after passage through hot AgNCO were passed through a cold trap (−95 °C, toluene/liquid N$_2$) to remove the more involatile B(NCO)$_3$. The products which enter the spectrometer then consist of three major components, BF$_3$, BF$_2$NCO, and BF(NCO)$_2$, the former having well-known PE and IR spectra.[27-29] Attempts to separate these compounds further were unsuccessful, and indeed, considerable polymerization was observed. As a final point, it should be noted that the last trap (−95 °C) efficiently collects B(NCO)$_3$, which forms a white solid at room temperature. It was subsequently found that warming this solid gave essentially pure B(NCO)$_3$ in the gas phase, and thus comprises a convenient source of this material.[2] Cocondensing BF$_3$ with this solid in an attempt to achieve a redistribution reaction and formation of fluoroisocyanatoboranes was unsuccessful.

Computational Methods

Ab initio calculations were performed at the 6-31G* level using RHF wave functions; all structures were fully optimized by means of analytic gradient procedures within planar C_s or C_{2v} symmetry. All stationary points were checked by frequency calculations to identify them as either potential energy minima or transition states (zero or one negative frequency, respectively). Although we have previously[15] used 6-311G** basis sets and correlation (MP2/6-31G*) for the structures and energies of F$_2$BNCO, we have, due to computational restraints with FB(NCO)$_2$, restricted ourselves herein to 6-31G* as the best basis set for both molecules. Experience gained previously[15] indicates that this level of theory is likely to underestimate the bend at nitrogen but, in terms of Koopmans' IPs and vibrational frequencies, will show only small differences compared to higher level calculations. Some calculations were also performed with the smaller 3-21G* basis set; these invariably led to structures with linear, or close to linear, BNCO chains and are not discussed here. The harmonic vibrational frequencies were used for comparison with the experimental IR spectra. To this end, all calculated frequencies were multiplied by a scaling factor of 0.9 to account partially for anharmonic effects. The ab initio calculations were performed using Gaussian 86[30] on an IBM 3081K at the University of Guelph.

Results

The PE spectra obtained from the reaction scheme described above are shown in Figure 1. The top spectrum (1a) shows an excess of BF$_3$, and the bottom spectrum (1b) shows less of this species due to slightly different conditions, determined principally by the absolute temperature of the first (−132 °C) trap. In Figure 1a sharp bands due to HNCO (11.7 eV)[6] and CO$_2$ (13.8 and 18.0 eV)[31] are also evident. Once bands of BF$_3$ have been identified (strong bands hatched on the figure), it is clear that the resulting spectra consist of only two species, because of the change in the relative intensities of the two broad bands between 11 and 13 eV, when recorded under different conditions.

The mid-IR spectrum of this same reaction is shown in Figure 2a; strong bands at 1495, 1450, 700, and 480 cm^{-1} belong to excess BF$_3$,[28,29] and the lower spectrum (Figure 2b) shows digital subtraction of most of the BF$_3$.

Discussion

Calculated Structures. Before trends and assignments in the ultraviolet photoelectron and FTIR spectra of these molecules are discussed, it is necessary to establish their structures and conformations. A recent body of evidence suggests care must be taken with ab initio methods if accurate representation of the structures of $>C{=}C{=}C{=}O$[16,17] and $-N{=}C{=}O$[15,20,32-34] molecules is required. The present calculations for both linear and nonlinear BNCO chains give the planar structures shown in Figures 3 and 4 for F$_2$BNCO and FB(NCO)$_2$; the corresponding

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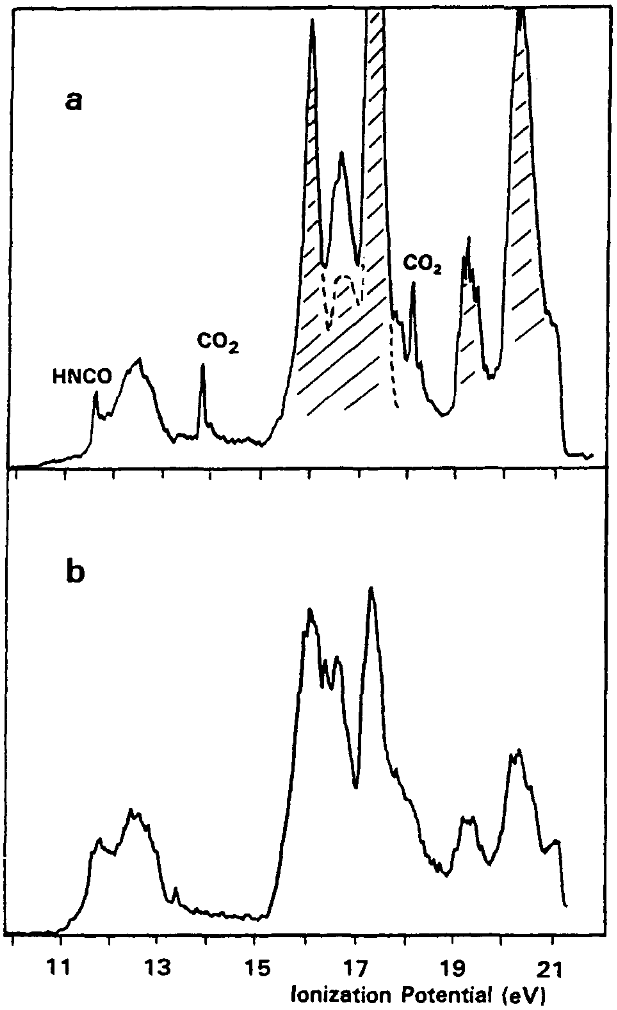

Figure 1. HeI photoelectron spectra of the reaction between gaseous BCl_3/BF_3 and solid AgNCO at 110 °C: (a) spectrum with excess BF_3 (hatched); (b) spectrum recorded under different conditions with less BF_3, illustrating changes in intensities on the first two bands.

total energies at various levels are given in Table I. Also shown in Figure 3 are the higher level 6-311G* and MP2/6-31G* calculations[15] on F_2BNCO for comparison. For both molecules the optimum structures have BNCO chains bent at nitrogen, with a smaller trans-bend at carbon. As mentioned previously,[15] the BNC angle for the difluoro species is 145.6° (6-31G*), with only 1.47 kJ mol^{-1} separating linear (C_{2v}, TS) and bent (C_s, minimum) structures. Possible transition states corresponding to rotation about the BN bond could not be located, as these reverted to linear structures. This level of theory also performs well for the isoelectronic (and bent) difluoropropadienone molecule, F_2CCCO, recently investigated by microwave spectroscopy,[18] although the $C_1C_2C_3$ angle is smaller (experiment, 130.6°; calculated, 6-31G*, 132.8°). The higher level 6-311G* and MP2/6-31G* calculations for F_2BNCO settle down to slightly more bent structures.

For the biisocyanato species, the structure with linear BNCO chains has two negative Hessian eigenvalues, corresponding to in-plane bending at the two nitrogen atoms, and the most inferior total energy. Of the three bent structures shown in Figure 4, U (C_{2v}), W (C_{2v}), and sickle (C_s), the first is a higher energy transition state (one negative Hessian eigenvalue), and of the remaining two, both of which are minima, the sickle form has the slightly lower energy by 1.0 kJ mol^{-1}. The origin of this ordering stems from steric interaction of the extended NCO groups. The BNC angles in the asymmetric C_s structure are 143.6° and 146.0° for the outward and inward pointing NCO groups. It should be noted that calculated frequencies (and indeed, IPs) for the W structure are very similar, and we cannot therefore exclude the presence of this species. The subsequent discussion focuses on the lowest energy sickle structure. The lower level calculations

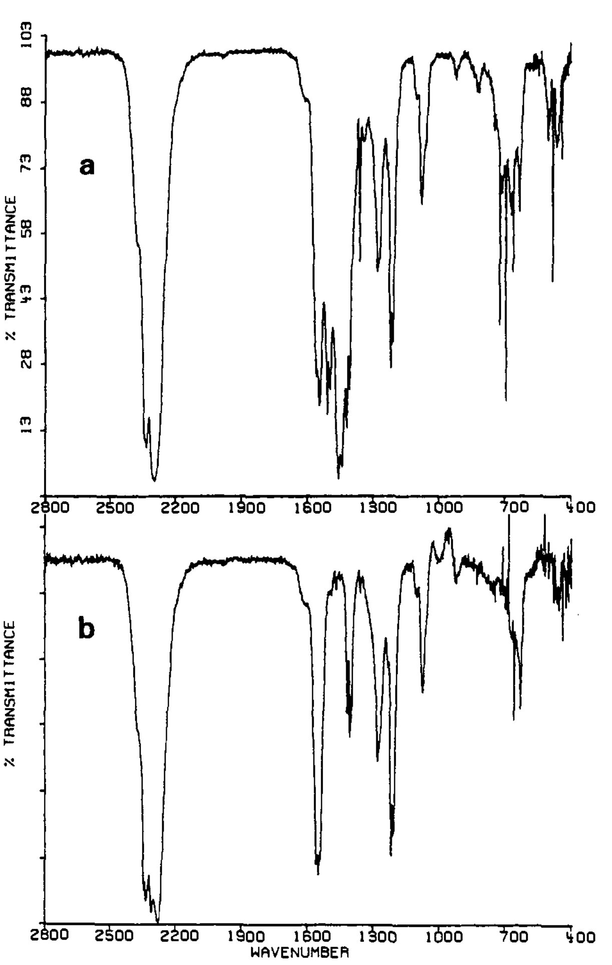

Figure 2. Infrared spectra of the BCl_3/BF_3 and AgNCO reaction between 2800 and 400 cm^{-1}: (a) spectrum with excess BF_3; (b) spectrum with BF_3 subtracted.

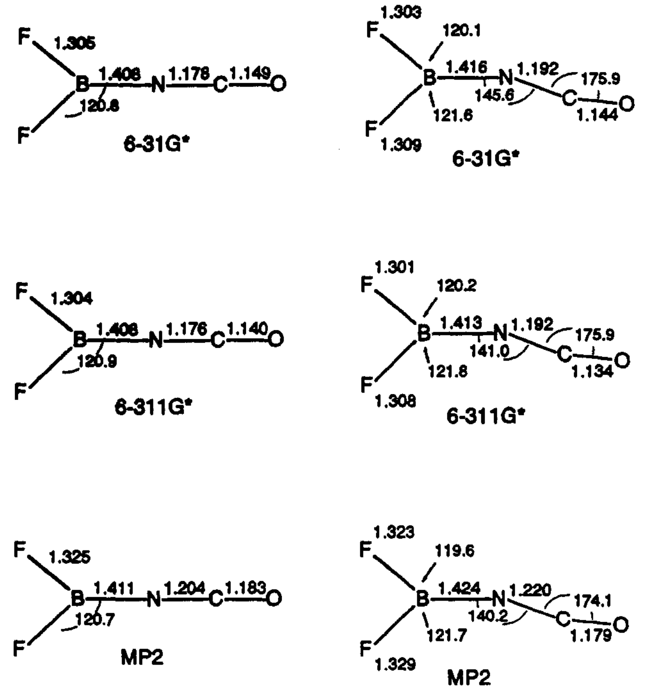

Figure 3. 6-31G*, 6-311G*, and MP2/6-31G* optimized structures for bent and linear F_2BNCO.

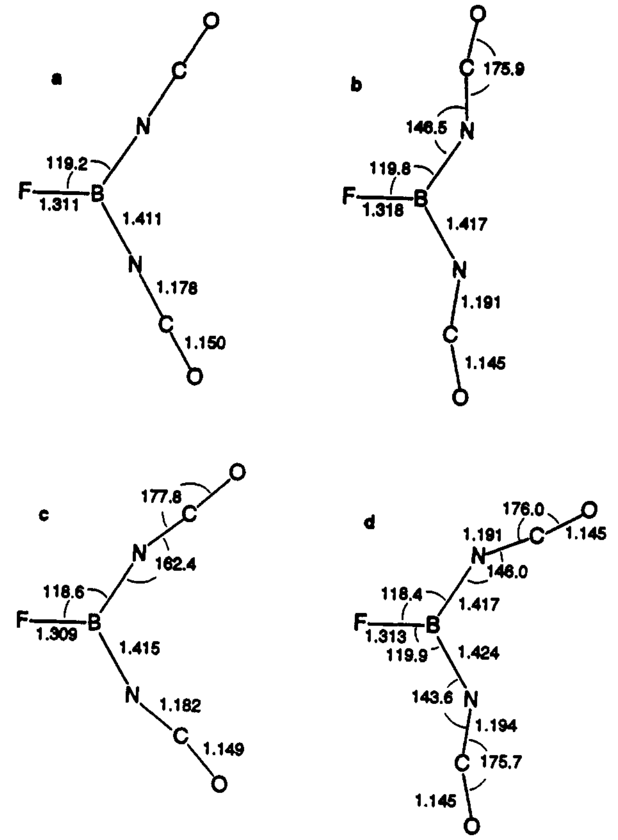

Figure 4. Optimized structures for $FB(NCO)_2$ at the 6-31G* HF level: (a) linear C_{2v} (high-lying saddle point); (b) W C_{2v} (minimum); (c) U C_{2v} (TS); (d) sickle C_s (minimum).

Table I. Total Energies (hartree) at Various Levels of Theory for F_2BNCO and $FB(NCO)_2$

level	symmetry	energy
	F_2BNCO	
6-31G*	C_{2v}[a]	−390.926 29
6-31G*	C_s[b]	−390.926 85
6-311G*	C_{2v}[a]	−391.025 54
6-311G*	C_s[b]	−391.027 01
MP2/6-31G*	C_{2v}[a]	−391.812 22
MP2/6-31G*	C_s[b]	−391.813 59
	$FB(NCO)_2$	
6-31G*	C_{2v} (linear)[c]	−458.656 91
6-31G*	C_{2v} (U)[a]	−458.657 06
6-31G*	C_{2v} (W)[b]	−458.657 75
6-31G*	C_s (sickle)[b]	−458.658 14

[a] One negative eigenvalue. [b] Zero negative eigenvalues. [c] Two negative eigenvalues.

(3-21G*) prefer essentially linear BNCO structures, as, indeed, they do for the CCCO chain of F_2CCCO.

Photoelectron Spectra, Ionization Energies, and ab Initio Calculations. The PE spectra (Figure 1) consist principally of three species, a mixture of BF_3, F_2BNCO, and $FB(NCO)_2$. BF_3 can be easily identified, leaving the combined spectra of the two new molecules. The basis for assignment to these particular molecules is the positions of the bands compared with those in the ultraviolet photoelectron spectra of the chloroisocyanatoboranes,[1] the comparison with calculations, and the results of the FTIR work (below).

As it turns out, specific orbital assignments are not feasible for these molecules, because the bands are broad, and although the fluorine-based IPs no longer obscure the first group of IPs as they did in the chloro case, they do tend to cluster (in both molecules) in the 15–19-eV range, precisely where the spectrum[27] of BF_3 occurs.

Table II. Experimental and Theoretical[a] IPs (eV) for F_2BNCO and $FB(NCO)_2$

F_2BNCO		$FB(NCO)_2$	
expt	theor	expt	theor
12.6	12.10(a″)	11.8	11.56(a″)
12.6	12.12(a′)	11.8	11.75(a′)
		12.6	12.39(a′)
		12.6	12.55(a″)
15.5–21[b]	16.43(a′)	15.5–21[b]	16.52(a′)
	16.77(a″)		16.84(a″)
	16.98(a″)		16.88(a′)
	17.03(a′)		16.93(a″)
	17.04(a′)		16.97(a′)
	18.33(a″)		17.71(a″)
	18.87(a′)		18.71(a′)
	19.55(a′)		18.80(a′)
	20.39(a′)		19.44(a′)
	22.24(a′)		20.77(a′)

[a] Theoretical values are 0.92 × 6-31G* Koopmans' values. For both molecules the minimum-energy C_s structures are used: F_2BNCO, E_T = −390.926 85 hartree at the 6-31G* level; $FB(NCO)_2$, E_T = −458.658 14 hartree at the 6-31G* level. [b] See text for discussion of this region. Some individual bands can be observed at 16.0, 16.5, and 17.6 eV but cannot be explicitly assigned to F_2BNCO or $FB(NCO)_2$.

The experimental and calculated IPs are shown in Table II for both F_2BNCO and $FB(NCO)_2$; the 6-31G* values for the minimum-energy structures (C_s in both cases) are multiplied by 0.92 to correct partially for deficiencies in Koopmans' theorem,[35] which often occur in the presence of low-lying virtual orbitals. What is clear from these results, and Figure 1, is that the second peak centered at 12.6 eV consists of the closely spaced first two IPs of F_2BNCO (corresponding to the out-of- and in-plane π NCO nonbonding orbitals; in Cl_2BNCO[1] these are located in the 11.5–12.0-eV range). The first peak in the spectra at 11.8 eV corresponds to the first two IPs of $FB(NCO)_2$, with the next two peaks, calculated less than 1 eV away, hidden under the first two IPs of F_2BNCO at 12.6 eV. This means that spectrum **1a** is F_2BNCO rich, whereas 1b is $FB(NCO)_2$ rich; in neither case is a completely clean spectrum obtained. It is also apparent that in both spectra, in the region 15–21 eV, there is considerable complexity due to the occurrence of three principal types of bands. These are (a) fluorine-based orbitals (compare strong peaks of BF_3 at 16.0, 16.6, 17.3, 19.3, and 20.3 eV,[26] hatched in Figure 1a, or the fluorine-based bands at 15–19 eV in F_2BNH_2[36]), (b) broad bands corresponding to NCO π bonding based orbitals, which are centered at 16.45 and 16.2 eV in Cl_2BNCO and $ClB(NCO)_2$, respectively, and, finally, (c) NCO $p\sigma$ based orbitals, which occur at 17.6 eV in both Cl_2BNCO and $ClB(NCO)_2$.[1] The sum total of these bands makes it impossible to assign any bands at all in this region, where the calculations show ten IPs for each molecule; Table II illustrates the calculated denseness of IPs.

No specific assignments can be made for the ultraviolet photoelectron spectra of these two molecules, and nothing can be extracted from the experimental data regarding linearity/nonlinearity of the BNCO chains. However, UPS does indicate that these molecules can be made and that the observed IPs are in accord with the results of the ab initio calculations.

Infrared Spectra. (a) Assignment of Observed Bands to Individual Molecules. The FTIR spectrum from 2800–400 cm^{-1} shown after the subtraction of excess BF_3 (Figure 2b) confirms the formation of isocyanate molecules; this is evident from the strong bands corresponding to ν_{as} NCO and ν_s NCO around 2340 and 1560 cm^{-1}, respectively. Once again this spectrum represents a mixture of the two molecules, but by careful analysis of a considerable number of spectra recorded under different conditions, it is feasible to identify bands specifically associated with

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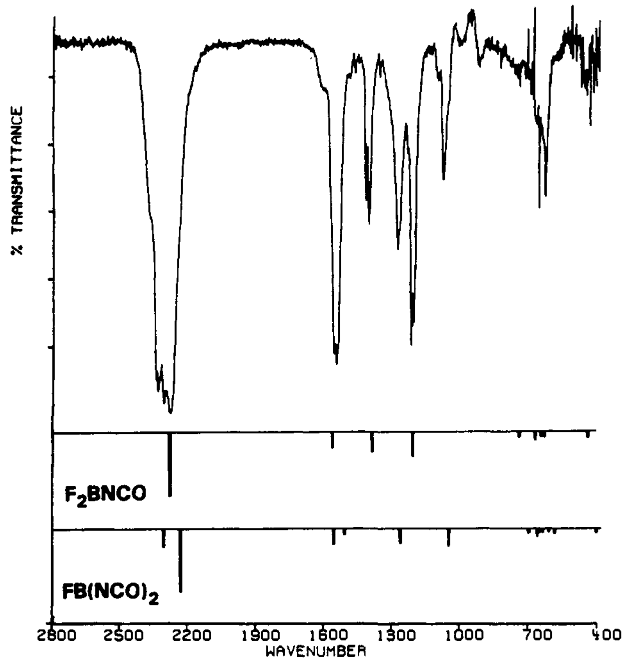

Figure 5. Infrared spectrum of the $BCl_3/BF_3/AgNCO$ reaction with BF_3 subtracted showing scaled 6-31G* frequencies, and calculated intensities for the two molecules F_2BNCO and $FB(NCO)_2$.

either F_2BNCO or $FB(NCO)_2$. It is also clear that a small amount of $B(NCO)_3$ is present, contributing some intensity (below 2200 cm^{-1}) to the wing of ν_{as} NCO and to the band centered at 1070 cm^{-1}. The 2340- and 1560-cm^{-1} features then consist of three fundamentals each, of which two correspond to the bisisocyanato species. Between 1500 and 1000 cm^{-1} discrete bands can be associated fairly readily with a particular molecule. Since F_2BNCO has larger rotational constants, some bands have distinct rotational profiles, and this is especially true for the B-type band at 1413 cm^{-1} and the A-type band at 1213 cm^{-1}, both of which are assigned to the F_2BNCO molecule. The maximum PR separations calculated for these bands using the equations of Seth-Paul[37] are 10.4 and 12.5 cm^{-1}, respectively, in good accord with experimental separations of 11.4 and 12.1 cm^{-1}. The band at 1276 cm^{-1}, with the suggestion of a weak Q branch, is assigned to $FB(NCO)_2$. Below 800 cm^{-1}, the intensities, as expected, fall off, although there are several weak features. Although many infrared-active bands are expected in this region, only one distinct band is definitely observed with a prominent Q branch at 659 cm^{-1}; this is assigned to a C-type band of F_2BNCO. It is feasible that the prominent feature at 632 cm^{-1} is associated with $FB(NCO)_2$, although its intensity is probably exaggerated by the close C-type band and an overlapping band of $B(NCO)_3$.

Table III. Observed and Calculated Vibrational Frequencies (cm^{-1}) and Assignments for F_2BNCO

obsd	calcd[a]	intensity[b]	band type[c]	assignment and approximate description[d]
2333	2275 (A′)	1783	A	ν_1 NCO asym str
1569/1553[e]	1546 (A′)	384	A	ν_2 NCO sym str + BN str
1413	1381 (A′)	465	B	ν_3 BF_2 asym str
1213	1199 (A′)	525	A	ν_4 BF_2 sym str
NO[d]	733 (A′)	30	A	ν_5 BF_2 sym str + BN str
659	652 (A″)	166	C	ν_{10} BNCO oop bend
NO	632 (A′)	51	B	ν_6 NCO in-plane bend
NO	631 (A″)	31	C	ν_{11} BF_2 wag + NCO oop bend
NO	440 (A′)	29	B	ν_7 BF_2 asym bend
NO	398 (A′)	7.6	A	ν_8 BF_2 sym bend
NO	83 (A″)	0.06	C	ν_{12} BNC oop bend
NO	61 (A′)	0.9	B	ν_9 BNC in-plane bend

[a] The values shown are for the best energy C_s structure and are 0.9 × 6-31G* calculated values. Symmetries are in parentheses. [b] Intensity in km mol^{-1} [c] Within C_s symmetry all in-plane vibrations are A′ and all out-of-plane vibrations are A′. The *a* principal axis is approximately along the (bent) BNCO chain. [d] oop = out-of-plane; NO = not observed. [e] In this region there are also two bands of $FB(NCO)_2$. Only one of these frequencies is attributable to F_2BNCO, but it is not known which.

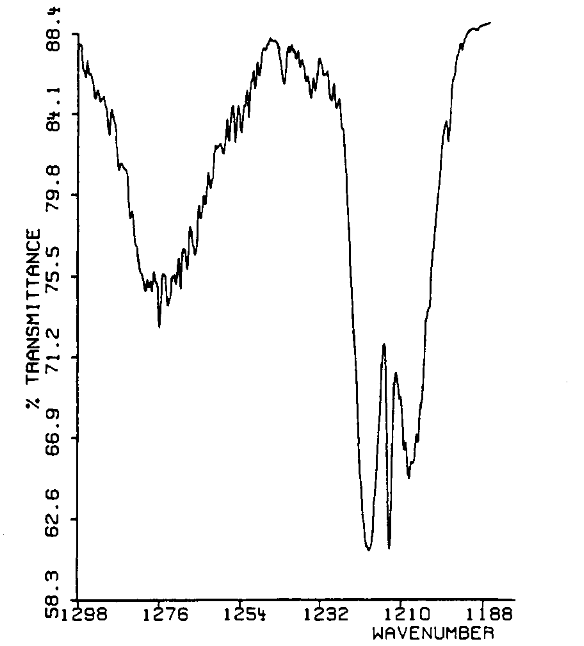

Figure 6. Expansion of the region between 1188 and 1298 cm^{-1} showing the ν_5 and ν_4 fundamentals of $FB(NCO)_2$ and F_2BNCO at 1276 and 1213 cm^{-1}.

(b) Vibrational Assignments. Specific vibrational assignments are assisted by the scaled frequency calculations (6-31G*) for F_2BNCO and $FB(NCO)_2$, the gas-phase rotational profiles where observed, and a comparison with similar molecules. Figure 5 shows the same spectrum as the lower half of Figure 2, together with the calculated frequencies and intensities, and displays impressive agreement for the limited number of bands seen by experiment. The observed positions together with the scaled calculated frequencies, calculated intensities, and approximate descriptions of the modes are given in Table III for bent F_2BNCO. Apart from the ν_1 fundamental at 2333 cm^{-1}, all bands are within 32 cm^{-1} of theory, with especially excellent agreement for the distinctive ν_3, ν_4, and ν_{10} fundamentals observed at 1413, 1213, and 659 cm^{-1}, respectively. This correspondence, together with the measured rotational profiles, confirms the assignment to the F_2BNCO molecule. The strong B- and A-type bands correspond to the BF_2 asymmetric (ν_3) and symmetric (ν_4) stretching frequencies. The latter is shown in expanded form in Figure 6. The ultimate resolution of our interferometer is only 0.5 cm^{-1}, and so no rotational structure is observed. However, with calculated rotational constants for this prolate asymmetric rotor ($\kappa = -0.93$) of A = 10.496 GHz, B = 1.994 GHz, and C = 1.676 GHz, it should be feasible to extract some detail using current high-resolution instruments. Given that all of the important low-energy bending vibrations are too weak to be seen (see Table III and Figure 5 for intensities), the question of linearity/nonlinearity in F_2BNCO could best be answered by a detailed rotational analysis of ν_3, ν_4, or ν_{10}. Preliminary work on obtaining ground-state constants via a microwave experiment[38] has been hampered by the very low dipole moment calculated for this molecule (0.16 D, 6-31G*; 0.18 D, MP2/6-31G*).

The $FB(NCO)_2$ molecule has two fundamentals in the ν_{as} NCO region (Table IV), a weaker one to higher wavenumber (2377 cm^{-1}) of ν_1 of F_2BNCO and one to lower wavenumber (2294 cm^{-1}). Although the scaled values, as with F_2BNCO, are

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Table IV. Observed and Calculated Vibrational Frequencies (cm^{-1}) and Assignments for $FB(NCO)_2$

obsd	calcd[a]	intensity[b]	band type[c]	assignment and approximate description[d]
2377	2296 (A′)	684	B	ν_1 NCO asym str
2294	2233 (A′)	3420	A	ν_2 NCO asym str
1553/1569[e]	1542 (A′)	642	A	ν_3 NCO sym + BN str
(1560)[e]	1510 (A′)	161	B	ν_4 NCO sym + BN str
1276	1259 (A′)	462	B	ν_5 BF str
NO[d]	1052 (A′)	646	A	ν_6 BN str + NCO str
NO	692 (A′)	54	B	ν_7 BN,BF str + NCO in-plane bend
NO	652 (A″)	199	C	ν_{14} NCO oop bend
NO	651 (A′)	81	A	ν_8 NCO in-plane bend
NO	645 (A″)	0.3	C	ν_{15} NCO oop bend
NO	608 (A″)	39	C	ν_{16} FBN_2 wag
NO	580 (A′)	0.9	B	ν_9 NCO in-plane bend
NO	403 (A′)	33	A	ν_{10} BF rock + BN_2 sym bend
NO	380 (A′)	10	B	ν_{11} BN_2 sym bend
NO	97 (A″)	0	C	ν_{17} BNC oop bend
NO	74 (A′)	0.8	A	ν_{12} BNC in-plane bend
NO	69 (A″)	0.2	C	ν_{18} BNC oop bend
NO	41 (A′)	0.5	B	ν_{13} BNC in-plane bend

[a] The values shown are for the best energy C_s structure (sickle) and are 0.9 × 6-31G* calculated values. Symmetries are in parentheses. [b] Intensity in km mol^{-1}. [c] Within C_s symmetry all in-plane vibrations are A′ and all out-of-plane vibrations are A′. The *a* principal axis is approximately perpendicular to the BF axis. [d] oop = out-of-plane; NO = not observed. [e] In this region there is one band of F_2BNCO. It is not known which two of the three bands between 1550 and 1570 cm^{-1} is attributable to $FB(NCO)_2$.

calculated about 60–80 cm^{-1} too low, the calculated separation for these fundamentals in the sickle structure is 63 cm^{-1}, and this agrees, by and large, with the experimental separation (83 cm^{-1}). Around 1560 cm^{-1} the strong band conceals one A-type band associated with the ν_2 fundamental of F_2BNCO and one A- and one B-type band associated with $FB(NCO)_2$. Since these three bands are all calculated within 36 cm^{-1} of each other, a specific assignment cannot be made in this region. The quoted values of 1569 and 1553 cm^{-1} correspond to weak Q branches and could belong to either molecule. Below 1400 cm^{-1} the band at 1276 cm^{-1} can be definitely associated with $FB(NCO)_2$ and is assigned to ν_5, the BF symmetric stretch (located at 1312 cm^{-1} in $FBCl_2$[39] and estimated at 1465 cm^{-1} in $FB(OMe)_2$[40]). This band has a weak Q branch (Figure 6) and is close to the calculated value of 1259 cm^{-1}. Additional bands associated with $FB(NCO)_2$ are uncertain. There is a band computed with reasonable intensity around 1050 cm^{-1}, and although a peak does exist at 1070 cm^{-1}, this can be shown to be due to a combination of $B(NCO)_3$ and an unknown impurity. The whereabouts of the missing band is unclear; it is, however, a fundamental involving extensive coupling of all heavy atoms and may not be well represented in the ab initio calculation. Below 1000 cm^{-1} the only other band with sufficient intensity, and distinctiveness, would be a C-type band predicted in the region of 652 cm^{-1}. In fact, as noted above, such a band near here was assigned to a C-type band (ν_{10}) of F_2BNCO, purely on the basis of what appeared to be a relatively wide rotational profile. The feature at 632 cm^{-1} on the P branch of ν_{10} of F_2BNCO is possibly ν_{14} of $FB(NCO)_2$. Following subtraction of BF_3, a feature also remains at 456 cm^{-1}, perhaps also associated with $FB(NCO)_2$. Clearly these bands, and the adjacent region, require further investigation at higher resolution in order to substantiate these assignments and locate other fundamentals. The calculated rotational constants for this molecule (sickle structure) are $A = 4.162$ GHz, $B = 1.053$ GHz, and $C = 0.840$ GHz, with a calculated dipole moment of 0.23 D.

An interesting and intriguing aspect of the vibrational spectra of these two molecules is the description of the vibrational modes, and this is reflected in the somewhat vague terminology used in Tables III and IV. This is simply because vibrations involving BF, BN, and NCO stretching and bending motions are all coupled together, with the requisite atoms, B, C, N, O, and F, comprising almost the complete first row of the periodic table. For F_2BNCO the asymmetric and symmetric BF_2 stretching frequencies at 1413 and 1213 cm^{-1} are in reasonable agreement with those observed for F_2BCl[39] at 1421 and 1242 cm^{-1} and for F_2BH[41,42] at 1404 and 1167 cm^{-1}. However, the position of the BN stretching frequency is not at all clear, since it is strongly coupled to ν_s NCO and ν_s BF_2. If H_2BNH_2 is taken as a simple molecule containing a BN moiety, intermediate between a single and double bond, then a frequency around 1337 cm^{-1} would be expected.[43] Unfortunately, a band associated with BN stretching in the closely related F_2BNH_2 molecule was not identified from the IR spectrum.[44] From the work described here, a band involving BN stretching in F_2BNCO can be identified (from the calculated eigenvectors) with calculated values of 1546 and 733 cm^{-1}, the former very high, and with a substantial NCO contribution, and the latter very low, with a BF_2 contribution. A key issue for all such BNCO molecules is thus the potential energy distribution, and it is with this in mind that normal coordinate analyses of $B(NCO)_3$, F_2BNCO, $FB(NCO)_2$, and the corresponding chloro-containing species are being undertaken.[2]

Conclusions

We have provided the first definitive experimental identification of the F_2BNCO and $FB(NCO)_2$ molecules, albeit in a mixture. These molecules have a very strong tendency to polymerize and may not be separable without substantial loss. HeI photoelectron spectra have been obtained, together with mid-IR spectra at 0.5–2-cm^{-1} resolution. Broad bands in the PE spectrum, typical for isocyanates, permit only a global assignment to be made for both molecules, based on the ab initio calculations. Similarly, in the infrared measurements, only about 5 bands could be unambiguously identified for each molecule, out of a total of 12 and 18 bands for F_2BNCO and $FB(NCO)_2$. Those bands that were observed were in excellent agreement with theory, and rotational profiles for F_2BNCO unambiguously confirm the identification of this molecule. Severe coupling of vibrational modes is noted and will necessitate a normal coordinate analysis for a series of $>B{-}N{=}C{=}O$ molecules. Although unambiguous structures cannot, with confidence, be evaluated from the photoelectron spectra or the low-resolution infrared spectra, the results of the ab initio calculations indicate that bent structures are favored, and in bisisocyanato case, an asymmetric (sickle, C_s) structure is the most preferred. It is to be noted that in the $F_xB(NCO)_{3-x}$ series increasing isocyanation leads to loss of $p\pi$–$p\pi$ bonding between N and B, longer BN bonds, and an increasing trend toward nonlinearity in the BNCO chain. The NCO group thus has more π donating ability than F; this notion is in accord with earlier conclusions based on displacement reactions.[11] This is supported by the photoelectron spectrum[1] of $B(NCO)_3$, which points to a C_{3h} structure. Comparable $p\pi$ effects have also been seen through changes in BN π bonding with halogen substitution in the X_2BNH_2 series.[36]

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