Crystal and Molecular Structures of Trifluoroacrylonitrile, $F_2C{=}CF{-}CN$, and Trifluorovinyl Isocyanide, $F_2C{=}CF{-}NC$, by Low-Temperature X-ray Crystallography and ab Initio Calculations

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Received March 8, 2000

The structures of trifluoroacrylonitrile, $F_2C{=}CF{-}CN$, monoclinic, $P2_1/n$ (no. 14), $a = 8.595(4)$, $b = 8.748(1)$, $c = 5.421(1)$ Å, $\beta = 102.83(2)°$, $Z = 4$, and its thermally unstable isomer trifluorovinyl isocyanide, $F_2C{=}CF{-}NC$, monoclinic, $P2_1/n$, $a = 8.501(2)$, $b = 8.828(2)$, $c = 5.599(2)$ Å, $\beta = 101.11(2)°$, $Z = 4$ were determined by X-ray crystal structure analysis at 113 and 128 K, respectively, from single crystals grown by partial melting and gradient cooling in small glass capillaries. Selected experimental bond lengths of $F_2C{=}CF{-}CN/F_2C{=}CF{-}NC$ are as follows: C=C 1.326(1)/1.304(2), C≡N 1.158(1)/1.167(2) Å. The C−F bond lengths of the CF_2 group are significantly shorter than those of the CF(NC) and CF(CN) units, respectively. The vibrational frequencies and molecular geometries of this cyanide/isocyanide pair were also calculated by ab initio methods for comparison with the experimental results, which were found to be in general agreement.

Introduction

Despite the great technological importance of fluorinated alkenes, solid-state structural information on these compounds based on X-ray crystal structure determination is very limited. For small, highly fluorinated alkenes crystallographic data are available only for potassium hydrogen difluorofumarate,[1] potassium hydrogen difluoromaleate,[1] 1,2-difluorodinitroethene,[2] perfluorocyclopropene,[3] a chromium complex of trifluorovinyl isocyanide,[4] and very recently bis(trifluorovinyl)mercury.[5] Structural information in the gaseous phase is available for several simple fluorinated alkenes[6] like C_2F_4[7] and C_2F_3H.[8] In addition, it is well documented that the replacement of hydrogen by fluorine in organic molecules drastically changes the reactivity and other properties of the molecules.[9] This is accompanied by structural changes. Although several well-established methods exist for the synthesis of hydrocarbon isocyanides,[10] only a few fluorinated isocyanides have been synthesized so far, mostly in small amounts by specially developed methods.[11] In addition α-fluorinated isocyanides like trifluoromethyl isocyanide tend to polymerize in condensed phase even at very low temperature.[12] Trifluorovinyl isocyanide was recently prepared for the first time in milligram quantities by flash vacuum pyrolysis of pentacarbonyl (trifluorovinyl isocyanide) chromium.[4] Although perfectly stable in the gas phase at ambient temperature and low pressure without any sign of isomerization to the thermodynamically more stable nitrile, trifluorovinyl isocyanide polymerizes readily in condensed phase. In a continuation of our work on fluorinated isocyanides,[11] we report on the X-ray crystal structure determination of $F_2C{=}CF{-}NC$. To study the structural difference between the isocyanide and the cyanide isomer, the structure

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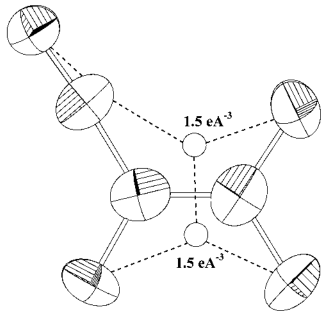

Figure 1. ORTEP[59] diagram of the $F_2C=CF-NC$ molecule from the first refinement with the positions of the difference Fourier peaks that lead to the disorder model.

of $F_2C=CF-CN$ was investigated, too. This experimental work was supplemented by ab initio calculations of the two isomeric compounds.

Experimental Section

Preparation. Trifluorovinyl isocyanide[4] was prepared by flash vacuum pyrolysis of $(CO)_5Cr(CNCF=CF_2)$, and its purity was checked by IR and ^{19}F NMR spectroscopy. Trifluoroacrylonitrile was prepared by passing $F_3C-CHF-CN$[9d] over dry KOH in a U-tube by slow evaporation from a sample held at −60 °C. The volatile products were collected in a trap kept at −196 °C resulting in a mixture of $F_3C-CHF-CN$ and $F_2C=CF-CN$. This procedure was repeated three times, after which IR and ^{19}F NMR spectroscopy showed only the signals of $F_2C=CF-CN$. ^{19}F NMR: $\delta_A = -79.3$ ($^2J_{FF} = 27$ Hz, $^3J_{FF} = 35$ Hz), $\delta_B = -103.5$ ($^2J_{FF} = 27$ Hz, $^3J_{FF} = 117$ Hz), $\delta_C = -191.1$ ($^3J_{FF} = 35$ Hz, $^3J_{FF} = 117$ Hz); IR (gaseous): 2250 (w), 1760 (s), 1362 (s), 1273 (s), 1134 (vs), 1089 (w) cm^{-1}.

Crystal Structure Determinations. $F_2C=CF-CN$ and $F_2C=CF-NC$ were condensed into glass capillaries of 0.5-mm diameter and 0.01-mm wall thickness by using a glass vacuum line. A column of 3−4 mm of the liquid was cooled with liquid nitrogen, and the capillary was sealed under vacuum at a length of 30 mm. After warming to −78 °C in a dry-ice acetone bath, the capillary was mounted on an insulated arcless goniometer head while maintaining the sample at −78 °C to avoid decomposition of the thermally very unstable isocyanide. The samples were mounted in the stream of cold nitrogen gas of an integrated cooling device[13] onto a computer-controlled Siemens four-circle single-crystal diffractometer using Mo Kα radiation with Nb filter. Single crystals were grown by setting the temperature of the gas stream to a few degrees below the melting point of each compound, that is, to −111 and −135 °C, respectively (mp = −108 °C for $F_2C=CF-CN$; mp = −130 °C for $F_2C=CF-NC$). The major part of the sample column was molten from its lower side using a coaxial coil of heating wire. By using an electronic control device for the heat output of the coil the phase borderface was moved very slowly in the opposite, downward direction. Finally the crystal was annealed at the preset temperature. After the crystals had been cooled slowly to 113 K and 128 K, respectively, the X-ray intensity data were collected.

The data were Lp corrected and reduced to F_o^2. The structure solution was obtained by direct methods (SHELXS-86)[14] for both compounds. Full-matrix least-squares refinement based on F^2 (SHELXL-93)[15] with anisotropic thermal displacement parameters converged at $R(F) = 0.057$ for $F_2C=CF-CN$ and at $R(F) = 0.100$ for $F_2C=CF-NC$. Because the difference Fourier maps exhibited two maxima on a line almost perpendicular to the C1−C2 bond as shown in Figure 1 for both compounds, the crystal structure was assumed to be disordered in both cases. The refinements of the disorder model with anisotropic thermal displacement parameters for the major molecule (site occupation factor (sof) = 0.946 for $F_2C=CF-CN$, sof = 0.844 for $F_2C=CF-NC$) and isotropic displacement parameters for the minor one, the bond lengths of which were restrained to the major molecule, converged at $R(F) = 0.042$ and $R(F) = 0.046$, respectively.

Table 1. Crystallographic Data of $F_2C=CF-CN$ and $F_2C=CF-NC$

	$F_2C=CF-CN$	$F_2C=CF-NC$
formula	C_3F_3N	C_3F_3N
Fw	107.04	107.04
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	8.595(4)	8.501(2)
b (Å)	8.7480(10)	8.828(2)
c (Å)	5.4210(10)	5.599(2)
β (deg)	102.83(2)	101.11(2)
V (Å^3)	397.4(2)	412.3(2)
Z	4	4
T (K)	113	128
λ (Å)	0.71069	0.71069
ρ_{calcd} (g cm^{-3})	1.789	1.724
μ (cm^{-1})	2.10	2.02
final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0416$, $wR_2{}^b = 0.139$	$R_1 = 0.0457$, $wR_2 = 0.1423$
final R indices (all data)	$R_1 = 0.0676$, $wR_2 = 0.149$	$R_1 = 0.0835$, $wR_2 = 0.1637$

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) of $F_2C=CF-CN$

	X-ray	HF/6-31G*	MP2/6-31G*
C1−C2	1.326(1)	1.314	1.338
F1−C1	1.307(1)	1.290	1.319
F2−C1	1.303(1)	1.288	1.316
F3−C2	1.337(1)	1.324	1.348
C2−C3	1.419(1)	1.431	1.420
C3−N1	1.158(1)	1.135	1.182
C2−C3−N1	178.97(8)	180	180
F1−C1−C2	123.60(5)	123.6	122.9
F2−C1−C2	123.60(6)	123.8	123.7
F1−C1−F2	112.79(6)	112.6	113.4
C1−C2−F3	119.61(6)	120.0	119.5
C1−C2−C3	123.67(5)	123.3	122.9
C3−C2−F3	116.71(5)	116.7	117.6

Table 3. Bond Lengths (Å) and Angles (deg) of $F_2C=CF-NC$

	X-ray	HF/6-31G*	MP2/6-31G*
C1−C2	1.304(2)	1.309	1.336
F1−C1	1.305(2)	1.295	1.319
F2−C1	1.311(2)	1.294	1.318
F3−C2	1.325(2)	1.318	1.342
N1−C2	1.373(2)	1.361	1.363
N1−C3	1.167(2)	1.159	1.194
C2−N1−C3	179.6(3)	180	180
F1−C1−C2	124.2(2)	123.6	123.1
F2−C1−C2	123.3(2)	123.5	123.1
F1−C1−F2	112.5(2)	112.9	113.4
C1−C2−F3	120.7(2)	120.5	120.6
C1−C2−N1	123.7(2)	123.9	122.9
N1−C2−F3	115.5(2)	115.6	116.5

Crystal data, experimental conditions, and refinement values are listed in Table 1. The experimental bond lengths and angles for the two compounds are presented in Tables 2 and 3 together with the corresponding values from the ab initio calculations. The molecular structures of $F_2C=CF-NC$ and $F_2C=CF-CN$, and the corresponding atomic numbering schemes are depicted in Figures 2 and 3, respectively. Figure 2 is a superposition of the major molecule of $F_2C=CF-NC$ from the disorder model with the molecule from the refinement disregarding disorder in the crystal lattice (empty ellipsoids).

Ab Initio Calculations. The geometries of trifluorovinyl cyanide (trifluoroacrylonitrile) and trifluorovinyl isocyanide were fully optimized in C_S symmetry at the Hartree−Fock and MP2 levels with the 6-31G* basis set using the ab initio programs GAUSSIAN 88,[16] GAUSSIAN 92,[17] and GAUSSIAN 94.[18] The $C-C\equiv N$ bond angle in the cyanide and the $C-N\equiv C$ bond angle in the isocyanide were held at 180°. This

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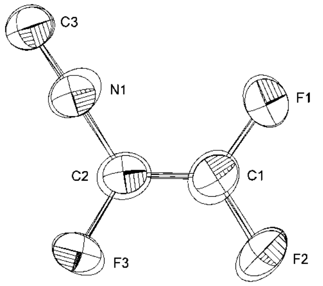

Figure 2. ORTEP[59] diagram. Superposing the $F_2C{=}CF{-}NC$ molecule from the refinement disregarding the disorder (empty ellipsoids) with the major molecule from the disorder model, 50% probability ellipsoids for both.

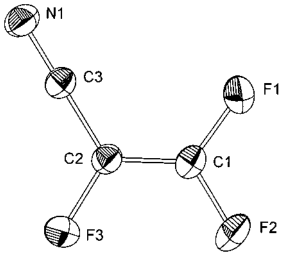

Figure 3. ORTEP[59] diagram of the major $F_2C{=}CF{-}CN$ molecule of the disorder model, 50% probability ellipsoids.

Table 4. Calculated Normal Mode Vibrational Frequencies (cm^{-1}) of $F_2C{=}CF{-}CN$ and $F_2C{=}CF{-}NC$ at the MP2/6-31G* Level Compared with Experimental Data[a]

fundamental	symmetry	$F_2C{=}CF{-}CN$ calcd	$F_2C{=}CF{-}CN$ exptl[48]	$F_2C{=}CF{-}NC$ calcd	$F_2C{=}CF{-}NC$ exptl[4]
ν_1	a′	2222 (5)	2248 (w)	2162 (103)	2111 (s)
ν_2	a′	1846 (140)	1772 (s)	1867 (107)	1801 (s)
ν_3	a′	1415 (133)	1366 (s)	1415 (128)	1363 (s)
ν_4	a′	1321 (168)	1271 (s)	1332 (191)	1279 (vs)
ν_5	a′	1156 (178)	1134 (s)	1177 (239)	1147 (vs)
ν_6	a′	742 (2)	730 (vw)	758 (1)	719 (m)
ν_7	a′	597 (<1)		574 (1)	
ν_8	a′	511 (2)		522 (2)	
ν_9	a′	448 (4)		422 (1)	
ν_{10}	a′	252 (3)		240 (4)	
ν_{11}	a′	134 (5)		126 (3)	
ν_{12}	a″	589 (4)		549 (1)	
ν_{13}	a″	505 (<1)		461 (5)	
ν_{14}	a″	303 (8)		275 (3)	
ν_{15}	a″	144 (2)		148 (1)	

[a] The values in parentheses are relative intensities.

is a satisfactory approximation, because the molecular structure determinations of various isocyanides[19−23] and nitriles[19,24−26] have shown little or no deviation from 180° of these bond angles. Whereas in the crystal structures of transition metal complexes of isocyanides[27] and nitriles,[28] the C−N−C angle is more flexible than the corresponding angle (C−C−N) in nitriles (cyanides) for both steric and electronic reasons. In addition, a test calculation performed on trifluorovinyl isocyanide at the MP2 level with the 6-31G* basis set showed that the $C{-}N{\equiv}C$ angle optimized to 179.1° with a reduction in energy by only 0.01 kJ/mol compared with the linear structure. Transition state structures for the isomerization of trifluorovinyl isocyanide to trifluoroacrylonitrile were performed at both the HF- and MP2/6-31G* levels of theory. Frequency calculations on the optimized geometries were performed at the MP2 level with the 6-31G* basis set; minima were verified by the absence of negative eigenvalues, whereas transition states were verified by the presence of one negative eigenvalue (i.e., one negative vibrational frequency). The geometric parameters are shown in comparison with the experimental results in Tables 2 and 3, and the calculated and observed vibrational frequencies are given in Table 4.

Previous successful matches between theory and experiment from our laboratory and others serve as a benchmark for the choice of basis sets for the current calculations. For example, a computational study of the possible isomers and conformations of *N*-trifluoromethylformamide, $CF_3NHC(O)H$, and *N*-hydroxmethylidenetrifluoromethylamine, $CF_3N{=}C(H)OH$, performed with a 6-31G** basis set[29] (same as 6-31G* above with no hydrogen atoms) reproduced the experimental preference for the *E*-isomer of $CF_3NHC(O)H$ along with detectable amounts of the isomeric imine $CF_3N{=}C(H)OH$.[30] A different computational study of the series of fluorinated and nonfluorinated methyl cyanides and isocyanides $CF_{3-x}H_x{-}CN$ and $CF_{3-x}H_x{-}NC$ at both the HF- and MP2/6-31G** levels of theory[31] has successfully reproduced many experimental properties of both $CF_3{-}NC$, including its structure, vibrational spectra, and excellent π-acceptor ligand properties,[11] and $CF_2H{-}NC$, particularly its vibrational spectra.[32] With the exception of $CF_2H{-}NC$ and $CFH_2{-}NC$, experimental geometric parameters are known for all of the fluorinated and nonfluorinated methyl cyanides and isocyanides[33−37]; and, in general, the calculated geometric parameters at the HF- and MP2/6-31G* levels bracket the experimental values, with bond distances typically being too short at the HF level but too long at

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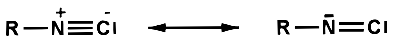
the MP2 level. In addition, the calculated CF_3-NC to CF_3-CN isomerization energy of −81.4 kJ/mol at the MP2/6-31G* level adequately reproduces the experimentally determined value of −96 kJ/mol from photoelectron spectroscopy using the core electron approximation.[38] Furthermore, activation barriers of 226.7 and 308.1 kJ/mol were calculated for the unimolecular rearrangement of CF_3-NC and CF_3-CN, respectively, from a transition state calculation at the MP2/6-31G* level; the magnitude of these barriers is supported by experimentation as well.[39] Trifluoromethyl isocyanide starts to isomerize to the nitrile at about 750 K, and the isomerization is about 50% complete at 1000 K in the dilute gas phase.[39] Finally, a computational study of SF_5-CN and SF_5-NC at the HF- and MP2/6-31G* levels[31] has again successfully reproduced the structural and spectroscopic aspects of this cyanide/isocyanide pair.[40−43] Scaling factors derived from several the aforementioned computational versus experimental studies have allowed for a prediction of the experimental vibrational frequencies of the yet-to-be synthesized molecule CFH_2-NC [$\nu(N{\equiv}C)_{calcd} \approx 2140$ cm^{-1}].[31]

Results and Discussion

Because trifluoroacrylonitrile and trifluorovinyl isocyanide are both gases at ambient temperature, each material had to be condensed into X-ray capillaries and transferred to the diffractometer without raising the temperature above −78 °C, especially to avoid the polymerization of the latter. Nevertheless, low-temperature crystallization of the thermally stable trifluoroacrylonitrile (mp −108 °C) and the thermally unstable, isomeric trifluorovinyl isocyanide (mp −130 °C) made the X-ray crystal structure determination of both compounds possible. Both isomers crystallize in the same monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit and similar lattice constants (see Table 1). Structure solution by direct methods and refinement by full-matrix least-squares revealed the expected molecular structures, but with unsatisfactory R values. An examination of the difference Fourier map of both compounds gave two strong maxima on a line perpendicular to the C1−C2 bond (Figure 1) as described above. These peaks were located in correct distances to the fluorine, carbon, and nitrogen atoms, respectively. In addition, the distances between neighboring fluorine atoms were similar. Thus, a disorder model was assumed with a second molecule oriented perpendicular to the first, which allowed all atoms except C1 and C2 to practically remain at their original positions. This model could be refined using full-matrix least-squares with population parameters of 0.95 and 0.05 for trifluoroacrylonitrile and 0.85 and 0.15 for trifluorovinyl isocyanide, respectively. Because of the small site occupancy of the minor molecules, it was necessary to restrain the geometries of the disordered molecules to those of the major molecules and to use isotropic temperature factors for the minor molecules.

The assumption of this disorder model has strong effects not only on the R values but even more importantly on the geometry of the molecules and the thermal parameters of the atoms as illustrated in Figure 2 for trifluorovinyl isocyanide. Without taking into account the disorder problem, the thermal ellipsoids of the fluorine and nitrogen atoms are extended in the direction of the disordered molecule, whereas the thermal ellipsoid of the isocyanide carbon atom shows no change. The same is true for the fluorine atoms and cyanide carbon atom of trifluoroacrylonitrile, whereas the thermal ellipsoid of the nitrogen atom now shows virtually no change. The most strongly influenced geometric parameters are the F−C−F and F−C−N (F−C−C) bond angles and the length of the C−C double bond. The angles F1−C1−F2 and C3−C2−F3 (N1−C2−F3) are too large in the nondisorder model, whereas the C1−C2 distance refines to too short a distance in both isomers. The reason for the opening of the angles in the nondisorder model is evident from Figure 2.

Scheme 1



I II

In connection with the existing disorder problem, the estimated standard deviations given by the structure refinement program seem to be too small. It is evident that most of the experimental geometric parameters lie between the theoretical values obtained by the HF/6-31G* and the MP2/6-31G* calculation, with HF/6-31G* typically giving the shorter values for bond lengths. This is especially true for the CN and NC triple bonds, which are estimated by the MP2 method to be unrealistically long. On the other hand, the experimental values agree well with those of earlier structure determinations of isocyanides[19−23] and nitriles,[19,24−27] especially if one takes into account that the present low-temperature experiments have these distances about 0.015 Å longer and more accurate than room-temperature measurements (cf. ref 19). Nevertheless, both theoretical calculations reflect all the general trends observed in the experimental data. The carbon−fluorine bond lengths C1−F1 and C2−F2 are shorter than C2−F3 for both molecules. The bond length of the carbon−carbon double bond seems to be shorter for the isocyanide, but taking into account that the value of this bond length is influenced strongly by the disorder problem, it is questionable whether this difference is significant. In comparison, a C═C double bond length of 1.313(3) Å was found in the trifluorovinyl isocyanide complex $(CO)_5Cr(CN-CF{=}CF_2)$ by low-temperature X-ray crystallography.[4] In both the cyanide and the isocyanide, the F−C−F angle of 112.79(6)° in $F_2C{=}CF-CN$ and 112.5(2)° in $F_2C{=}CF-NC$ are well below 120°, which results in corresponding F−C−C bond angles of 123.3(2) to 124.2(2)°. The bond angles C1−C2−C3 [123.67(5)°] and C1−C2−N1 [123.7(2)°] are very similar for the nitrile and the isocyanide, respectively. The almost linear nitrile and isocyanide moieties with bond angles of 178.97(8)° and 179.6(3)°, respectively, are in excellent accord with the symmetry constraints placed on the ab initio calculations. As expected,[19] the C≡N triple bond is slightly shorter for the nitrile than for the isocyanide both experimentally and computationally, as explained by the contribution of resonance form II (Scheme 1) in the isocyanide.

As expected, the nitrile $F_2C{=}CF-CN$ is more stable than the isocyanide $F_2C{=}CF-NC$ by 114.0 kJ/mol (MP2/6-31G* level), whereas a transition state calculation at the same level of theory produced activation barriers corresponding to 268.1 and 154.1 kJ/mol for a unimolecular rearrangement starting from the nitrile and the isocyanide, respectively. This is in perfect agreement with the observation that trifluorovinyl isocyanide is perfectly stable in the gas phase at low pressure and that no isomerization to the nitrile takes place at ambient temperature. However, concentrated solutions and neat $F_2C{=}CF-NC$ tend to polymerize to a material with a structure thus far unknown.

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The charge distribution of the nitrile and the isocyanide can be considered by representing the molecule as $[C_2F_3]^{0.124+}[CN]^{0.124-}$ and $[C_2F_3]^{0.319+}[NC]^{0.319-}$, respectively, where the charges come from the sum of the atomic charges (MP2/6-31G* level) on the trifluorovinyl and $-C{\equiv}N$ or $-N{\equiv}C$ moieties. As demonstrated previously for other cyanide/isocyanide pairs,[44-46] the ionic character in trifluorovinyl isocyanide is more than double that in the respective cyanide (nitrile). Because the ionic character of the isocyanide moiety in trifluorovinyl isocyanide approaches that of a fluorine atom (atomic charges at the MP2/6-31G* level), the predicted dipole moment of 1.015 D for trifluorovinyl isocyanide is significantly less than that of 2.503 D for trifluoroacrylonitrile. The greatly reduced dipole moment of trifluorovinyl isocyanide versus that of its nonfluorinated counterpart $CH_2{=}CH\text{-}NC$ (3.56 D exptl,[47] 3.138 D calcd[46]) is in complete accord with its significantly lower boiling point (bp 11 vs. 77 °C, respectively) as has been previously pointed out for the fluorinated/nonfluorinated pair $CF_3{-}NC/CH_3{-}NC$.[11,12] Further details on these calculations as well as calculations of the entire series $C_2F_{(3-x)}H_x{-}CN$ and $C_2F_{(3-x)}H_x{-}NC$ will be the subject of another paper.[31]

The calculated normal-mode vibrational frequencies of trifluoroacrylonitrile and trifluorovinyl isocyanide are shown without scaling in Table 4 in comparison with the experimental vibrational frequencies.[4,48] Of the fifteen normal vibrational modes, eleven are a′ and four are a″ in symmetry as imposed by the C_S symmetry point group. The vibrational frequencies ν_1 and ν_2 can easily be assigned to the $\text{-}C{\equiv}N$ ($\text{-}N{\equiv}C$) and $C{=}C$ stretching modes, respectively. The computed spectrum of the isocyanide also indicates that the intensity of both bands should be strong in the infrared, as indicated by the calculated intensities shown in Table 4, and this prediction is confirmed experimentally.[4] On the other hand, ν_1 for the cyanide (nitrile) is predicted to be weak, whereas ν_2 is predicted to be strong, which again is borne out by the experimental spectrum. The frequencies were not scaled because different functional groups generally require different scaling factors.[49] This point is vividly displayed by the fact that a 97.7% scaling factor is required for the calculated isocyanide stretching frequency in $F_2C{=}CF{-}NC$ to match the experimental value, whereas a 101% scaling factor is required for the calculated cyanide stretching frequency in $F_2C{=}CF{-}CN$ to match its experimental value. Similar scaling factors have been found previously for the isocyanide and cyanide moieties both in the series of fluorinated methyl isocyanides and cyanides as well as with $SF_5{-}NC$ and $SF_5{-}CN$.[31]

Table 5. Geometrical Parameters (Å, deg) of Acrylonitrile[56,57] and Vinylisocyanide[57]

$H_2C{=}CH{-}CN$	MW, ED	HF/6-31G*	MP2/6-31G*
$C{=}C$	1.343(4)	1.320	1.341
$C{-}C$	1.438(3)	1.443	1.432
$C{\equiv}N$	1.167(4)	1.136	1.182
$C{-}H$	–	1.074	1.084−1.086
$C{-}C{-}N$	178.2(10)	179.2	179.2
$C{-}C{-}C$	121.7(5)	122.2	122.1
$H{-}C{-}H$	123(30)	117.3	117.5
$H_2C{=}CH{-}NC$	MW	HF/6-31G*	MP2/6-31G*
$C{=}C$	1.338(4)	1.316	1.336
$C{-}N$	1.379(6)	1.385	1.386
$N{\equiv}C$	1.174(6)	1.157	1.192
$C{-}H$	1.085 (fixed)	1.073−1.074	1.083−1.085
$C{-}N{-}C$	178.2(12)	177.7	177.7
$C{-}C{-}N$	122.5(7)	123.0	122.0
$H{-}C{-}H$	120 (fixed)	118.2	118.5

The usefulness of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of an isocyanide in estimating its σ-donor and π-acceptor properties has already been discussed in detail[50] and more specifically for $CF_3{-}NC$.[11] The remarkable correlation between these properties and the bending of the $C{-}N{\equiv}C$ angle of an isocyanide ligand in metal complexes has also been documented,[51,52] especially with respect to the organometallic chemistry of $CF_3{-}NC$.[11] Both the longer $Cr{-}C$(isocyanide) bond distance versus the $Cr{-}C$(carbonyl) bond distance as well as the 173.6(2)° $C{-}N{\equiv}C$ bond angle in $(CO)_5Cr(CN{-}CF{\equiv}CF_2)$ [cf. 142(4)° $C{-}N{\equiv}C$ bond angle in $(CO)_5Cr(CN{-}CF_3)^{52}$] clearly indicate a lower π-acceptor to σ-donor ratio for the trifluorovinyl isocyanide ligand than for the $CF_3{-}NC$ ligand.[11] According to molecular orbital (MO) theory, σ-donation should increase as the energy of the HOMO increases and π-acceptance should increase as the energy of the LUMO decreases. The energies of the HOMO and LUMO in $F_2C{=}CF{-}NC$ are −10.55 eV and 2.83 eV, respectively, at the MP2/6-31G* level versus the corresponding values for $CF_3{-}NC$ of −14.24 and 3.83, respectively.[29] This initially implies that the $F_2C{=}CF{-}NC$ should be both a better π-acceptor and a better σ-donor than $CF_3{-}NC$; however, one needs to examine the actual HOMO and LUMO coefficients and/or diagrams more closely. Further inspection of the HOMO and LUMO shows that the largest component of the HOMO is actually the olefinic π-bond, whereas the LUMO is predominately displaying conjugation between the two multiple bonds. In terms of ligand character, the σ-donor orbital of $F_2C{=}CF{-}NC$ is actually the second highest occupied MO (SHOMO) at −13.95 eV, and the π-acceptor orbital is the second lowest unoccupied MO (SLUMO) at 3.86 eV. This trend is consistent with the observation that a $(Ph_3P)_2Pt$ fragment can coordinate to the olefinic double bond in $(CO)_5Cr(CN{-}CF{=}CF_2)$.[53] Furthermore, a similar trend has been observed both experimentally and computationally for $HC{\equiv}C{-}NC$[54] as well as computationally for $FSO_2{-}NC$ and $CF_3SO_2{-}NC$.[55] Therefore, it becomes clear that one must use extreme caution when trying to ascertain the ligand properties of an isocyanide ligand from HOMO/LUMO energies, especially when the isocyanide moiety has the opportunity to be conjugated with its R group.

A comparison of the geometrical parameters of trifluoroacrylonitrile and trifluorovinyl isocyanide with the structural

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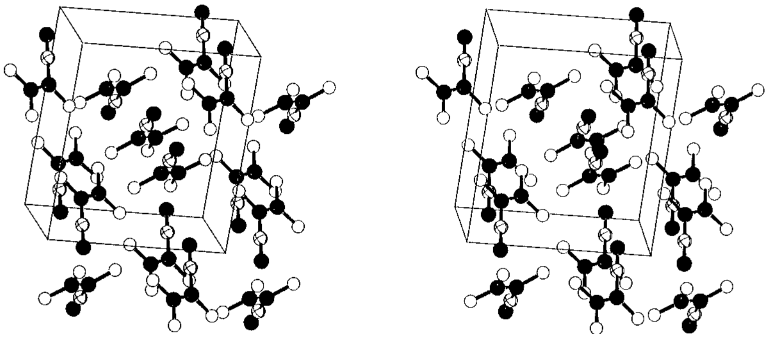

Figure 4. SCHAKAL[60] diagram of the packing in the lattice of the major molecules of $F_2C{=}CF{-}NC$ from the disorder model.

parameters of acrylonitrile[56,57] and vinyl isocyanide[57] (see Table 5) demonstrates that the C═C double bond length and the H─C─H and F─C─F bond angles are influenced the most by fluorine substitution. In both fluorinated compounds, the C═C double bond is significantly shorter than in the hydrogen-substituted analogues. Although the H─C─H bond angle in both $H_2C{=}CH{-}CN$ and $H_2C{=}CH{-}NC$ was approximately 120°, the F─C─F bond angle was determined to be 112.79(6) and 112.5(2)° for $F_2C{=}CF{-}CN$ and $F_2C{=}CF{-}NC$, respectively. Other analogous bonds were found to be slightly shorter for the fluorinated compound; however, this effect can well be caused by libration effects in the solid-state structure. Similar discrepancies in the geometrical parameters that resulted from the ab initio calculations, depending on the level of theory, were observed for both vinyl isocyanide[57] and trifluorovinyl isocyanide. Recently, calculations on acrylonitrile (vinylcyanide) with polarization functions on the hydrogen atoms as well (MP2/6-31G** geometry optimization) have appeared[58]; however, the geometric parameters are virtually unchanged from those shown in Table 5 at the MP2/6-31G* level.

Figure 4 shows the packing of the trifluorovinyl isocyanide molecules in the crystal lattice. The packing can be described as follows: the molecules are oriented in rows along the $a-c$ direction in a head-to-tail fashion, where adjacent molecules are generated by the n glide plane, having their molecular planes perpendicular to each other. For the $F_2C{=}CF{-}NC$ molecules within a row, intermolecular fluorine contact distances of 3.02 Å (F3─F1) and 3.05 Å (F2─F3) are observed. An additional fluorine−fluorine contact distance of 3.06 Å (F1─F3) arises from the glide plane related molecule translated in the c direction and belonging to the neighboring row. The rows neighboring in b direction are related by a 2_1 screw axis and run in opposite direction. The shortest, nonbonded contact distances between these rows are found for F1─F2, 3.10 Å; C3─C1, 3.30 Å; and C3─C2, 3.33 Å. The latter contact distances represent an interaction of the isocyano (nitrile group for N1─C1 and N1─C2 contacts) with the π-system of the carbon−carbon double bond. As $F_2C{=}CF{-}NC$ and $F_2C{=}CF{-}CN$ crystallize isomorphically, a similar packing with only minor differences in contact distances was found for both compounds (see Table 6).

Table 6. Short Intermolecular Distances (Å)

	$F_2C{=}CF{-}CN$		$F_2C{=}CF{-}NC$
F1−F3	2.933(1)		3.023(3)
F2−F3	3.112(2)		3.046(4)
F1−F3	3.022(1)		3.063(3)
F1−F2	3.008(1)		3.102(3)
F1−F1	3.176(1)		3.215(3)
N1−C1	3.167(1)	C3−C1	3.300(4)
N1−C2	3.245(1)	C3−C2	3.331(5)
N1−C1	3.257(1)	C3−C1	3.415(4)

Conclusions

The crystal and molecular structures of trifluoroacrylonitrile, $F_2C{=}CF{-}CN$, and trifluorovinyl isocyanide, $F_2C{=}CF{-}NC$, has been solved by low-temperature X-ray crystallography, thereby adding to the limited number of solid-state structures that are known for fluorinated olefins. During the solution of these structures, it became necessary to use a disorder model to obtain both acceptable refinements as well as bond distances and angles. Ab initio calculations not only concurred with the need for the use of the disorder model in the structure solutions, but also afforded a better understanding of the bonding and spectroscopic properties in this cyanide/isocyanide pair, especially in terms of drawing caution to ascertaining the ligating properties of an isocyanide ligand solely from HOMO/LUMO energies.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The Alabama Supercomputer Network is gratefully acknowledged for computer time as well as The University of Alabama for use of their mainframe computer; Dr. Jeff Erickson and Dr. Bill Hunter are acknowledged for technical assistance in maintaining the GAUSSIAN programs.

Supporting Information Available: X-ray coordinates and anisotropic thermal parameters as well as calculated atomic charges/dipole moments for $F_2C{=}CF{-}CN$ and $F_2C{=}CF{-}NC$, the transition state structure for the unimolecular rearrangement of $F_2C{=}CF{-}NC$ to $F_2C{=}CF{-}CN$, and the atomic charges/dipole moment for that transition state structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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