# Low-temperature crystallization and structure determination of *N*-(trifluoromethyl)formamide, *N*-(2,2,2-trifluoroethyl)formamide and 2,2,2-trifluoroethyl isocyanide

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## Abstract

Crystals of *N*-(trifluoromethyl)formamide, $C_2H_2F_3NO$, (I), *N*-(2,2,2-trifluoroethyl)formamide, $C_3H_4F_3NO$, (II), and 2,2,2-trifluoroethyl isocyanide, $C_3H_2F_3N$, (III), were grown *in situ* on an X-ray diffractometer and analysed by single-crystal X-ray diffraction methods at low temperatures. Crystal data: (I) orthorhombic, $P2_12_12_1$, $a = 4.547$ (2) Å, $b = 5.947$ (3) Å, $c = 14.731$ (9) Å, $V = 398.3$ (4) Å$^3$, $Z = 4$, $M_r = 113.05$, $T = 143$ K, $D_x = 1.885$ Mg m$^{-3}$; (II) monoclinic, $P2_1/n$, $a = 4.807$ (1) Å, $b = 16.707$ (3) Å, $c = 6.708$ (1) Å, $\beta = 109.90$ (1)°, $V = 506.6$ (2) Å$^3$, $Z = 4$, $M_r = 127.07$, $T = 141$ K, $D_x = 1.666$ Mg m$^{-3}$; (III) orthorhombic, $P2_12_12_1$, $a = 5.668$ (2) Å, $b = 9.266$ (3) Å, $c = 8.626$ (2) Å, $V = 453.0$ (2) Å$^3$, $Z = 4$, $M_r = 109.06$, $T = 163$ K, $D_x = 1.599$ Mg m$^{-3}$. The results showed that in the crystal both formamides (I) and (II) are exclusively present in the form of the *Z* isomer, although measurements of solutions of (I) have shown that the *E* isomer prevails [Lentz *et al.* (1987). *Angew. Chem.* **99**, 951–953]. In addition *ab initio* calculations for (I) predicted the *E* isomer to be the more stable one. In compound (III) the isocyanide group is staggered with respect to the trifluoroethyl group. In the crystal packing of (I) and (II) intermolecular N—H···O hydrogen bonds generate infinite chains. In (I), these chains are linked to form sheets by C—H···O contacts. In the crystal structure of (III) each isocyanide dipole is surrounded by four electronegative F atoms with intermolecular C···F contacts between 3.4 and 3.5 Å.

## 1. Introduction

The crystal structure of formamide was first determined by film methods (Ladell & Post, 1954) four decades ago. Higher accuracy was provided by low-temperature X-ray experiments (Ottersen, 1975; Stevens, 1978), which also reported the experimental and theoretical charge-density distribution of formamide. In addition a complex between formic acid and formamide was studied by X-ray crystallography (Nahringbauer & Larsson, 1969). In two further studies formamide is present in the crystal as a solvate (Betz & Bino, 1988; Khorami *et al.*, 1980).

Moreover, in the literature there is a wide variety of organic molecules which provide experimental data for interesting features of the terminal formamide group, such as its planarity, the relative lengths of the C—N and C=O bonds, the conformational isomers, and the formation of hydrogen bonds. Of the 45 crystal structures of molecules containing an *N*-monosubstituted formamide fragment in the Cambridge Structural Database (Allen & Kennard, 1993), 39 possess an almost planar formamide moiety in a *Z* orientation with O—C—N—C torsion angles close to 0°. Five of the remaining molecules are present as the *E* isomer with O—C—N—C torsion angles around 180°. One case (Adams, 1979), in which the *N*-methylformamide molecule is present as a solvate, exhibits an O—C—N—C torsion angle of 72° and a non-planar formamide moiety. The *E* isomer, however, is the thermodynamically more stable isomer of *N*-(trifluoromethyl)formamide in both the neat liquid and in solutions in non-polar solvents according to NMR spectroscopy studies (Lentz *et al.*, 1987), whereas for *N*-methylformamide the *Z* isomer prevails. This finding is in agreement with recent *ab initio* calculations (Madappat *et al.*, 1993).

In order to establish whether the *E* or *Z* isomer of *N*-(trifluoromethyl)formamide, (I), is present in the solid state we grew crystals of $CF_3$—NH—CHO *in situ* and executed an X-ray structure analysis. The influence of $\beta$ fluorine substitution *versus* $\alpha$ substitution in the structure of $F_3C$—$CH_2$—NH—CHO, (II), was also analysed. For comparison, a crystal structure analysis of $F_3C$—$CH_2$—NC, (III), was performed and the structure was compared with those of simple isocyanides.

## 2. Experimental

### 2.1. *Synthesis and crystallization*

(I) (Lentz *et al.*, 1987), (II) and (III) (Sergeev & Englin, 1971) were prepared according to literature methods. The purity of the compounds was checked by $^1H$ and $^{19}F$ NMR spectroscopy.

Table 1. *Experimental details*

|  | (I) | (II) | (III) |
|---|---|---|---|
| **Crystal data** | | | |
| Chemical formula | $C_2H_2F_3NO$ | $C_3H_4F_3NO$ | $C_3H_2F_3N$ |
| Chemical formula weight | 113.05 | 127.07 | 109.06 |
| Cell setting | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_1/n$ | $P2_12_12_1$ |
| $a$ (Å) | 4.547 (2) | 4.807 (1) | 5.668 (2) |
| $b$ (Å) | 5.947 (3) | 16.707 (3) | 9.266 (3) |
| $c$ (Å) | 14.731 (9) | 6.708 (1) | 8.626 (2) |
| $\beta$ (°) | | 109.90 (1) | |
| $V$ (Å$^3$) | 398.3 (4) | 506.6 (2) | 453.0 (2) |
| $Z$ | 4 | 4 | 4 |
| $D_x$ (Mg m$^{-3}$) | 1.885 | 1.666 | 1.599 |
| $F(000)$ | 224 | 256 | 216 |
| Temperature of crystallization (K) | 250 | 266 | 169 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| Wavelength (Å) | 0.71068 | 0.71068 | 0.71068 |
| $\mu$ (mm$^{-1}$) | 0.232 | 0.192 | 0.185 |
| Temperature of measurement (K) | 143 (1) | 141 (1) | 163 (1) |
| Crystal form | | Cylinder, diameter 0.5 mm | |
| | | | |
| **Data collection** | | | |
| Diffractometer | | Siemens four-circle with $N_2$ gas stream cooling device | |
| No. of orientation reflections | 58 | 37 | 76 |
| $2\theta$ range (°) | 20–35 | 20–46 | 20–44 |
| Data collection method | $\omega/2\theta$ scans | $\omega/2\theta$ scans | $\omega/2\theta$ scans |
| Scan width $\Delta\omega$ (°) | $1.78 + 0.4\tan(2\theta)$ | $1.70 + 0.4\tan(2\theta)$ | $1.58 + 0.4\tan(2\theta)$ |
| Time per step (s) to reach $I/\sigma(I) > 50$ | 0.5–2.0 | 0.5–2.0 | 0.5–2.0 |
| Absorption correction | None | None | None |
| No. of measured reflections | 2446 | 2983 | 1856 |
| No. of independent reflections | 1170 | 1484 | 1556 |
| No. of observed reflections | 779 | 1018 | 1092 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| No. of reflections with $F_o < 4\sigma(F_o)$ | 391 | 466 | 464 |
| $R_{int}$ | 0.0498 | 0.0308 | 0.0220 |
| $\theta_{max}$ (°) | 30.02 | 30.08 | 34.98 |
| Range of $h, k, l$ | $0 \rightarrow h \rightarrow 6$ | $-6 \rightarrow h \rightarrow 4$ | $-4 \rightarrow h \rightarrow 9$ |
| | $-8 \rightarrow k \rightarrow 8$ | $-23 \rightarrow k \rightarrow 19$ | $-14 \rightarrow k \rightarrow 14$ |
| | $-20 \rightarrow l \rightarrow 20$ | $-9 \rightarrow l \rightarrow 9$ | $-11 \rightarrow l \rightarrow 13$ |
| No. of standard reflections | 4 | 3 | 4 |
| Frequency of standard reflections | Every 90 min | Every 90 min | Every 90 min |
| Intensity decay (%) | 4 | 4 | 58 |
| | | | |
| **Refinement** | | | |
| Refinement on | $F^2$ | $F^2$ | $F^2$ |
| Function minimized | | $\sum w(F_o^2 - F_c^2)^2$ | |
| $R[F^2>2\sigma(F^2)]$ | 0.0696 | 0.0508 | 0.0329 |
| $wR(F^2)$† | 0.1708 | 0.1619 | 0.0839 |
| $S$‡ | 1.105 | 1.085 | 1.044 |
| No. of reflections used in refinement | 1170 | 1484 | 1556 |
| No. of parameters used | 70 | 89 | 72 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.5432P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.5432P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.5432P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{max}$ | 0.086 | 0.043 | 0.006 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.403 | 0.295 | 0.219 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | $-0.389$ | $-0.292$ | $-0.143$ |
| Extinction method | None | None | None |
| Source of atomic scattering factors | | *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4) | |

Table 1 (cont.)

| | (I) | (II) | (III) |
|---|---|---|---|
| Computer programs | | | |
| Data collection | Siemens software | Siemens software | Siemens software |
| Cell refinement | Siemens software | Siemens software | Siemens software |
| Data reduction | In-house program | In-house program | In-house program |
| Structure solution | *SHELXS*86 (Sheldrick, 1985) | *SHELXS*86 (Sheldrick, 1985) | *SHELXS*86 (Sheldrick, 1985) |
| Structure refinement | *SHELXL*97 (Sheldrick, 1997) | *SHELXL*93 (Sheldrick, 1993) | *SHELXL*93 (Sheldrick, 1993) |

† $wR(F^2) = \left[ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$    ‡ $S = \left[ \sum w(F_o^2 - F_c^2)^2 / (n - p) \right]^{1/2}$ where $n$ is the number of reflections and $p$ is the number of parameters.

Since all three compounds are liquid at room temperature, *in situ* crystallization directly on the diffractometer was required for single-crystal X-ray analysis. This was carried out following a procedure described by Luger & Buschmann (1984). A thin-walled, closed glass capillary containing a column of sample fluid 3–4 mm long at the tip was cooled in the nitrogen gas stream of a low-temperature device yielding poly-crystalline material far below the melting point. Single-crystal growth was then achieved by partial melting (∼85%) of the polycrystalline material in the direction against the gas stream with a heating coil at a temperature just below the melting point and by subsequent very slow, electronically controlled reduc-tion of the heat output from the coil. This process was repeated several times for each compound. However, the inspection of oscillation photographs and reflection searches indicated that this never resulted in only one single crystal. In the most favourable attempts only a few crystals were grown. For each of the three compounds it was possible to identify a small number of reflections from one single crystal by careful inspection of the reflection distribution in reciprocal space on a graphic screen. These were then used to identify the unit cell and in a further step to centre a sufficient number of high-order reflections from this crystal to obtain an accurate orientation matrix and lattice constants. Intensity-data collection followed routinely.

### 2.2. Data collection, structure determination and refine-ment

The experimental conditions, details of the data collection and results of the structure refinements for the three compounds are summarized in Table 1. A correction for the systematic decay in the intensities of the standard reflections for (III) was applied. Lorentz and polarization corrections were also applied to the data. H atoms were located from difference Fourier syntheses after anisotropic atomic displacement para-meters were refined for non-H atoms. Their positions and isotropic displacement parameters were included in the following cycles of structure refinement. In (I), the H-atom displacement parameters were fixed at 1.2 times the equivalent isotropic displacement parameter of the heavy atom to which they are attached.

### 3. Results and discussion

The crystal growth directions for (I) and (III) in the glass capillary coincide approximately with the reciprocal lattice vectors (100) and (101), respectively. No trivial combination of Miller indices could be assigned to the growth direction for (II).

The small decrease observed in the intensities of the standard reflections for crystals (I) and (II) attests to the relative stability of these compounds under the experi-
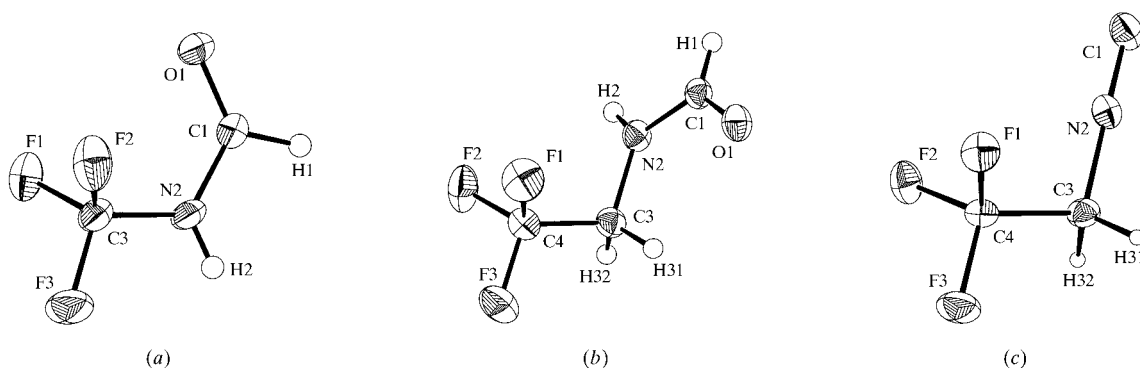


Fig. 1. *ORTEP*II (Johnson, 1976) views of the title compounds with the atomic numbering schemes. Displacement ellipsoids are scaled to include 50% probability for (*a*) (I) and (*b*) (II), and 40% for (*c*) (III). H atoms are illustrated as spheres of arbitrary size.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| (I) | | | | |
| O1 | 1.0942 (7) | 0.5366 (6) | 0.4321 (3) | 0.029 (1) |
| C1 | 0.8260 (9) | 0.5368 (8) | 0.4309 (3) | 0.025 (1) |
| H1 | 0.70 (2) | 0.66 (1) | 0.46 (1) | 0.030 |
| N2 | 0.6592 (8) | 0.3786 (6) | 0.3883 (3) | 0.026 (1) |
| H2 | 0.49 (2) | 0.38 (1) | 0.38 (1) | 0.031 |
| C3 | 0.7820 (9) | 0.1974 (7) | 0.3408 (3) | 0.026 (1) |
| F1 | 0.9606 (7) | 0.0725 (4) | 0.3916 (2) | 0.034 (1) |
| F2 | 0.9435 (9) | 0.2611 (5) | 0.2699 (2) | 0.040 (1) |
| F3 | 0.5689 (7) | 0.0657 (6) | 0.3109 (3) | 0.060 (1) |
| | | | | |
| (II) | | | | |
| O1 | 1.0908 (3) | 0.2117 (1) | 0.3539 (2) | 0.027 (1) |
| C1 | 0.9939 (4) | 0.2445 (1) | 0.4805 (3) | 0.021 (1) |
| H1 | 1.016 (6) | 0.298 (2) | 0.509 (4) | 0.027 (6) |
| N2 | 0.8317 (3) | 0.2082 (1) | 0.5793 (2) | 0.022 (1) |
| H2 | 0.766 (5) | 0.235 (1) | 0.666 (4) | 0.013 (5) |
| C3 | 0.7452 (4) | 0.1256 (1) | 0.5396 (2) | 0.023 (1) |
| H31 | 0.780 (7) | 0.108 (2) | 0.411 (5) | 0.034 (7) |
| H32 | 0.550 (7) | 0.121 (2) | 0.524 (5) | 0.041 (8) |
| C4 | 0.9133 (4) | 0.0737 (1) | 0.7229 (3) | 0.026 (1) |
| F1 | 1.2041 (3) | 0.0744 (1) | 0.7593 (2) | 0.040 (1) |
| F2 | 0.8787 (4) | 0.0967 (1) | 0.9037 (2) | 0.041 (1) |
| F3 | 0.8245 (4) | −0.0020 (1) | 0.6893 (3) | 0.042 (1) |
| | | | | |
| (III) | | | | |
| C1 | −0.0245 (3) | 0.2436 (2) | −0.1439 (2) | 0.054 (1) |
| N2 | 0.0359 (2) | 0.1328 (1) | −0.1005 (1) | 0.042 (1) |
| C3 | 0.1126 (3) | −0.0044 (1) | −0.0460 (2) | 0.042 (1) |
| H31 | 0.276 (4) | 0.000 (2) | −0.0088 (2) | 0.051 (5) |
| H32 | 0.103 (4) | −0.074 (2) | −0.127 (2) | 0.057 (5) |
| C4 | −0.0476 (3) | −0.0568 (2) | 0.0807 (1) | 0.039 (1) |
| F1 | −0.0465 (2) | 0.0293 (1) | 0.2027 (1) | 0.056 (1) |
| F2 | −0.2697 (2) | −0.0675 (1) | 0.0346 (1) | 0.058 (1) |
| F3 | 0.0198 (3) | −0.1866 (1) | 0.1278 (1) | 0.073 (1) |

mental conditions. However, the crystal of (III) was strongly affected by X-ray damage, resulting in a decay of 58% of the reflection intensities during a few days of measurement. The atomic numbering schemes and the molecular structures of the three compounds are shown in Fig. 1. Fractional atomic coordinates are given in Table 2. Bond lengths, angles and torsion angles are listed in Table 3.†

### 3.1. N-(Trifluoromethyl)formamide, (I)

The molecular structure as present in the crystal is displayed in Fig. 1(*a*). All atoms except for F1 and F2 lie in a common plane with an average deviation of 0.021 Å from the least-squares plane.

Experimental and theoretical studies have investigated the rotational isomerism about $sp^2$–$sp^3$ bonds in small molecules (Karabatsos & Fenoglio, 1970). For

acetaldehyde and acetamide molecules there are only two different conformations: eclipsed or staggered. For methylformamide and (trifluoromethyl)formamide, Z or E conformations are possible, with the methyl group *cis* or *trans* to the carbonyl O atom; for each, the methyl group may be eclipsed or staggered with respect to the C—N bond.

As Fig. 1(*a*) shows, the molecule adopts the Z conformation and the trifluoromethyl group is in an almost staggered orientation with respect to the formamide C—N bond (see also Fig. 2). There is a small torsion of the $CF_3$ group around the C—N bond by approximately 3°, as can be seen from the F—C—N—C torsion angles. The C═O and C—N bond lengths in the formamide group are 1.219 (5) and 1.366 (6) Å, and these values are in the range observed in other form-amide-containing compounds investigated by X-ray diffraction methods (Coetzer *et al.*, 1972; Eggleston, 1990; Ohki *et al.*, 1975; Vrabel *et al.*, 1985; Boeyens *et al.*, 1977; Hall & Brown, 1971; Morffew & Tickle, 1981; Chen & Parthasarathy, 1977; Valle *et al.*, 1992; Grunewald *et al.*, 1991), where the C═O distances range from 1.191 (6) to 1.242 (6) Å and the C—N distances range from 1.314 (6) to 1.350 (10) Å. Moreover, in all these structures, if the N atom is linked to a terminal $Csp^3$ atom the conformation is Z. In these cases the observed N2—C3 bond lengths range from 1.432 (9) to 1.469 (9) Å, compared to 1.402 (5) Å in (I). The noticeable shortening of about 0.04 Å is related to the presence of the electronegative F atoms. A rather normal value of 1.440 (2) Å is found for (II). Comparison of our experimental data with *ab initio* calculations (Madappat *et al.*, 1993) (see Table 3) shows that the
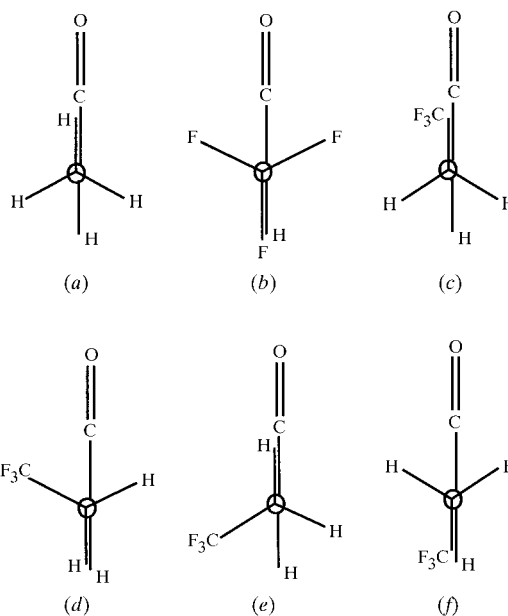
Fig. 2. Newman projections down the C—N axis for (*a*) methylform-amide, (*b*) (I) and (*c*–*f*) (II).

Table 3. *Bond lengths (Å), angles and torsion angles (°)*

Theoretical calculations are at the *ab initio* level HF/6-31G(*d,p*). In the calculations for (I), performed by Madappat *et al.* (1993), the molecular geometry was constrained to C$_s$ symmetry.

| (I) | X-ray | Theory | (II) | X-ray | Theory | (III) | X-ray | Theory |
|---|---|---|---|---|---|---|---|---|
| O1—C1 | 1.219 (5) | 1.185 | O1—C1 | 1.228 (2) | 1.192 | C1—N2 | 1.145 (2) | 1.155 |
| C1—N2 | 1.366 (6) | 1.370 | C1—N2 | 1.329 (2) | 1.355 | N2—C3 | 1.424 (2) | 1.413 |
| C1—H1 | 1.01 (6) | 1.090 | C1—H1 | 0.90 (3) | 1.091 | C3—C4 | 1.502 (2) | 1.514 |
| N2—C3 | 1.402 (5) | 1.406 | N2—C3 | 1.440 (2) | 1.436 | C3—H31 | 0.98 (2) | 1.081 |
| N2—H2 | 0.96 (7) | 0.994 | N2—H2 | 0.87 (2) | 0.994 | C3—H32 | 0.96 (2) | 1.081 |
| C3—F1 | 1.332 (5) | 1.314 | C3—C4 | 1.498 (3) | 1.510 | C4—F1 | 1.321 (2) | 1.316 |
| C3—F2 | 1.330 (5) | 1.314 | C3—H31 | 0.98 (3) | 1.079 | C4—F2 | 1.324 (2) | 1.316 |
| C3—F3 | 1.320 (5) | 1.317 | C3—H32 | 0.91 (3) | 1.084 | C4—F3 | 1.326 (2) | 1.322 |
| | | | C4—F3 | 1.329 (2) | 1.322 | | | |
| | | | C4—F1 | 1.334 (2) | 1.318 | | | |
| | | | C4—F2 | 1.335 (2) | 1.328 | | | |
| O1—C1—N2 | 124.0 (5) | 124.9 | O1—C1—N2 | 124.5 (2) | 125.04 | C1—N2—C3 | 179.5 (2) | 179.82 |
| O1—C1—H1 | 124 (4) | | O1—C1—H1 | 123 (2) | 122.56 | N2—C3—C4 | 110.1 (1) | 111.30 |
| N2—C1—H1 | 112 (4) | 111.7 | N2—C1—H1 | 113 (2) | 112.40 | N2—C3—H31 | 111 (1) | 109.93 |
| C1—N2—C3 | 122.6 (4) | 123.7 | C1—N2—C3 | 121.7 (2) | 122.45 | N2—C3—H32 | 110 (1) | 109.94 |
| C1—N2—H2 | 125 (3) | | C1—N2—H2 | 120 (2) | 118.54 | C4—C3—H31 | 110 (1) | 108.22 |
| C3—N2—H2 | 112 (3) | 116.3 | C3—N2—H2 | 118 (2) | 118.86 | C4—C3—H32 | 107 (1) | 108.23 |
| F1—C3—N2 | 113.0 (4) | 112.3 | N2—C3—C4 | 111 (2) | 111.58 | H31—C3—H32 | 109 (2) | 109.16 |
| F2—C3—N2 | 113.2 (4) | 112.3 | N2—C3—H31 | 110 (2) | 108.69 | F1—C4—C3 | 112.5 (1) | 111.83 |
| F3—C3—N2 | 109.2 (4) | 108.2 | N2—C3—H32 | 109 (2) | 111.19 | F2—C4—C3 | 112.4 (1) | 111.83 |
| F2—C3—F3 | 108.2 (4) | | C4—C3—H31 | 109 (2) | 108.69 | F3—C4—C3 | 110.0 (1) | 108.77 |
| F1—C3—F3 | 107.7 (4) | | C4—C3—H32 | 107 (2) | 107.55 | F2—C4—F3 | 107.3 (1) | 108.07 |
| F1—C3—F2 | 105.3 (4) | | H31—C3—H32 | 110 (3) | 109.08 | F1—C4—F3 | 107.6 (1) | 108.09 |
| | | | F1—C4—C3 | 112.6 (2) | 112.40 | F1—C4—F2 | 106.8 (1) | 108.12 |
| | | | F2—C4—C3 | 112.3 (2) | 110.95 | | | |
| | | | F3—C4—C3 | 111.0 (2) | 110.42 | | | |
| | | | F3—C4—F2 | 107.2 (2) | 107.53 | | | |
| | | | F3—C4—F1 | 107.2 (2) | 108.02 | | | |
| | | | F1—C4—F2 | 106.1 (2) | 107.33 | | | |
| O1—C1—N2—C3 | 0.3 (8) | 0 | O1—C1—N2—C3 | −2.2 (3) | 3.00 | N2—C3—C4—F1 | −62.1 (2) | −60.73 |
| C1—N2—C3—F1 | 56.6 (6) | 60 | N2—C3—C4—F1 | −62.3 (2) | −61.50 | N2—C3—C4—F2 | 58.5 (2) | 60.69 |
| C1—N2—C3—F2 | −62.9 (6) | −60 | N2—C3—C4—F2 | 57.4 (2) | 58.68 | N2—C3—C4—F3 | 178.0 (1) | 179.97 |
| C1—N2—C3—F3 | 176.5 (5) | 60 | N2—C3—C4—F3 | 177.5 (2) | 177.80 | | | |
| | | | C1—N2—C3—C4 | 107.5 (2) | 109.02 | | | |

differences are at most 0.02 Å for bond lengths and 1.3° for the C—N—C angle. It is interesting to note that the F3—C3—N2 bond angle is 4° smaller than the other two F—C—N angles in both the experimental and theoretical investigations. This is probably caused by an attraction between F3 and H2 or a steric repulsion between the carbonyl C═O group and the F atoms F1 and F2.

The conformational preferences and rotational barriers of many molecules in which a methyl group is attached to an unsaturated fragment have been studied by *ab initio* calculations (Pross *et al.*, 1980; Hehre *et al.*, 1976; Radom & Riggs, 1982) and by experimental methods such as microwave (Butcher & Wilson, 1964; Pickett & Scroggin, 1974) and NMR spectroscopy (Abraham & Pople, 1960). For example, in the acetaldehyde and acetamide molecules, the eclipsed conformation is preferred. However, the internal rotation barrier of the methyl group in acetamide, 2.2 kJ mol$^{-1}$, is only half of that found for acetaldehyde (Pross *et al.*, 1980; Hehre *et al.*, 1976). In methylformamide, which prefers the eclipsed *Z* conformation (see

Fig. 2), the energy difference between the staggered and the eclipsed methyl-group arrangement is only 0.50 kJ mol$^{-1}$ according to *ab initio* calculations at the Hartree–Fock 4-31G level (Radom & Riggs, 1982). An electrostatic attraction between a methyl H atom and the negatively charged O atom is thought to stabilize this conformation. An interaction of this type is not possible in the trifluoro derivative. In its staggered conformation, the repulsion between the negatively charged F atom and the carbonyl O atom is minimized, leading to an energy difference between the staggered and eclipsed *Z* conformations of 14.05 kJ mol$^{-1}$, obtained from a calculation with the same basis set as above (Madappat *et al.*, 1993).

The molecular arrangement in the crystal is displayed in Fig. 3. Molecules translated by one unit cell along the *a* direction are held together by N—H···O hydrogen bonds, forming an infinite chain parallel to **a**. A neighbouring chain generated by the twofold screw axis in the *a* direction is close enough to permit C—H···O interactions between the chains with a C···O distance of 3.41 (1) Å, which is slightly larger than the C···O van

der Waals distance (3.2 Å). In this way a sheet-like bilayer arrangement is generated with a head-to-head arrangement of the amide groups and the $CF_3$ groups on the outside of the sheet (Fig. 3$a$). These infinite sheets form a herringbone pattern in the crystal which can be visualized best when plotted onto the $bc$ plane (Fig. 3$b$). The shortest sheet-to-sheet distances are intermolecular F$\cdots$F contacts of 3.047 (6) Å.

### 3.2. N-(Trifluoroethyl)formamide, (II)

Fig. 1($b$) shows that the molecule of (II) also has a $Z$ conformation in the crystal. With respect to the form-amide plane, an eclipsed conformation is present with a $cis$ arrangement of H31 with C1 and a $gauche$ position of C4 relative to H2. As the Newman projection (Fig. 2) and torsion angles show, there is a slight deviation of $\sim 14°$ from an ideal eclipsed conformation. A similar deviation ($\sim 11°$) was observed for propionaldehyde (Karabatsos & Fenoglio, 1970; Butcher & Wilson, 1964; Pickett & Scroggin, 1974; Abraham & Pople, 1960). The electrostatic attraction between H31 and O1 mentioned above for methylformamide can take place here and may stabilize the present conformation. Theoretical studies of alternative conformations around the C3—N2 bond are discussed in §4. For the $Csp^3$—$Csp^3$ bond C4—C3 the expected staggered conformation is present.

The N—H$\cdots$O(amide) hydrogen bond found in (I) is also present in the crystal of (II) (Fig. 4). However, in (II) the interaction occurs $via$ the $n$-glide plane, so that an infinite chain in the diagonal direction of the $ac$ plane is generated where adjacent molecules have antiparallel orientations [they are oriented parallel in (I)]. The C—H$\cdots$O contact seen in (I) is missing in (II). Fig. 4 shows that there is a small layer ($\sim 1.7$ Å width) around $y = \frac{1}{4}, \frac{3}{4}, \ldots$ where the formamide groups are concentrated with the trifluoromethyl groups on alternating sides of this layer. Thus the broad region between $y = \frac{1}{4}$

and $y = \frac{3}{4}$ is occupied by head-to-head positioned $CF_3$—$CH_2$ groups with closest intermolecular F$\cdots$F contacts of 3.055 (2) Å.

### 3.3. 2,2,2-Trifluoroethyl isocyanide, (III)

The molecular structure of (III) in the crystal is shown in Fig. 1($c$). The molecule has a staggered conformation between the $CF_3$ and the $CH_2(NC)$ fragment (the torsion angle N2—C3—C4—F3 is 178.0 (1)°; see Table 3). The N$\equiv$C bond length is 1.145 (2) Å and the C—N$\equiv$C bond angle is 179.5 (2)°, which indicate the triple-bond character of the N$\equiv$C bond and the linear conformation of the isocyanide group. The same conformation of the isocyanide group is observed in a series of organic compounds (Blasio $et$ $al.$, 1976; Baker $et$ $al.$, 1976; Hagadone $et$ $al.$, 1979; Hahn & Tamm, 1991; Lane $et$ $al.$, 1994; Das & Mazumdar, 1995; Buschmann $et$ $al.$, 1995; Britton $et$ $al.$, 1981; Dyrbusch & Egert, 1992) investigated by X-ray diffraction methods, where the N$\equiv$C bond lengths range from 1.14 to 1.16 Å. It should be pointed out that these values are smaller than those obtained by other experimental techniques, $e.g.$ 1.171 (3) Å (Christen $et$ $al.$, 1984) in $CF_3NC$ and 1.166 (1) Å (Halonen & Mills, 1978) in $CH_3NC$, both in the gas phase. Computationally, the N$\equiv$C bond lengths range from 1.153 to 1.158 Å in the compounds $CF_3NC$, $CHF_2NC$, $CH_2FNC$ and $CH_3NC$ at the HF/6-31G** level (Lentz, 1994).

The C—$N_{iso}$ single-bond length is 1.424 (2) Å, which compares well with other $Csp^3$—$N_{iso}$ bond lengths (Blasio $et$ $al.$, 1976; Baker $et$ $al.$, 1976; Hagadone $et$ $al.$, 1979; Hahn & Tamm, 1991; Lane $et$ $al.$, 1994; Das & Mazumdar, 1995; Buschmann $et$ $al.$, 1995), which lie between 1.41 and 1.46 Å, and are, as expected, longer than those observed for $Csp^2$—$N_{iso}$ bonds of about 1.39 (1) Å (Lane $et$ $al.$, 1994; Britton $et$ $al.$, 1981; Dyrbusch & Egert, 1992).
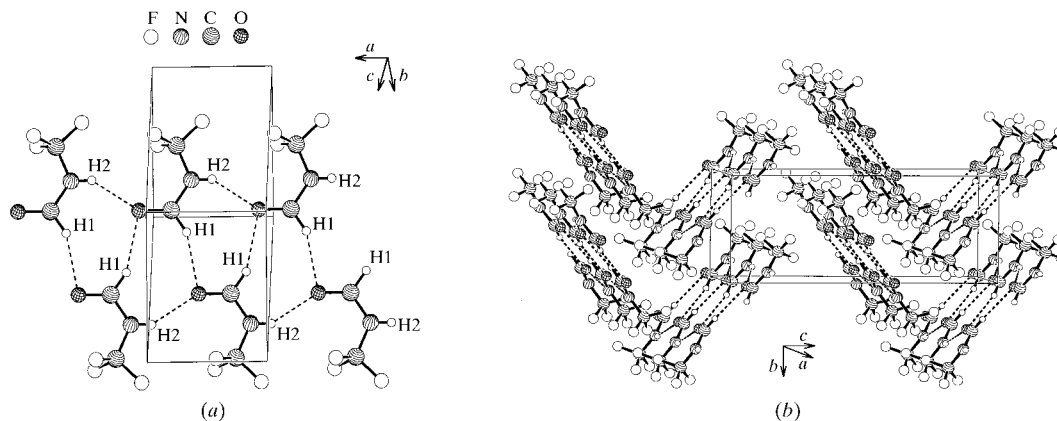


Fig. 3. ($a$) An illustration of the bilayer sheets in the crystal structure of (I). Only molecules related by the translations and $2_1$ screw axis along the $a$ axis are drawn. The hydrogen bonds forming the sheet-like arrangement are N—H$\cdots$O′, H$\cdots$O′ 2.13 (8), N$\cdots$O′ 2.81 (1) Å, N—H$\cdots$O′ 144 (6)° (symmetry operation for the primed atom: $-1 + x, y, z$); C—H$\cdots$O″, H$\cdots$O″ 2.47 (6), C$\cdots$O″ 3.41 (1) Å, C—H$\cdots$O″ 154 (5)° (symmetry operation for the double-primed atom: $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$). ($b$) View of the crystal structure of (I) approximately down the $a$ axis illustrating the herringbone pattern.

The molecule has approximately $C_s$ symmetry, the symmetry plane being defined by the atoms C1, N2, C3, C4 and F3 with a deviation from the least-squares plane of 0.01 Å. The C—F bond lengths are equal within the s.u.'s and compare well with the values observed in (I) and (II) (~1.333 Å). The F—C—C angle for F3, the F atom *trans* to the isocyanide group, is 2.5° smaller than for F1 and F2. This is most likely to be due to repulsive forces between the N atom and the F atoms F1 and F2.

A stereoview of the structure along the $c$ axis is shown in Fig. 5. The shortest intermolecular F$\cdots$F distances range between 2.93 and 3.06 Å, and are slightly smaller than those observed in the two other title compounds. The closest intermolecular approach of the isocyanide groups occurs *via* a 2$_1$ screw axis along **a** generating a shortest C1$\cdots$N2 contact of 3.46 Å. According to *ab initio* calculations (Lane *et al.*, 1994), isocyanide dipoles have a magnitude of 3.7 D (1 D $\simeq 3.33564 \times 10^{-30}$ C m) and will result in a dipole–dipole interaction energy of 38 kJ mol$^{-1}$ when aligned in opposite directions and

separated by 3.5 Å. In the present crystal structure, the dipoles deviate significantly from an antiparallel orientation, making a contribution by the dipole–dipole interaction to an effective stabilization of the structure unlikely. Instead, each isocyanide group is trapped in an electronegative environment formed by four F atoms belonging to two neighbouring molecules (see Fig. 5), one generated by the same 2$_1$ screw axis mentioned above and the second one by the 2$_1$ screw axis along **c**. The four intermolecular C1$\cdots$F distances (3.42–3.47 Å) are all shorter than the intramolecular C1$\cdots$F distances (3.55–3.59 Å). The C$_{iso}\cdots$F attractive interactions obviously play a more important role in this crystal structure than the dipole–dipole attractive interactions.

### 4. Theoretical calculations

Full optimizations of molecules (II) and (III) were carried out starting from the corresponding structural data obtained by X-ray diffraction. The *ab initio* calculations were performed using the *GAUSSIAN*92 program package (Frisch *et al.*, 1993) at the Hartree–Fock level of theory utilizing the basis set 6-31G($d$,$p$) to permit comparison with the values obtained for (I) by Madappat *et al.* (1993). Threshold limits of 0.00045 and 0.0018 a.u. for the maximum force and displacement, respectively, were applied as convergence criteria.

Comparison of our experimental data with the results of *ab initio* calculations for (I) and (II) shows that, except for those atoms which participate in hydrogen bonds, the differences are at most 0.02 Å for bond lengths and 1.4° for bond angles. For compound (III), these differences are even smaller: 0.01 Å for bond lengths and 1.2° for bond angles (see Table 3).

In the trifluoromethyl groups, the differences in the F—C—N and F—C—C bond angles for (I) and (III), respectively, are reflected by both experiment and theory. However, in (II) minor differences in these angles occur between the experimental values for the solid state and *ab initio* calculations for the molecule in the gas phase.

In addition to the experimental geometry, three further conformations were optimized for molecule (II) in which the torsion angle C4—C3—C2—C1 was given starting values of 0, 180 and 60° (see Fig. 2$c$). In all cases convergence was achieved at a geometry very close to the experimental one (see Table 3). Only by keeping these torsion angles fixed during optimization was it possible to compare the energies of the possible conformations; the *cis* conformation is definitely the less stable (by 9.88 kcal mol$^{-1}$; 1 kcal = 4.184 kJ). This increase in energy is accompanied by the opening of the bond angles O1—C1—N2 127.4, C1—N2—C3 130.8 and N2—C3—C4 118.4°, clearly indicating strong repulsion forces between the O and F atoms. The energy minimum of the *trans* conformation, on the other hand, lies only 1.72 kcal mol$^{-1}$ above the fully optimized conformation.
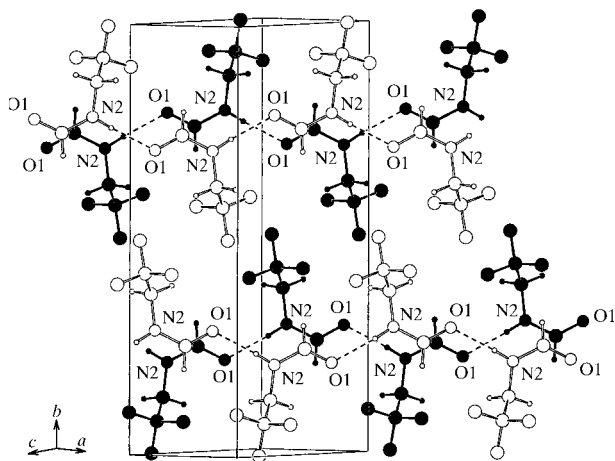


Fig. 4. View of the crystal structure of (II) approximately along the *ac* diagonal. The molecules within each chain in the foreground (white) or in the background (black) are related by *n*-glide planes and form N—H$\cdots$O' hydrogen bonds with H$\cdots$O' 1.96 (2), N$\cdots$O' 2.82 (2) Å and N—H$\cdots$O' 175 (2)° (symmetry operation for the primed atom: $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$).
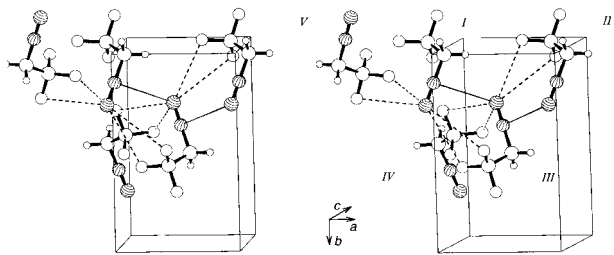


Fig. 5. Stereoview of the packing of (III) approximately along the *c* axis. Molecules generated by the following symmetry operations are drawn: (*I*) $x, y, z$; (*II*) $1 + x, y, z$; (*III*) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (*IV*) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (*V*) $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$. The shortest intermolecular contacts between isocyanide atoms (C1$\cdots$N1) are drawn as solid lines and the C1$\cdots$F contacts as dashed lines.

Finally, the *gauche* conformation (where C4—C3—C2—C1 was held at 60°) shows, as expected, a distortion of the experimental bond angles like that observed for the *cis* conformation.

## 5. Concluding remarks

Our results confirm the presence of the *Z* conformation in the crystal structures of (I) and (II), although the *E* isomer had been predicted to be the energetically more stable one in the case of (I). This finding is in agreement with a wide variety of related organic molecules analysed in the crystalline state. The planarity of the formamide group is retained in both (I) and (II). Moreover, our observations suggest that intermolecular hydrogen bonds between the N atom and the carbonyl O atom determine the molecular packing in (I) and (II), giving rise to infinite chains of molecules. In (I), this is further reinforced by C—H···O contacts which link the chains into sheets. The isocyanide fragment in (III) shows the expected geometry. The crystal structure of (III) is characterized by an interaction between the isocyanide dipoles and the surrounding electronegative F atoms.

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