

3,3-Bis(difluoroaminomethyl)oxetane,
a promising new energetic materialRichard Gilardi,^{a*} Robin N.
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Key indicators

Single-crystal X-ray study

T = 93 K

Mean $\sigma(\text{C}-\text{C}) = 0.001 \text{ \AA}$

R factor = 0.036

wR factor = 0.102

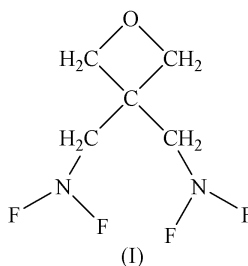
Data-to-parameter ratio = 12.2

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, a promising new energetic material, 3,3-bis(difluoroaminomethyl)oxetane, $(\text{F}_2\text{NCH}_2)_2\text{C}(\text{CH}_2)_2\text{O}$ or $\text{C}_5\text{H}_8\text{F}_4\text{N}_2\text{O}$, contains two difluoroamine (NF_2) substituents, rather uncommon energetic groups, which tend to be disordered in crystal structures. The molecule occupies a special position on a twofold axis, and its two equivalent difluoroamine groups show no signs of disorder.

Comment

Energetic polymers appropriate for use as elastic binders in solid propellants can be made by adding energetic groups to oxetane, the four-membered ring in the title molecule, (I). If a mixture of different oxetanes and an appropriate catalyst are used for starting materials, copolymerization of the oxetanes occurs; this is a promising method for designing energetic materials with specific handling properties, while also adding energy to be released during combustion. The crystal structures of two energetic oxetanes were reported by George & Gilardi (1986), where the substituent arms contained the conventional energetic nitramine ($\text{N}-\text{NO}_2$) and nitrate ($\text{O}-\text{NO}_2$) groups.



In (I), the added energetic moieties are the more unconventional difluoroamine (NF_2) groups.

Fluoroamine-rich materials are a newly emergent area of energetic materials synthesis, and they are expected to lead to significant increases in propellant and explosive energy densities. Difluoroamines (NF_2 compounds) are predicted by theoretical calculations to perform especially well as propellants (Miller, 1996).

The difluoroamine grouping can be a very sensitive and dangerous addition to organic molecules. Compounds containing it should only be synthesized in an explosion-proofed laboratory by an experienced explosives chemist. As a result, there are not many structure determinations of the NF_2 group in the literature. However, in recent years, several quite stable compounds containing NF_2 [such as (I)] have been discovered. Butcher *et al.* (2002) reported four such compounds, and reviewed the five prior reports of NF_2 -

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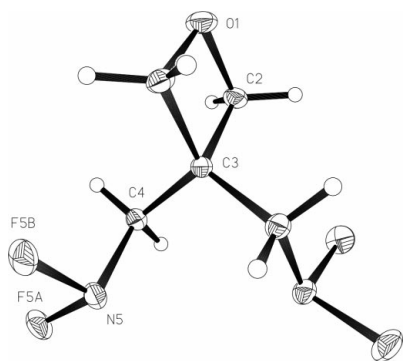


Figure 1
The molecule of (I), showing 50% probability atomic displacement ellipsoids.

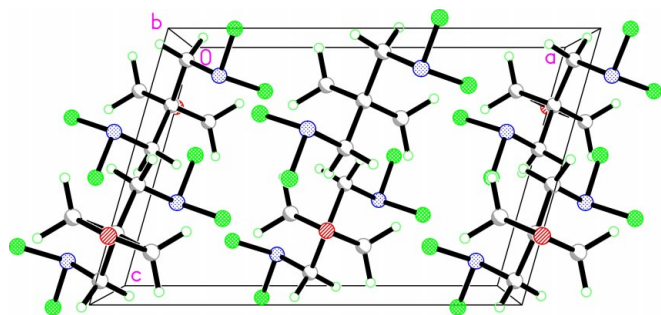


Figure 2
The packing of (I), viewed down the *b* axis of the unit cell. The six planar oxetane rings, located on the twofold axes at $x = 0, \frac{1}{2}$ or 1, and $z = \frac{1}{4}$ or $\frac{3}{4}$, overlap because they are seen edge-on in this view.

containing molecules. Their conclusions were that the NF_2 group always displays an extremely pyramidal structure, with an average F—N—F angle of $100.1(7)^\circ$ and an average C—N—F angle of $105.2(7)^\circ$. Both are considerably smaller than the usual sp^3 ‘tetrahedral’ angle of 109.5° .

In molecule (I), which occupies a special position on a twofold axis, the corresponding angles, F5A—N5—F5B , C4—N5—F5A and C4—N5—F5B , are $100.85(7)$, $103.92(8)$ and $104.44(8)^\circ$ (Fig. 1), so the NF_2 group in this molecule is also pyramidalized ‘beyond tetrahedral’. The N—F distances in (I) are $1.412(1)$ and $1.425(1)$ Å, slightly longer than noted for N—F in prior determinations [mean $1.392(9)$ and range 1.358 – 1.413 Å; Butcher *et al.*, 2002]. The single independent C—NF_2 distance in (I) is $1.475(1)$ Å, slightly shorter than those reported by Butcher *et al.* (2002), which averaged $1.500(7)$ Å, with a range of 1.489 – 1.511 Å.

Perfluorinated groups are often ‘floppy’ or extreme in their thermal vibrations, and sometimes even display a disordered mix of conformations [see Flippen-Anderson *et al.* (2001) for database statistics on $-\text{CF}_3$, and BF_4^- and PF_6^- anion disorders]. Librational disorder was especially pronounced in the crystal structure of 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine, a very energetic compound, known as HNFx, containing four NF_2 groups (Chapman *et al.*, 1999); its refinement required disordered NF_2 -group conformer pairs differing in rotation about the C—NF_2 bond by approximately 120° , and the application of group-similarity constraints to all conformers.

Molecule (I) shows no sign of disorder or large vibrations; the principal axes of the atomic displacement ellipsoids for the F atoms are comparable to those on the ring O atom at the opposite end of the molecule. Although there are no particularly close intermolecular approaches (a packing diagram is shown in Fig. 2), the pendant NF_2 groups are effectively constrained by inter- and intramolecular neighboring atoms at or near usual van der Waals contact distances (Rowland & Taylor, 1996).

Experimental

The title compound was synthesized at Aerojet Propulsion by Dr Manser. Details of the synthesis will be reported elsewhere. Crystals were grown at the Naval Research Laboratory from 2-butanone by slow evaporation.

Crystal data

$\text{C}_5\text{H}_8\text{F}_4\text{N}_2\text{O}$
 $M_r = 188.13$
Monoclinic, $C2/c$
 $a = 10.3304(13)$ Å
 $b = 10.6065(13)$ Å
 $c = 6.8638(8)$ Å
 $\beta = 105.931(2)^\circ$
 $V = 723.18(15)$ Å³
 $Z = 4$

$D_x = 1.728$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2766 reflections
 $\theta = 2.9$ – 28.5°
 $\mu = 0.19$ mm⁻¹
 $T = 93(2)$ K
Rounded chunk, colorless
 $0.70 \times 0.65 \times 0.60$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: by integration (Wunsch & Prewitt, 1965)
 $T_{\min} = 0.858$, $T_{\max} = 0.919$
2995 measured reflections

877 independent reflections
840 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$
 $\theta_{\max} = 28.2^\circ$
 $h = -12 \rightarrow 13$
 $k = -14 \rightarrow 14$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.102$
 $S = 1.00$
877 reflections
72 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.609P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.26$ e Å⁻³

All four H atoms are bonded to methylene C atoms. Their positional parameters were refined and their U_{iso} values were set equal to $1.2U_{\text{eq}}$ of the parent C atom. The C—H bond distances range from $0.93(2)$ to $0.99(2)$ Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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