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The structural chemistry of energetic compounds containing geminal-difluoramino groups

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Abstract

This report discusses the structural chemistry of four molecules containing geminal-difluoramine (NF_2) groups. They are: 1,1,4,4-tetrakis(difluoramino)cyclohexane (**1**), monoclinic, $P2_1/n$, $a = 6.277(1)$, $b = 10.502(2)$, $c = 7.910(1)$ Å, $\beta = 99.50(1)^\circ$; 1-{3-[5,5-bis(difluoramino)-2-oxopyrrolidinyl]-2-oxopropyl}pyrrolidine-2,5-dione (**2**), monoclinic, $P2_1/c$, $a = 12.994(1)$, $b = 8.4799(8)$, $c = 13.142(1)$ Å, $\beta = 102.998(7)^\circ$; 1-[2,2-bis(difluoramino)propyl]-pyrrolidine-2,5-dione (**3**), monoclinic, $P2_1$, $a = 6.488(1)$, $b = 9.508(2)$, $c = 8.612(1)$ Å, $\beta = 105.52(1)^\circ$; and 2-[2,2-bis(difluoramino)propyl]isoindoline-1,3-dione (**4**), orthorhombic, $Pbca$, $a = 15.718(1)$, $b = 7.0818(5)$, $c = 22.039(2)$ Å. The pyramidal difluoramine group sometimes displays extensive torsional disorder in crystals, but in each of the structures reported here, the geminal-NF_2 groups are primarily ordered, due to interactions with their steric environments. There are increases in the thermal parameters of the fluorine atoms indicating libration in some cases, where there are fewer steric demands in the NF_2 environment. The conformation adopted by each NF_2 group can be explained in terms of minimization of non-bonded $F \cdots H$ and $F \cdots F$ contacts. All NF_2 groups are nonplanar and show unusual metrical parameters compared to amines containing no fluoro substituents. The interior F–N–F and C–N–F angles are very small, indicating a high degree of pyramidalization. This type of behavior has been attributed to pπ–s resonance and electrostatic effects. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Difluoramines; Propellant ingredients; Crystal structures

1. Introduction

In a 1995 plenary lecture on “New Energetic Materials” [1], Richard S. Miller emphasized that fluorine-rich energetic materials were an emerging area of energetic materials science, and that “fluorine and oxygen rich energetic crystals and polymers will provide a new approach to increasing composite propellant and explosive energy density and energy release rates”. Recent synthetic developments in the search for higher performance energetic compounds have led to dinitramide salts [2–7] and, more recently, pentafluorosulfanylnitramide salts [8]. However,

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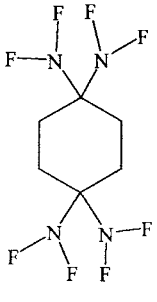
the potential to achieve full metal combustion/detonation in advanced energetic compositions is limited by the use of conventional energetic oxidizers that contain only nitro, nitrato, or nitramino functional moieties [9].

One possible component in energetic compounds is the difluoramino (NF_2) group. This group has several advantages over nitramines; it has a higher intrinsic density and its energy content is higher (especially when combined with boron or aluminum). In addition, incorporation of fluorine derivatives into advanced metallized energetic materials leads to the formation of gaseous oxy fluorides, rather than to the formation of oxide coatings on the metal surfaces which degrade the performance of these energetic materials. Moreover, difluoramino compounds are predicted to perform extremely well by theoretical computations of explosive (detonation pressure) and propellant (impulse) performance parameters. According to a recent report, some of these benefits have been experimentally verified [10].

The incorporation of the difluoramino (NF_2) group into structures that maintain high density and acceptable thermal and processing properties would thus provide new capabilities for propulsion and weapon technologies. In the design of this new generation of advanced energetic materials, calculations indicate that it is advantageous to include oxygen oxidizer groups, such as the nitramino group, to oxidize the carbon atoms to gaseous propellant products such as carbon monoxide [9].

In spite of this technological interest, there has been very little published about the structural chemistry of this unusual group. One very energetic target, the HMX analog 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine (HNFX) has been synthesized and structurally characterized [11] and was found to contain disordered NF_2 groups (rotated by approximately 120°), which made it difficult to obtain reliable parameters for the group. This article reports the structural chemistry of 1,1,4,4-tetrakis (difluoramino)-cyclohexane (**1**), 1-{3-[5,5-bis(difluoramino) -2-oxo-pyrrolidinyl]-2-oxopropyl} pyrrolidine-2,5-dione (**2**), 1-[2,2-bis(difluoramino)propyl]-pyrrolidine-2,5-dione (**3**), and 2-[2,2-bis(difluoramino)propyl]-isoindoline-1, 3-dione (**4**), containing predominantly ordered *geminal*-difluoramine groups.



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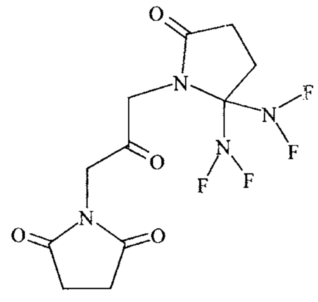

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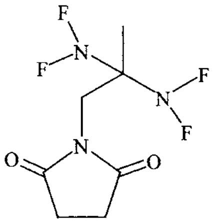

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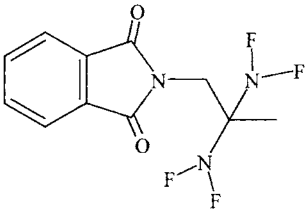

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2. Experimental

2.1. Data collection

Crystals of **1** were synthesized [12] by Dr. Baum, while crystals of **2**–**4** were synthesized [2] [13] by Drs. Trivedi and Adolph [also from the Energetic Materials Research & Technology Department, Naval Surface Warfare Center, Indian Head, MD 20640, USA]. Clear, colorless crystals of **1**–**4** were glued to the ends of thin glass fibers and transferred to a Nicolet R3 m/V (**1**) or a Siemens P4S diffractometer (**2**–**4**), both equipped with Cu Kα radiation and a graphite monochromator. Cell dimensions and an orientation matrix for data collection for all crystals were obtained from a least-squares refinement of the setting angles of 25–50° accurately centered reflections. These are listed with other relevant crystal data in Table 1.

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[2] Compound **2** was first synthesized by Dr. Horst Adolph. Full details of his synthetic procedure will be published in a later communication. Compound **3** & **4** was prepared by Dr. Trivedi using method analogous to that reported for **4** (see [13]).

Table 1
Crystal data and structure refinement

Crystal data	Crystal structure			
	1	**2**	**3**	**4**
Crystal shape	Colorless plate	Colorless plate	Colorless needle	Colorless plate
Chemical formula	$C_6H_8F_8N_4$	$C_{11}H_{12}F_4N_4O_4$	$C_7H_9F_4N_3O_2$	$C_{11}H_9F_4N_3O_2$
Formula weight	288.16	340.25	243.17	291.21
Temperature (K)	223	293	293	293
System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_1$	*Pbca*
a (Å)	6.277(1)	12.994(1)	6.488(1)	15.718(1)
b (Å)	10.502(2)	8.4799(8)	9.508(2)	7.0818(5)
c (Å)	7.910(1)	13.142(1)	8.612(1)	22.039(2)
β (°)	99.50(1)	102.998(7)	105.52(1)	–
V (Å^3), Z	514.3(1), 2	1411.0(2), 4	511.9(2), 2	2453.2(3), 8
Density (mg/mm^3)	1.861	1.602	1.578	1.577
μ (mm^{-1})	2.030	1.388	1.467	1.342
θ range (°)	3.00–55.99°	3.49–57.50	5.33–57.49	4.90–57.99
Number measured[a]	844	2104	1544	3352
Number unique	660 ($R_{\text{int}} = 1.90\%$)	1934 ($R_{\text{int}} = 1.30\%$)	749 ($R_{\text{int}} = 1.80\%$)	1702 ($R_{\text{int}} = 4.06\%$)
Number observed	601 ($F > 4\sigma(F)$)	1760 ($F > 4\sigma(F)$)	729 ($F > 4\sigma(F)$)	1167 ($F > 4\sigma(F)$)
Data/restraints/parameters	660/6/117	1934/0/209	749/1/147	1702/6/203
Absorption correction	–	Integration	Integration	Integration
$T_{\max}$, $T_{\min}$	–	0.872, 0.579	0.865, 0.725	0.954, 0.448
Goodness of fit on F^2	1.082	1.038	1.070	1.054
R indices [$I > 2\sigma(\mathrm{I})$] ($\times 100$)	R_1 5.44, wR_2 15.72	R_1 4.71, wR_2 13.46	R_1 4.42, wR_2 12.47	R_1 6.65, wR_2 17.30
R indices (all data) ($\times 100$)	R_1 5.74, wR_2 16.11	R_1 5.07, wR_2 13.86	R_1 4.47, wR_2 12.58	R_1 9.27, wR_2 20.05

[a] All structures were collected on a Siemens diffractometer using Cu Kα radiation (1.54178 Å) and $\theta/2\theta$ scans.

2.2. Structure solution and refinement

The structures were solved by direct methods using the SHELXTL package of computer programs [14,15]. Neutral atom scattering factors were used [16] with corrections for real and imaginary anomalous dispersion [17]. All structures were refined by full-matrix least-squares methods based on F^2 using SHELXL [3] and used all of the unique data. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were located in difference Fourier syntheses and refined isotropically.

Fractional coordinates and equivalent thermal factors for **1** through **4** are listed in Tables 2–5.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for **1**[a]

	x	*y*	*z*	*U* (eq.)
C(1)	3885(4)	5705(2)	3500(3)	26(1)
N(1eq)	3836(3)	6646(2)	2049(3)	43(1)
F(3a)	3151(7)	5905(4)	581(4)	57(1)
F(4a)	6029(5)	6778(5)	1920(6)	69(2)
F(3b)	3628(9)	5971(5)	498(5)	62(2)
F(4b)	5984(6)	7056(5)	2178(7)	61(2)
N(1ax)	1617(3)	5417(2)	3701(3)	39(1)
F(1)	578(3)	4890(2)	2171(3)	68(1)
F(2)	537(3)	6584(2)	3676(2)	55(1)
C(2)	4881(4)	6395(3)	5135(3)	32(1)
C(3)	4987(5)	5552(3)	6714(3)	33(1)

[a] *U* (eq.) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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[3] SHELXL, is contained in the SHELXTL suite of crystallographic programs [14]. It is a full-matrix least-squares refinement package that uses all data and refines on F^2 rather than the traditional *F*. The various criteria used in this refinement process are defined as follows: $R(F) = \sum |F_o - F_c| / \sum F_o$, and $R(F^2) = \left\{\sum[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\right\}^{1/2}$, where $w = 1/[\sigma^2(F_o) + (a\mathrm{P})^2 + b\mathrm{P}]$ and *a* and *b* are variable parameters whose optimal values are suggested by the program during the refinement process.

The goodness-of-fit parameter (*s*) is based on F^2 and defined as: $s = \left\{\sum[w(F_o^2 - F_c^2)^2]/[n - p]\right\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**[a]

	x	*y*	*z*	*U* (eq.)
F(1)	6900(2)	3067(3)	5516(2)	92(1)
F(2)	6481(1)	697(3)	4988(2)	84(1)
F(3)	7803(2)	1200(2)	3138(1)	75(1)
F(4)	9156(2)	119(2)	4134(1)	69(1)
O(1A)	9787(2)	1776(2)	7379(2)	52(1)
O(1B)	7650(2)	−1647(2)	9507(2)	67(1)
O(2B)	5423(2)	−3120(6)	6504(2)	125(2)
O(3)	7310(2)	478(2)	7298(2)	54(1)
N(1)	6966(2)	2055(4)	4701(2)	67(1)
N(2)	8101(2)	415(3)	4092(2)	48(1)
N(1A)	8598(2)	1044(2)	5902(2)	33(1)
N(1B)	6703(2)	−2354(3)	7902(2)	44(1)
C(1A)	8121(2)	1667(3)	4902(2)	38(1)
C(2A)	8725(2)	3173(3)	4779(2)	51(1)
C(3A)	9350(3)	3549(4)	5876(3)	62(1)
C(4A)	9298(2)	2079(3)	6502(2)	41(1)
C(5A)	8462(2)	−538(3)	6275(2)	34(1)
C(6)	7719(2)	−641(3)	7000(2)	36(1)
C(1B)	6806(3)	−1945(3)	8928(2)	50(1)
C(2B)	5734(3)	−1928(5)	9154(3)	75(1)
C(3B)	5003(3)	−2533(8)	8183(3)	100(2)
C(4B)	5677(3)	−2707(5)	7405(3)	74(1)
C(5B)	7545(2)	−2311(3)	7349(2)	47(1)

[a] *U* (eq.) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**[a]

	x	*y*	*z*	*U* (eq.)
F(1)	7790(6)	2069(5)	11710(5)	99(1)
F(2)	6379(8)	893(5)	13258(5)	111(2)
F(3)	8047(6)	4369(5)	13375(5)	106(2)
F(4)	5460(9)	4711(6)	14386(5)	134(2)
O(1)	4555(5)	2478(3)	8249(4)	58(1)
O(2)	102(5)	5018(4)	10426(4)	67(1)
N	2672(5)	3717(4)	9705(4)	42(1)
N(1)	5804(8)	1756(5)	11893(6)	70(1)
N(2)	6524(8)	3608(6)	13898(5)	76(1)
C(1)	2882(7)	2938(4)	8385(5)	45(1)
C(2)	712(7)	2801(6)	7233(5)	59(1)
C(3)	−748(7)	3674(7)	7938(6)	68(1)
C(4)	604(7)	4251(5)	9482(5)	51(1)
C(5)	4488(6)	4119(4)	11013(5)	45(1)
C(6)	4913(6)	3084(5)	12427(5)	46(1)
C(7)	2933(9)	2643(8)	12896(7)	76(2)

[a] *U* (eq.) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4**[a]

	x	*y*	*z*	*U* (eq.)
F(1)	2855(2)	3082(7)	4642(2)	133(2)
F(2)	3501(2)	5687(6)	4782(1)	122(1)
F(3)	4100(30)	1190(50)	4763(18)	210(20)
F(4)	5285(16)	2010(70)	4383(9)	173(19)
F(3A)	4270(7)	959(10)	4658(6)	121(4)
F(4A)	5347(3)	2508(19)	4361(4)	113(3)
O(1)	4850(2)	3072(5)	2535(1)	82(1)
O(2)	2116(2)	2882(5)	3213(1)	72(1)
N	3553(2)	2955(5)	3028(1)	54(1)
N(1)	3257(3)	4473(7)	4304(2)	88(1)
N(2)	4546(3)	2819(7)	4607(2)	95(1)
C(1)	4089(2)	3276(5)	2526(2)	58(1)
C(2)	3522(2)	3829(5)	2026(2)	51(1)
C(3)	3697(3)	4286(6)	1424(2)	66(1)
C(4)	3020(3)	4651(6)	1048(2)	70(1)
C(5)	2198(3)	4581(6)	1255(2)	66(1)
C(6)	2010(2)	4115(6)	1852(2)	58(1)
C(7)	2692(2)	3758(5)	2230(2)	49(1)
C(8)	2702(2)	3175(5)	2876(2)	53(1)
C(9)	3843(3)	2145(6)	3596(2)	65(1)
C(10)	4065(2)	3615(7)	4080(2)	62(1)
C(11)	4573(3)	5306(8)	3841(2)	83(2)

[a] *U* (eq.) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

Figs. 1–4 show the molecular unit and atomic numbering scheme used. These four compounds all contain geminal difluoramino groups in a similar environment, i.e. attached to an sp^3 carbon. In a series of molecules containing the difluoramino group that have been structurally characterized in this laboratory, most contain disordered NF_2 groups [11,18]. The four molecules reported herein are characterized by the fact that they all contain at least one ordered NF_2 moiety. Since a major focus of this paper is the structure of the NF_2 group, Table 6 lists important metrical parameters observed for this group. Table 7 lists these same parameters for those published structures [11,19–22] that contain the NF_2 moiety. One molecule [11] reported in Table 7 was refined with group-similarity constraints due to the extensive disorder of its NF_2 groups. Because of the disorder, its metrical parameters are less certain, but fit into the pattern shown by Table 6.

Fluorinated organic molecules exhibit unusual chemical reactivity and unusual physical properties that

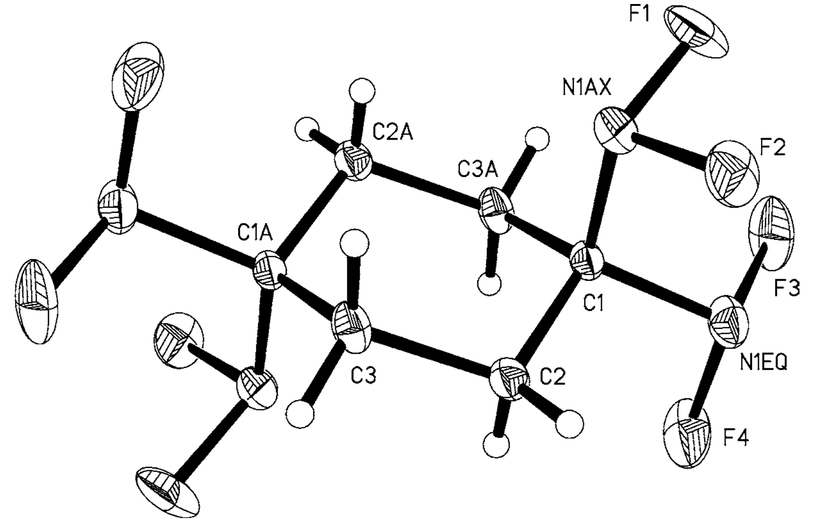


Fig. 1. Formula unit for 1,1,4,4-tetrakis(difluoramino)cyclohexane (**1**) showing the labeling scheme used. The N1eq-F3,F4 fluoramino group was modeled with a 52%:48% occupancy disorder pair torsionally displaced by 14.0°. The major form is shown here.

place these compounds in a class of their own and many fluorocarbon properties remain puzzling and defy theoretical understanding [23]. Since the majority of structures containing the difluoramino moiety are disordered it is of interest to examine each structure in turn to see what factors are influencing these groups to be ordered in the solid state.

In **1**, the geminal difluoramino groups are axial and equatorial. In the case of the axial NF_2 two conformations are possible; one in which the nitrogen lone pair is directed over the ring and one in which one of the fluorine atoms is directed over the ring (i.e. a 120° rotation about the C–N bond). In this latter conformation there would be two non-bonded $F\cdots H$ axial contacts of 1.9–2.0 Å, which is well below the sum of the van der Waals radii [24] for these two atoms (2.54 Å based on analysis of data contained in the Cambridge Structural Database [25]). Thus this NF_2

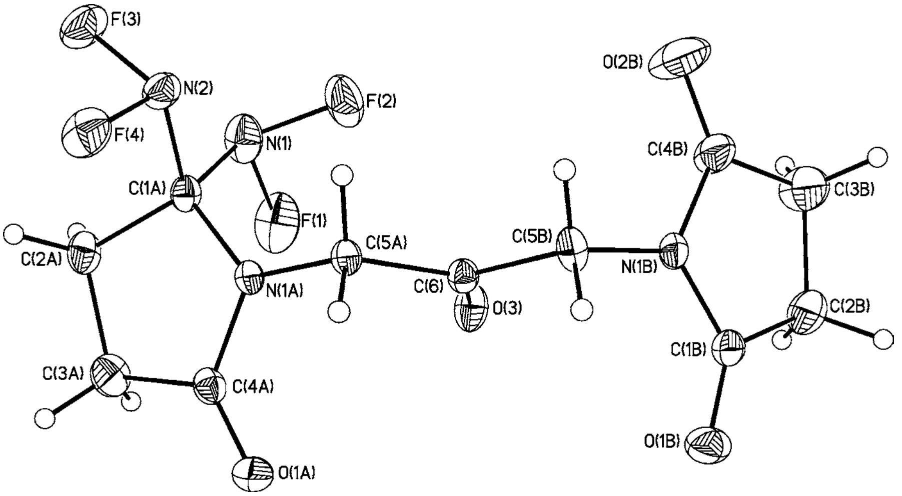


Fig. 2. Formula unit for 1-{3-[5,5-bis(difluoramino)-2-oxopyrrolidinyl]-2-oxopropyl}pyrrolidine-2,5-dione (**2**) showing the labeling scheme used.

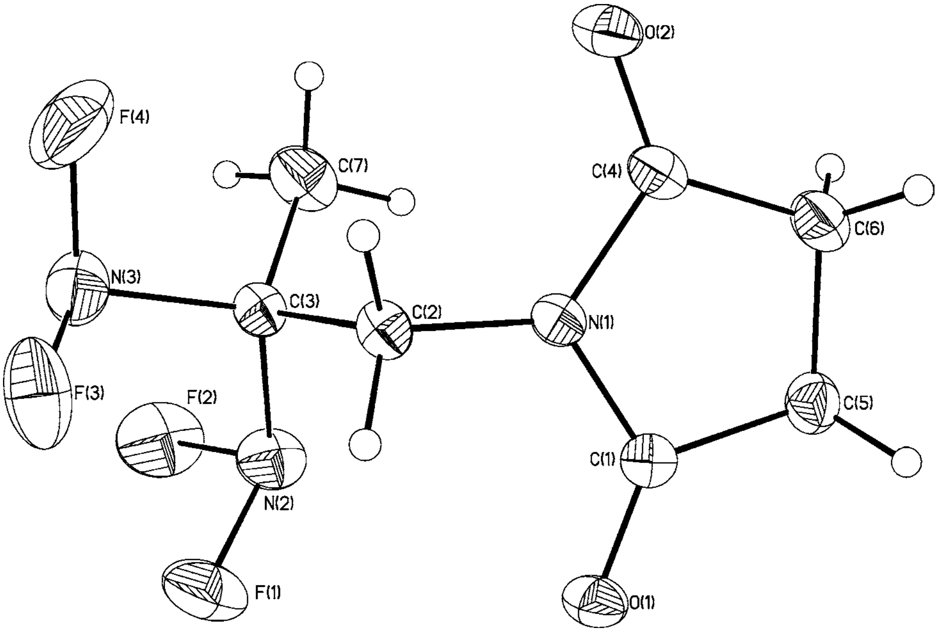


Fig. 3. Formula unit for 1-[2,2-bis(difluoramino)propyl]-pyrrolidine-2,5-dione (**3**) showing the labeling scheme used.

group is sterically restricted to just one conformation, and serves as an anchor to constrain the freedom of the other NF_2 group to adopt multiple conformations. The conformation adopted by this group relative to that adopted by the first NF_2 group can be explained by considering the steric consequences of the alternatives. If the second group were rotated by 120° there would be non-bonded F···F contacts of only 2.2 and 2.4 Å between the geminal NF_2 groups. This is considerably less than the usual F···F van der Waals radius sum, 2.9 Å [24]. In the observed conformation, the closest F···F contacts are $F_1 \cdots F_3$ at 2.59 Å for geminal neighbors, and an intermolecular contact, $F_1 \cdots F_4$, at 2.94 Å.

In **2**, one of the two NF_2 groups is in a sterically constrained position. The lone pair on N2 is directed

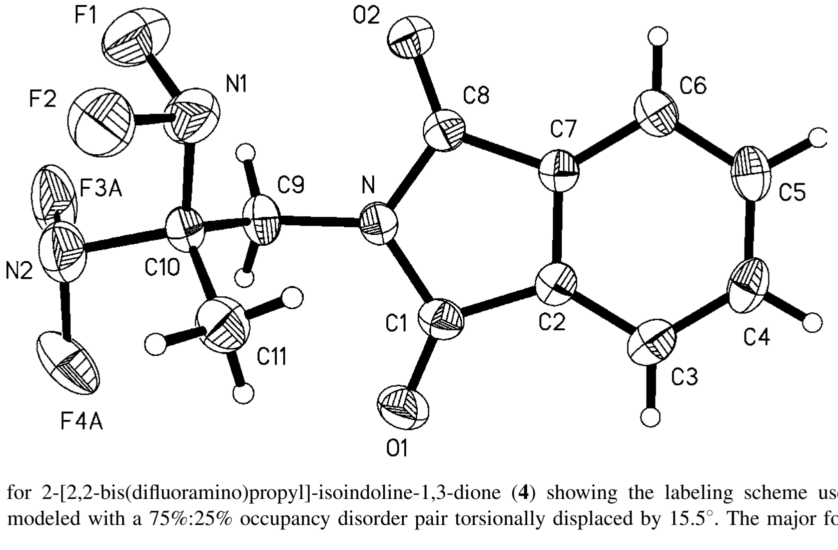


Fig. 4. Formula unit for 2-[2,2-bis(difluoramino)propyl]-isoindoline-1,3-dione (**4**) showing the labeling scheme used. The N2–F3a,F3b fluoramino group was modeled with a 75%:25% occupancy disorder pair torsionally displaced by 15.5°. The major form is shown here.

Table 6
Selected metrical parameters for the NF_2 groups

Parameter	**1**	**2**	**3**	**4**	Average
N1–F1 (Å)[a]	1.391(3)	1.391(4)	1.372(6)	1.387(5)	1.395(9)
N1–F2 (Å)	1.399(3)	1.405(4)	1.400(6)	1.413(5)	
C–N1	1.489(3)	1.500(4)	1.511(6)	1.492(5)	1.500(7)
F1–N1–F2 (°)	100.4(2)	100.9(2)	100.1(4)	99.0(4)	100.1(7)
Pyramidalization[b]	62.2	67.0	63.4	65.3	64.5(18)
C–N2	1.511(3)	1.500(4)	1.496(6)	1.497(6)	
N2–F3 (Å)[c]	1.404(4)	1.395(3)	1.394(7)	1.389(8)	1.394(9)
N2–F4 (Å)	1.406(4)	1.382(3)	1.381(7)	1.387(7)	
F3–N2–F4 (°)	99.5(3)	101.3(2)	99.2(5)	99.5(8)	99.8(4)
Pyramidalization[b]	66.6	66.9	66.4	67.0	66.8(19)
C–N–F (°)[d]	105.7(22)	104.4(7)	105.8(20)	105.5(4)	105.4(6)

[a] N1–F1, if more than one NF_2 group, the most ordered of the NF_2 groups.

[b] Pyramidalization is defined as the angle between the C–N bond and the NF_2 plane (54.7° for a regular tetrahedron).

[c] N2–F1, if more than one NF_2 group, the least ordered of the NF_2 groups.

[d] Average C–N–F angle for all of the C–NF_2 groups in each molecule.

towards the hydrogen atom, H5AB, attached to C5 (N2 · · · H5AB, 2.479 Å). Again, if this groups were rotated by 120° there would be short non-bonded F · · · H contacts of 1.9–2.0 Å. Thus this group is constrained and restricts the conformational freedom of the other geminal NF_2 in a similar manner to that in **1**.

In **3** and **4**, the NF_2 moieties are in similar steric environments. In both cases the NF_2 group (N2, F3, and F4) that is in the less sterically demanding conformation is antiperiplanar to the plane of the pyrrolidine ring. In the case of **4** this allows this NF_2 to adopt two slightly different conformations (F3/F4 and F3A/F4A), while in the case of **3** the thermal parameters of F3 and F4 are larger than those of F1 and F2. For the other geminal NF_2 groups in **3** and **4**, the lone pair of the nitrogen is directed over the pyrrolidine ring thus minimizing contacts (N1 · · · H7D, 2.507 Å in **3**; N1 · · · H11B, 2.423 Å in **4**). This is similar to the situation found in **1** and other saturated ring compounds [11,18] where the equatorial NF_2 moieties are in less sterically demanding environments and thus show a tendency towards large librations and/or disorder.

Table 6 summarizes the metrical parameters of the NF_2 moieties. From these it can be seen that, while this moiety contains an sp^3 hybridized nitrogen atom, it has metrical parameters that are not within the normal

Table 7
Selected metrical parameters for the NF_2 groups in published structures

Parameter	[11]	[19]	[20]	[21]	[22]	Average
N1–F1 (Å)[a]	1.388	1.407	1.401	1.404	1.358	1.389(11)
N1–F2 (Å)	1.380	1.417	1.417	1.391	1.367	
F1–N1–F2 (°)	101.0	100.1	99.8	102.3	101.6	100.9(9)
Pyramidalization[b]	65.3	63.7	67.1	65.5	67.4	66.1(3)
N2–F3 (Å)[c]	1.388		1.380		1.363	
N2–F4 (Å)	1.380		1.400		1.379	
F3–N2–F4 (°)	101.0		99.8		101.6	
Pyramidalization[b]	65.3		67.7		66.7	
C–N–F (°)[d]	105.4	106.5	104.3	105.1	104.3	105.1(8)

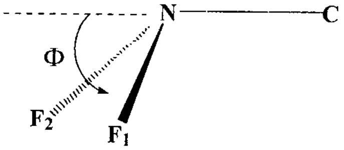
[a] N1–F1, if more than one NF_2 group, the most ordered of the NF_2 groups.

[b] Pyramidalization defined as the angle between the C–N bond and the NF_2 plane (54.7° for a regular tetrahedron).

[c] N2–F1, if more than one NF_2 group, the least ordered of the NF_2 groups.

[d] Average C–N–F angle for all C–NF_2 groups.

range found for this atom (in particular for the F–N–F angle). A search was made of the Cambridge Structural Database [25] for N–$(CH_3)_2$ fragments to provide a statistical base for comparison. This gave 4052 hits and a mean CH_3–N–CH_3 angle of 114.82 (6)°. The mean F–N–F angle of 100.1(7)° observed in these compounds is considerably less than the tetrahedral angle and may be due to the high electronegativity of the fluorine atom [23]. The other interesting aspect of the structural chemistry of these NF_2 derivatives is the high degree of pyramidalization observed at the nitrogen atom. This is shown in the diagram below.



The pyramidal angle is defined as being the angle between the plane of the NF_2 moiety and the line of the extended C–N bond. If the nitrogen were considered to be sp^3 hybridized and thus have bond angles of 109.5° then this angle would be expected to be one-half of the tetrahedral angle, i.e. 54.75°. In these NF_2 derivatives the average pyramidalization is 65.9(22)° with a low and high value of 62.2 and 69.5°, respectively.

Density functional theory has been used to compute optimized geometries for several difluoramines [26]. In this study, F–N–F angles of from 98 to 104° and N–F distances from 1.378 to 1.563 Å were observed. The unusual metrical parameters observed upon geminal fluorination have been attributed to both pπ–s resonance [27] and electrostatic effects [28].

4. Conclusion

It has been shown that the four structures reported here contain ordered *geminal*-NF_2 groups owing to their steric environments. There is an increase in the thermal parameters of the fluorine atoms in those cases where there is some relaxation in the steric demands of the NF_2 environment; in other words, this group is 'floppy' and moves a lot unless it is constrained by inter- or intra-molecular neighbors. The conformation adopted by each NF_2 group can be explained in terms of minimization of non-bonded F···H and F···F contacts. The structural characteristics of the NF_2 groups are tabulated and described herein. All NF_2 groups contain highly pyramidalized nitrogen centers, characterized by small values for the F–N–F and CNF angles (significantly less than 109.5°, the tetrahedral norm). This type of behavior has been attributed to pπ–s resonance [27] and electrostatic effects [28].

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