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Low-temperature redetermination of 1,3-bis(pentafluorophenyl)triazene

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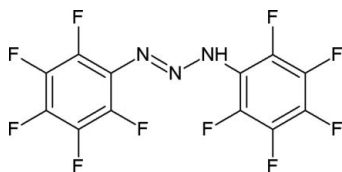
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.039; wR factor = 0.107; data-to-parameter ratio = 13.3.

The crystal structure of the title compound, $(\text{C}_6\text{F}_5)_2\text{N}_3\text{H}$, is stabilized by $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding, forming centrosymmetric dimers organized in a herringbone motif. Important geometrical parameters are $\text{N}-\text{N} = 1.272$ (2) and 1.330 (2) Å and $\text{N}-\text{N}-\text{N} = 112.56$ (15)°. The dihedral angle between C_6F_5 groups is 21.22 (9)°. The room temperature structure was reported by Leman *et al.* (1993). *Inorg. Chem.* **32**, 4324–4336]. In the current determination, the data were collected to a higher θ angle, resulting in higher precision for the $\text{C}-\text{C}$ bond lengths (0.001–0.005 versus 0.003 Å).

Related literature

Average bond lengths were obtained from the Cambridge Structural Database (Allen, 2000); For the synthesis of nitroformazans, see: Pelkis *et al.* (1957); and for the synthesis of triazenes, see: Brooke *et al.* (1965). For use of triazenes in both synthesis and as metal coordinating ligands, see: Leman *et al.* (1993).



Experimental

Crystal data

 $\text{C}_{12}\text{HF}_{10}\text{N}_3$
 $M_r = 377.16$

 Monoclinic, $P2_1/c$
 $a = 9.9930$ (8) Å

 $b = 9.4850$ (8) Å

 $c = 12.9200$ (11) Å

 $\beta = 95.585$ (2)°
 $V = 1218.79$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.23$ mm⁻¹
 $T = 100$ K
 $0.3 \times 0.19 \times 0.15$ mm

Data collection

 Bruker X8 APEXII 4K Kappa CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2004)
 $T_{\min} = 0.933$, $T_{\max} = 0.966$

 12525 measured reflections
 3013 independent reflections
 2177 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.107$
 $S = 1.07$
 3013 reflections

 226 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H3}\cdots\text{N1}^i$	0.88	2.23	3.076 (2)	162

 Symmetry code: (i) $-x + 1, -y, -z + 1$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus and XPREP (Bruker, 2004); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2288).

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Low-temperature redetermination of 1,3-bis(pentafluorophenyl)triazene

Karel G. von Eschwege and Annemarie Kuhn

S1. Comment

A series of dithizones with varying number of fluorines on the phenyl rings were synthesised. During this process the nitroformazan precursor is initially prepared from the substituted aniline, as described by Pelkis *et al.*, 1957. In the final step the nitro group is substituted by sulfur, to form dithizone. However, during the first step to prepare pentafluorophenyldithizone it was found that, contrary to expectation, a triazene formed instead of the usual nitroformazan. Previous studies show the extensive use of triazenes in both synthesis and as metal coordinating ligand, as illustrated by Leman *et al.*, 1993. Triazenes, in general, are traditionally synthesised slightly different, according to a method by Brooke *et al.*, 1965.

The title compound (Fig.1) and geometrical data are within expected values (average values obtained from the Cambridge Structural Database; Allen, 200). The C₆F₅ groups are twisted out of the plane formed by the N—N=N fragment 30.91 (16)° for ring C1—C6 and 38.49 (13)° for ring C7—C12. Hydrogen bonding (Fig. 2, Table 1) creates a centrosymmetric dimers that organise in a herring-bone motif along the *c* axis (Fig. 3).

S2. Experimental

Reagent chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. For the synthesis 2,3,4,5,6 pentafluoroaniline (5 g, 27.3 mmol) was added to a mixture of concentrated hydrochloric acid (20 mL) and water (35 mL) at 273 K, and diazotized by the slow addition of sodium nitrite (3 g, 43 mmol), stirring for 30 min. The resulting solution was added, with stirring, to a cold mixture of sodium acetate (80 g), glacial acetic acid (45 mL) and water (25 mL). Nitromethane (5.0 g, 82 mmol) was added after 10 min. While heating at 343 K and stirring for 20 h the colour changed to dark-red. Filtering the precipitated 1,3 bis-pentafluorophenyltriazene off, gave the product in 52% yield. Crystals suitable for X-ray crystallography were grown from a mixture of dichloromethane and methanol. Although this method is typically used for the preparation of nitroformazan as precursor for the synthesis of dithizone, nitromethane did not serve here as coupling reagent in the synthesis of this highly fluorinated compound. The unexpected outcome is ascribed to the large electron-withdrawing capacity of the five fluorines on each phenyl ring.

S3. Refinement

The imine H atom was placed in a geometrically idealized position (C—H = 0.88) and constrained to ride on the parent atom with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest residual electron density peak of 0.36 e.Å is 0.70 Å from C9 and the deepest hole of -0.31 e.Å is 0.37 Å from H3 representing no physical meaning.

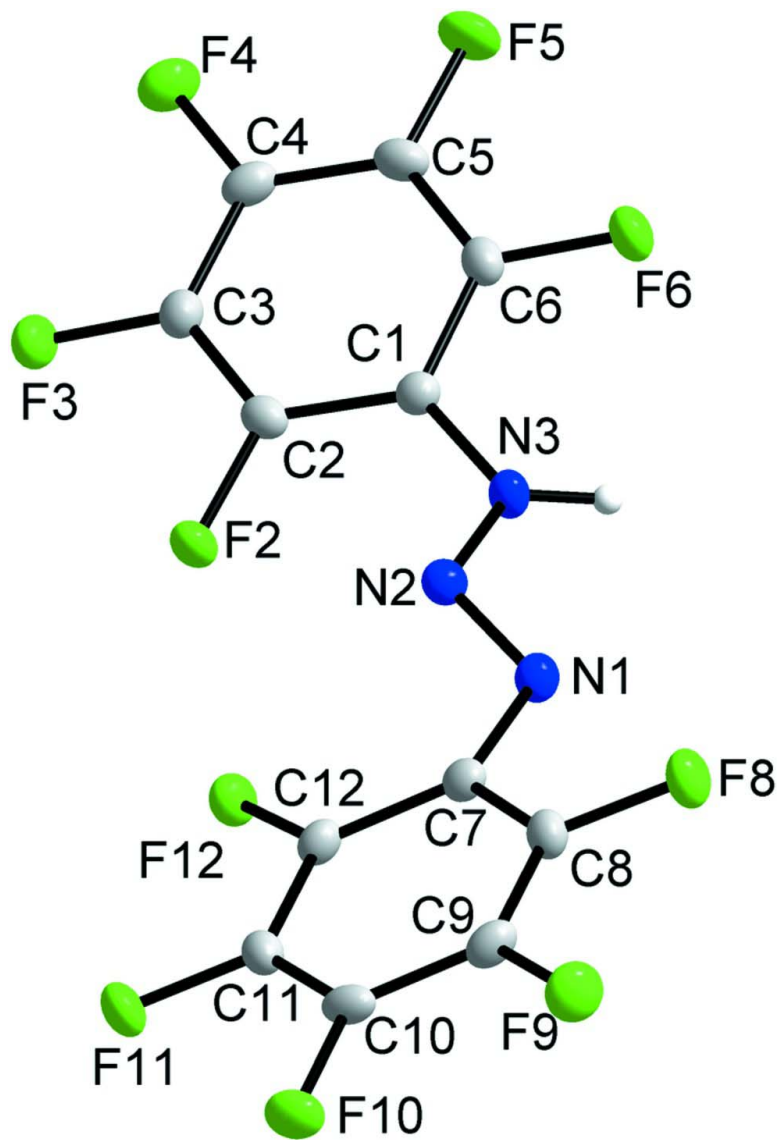


Figure 1

A view of (I). Displacement ellipsoids are drawn at the 30% probability level.

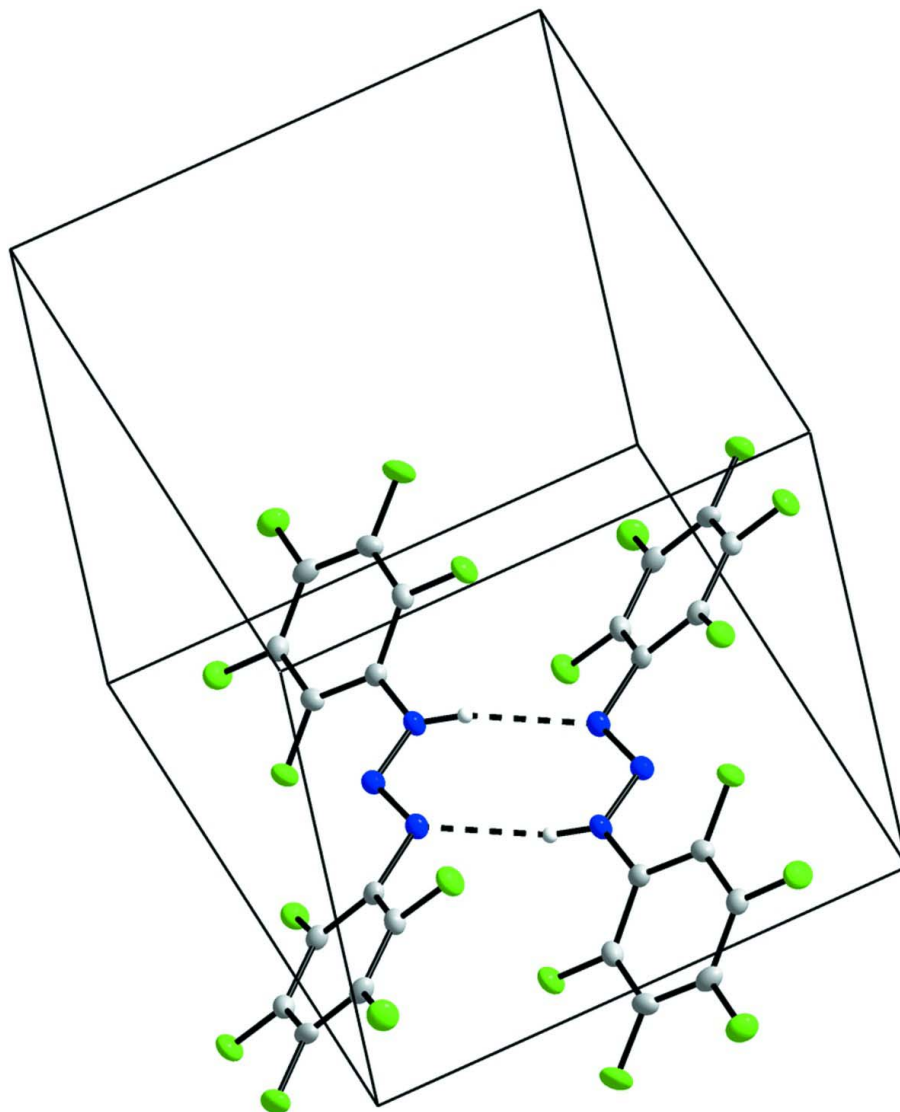


Figure 2
Hydrogen bonding of (I) showing the dimeric units formed.

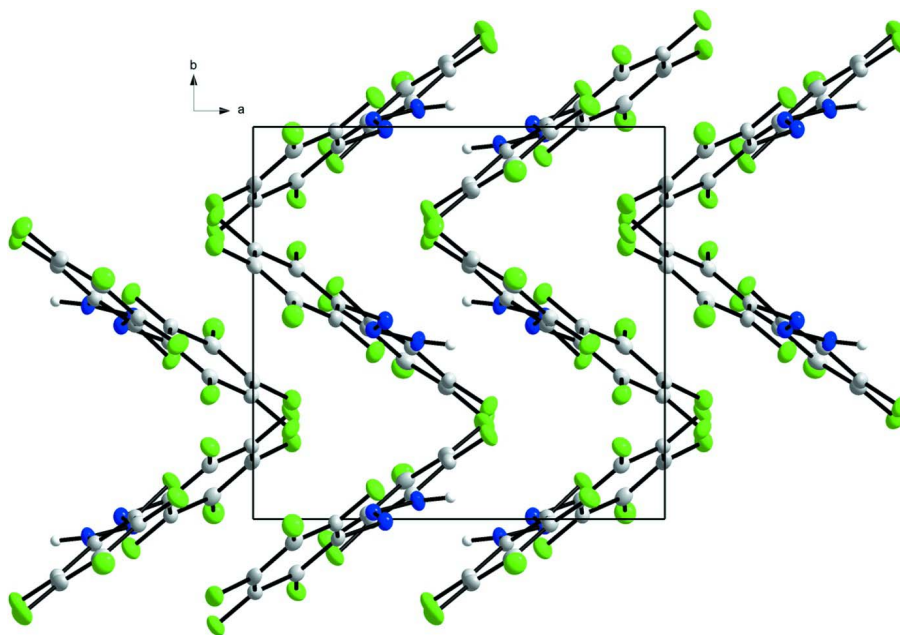


Figure 3

Packing diagram of (I) showing the herring-bone motif.

1,3-bis(pentafluorophenyl)triazene

Crystal data

$C_{12}HF_{10}N_3$

$M_r = 377.16$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 9.9930$ (8) Å

$b = 9.4850$ (8) Å

$c = 12.9200$ (11) Å

$\beta = 95.585$ (2)°

$V = 1218.79$ (18) Å³

$Z = 4$

$F(000) = 736$

$D_x = 2.055$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2521 reflections

$\theta = 3.5\text{--}28.1^\circ$

$\mu = 0.23$ mm⁻¹

$T = 100$ K

Cuboid, red

$0.3 \times 0.19 \times 0.15$ mm

Data collection

Bruker X8 APEXII 4K Kappa CCD
diffractometer

Graphite monochromator

Detector resolution: 8.4 pixels mm⁻¹

φ scans

Absorption correction: multi-scan

(*SADABS*; Bruker; 2004)

$T_{\min} = 0.933$, $T_{\max} = 0.966$

12525 measured reflections

3013 independent reflections

2177 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -12 \rightarrow 13$

$k = -12 \rightarrow 12$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.107$

$S = 1.07$

3013 reflections

226 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.6444P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The intensity data was collected on a Bruker X8 Apex II 4 K Kappa CCD diffractometer using an exposure time of 10 s/frame. A total of 1126 frames were collected with a frame width of 0.5° covering up to $\theta = 28.33^\circ$ with 98.8% completeness accomplished.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.32054 (15)	-0.00606 (18)	0.51342 (13)	0.0176 (4)
N2	0.29181 (15)	0.01759 (18)	0.41693 (13)	0.0170 (4)
N3	0.39984 (15)	0.04639 (18)	0.36826 (13)	0.0187 (4)
H3	0.4793	0.0554	0.4034	0.022*
C1	0.38491 (18)	0.0620 (2)	0.26046 (15)	0.0161 (4)
C2	0.28659 (18)	-0.0055 (2)	0.19428 (16)	0.0170 (4)
C3	0.27844 (18)	0.0129 (2)	0.08793 (16)	0.0183 (4)
C4	0.37001 (19)	0.0977 (2)	0.04420 (16)	0.0198 (4)
C5	0.46978 (19)	0.1626 (2)	0.10765 (16)	0.0199 (4)
C6	0.47531 (18)	0.1467 (2)	0.21357 (16)	0.0184 (4)
C7	0.20622 (17)	-0.0486 (2)	0.56306 (15)	0.0156 (4)
C8	0.20040 (18)	-0.0106 (2)	0.66629 (16)	0.0178 (4)
C9	0.09951 (19)	-0.0571 (2)	0.72416 (15)	0.0190 (4)
C10	0.00216 (18)	-0.1471 (2)	0.67859 (16)	0.0187 (4)
C11	0.00446 (18)	-0.1863 (2)	0.57591 (16)	0.0174 (4)
C12	0.10529 (18)	-0.1381 (2)	0.51888 (15)	0.0165 (4)
F2	0.19834 (11)	-0.09374 (13)	0.23200 (9)	0.0218 (3)
F3	0.18284 (12)	-0.05460 (13)	0.02754 (9)	0.0254 (3)
F4	0.36352 (12)	0.11346 (14)	-0.05941 (9)	0.0272 (3)
F5	0.56138 (12)	0.24230 (14)	0.06517 (10)	0.0283 (3)
F6	0.57237 (11)	0.21376 (13)	0.27471 (9)	0.0246 (3)
F8	0.29674 (11)	0.07433 (13)	0.71246 (9)	0.0241 (3)
F9	0.09641 (12)	-0.01701 (14)	0.82274 (9)	0.0269 (3)
F10	-0.09396 (11)	-0.19674 (13)	0.73422 (10)	0.0243 (3)
F11	-0.09111 (11)	-0.27180 (13)	0.53101 (10)	0.0245 (3)
F12	0.10472 (11)	-0.18344 (13)	0.42082 (9)	0.0218 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0153 (7)	0.0214 (9)	0.0163 (9)	0.0000 (6)	0.0024 (6)	-0.0012 (7)
N2	0.0160 (7)	0.0181 (9)	0.0172 (9)	0.0000 (6)	0.0031 (6)	-0.0005 (7)
N3	0.0142 (7)	0.0247 (10)	0.0172 (9)	-0.0037 (7)	0.0009 (6)	0.0012 (7)
C1	0.0152 (8)	0.0164 (10)	0.0167 (10)	0.0014 (7)	0.0017 (7)	0.0008 (8)
C2	0.0158 (8)	0.0147 (10)	0.0209 (11)	0.0001 (7)	0.0035 (7)	0.0003 (8)
C3	0.0173 (9)	0.0182 (10)	0.0190 (11)	0.0016 (8)	-0.0006 (8)	-0.0006 (8)
C4	0.0244 (10)	0.0200 (11)	0.0155 (10)	0.0055 (8)	0.0040 (8)	0.0026 (8)
C5	0.0193 (9)	0.0177 (11)	0.0236 (11)	0.0004 (8)	0.0070 (8)	0.0035 (9)
C6	0.0150 (8)	0.0167 (10)	0.0230 (11)	-0.0002 (7)	-0.0003 (8)	-0.0013 (8)
C7	0.0138 (8)	0.0171 (10)	0.0159 (10)	0.0027 (7)	0.0014 (7)	0.0014 (8)
C8	0.0144 (8)	0.0186 (11)	0.0199 (11)	0.0000 (7)	-0.0003 (7)	-0.0018 (8)
C9	0.0210 (9)	0.0226 (11)	0.0134 (10)	0.0053 (8)	0.0023 (8)	0.0014 (8)
C10	0.0163 (9)	0.0192 (11)	0.0215 (11)	0.0035 (8)	0.0060 (8)	0.0069 (8)
C11	0.0155 (8)	0.0152 (10)	0.0211 (11)	-0.0005 (7)	-0.0009 (7)	0.0004 (8)
C12	0.0176 (9)	0.0187 (10)	0.0130 (10)	0.0025 (7)	0.0004 (7)	-0.0002 (8)
F2	0.0208 (5)	0.0244 (7)	0.0203 (6)	-0.0077 (5)	0.0023 (5)	0.0023 (5)
F3	0.0293 (6)	0.0275 (7)	0.0183 (7)	-0.0069 (5)	-0.0036 (5)	-0.0011 (5)
F4	0.0334 (7)	0.0318 (8)	0.0171 (7)	0.0016 (6)	0.0055 (5)	0.0032 (5)
F5	0.0265 (6)	0.0308 (7)	0.0292 (7)	-0.0082 (5)	0.0106 (5)	0.0064 (6)
F6	0.0197 (5)	0.0285 (7)	0.0252 (7)	-0.0087 (5)	-0.0005 (5)	-0.0005 (5)
F8	0.0226 (6)	0.0298 (7)	0.0195 (7)	-0.0071 (5)	0.0004 (5)	-0.0053 (5)
F9	0.0304 (6)	0.0342 (8)	0.0168 (6)	-0.0011 (5)	0.0060 (5)	-0.0033 (5)
F10	0.0212 (6)	0.0270 (7)	0.0260 (7)	-0.0008 (5)	0.0098 (5)	0.0048 (5)
F11	0.0198 (5)	0.0260 (7)	0.0274 (7)	-0.0088 (5)	-0.0002 (5)	-0.0008 (5)
F12	0.0241 (6)	0.0249 (7)	0.0162 (6)	-0.0046 (5)	0.0018 (5)	-0.0029 (5)

Geometric parameters (\AA , $^\circ$)

N1—N2	1.272 (2)	C5—C6	1.373 (3)
N1—C7	1.422 (2)	C6—F6	1.349 (2)
N2—N3	1.330 (2)	C7—C8	1.388 (3)
N3—C1	1.394 (2)	C7—C12	1.397 (3)
N3—H3	0.88	C8—F8	1.349 (2)
C1—C6	1.391 (3)	C8—C9	1.385 (3)
C1—C2	1.394 (3)	C9—F9	1.332 (2)
C2—F2	1.341 (2)	C9—C10	1.382 (3)
C2—C3	1.380 (3)	C10—F10	1.340 (2)
C3—F3	1.336 (2)	C10—C11	1.380 (3)
C3—C4	1.380 (3)	C11—F11	1.341 (2)
C4—F4	1.342 (2)	C11—C12	1.383 (3)
C4—C5	1.373 (3)	C12—F12	1.337 (2)
C5—F5	1.345 (2)		
N2—N1—C7	112.19 (15)	F6—C6—C1	118.53 (18)
N1—N2—N3	112.56 (15)	C5—C6—C1	122.21 (18)

N2—N3—C1	118.78 (15)	C8—C7—C12	117.02 (17)
N2—N3—H3	120.6	C8—C7—N1	118.04 (17)
C1—N3—H3	120.6	C12—C7—N1	124.61 (18)
C6—C1—C2	116.55 (18)	F8—C8—C9	118.51 (18)
C6—C1—N3	119.05 (17)	F8—C8—C7	119.02 (17)
C2—C1—N3	124.38 (17)	C9—C8—C7	122.46 (18)
F2—C2—C3	117.62 (17)	F9—C9—C10	120.19 (17)
F2—C2—C1	120.85 (18)	F9—C9—C8	120.73 (18)
C3—C2—C1	121.51 (18)	C10—C9—C8	119.08 (18)
F3—C3—C2	119.36 (17)	F10—C10—C11	120.04 (18)
F3—C3—C4	120.34 (18)	F10—C10—C9	120.00 (18)
C2—C3—C4	120.28 (18)	C11—C10—C9	119.95 (17)
F4—C4—C5	120.47 (18)	F11—C11—C10	120.08 (17)
F4—C4—C3	120.24 (18)	F11—C11—C12	119.65 (18)
C5—C4—C3	119.27 (19)	C10—C11—C12	120.28 (18)
F5—C5—C6	120.39 (18)	F12—C12—C11	117.55 (17)
F5—C5—C4	119.46 (19)	F12—C12—C7	121.24 (17)
C6—C5—C4	120.14 (18)	C11—C12—C7	121.18 (18)
F6—C6—C5	119.25 (17)		
C7—N1—N2—N3	-174.92 (16)	N3—C1—C6—C5	177.51 (18)
N1—N2—N3—C1	174.28 (17)	N2—N1—C7—C8	-147.83 (18)
N2—N3—C1—C6	152.97 (18)	N2—N1—C7—C12	38.9 (3)
N2—N3—C1—C2	-29.0 (3)	C12—C7—C8—F8	179.22 (17)
C6—C1—C2—F2	177.31 (17)	N1—C7—C8—F8	5.4 (3)
N3—C1—C2—F2	-0.7 (3)	C12—C7—C8—C9	-0.5 (3)
C6—C1—C2—C3	-1.0 (3)	N1—C7—C8—C9	-174.24 (18)
N3—C1—C2—C3	-179.05 (18)	F8—C8—C9—F9	1.1 (3)
F2—C2—C3—F3	1.3 (3)	C7—C8—C9—F9	-179.21 (18)
C1—C2—C3—F3	179.65 (17)	F8—C8—C9—C10	-178.35 (17)
F2—C2—C3—C4	-177.26 (17)	C7—C8—C9—C10	1.3 (3)
C1—C2—C3—C4	1.1 (3)	F9—C9—C10—F10	-1.5 (3)
F3—C3—C4—F4	0.2 (3)	C8—C9—C10—F10	177.96 (17)
C2—C3—C4—F4	178.76 (17)	F9—C9—C10—C11	178.85 (17)
F3—C3—C4—C5	-178.06 (18)	C8—C9—C10—C11	-1.7 (3)
C2—C3—C4—C5	0.5 (3)	F10—C10—C11—F11	1.4 (3)
F4—C4—C5—F5	-0.1 (3)	C9—C10—C11—F11	-178.93 (17)
C3—C4—C5—F5	178.22 (18)	F10—C10—C11—C12	-178.43 (17)
F4—C4—C5—C6	179.63 (18)	C9—C10—C11—C12	1.2 (3)
C3—C4—C5—C6	-2.1 (3)	F11—C11—C12—F12	-2.0 (3)
F5—C5—C6—F6	1.1 (3)	C10—C11—C12—F12	177.86 (17)
C4—C5—C6—F6	-178.58 (18)	F11—C11—C12—C7	179.80 (17)
F5—C5—C6—C1	-178.10 (18)	C10—C11—C12—C7	-0.3 (3)
C4—C5—C6—C1	2.2 (3)	C8—C7—C12—F12	-178.17 (17)
C2—C1—C6—F6	-179.85 (17)	N1—C7—C12—F12	-4.9 (3)
N3—C1—C6—F6	-1.7 (3)	C8—C7—C12—C11	0.0 (3)
C2—C1—C6—C5	-0.6 (3)	N1—C7—C12—C11	173.28 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N3—H3 \cdots N1 ⁱ	0.88	2.23	3.076 (2)	162

Symmetry code: (i) $-x+1, -y, -z+1$.