| | | | | |
|---|---|---|---|---|
| O15 | 0.6413 (2) | 0.93930 (10) | 0.0747 (4) | 0.0331 (6) |
| O19 | 0.3091 (2) | 0.99390 (10) | 0.5199 (5) | 0.0382 (6) |
| N8 | 0.6712 (2) | 0.79920 (10) | −0.5981 (5) | 0.0298 (6) |
| C2 | 0.7835 (3) | 0.79050 (10) | −0.7568 (6) | 0.0325 (7) |
| C4 | 0.6137 (3) | 0.73810 (10) | −0.8353 (6) | 0.0360 (8) |
| C5 | 0.6217 (4) | 0.69050 (10) | −0.7765 (7) | 0.0380 (8) |
| C7 | 0.5628 (3) | 0.76570 (10) | −0.6090 (7) | 0.0396 (9) |
| C9 | 0.6640 (3) | 0.83420 (10) | −0.4253 (6) | 0.0280 (7) |
| C10 | 0.7622 (3) | 0.86850 (10) | −0.4344 (6) | 0.0312 (7) |
| C11 | 0.7506 (3) | 0.90240 (10) | −0.2632 (6) | 0.0306 (7) |
| C12 | 0.6425 (3) | 0.90340 (10) | −0.0802 (6) | 0.0290 (7) |
| C13 | 0.5454 (3) | 0.86980 (10) | −0.0710 (6) | 0.0325 (8) |
| C14 | 0.5564 (3) | 0.83560 (10) | −0.2424 (6) | 0.0319 (8) |
| C16 | 0.5271 (3) | 0.94480 (10) | 0.2533 (6) | 0.0293 (7) |
| C17 | 0.5473 (3) | 0.98980 (10) | 0.3631 (6) | 0.0317 (8) |
| C18 | 0.4551 (3) | 1.00020 (10) | 0.5934 (6) | 0.0304 (7) |
| C20 | 0.4781 (4) | 1.04590 (10) | 0.6872 (7) | 0.0425 (10) |
| C21 | 0.7069 (5) | 0.64030 (10) | −0.4822 (10) | 0.0580 (14) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| O1—C2 | 1.202 (4) | C4—C5 | 1.509 (4) |
| O3—C2 | 1.362 (4) | C4—C7 | 1.531 (5) |
| O3—C4 | 1.460 (4) | C9—C10 | 1.408 (4) |
| O6—C5 | 1.407 (4) | C9—C14 | 1.387 (4) |
| O6—C21 | 1.412 (5) | C10—C11 | 1.381 (4) |
| O15—C12 | 1.374 (4) | C11—C12 | 1.391 (4) |
| O15—C16 | 1.428 (4) | C12—C13 | 1.385 (4) |
| O19—C18 | 1.436 (3) | C13—C14 | 1.389 (4) |
| N8—C2 | 1.365 (4) | C16—C17 | 1.519 (4) |
| N8—C7 | 1.455 (4) | C17—C18 | 1.511 (4) |
| N8—C9 | 1.410 (4) | C18—C20 | 1.514 (4) |
| C2—O3—C4 | 110.0 (2) | N8—C9—C14 | 119.7 (3) |
| C5—O6—C21 | 111.0 (3) | C10—C9—C14 | 118.4 (3) |
| C12—O15—C16 | 118.9 (2) | C9—C10—C11 | 120.1 (3) |
| C2—N8—C7 | 112.1 (3) | C10—C11—C12 | 121.0 (3) |
| C2—N8—C9 | 125.0 (2) | O15—C12—C11 | 115.1 (3) |
| C7—N8—C9 | 122.7 (2) | O15—C12—C13 | 125.7 (3) |
| O1—C2—O3 | 120.8 (3) | C11—C12—C13 | 119.1 (3) |
| O1—C2—N8 | 129.5 (3) | C12—C13—C14 | 120.2 (3) |
| O3—C2—N8 | 109.7 (2) | C9—C14—C13 | 121.1 (3) |
| O3—C4—C5 | 109.3 (3) | O15—C16—C17 | 105.1 (2) |
| O3—C4—C7 | 105.1 (2) | C16—C17—C18 | 114.9 (2) |
| C5—C4—C7 | 114.0 (3) | O19—C18—C17 | 107.9 (2) |
| O6—C5—C4 | 109.6 (3) | O19—C18—C20 | 110.4 (3) |
| N8—C7—C4 | 102.2 (2) | C17—C18—C20 | 111.9 (3) |
| N8—C9—C10 | 121.9 (3) | | |
| C4—O3—C2—O1 | −178.4 (3) | C5—C4—C7—N8 | 129.6 (3) |
| C4—O3—C2—N8 | 2.7 (3) | O3—C4—C5—O6 | 60.1 (3) |
| C2—O3—C4—C5 | −130.9 (3) | C7—C4—C5—O6 | −57.1 (3) |
| C2—O3—C4—C7 | −8.2 (3) | O3—C4—C7—N8 | 10.1 (3) |
| C21—O6—C5—C4 | 172.1 (3) | N8—C9—C10—C11 | 179.4 (3) |
| C16—O15—C12—C11 | 174.8 (3) | C14—C9—C10—C11 | 0.3 (5) |
| C16—O15—C12—C13 | −3.8 (4) | N8—C9—C14—C13 | −179.4 (3) |
| C12—O15—C16—C17 | −172.2 (2) | C10—C9—C14—C13 | −0.3 (5) |
| C7—N8—C2—O1 | −174.3 (3) | C9—C10—C11—C12 | −0.1 (6) |
| C9—N8—C2—O1 | 0.4 (5) | C10—C11—C12—O15 | −178.7 (3) |
| C7—N8—C2—O3 | 4.5 (4) | C10—C11—C12—C13 | −0.1 (4) |
| C9—N8—C2—O3 | 179.2 (3) | O15—C12—C13—C14 | 178.6 (3) |
| C7—N8—C9—C10 | −173.7 (3) | C11—C12—C13—C14 | 0.1 (5) |
| C2—N8—C9—C14 | −168.7 (3) | C12—C13—C14—C9 | 0.1 (6) |
| C7—N8—C9—C14 | 5.4 (4) | O15—C16—C17—C18 | −169.2 (2) |
| C2—N8—C9—C10 | 12.2 (5) | C16—C17—C18—O19 | −56.7 (3) |
| C2—N8—C7—C4 | −9.2 (3) | C16—C17—C18—C20 | −178.4 (3) |
| C9—N8—C7—C4 | 176.0 (3) | | |

Table 3. *Hydrogen-bonding geometry* (Å, °)

| *D*—H···*A* | H···*A* | *D*—H···*A* |
|---|---|---|
| O19—H19···O19$^{i}$ | 2.850 (4) | 174.0 (50) |

Symmetry code: (i) $\frac{1}{2} - x, 2 - y, \frac{1}{2} + z$.

Most calculations were performed with *SHELX*76 (Sheldrick, 1976), the structure was solved using *SHELXS*86 (Sheldrick, 1985) and *PLATON* (Spek, 1990) was used for the generation of the CIF.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1994). **C50**, 1492–1494

# (*Z*,*Z*)-5-Anilino-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene-2-amine

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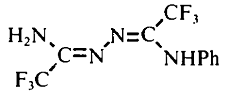
## Abstract

The title molecule, $C_{10}H_8F_6N_4$, has been characterized crystallographically, thus establishing its isomeric form. This form has a C═N—N═C substructure with a torsion angle of 145 (1)° about the N—N bond. There is an extensive hydrogen-bonding system, such that each

molecule is doubly bonded to each of two neighbours, related to the first by different twofold axes.

## Comment

The structure of (*Z*,*Z*)-5-chloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene-2-amine has recently been characterized crystallographically (Abdul-Ghani, Pritchard & Tipping, 1994). It reacts with aniline under anhydrous conditions to give the title molecule, (*Z*,*Z*)-5-anilino-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene-2-amine (I) and aniline hydrochloride. After purification by flash chromatography, the title molecule was recrystallized from *n*-pentane/dichloromethane (2:1 *v*/*v*).



(I)

A literature search (*CSSR*, 1984) revealed only one other molecule (Tinant, Declercq, van Meerssche, Bouvy, Janousek & Viehe, 1985), besides the chloro precursor of the title molecule (Abdul-Ghani, Pritchard & Tipping, 1994), possessing a similar CC(N)═N—N═C substructure to that of the title molecule. All three molecules have comparable bond lengths for this substructure. The title molecule and the chloro precursor are twisted about the N—N bond by similar amounts with torsion angles of 145(1) and 2 × 154(1)°, respectively (the chloro precursor has two molecules in the asymmetric unit), but the molecule of Tinant, Declercq, van Meerssche, Bouvy, Janousek & Viehe (1985) has two approximately planar C═N—N═C systems [177 and 180(1)°]. Hydrogen bonds observed in the title molecule are N3···H8—N8 (at $-x$, $y-x$, $\frac{2}{3}-z$) and N4···H72—N7 (at $y$, $x$, $1-z$) with N···N lengths of 3.00(1) and 2.99(1) Å, respectively. These hydrogen bonds generate two more by different twofold symmetry operations, such that the molecule at $x$, $y$, $z$ also has N8—H8···N3 and N7—H72···N4 hydrogen bonds and is doubly linked to each of the stated neighbours.

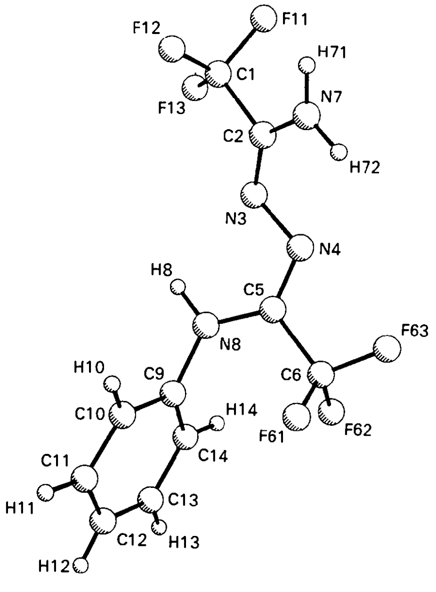


Fig. 1. The title molecule showing atom labelling.

## Experimental

*Crystal data*

$C_{10}H_8F_6N_4$
$M_r = 298.19$
Trigonal
$P3_221$
$a = 9.480$ (2) Å
$c = 24.792$ (2) Å
$V = 1929$ (1) Å$^3$
$Z = 6$
$D_x = 1.540$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6.5$–11.9°
$\mu = 0.151$ mm$^{-1}$
$T = 296$ K
Block
0.4 × 0.3 × 0.2 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3142 measured reflections
2075 independent reflections
773 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.038$
$\theta_{\max} = 24°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 8$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity variation: none

*Refinement*

Refinement on $F$
$R = 0.065$
$wR = 0.030$
$S = 2.37$
773 reflections
188 parameters
H-atom parameters not refined
Weights: default scheme in *TEXSAN* (Molecular Structure Corporation, 1985)

$(\Delta/\sigma)_{\max} = 0.07$
$\Delta\rho_{\max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.28$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{\text{eq}} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | Occupancy | $x$ | $y$ | $z$ | $B_{\text{eq}}$ |
|---|---|---|---|---|---|
| F11 | 0.85 (1) | −0.228 (02) | −0.4393 (14) | 0.4512 (06) | 9.5 (6) |
| F12 | 0.85 (1) | −0.031 (02) | −0.417 (02) | 0.4080 (09) | 11 (1) |
| F13 | 0.85 (1) | −0.198 (02) | −0.3597 (12) | 0.3710 (05) | 8.4 (7) |
| F61 | 1.00 | 0.4166 (09) | 0.4532 (08) | 0.4152 (03) | 8.8 (4) |
| F62 | 1.00 | 0.2015 (11) | 0.4654 (09) | 0.3945 (03) | 9.3 (5) |
| F63 | 1.00 | 0.2151 (09) | 0.3708 (08) | 0.4708 (02) | 9.0 (4) |
| N3 | 1.00 | 0.0008 (12) | −0.0634 (11) | 0.4038 (04) | 4.3 (5) |
| N4 | 1.00 | 0.0813 (12) | 0.0890 (11) | 0.4290 (04) | 4.6 (5) |
| N7 | 1.00 | 0.0383 (12) | −0.1668 (11) | 0.4872 (03) | 5.8 (6) |
| N8 | 1.00 | 0.2050 (10) | 0.1862 (11) | 0.3452 (03) | 5.2 (5) |
| C1 | 1.00 | −0.113 (02) | −0.348 (02) | 0.4132 (06) | 6.0 (8) |

| | | | | | |
|---|---|---|---|---|---|
| C2 | 1.00 | −0.014 (02) | −0.175 (02) | 0.4367 (05) | 4.1 (7) |
| C5 | 1.00 | 0.172 (02) | 0.202 (02) | 0.3969 (05) | 4.4 (7) |
| C6 | 1.00 | 0.257 (02) | 0.379 (02) | 0.4185 (06) | 7.1 (9) |
| C9 | 1.00 | 0.3135 (14) | 0.3121 (14) | 0.3082 (05) | 4.6 (6) |
| C10 | 1.00 | 0.461 (02) | 0.326 (02) | 0.2956 (05) | 7.6 (8) |
| C11 | 1.00 | 0.5649 (14) | 0.435 (02) | 0.2581 (05) | 8.1 (9) |
| C12 | 1.00 | 0.522 (02) | 0.5394 (14) | 0.2344 (05) | 6.8 (9) |
| C13 | 1.00 | 0.376 (02) | 0.529 (02) | 0.2443 (06) | 8 (1) |
| C14 | 1.00 | 0.2692 (14) | 0.414 (02) | 0.2818 (05) | 6.7 (7) |
| F14 | 0.15 (1) | −0.092 (10) | −0.362 (08) | 0.361 (02) | 9.0 |
| F15 | 0.15 (1) | −0.069 (10) | −0.458 (12) | 0.436 (03) | 9.0 |
| F16 | 0.15 (1) | −0.266 (07) | −0.414 (11) | 0.424 (04) | 9.0 |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| F11—C1 | 1.37 (2) | N8—C5 | 1.35 (2) |
| F12—C1 | 1.25 (3) | N8—C9 | 1.45 (1) |
| F13—C1 | 1.29 (2) | C1—C2 | 1.54 (2) |
| F61—C6 | 1.31 (2) | C5—C6 | 1.55 (2) |
| F62—C6 | 1.32 (2) | C9—C10 | 1.37 (2) |
| F63—C6 | 1.35 (2) | C9—C14 | 1.40 (2) |
| N3—N4 | 1.40 (1) | C10—C11 | 1.38 (2) |
| N3—C2 | 1.29 (2) | C11—C12 | 1.38 (2) |
| N4—C5 | 1.27 (1) | C12—C13 | 1.36 (3) |
| N7—C2 | 1.33 (1) | C13—C14 | 1.40 (2) |
| N4—N3—C2 | 110.1 (9) | N4—C5—N8 | 127 (1) |
| N3—N4—C5 | 113 (1) | N4—C5—C6 | 118 (1) |
| C5—N8—C9 | 128.3 (9) | N8—C5—C6 | 115 (1) |
| F11—C1—F12 | 104 (2) | F61—C6—F62 | 110 (1) |
| F11—C1—F13 | 104 (1) | F61—C6—F63 | 109 (1) |
| F11—C1—C2 | 106 (1) | F61—C6—C5 | 113 (2) |
| F12—C1—F13 | 113 (2) | F62—C6—F63 | 106 (2) |
| F12—C1—C2 | 113 (1) | F62—C6—C5 | 111 (1) |
| F13—C1—C2 | 115 (1) | F63—C6—C5 | 107 (1) |
| C2—C1—F14 | 116 (3) | N8—C9—C10 | 119 (1) |
| C2—C1—F15 | 112 (3) | N8—C9—C14 | 122 (1) |
| C2—C1—F16 | 112 (5) | C10—C9—C14 | 118 (1) |
| F14—C1—F15 | 102 (6) | C9—C10—C11 | 122 (2) |
| F14—C1—F16 | 110 (6) | C10—C11—C12 | 118 (2) |
| F15—C1—F16 | 104 (6) | C11—C12—C13 | 122 (1) |
| N3—C2—N7 | 132 (1) | C12—C13—C14 | 119 (2) |
| N3—C2—C1 | 113 (1) | C9—C14—C13 | 120 (1) |
| N7—C2—C1 | 115 (1) | | |

The structure was solved using direct methods (*MITHRIL*; Gilmore, 1984) in the space group $P3_2$ (No. 145) which requires two molecules in the asymmetric unit; the two molecules found were clearly related by a twofold axis at $(\frac{2}{3},y,\frac{1}{2})$. Space group $P3_2$ has equivalent $3_2$ axes at $(\frac{2}{3},\frac{1}{3},z)$ and $(0,0,z)$. A change to space group $P3_221$ (No. 154) was implied, but its $3_2$ axes were no longer equivalent; the added twofold axes pass through $(0,0,z)$. The solution of the present structure in $P3_221$ was achieved in two steps. First, $x$ and $y$ coordinates were reduced by $\frac{2}{3}$ and $\frac{1}{3}$, respectively, moving the known twofold axis to $(0,y-\frac{1}{3},\frac{1}{2})$, placing the molecules around the $3_2$ axis at $(0,0,z)$, but requiring a $z$ translation of $-\frac{1}{6}$ to bring the molecules to valid equivalent positions in $P3_221$. The known twofold axis was now at $(0,y-\frac{1}{3},\frac{1}{3})$, which may be redesignated as $(0,x,\frac{1}{3})$ which is acceptable in $P3_221$ and requires only one molecule per asymmetric unit. Data collection and cell refinement: CAD-4 software. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *CIF* (Hall, Allen & Brown, 1991).

The CAD-4 diffractometer was funded by the SERC which is also thanked for funding the Chemical Databank Services used for cystallographic literature searches.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Methyl-α-D-galacturonic Acid Methyl Ester

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## Abstract

The structure of methyl methyl-α-D-galacturonoate monohydrate, $C_8H_{14}O_7.H_2O$, has been redetermined. The sugar ring has the expected $^4C_1$ conformation. The orientation of the methoxy group is *gauche-trans* and

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