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Synthesis, molecular and crystal structures of 4-amino-3,5-difluorobenzonitrile, ethyl 4-amino-3,5-difluorobenzoate, and diethyl 4,4′-(diazene-1,2-diyl)bis(3,5-difluorobenzoate)

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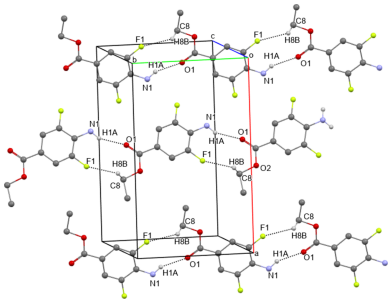
The crystal structures of two intermediates, 4-amino-3,5-difluorobenzonitrile, $C_7H_4F_2N_2$ (**I**), and ethyl 4-amino-3,5-difluorobenzoate, $C_9H_9F_2NO_2$ (**II**), along with a visible-light-responsive azobenzene derivative, diethyl 4,4′-(diazene-1,2-diyl)bis(3,5-difluorobenzoate), $C_{18}H_{14}F_4N_2O_4$ (**III**), obtained by four-step synthetic procedure, were studied using single-crystal X-ray diffraction. The molecules of **I** and **II** demonstrate the quinoid character of phenyl rings accompanied by the distortion of bond angles related to the presence of fluorine substituents in the 3 and 5 (*ortho*) positions. In the crystals of **I** and **II**, the molecules are connected by N—H···N, N—H···F and N—H···O hydrogen bonds, C—H···F short contacts, and π-stacking interactions. In crystal of **III**, only stacking interactions between the molecules are found.

1. Chemical context

Azobenzene and its derivatives have different absorbance depending on the molecular conformation (*trans* or *cis*) around the central N═N bond (Mostad & Rømming, 1971; Harada *et al.*, 1997) and molecular architecture. Recently, derivatives of azobenzene, known as pharmacophores, whose activity can be altered *via* the application of excitation sources with different wavelengths, started being used as molecular tools for controlling biological processes (Aggarwal *et al.*, 2020; Gutzeit *et al.*, 2021). The development of new pharmacophores can be achieved *via* alteration of the molecular properties by changing the chemical structure, shape, polarity, and other molecular characteristics.

It was indicated (Bléger *et al.*, 2012; Knie *et al.*, 2014) that fluorination of benzene rings in azobenzene in *ortho* positions to the N═N group along with the introduction of electron-withdrawing groups in a *para* position can help to achieve higher isomer conversion to the *cis* form when compared to other azobenzene derivatives. In addition, it was observed that the thermal stability of the *cis* isomers of *ortho* fluorinated azobenzenes compared to non-fluorinated materials was significantly increased from 5 h to 700 days (Bléger *et al.*, 2012).

Another interesting application of azobenzene-based organic materials was presented by Peng and co-workers (Peng *et al.*, 2022), who demonstrated that the non-centrosymmetric 2-amino-2′,4,4′,6,6′-pentafluoroazobenzene was a single-component ferroelectric. In that publication, it was stated that the above-mentioned material was the first single-



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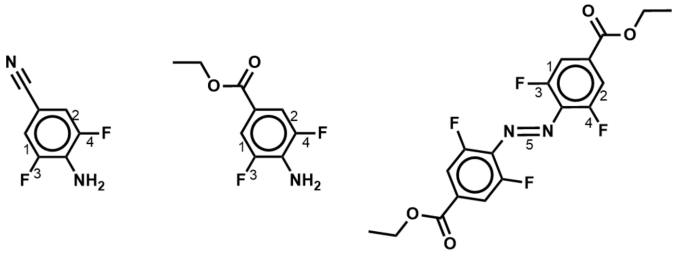
component organic ferroelectric that opened the way to the design and exploration of azobenzene-based ferroelectrics with promising applications in biofriendly ferroelectric devices.



(I) (II) (III)

Herein, the synthetic protocols for two intermediates, 4-amino-3,5-difluorobenzonitrile (**I**), ethyl 4-amino-3,5-difluorobenzoate (**II**), and an azobenzene derivative with the fluorine atoms in *ortho*-positions and ester group in a *para*-position, namely, diethyl-4,4′-(2,2′,6,6′-tetrafluoro)azobenzene dicarboxylate (**III**) obtained in four-step synthesis using a modified synthetic procedure (Appiah *et al.*, 2017) are reported along with the comprehensive X-ray structural study of these materials in the solid state. The synthesized azobenzene derivative might be used as a precursor for further development and application in photopharmacological studies. It has been shown that fluorinated azobenzenes can be used also for the synthesis of photoresponsive main-chain oligomers with azobenzene moieties incorporated in linear unsaturated or saturated polyolefins on a gram scale (Appiah *et al.*, 2017).

2. Structural commentary

The geometric parameters of molecule **I** (Table 1, Fig. 1) are very similar to those found in related structures lacking fluorine substituents. For example, a comparison of the geometrical parameters of **I** with those of 4-aminobenzonitrile (Merlino & Sartori, 1982; Heine *et al.*, 1994; Islor *et al.*, 2013; Alimi *et al.*, 2018) in which there are no fluorine substituents, shows their similarity. However, while in 4-aminobenzonitrile (Alimi *et al.*, 2018), the angles in the phenyl ring are almost the same (from 118.5 to 120.8°), in **I**, the C6—C5—C4 angle with the value 114.5 (1)° is more acute than the C7—C6—C5 [124.4 (1)°] and C5—C4—C3 [124.2 (1)°] angles, mainly due to the influence of highly electronegative fluorine substituents. It also can be noted, that the cyano group bond length C1≡N1 [1.146 (2) Å] is slightly longer than the literature value (1.136 Å; Allen *et al.*, 1987). Increased conjugation can lead to a slight reduction in bond order, potentially lengthening and somewhat weakening the triple bond compared to a non-conjugated nitrile (Allen *et al.*, 1987).

Likewise, the bond lengths and angles in **II** (Table 1, Fig. 1) are very similar to those reported previously for related structures, for instance, for the molecule of ethyl-4-aminobenzoate (similar to molecule **II**, without fluorine substituents) that was reported in several publications (Lynch & McClenaghan, 2002; Chan & Welberry, 2010; Patyk-Kaźmierczak & Kaźmierczak, 2020). The molecular structure in the most recent paper (Patyk-Kaźmierczak & Kaźmierczak, 2020) demonstrated equal distances of 1.390 Å between the carbon atoms in the phenyl ring.

Table 1
Selected bond lengths (Å) in molecules of **I**–**III**.

Bond/Compound	I	II	III
1	1.373 (2)	1.372 (4)	1.373 (3)
2	1.377 (2)	1.365 (4)	1.373 (3)
3	1.360 (1)	1.360 (3)	1.345 (2)
4	1.360 (1)	1.368 (3)	1.341 (2)
5	–	–	1.252 (3)

The geometric parameters of molecule **III** (Table 1, Fig. 1) are very similar to those found in related structures. There are few structures reported in the literature (Kerckhoffs *et al.*, 2022; Hermann *et al.*, 2017; Bushuyev *et al.*, 2016; Saccone *et al.*, 2014, and Aggarwal *et al.*, 2020) featuring *trans*-azobenzene with halogen substituents at the 2- and 6-positions. However, there are two structures that have been found to incorporate the diethyl-4,4′-azobenzene dicarboxylate moiety (Niu *et al.*, 2011; Gajda *et al.*, 2014). In both those structures, the molecules are planar. The title structure **III** is centrosymmetric, the phenyl rings are planar. The N1═N1′ distance [1.252 (3) Å] is very close to the distances presented in the literature. In the molecule of **II**, the C7═O1 distance is 1.212 (4) Å, and in the molecule of **III** the distance C7═O1 is equal to 1.211 (2) Å. Those values are close to the statistical mean value of 1.221 Å (Allen *et al.*, 1987).

For a convenient comparison of the molecular geometries of **I**–**III**, some bond lengths and their notations are presented in Scheme 1 and Table 1. From Table 1, it is clear that in all molecules the C—F bonds are characterized by very similar

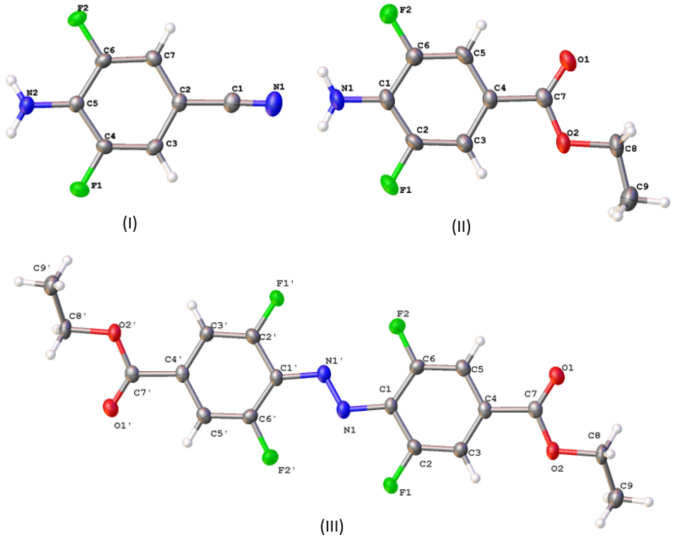


Figure 1
Molecular structures of **I**, **II**, **III** with the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (′) $1-x, 1-y, 2-z$ for **III**.

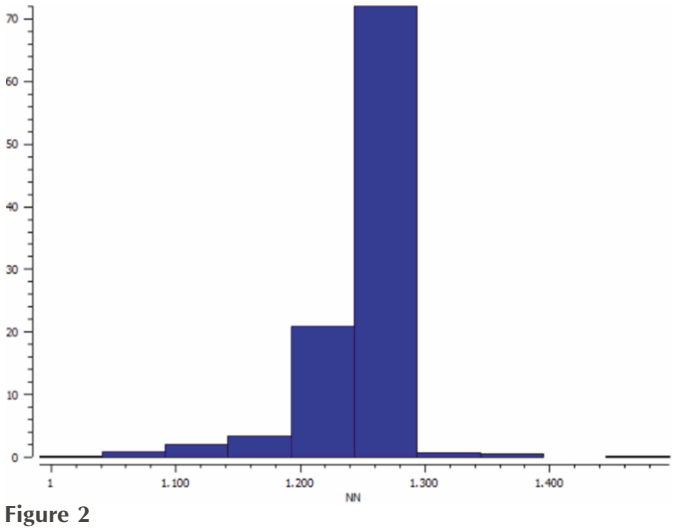


Figure 2
Histogram of N═N bond-length distribution in azobenzene derivatives.

bond lengths. As a result of the *para* position of the donor and acceptor substituents of the phenyl rings, it is expected that this ring should have quinoid character (Zyss, 1994). Indeed, bond lengths 1 and 2 (see Scheme 1 and Table 1) are reduced if compared with the other bond lengths in the phenyl rings (see supporting information).

The length of the double N═N bond in molecule **III** corresponds to a standard value for this series of compounds. Using CSD Version 5.45 (update of June 2024; Groom *et al.*, 2016), a statistical analysis of the N═N bonds in 2261 Ph—N═N—Ph fragments from 1733 crystal structures was carried out. A histogram of the bond-length distribution with a mean bond value of 1.246 Å, median 1.253 Å and su 0.034 Å is presented in Fig. 2. It clearly demonstrates that the central bond length in molecule **III** corresponds to the median value of such bonds.

The molecule of **III**, in contrast to the previously studied molecule of diethyl 4,4′-(diazenediyl)dibenzoate (DDB; Niu *et al.*, 2011) without F substituents, is not planar. The torsion angle that characterizes the position of the phenyl rings relative to the central C—N═N—C fragment is equal to 17.2 (3) ° in **III** and 0.2 (2) ° in DDB. It can be explained by the intramolecular steric interactions between F and N atoms in **III**, N1···F1 = 2.644 (2) Å and N1···F2 = 2.945 (2) Å, which are slightly shorter than sum of van der Waals radii (Batsanov, 2001). An overlay of molecules **III** and DDB demonstrates the molecular similarity with the exception of the orientation of the terminal Me groups (See Fig. 3).

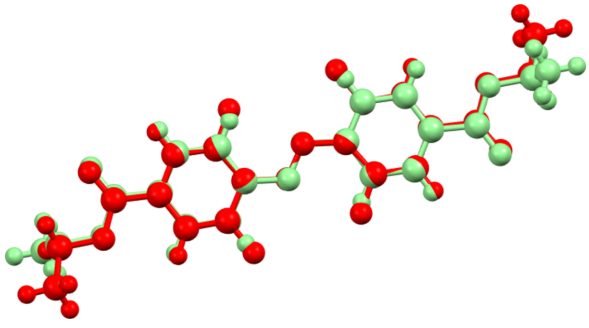


Figure 3
Overlay of molecules **III** (red) and DDB (green) with r.m.s. 0.121.

Table 2
Hydrogen-bond geometry (Å, °) for **I**.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1^{i}	0.82 (2)	2.28 (2)	3.0297 (17)	153 (2)
N2—H2B···F2^{ii}	0.88 (2)	2.38 (2)	3.2526 (15)	173.9 (19)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Table 3
Hydrogen-bond geometry (Å, °) for **II**.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.85 (3)	2.15 (4)	2.942 (3)	155 (3)
C8—H8B···F1^{ii}	0.99	2.46	3.015 (3)	115

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$.

3. Supramolecular features

The packing in the crystal of **I** is defined by weak N–H···N and N–H···F H-bonds (Fig. 4 and Table 2), and π-stacking interactions with interplanar distances between the overlapping phenyl rings equal to 3.3573 (8) Å and distances between the ring centroids equal to 3.7283 (4) Å. The parameters of the short contacts correspond to the average D···A distances for specific interactions [N—H···N = 2.9–3.0 Å (Prasad & Govil, 1980) and N—H···F = 2.427 Å (Taylor, 2017)]. Interplanar distances for stacking interactions are slightly shorter than the interplanar distance in graphite (3.42 Å), indicating the significant role of stacking interactions in this crystal. As a result of the hydrogen bonding, molecules of **I** form chains along the (101) direction.

In the crystal of **II**, N—H···O hydrogen bonds and C—H···F short contacts are found (Fig. 5, Table 3) as well as π–π-stacking interactions with interplanar distances between phenyl rings equal to 3.325 (3) Å and distances between ring centroids of 3.490 (3) Å. The parameters of the short contacts correspond to the average D···A distances for specific inter-

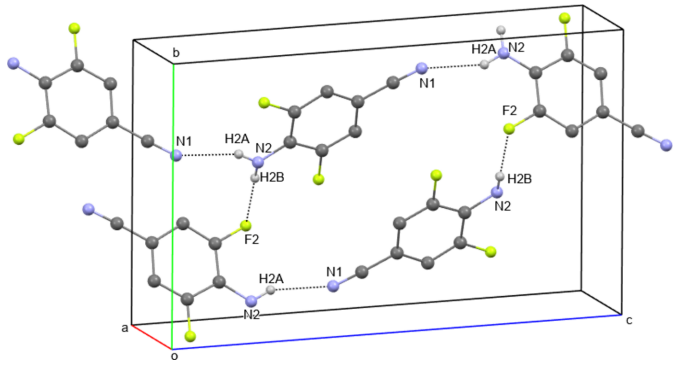


Figure 4
The packing in the crystal of **I**. Hydrogen bonds are shown as dotted lines. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

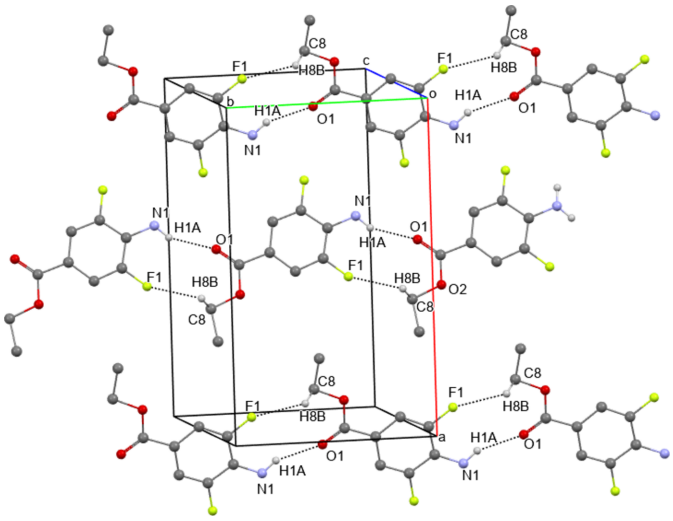


Figure 5
The packing in the crystal of **II**. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not participating in hydrogen bonding are omitted for clarity.

actions (N—H···O = 2.7–3.3 Å (Bakker *et al.*, 2023) and N—H···F = 2.427 (6) Å (Taylor, 2017)]. As a result of hydrogen bonding, molecules of **II** form chains along the *b*-axis direction. In the structures of both **I** and **II**, short intramolecular contacts of the type N–H···F are observed.

The relative orientations of the molecular cores in structure **III** (Fig. 6) and in the analogous crystal structure of *trans*-1,2-bis(4-bromo-2,6-difluorophenyl)diazene (Broichhagen *et al.*, 2015) are similar. In the crystal of **III**, the interplanar distance between the molecular core containing the phenyl rings and the N═N bond is 3.324 (13) Å and intercentroid distance is 4.6106 (17) Å. The nearest distance of the azo group N atom

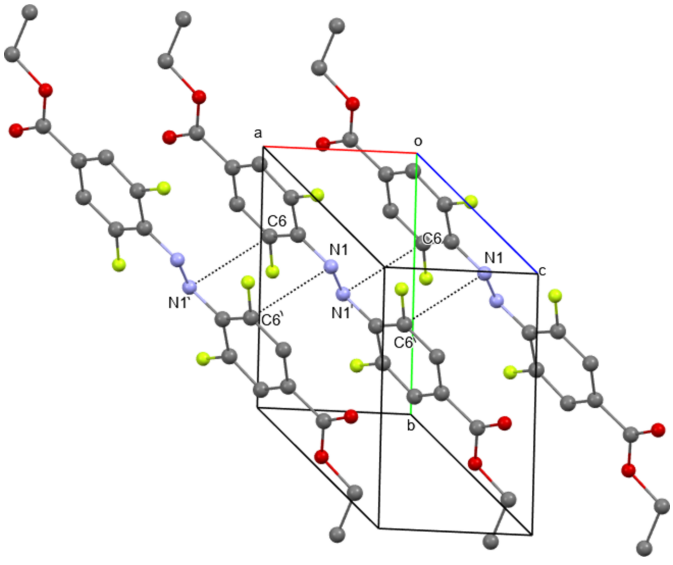


Figure 6
The packing in the crystal of **III**. Stacking short contacts are shown as dashed lines. Hydrogen atoms are omitted for clarity. N1···C6($-x$, $1-y$, $2-z$) = 3.184 (3) Å.

to the carbon atom in the phenyl ring N1···C6 is 3.184 (3) Å, and the distance to the ring centroid is 3.465 (19) Å. The distance between carbonyl atom O1 and the nearest C atom in the phenyl ring is 3.316 (2) Å and to the ring centroid is 3.351 (18) Å. As a result of π–π stacking, the molecules of **III** form chains along the [01$\bar{1}$] direction.

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.45, update of June 2024; Groom *et al.*, 2016) for 4-amino-3,5-difluorobenzonitrile (**I**) revealed that the structure had not previously been published. However, a similar structure without fluorine substituents in the ring, 4-amino-benzonitrile, had been described and demonstrated the possibility of different polymorphs [Alimi *et al.*, 2018 (BERTOH03); Merlino & Sartori, 1982 (BERTOH); Heine *et al.*, 1994 (BERTOH01); Islor *et al.*, 2013 (BERTOH02)] all of which crystallize in centrosymmetric space groups, except for BERTOH01 (Heine *et al.*, 1994) which crystallizes in the non-centrosymmetric $P2_12_12_1$ space group.

The novelty of 4-amino-3,5-difluorobenzoate (**II**) was also confirmed by the lack of this structure in the CSD. The closest analogue without fluorine substituents in the phenyl ring is ethyl 4-amino-benzoate (benzocaine), an anesthetic applied in medicine and the pharmaceutical industry and described as 19 database entries. Eight of the structures were reported by Patyk-Kaźmierczak & Kaźmierczak (2020) (QQQAXG11–18), which represent several polymorphs in the same $P2_1/c$ space group but with different cell parameters. Other structures were reported by Patel *et al.* (2017) (QQQAXG09–10) where two polymorphs of benzocaine were described in space groups $P2_12_12_1$ and $P2_1/c$. Earlier, these structures were mentioned by Chan & Welberry (2010) and Lynch & McClenaghan (2002).

The structure of diethyl-4,4′-(2,2′,6,6′-tetrafluoro)azobenzene dicarboxylate (**III**) had also not been deposited in the CSD. However, similar *tetra*-halogenated molecules with the halogens in *ortho* positions have been described (Kerckhoffs *et al.*, 2022; TETROD). It should be mentioned that molecules of *cis* and *trans* (*Z* and *E*) isomers were structurally characterized when it was possible to separate them and when the *cis* isomers had a long half-life to facilitate their isolation. The authors showed that it was possible to modify the stability of the *cis* isomers by introducing larger halogen atoms in the *ortho* positions and a heavier element substituent in the *para* position. If the azo-benzene molecules with small substituents (H, F) in the *ortho* positions are planar, with larger halogens (I) they are non-planar, and their *cis* isomers are more stable. It is important to mention that the *ortho*-tetrafluoroazobenzenes (DIQBOX; Hermann *et al.*, 2017) resulting from isomerization of the molecule, resulted in significant shape changes, with the *trans* isomer exhibiting elongation and the *cis* isomer adopting a more spherical shape. In addition, diethyl-4,4′-azobenzene dicarboxylate, which represents the non-halogenated analogue of compound **III** [Niu *et al.*, 2011 (AZUKAI); Gajda *et al.*, 2014 (AZUKAI01)], has a planar

Table 4
Experimental details.

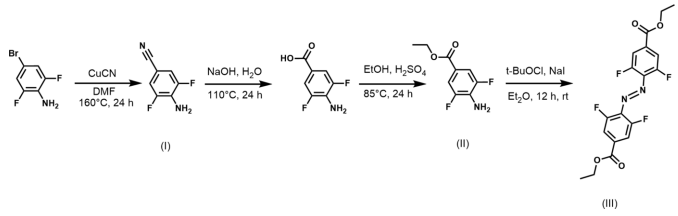
	I	II	III
Crystal data			
Chemical formula	$C_7H_4F_2N_2$	$C_9H_9F_2NO_2$	$C_{18}H_{14}F_4N_2O_4$
M_r	154.12	201.17	398.31
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $Pbcn$	Triclinic, $P\overline{1}$
Temperature (K)	100	100	100
a, b, c (Å)	3.7283 (4), 10.5275 (12), 16.9073 (19)	14.877 (3), 8.9995 (18), 13.635 (3)	4.6106 (17), 8.839 (3), 10.969 (4)
α, β, γ (°)	90, 94.604 (2), 90	90, 90, 90	99.330 (8), 99.431 (8), 96.442 (7)
V (Å^3)	661.46 (13)	1825.6 (6)	430.7 (3)
Z	4	8	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.14	0.13	0.14
Crystal size (mm)	0.36 × 0.22 × 0.12	0.21 × 0.13 × 0.11	0.57 × 0.13 × 0.1
Data collection			
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker *SMART* APEXII
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.661, 0.746	0.973, 0.986	0.926, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11242, 2140, 1775	29363, 1665, 1265	3269, 1913, 1414
R_{int}	0.029	0.114	0.023
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.738	0.600	0.649
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.130, 1.09	0.060, 0.131, 1.21	0.047, 0.150, 1.01
No. of reflections	2140	1665	1913
No. of parameters	108	136	132
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, −0.23	0.20, −0.27	0.28, −0.29

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2019), SHELXT (Sheldrick, 2015*a*), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

arrangement in the *trans* isomers. However, if the *ortho* positions are occupied by bulky iodine substituents, such as in diethyl 4,4′-diazenediylbis(3,5-diiodobenzoate), the molecule is non-planar in the *trans* form (TETROD; Kerckhoffs *et al.*, 2022). In addition, some non-halogenated and halogenated azobenzenes, both *cis* and *trans* isomers, have been studied [Hampson & Robertson,1941 (AZBENC); Mostad *et al.*, 1971 (AZBENC01); De Lange *et al.*, 1939 (AZOBEN); Chinnakali *et al.*, 1993 (WACHAJ); Harada *et al.*, 1997 (AZOBEN04–06; Bushuyev *et al.*, 2016 (SUWKIG); Saccone *et al.*, 2014 (PINLUV); Aggarwal *et al.*, 2020 (TUXNEI and TUXNAE)].

5. Synthesis and crystallization

The synthesis of molecules **I–III** is shown in the reaction scheme, and follows a slight modification of the procedure described previously (Appiah *et al.*, 2017). Starting materials were purchased from Ambeed Inc. and Sigma-Aldrich and used without further purification. To obtain 4-amino-3,5-difluorobenzonitrile (**I**), 4-bromo-2,6-difluoroaniline (50.0 g, 240 mmol, 1 eq.) and CuCN (64.5 g, 720 mmol, 3 eq.) were suspended in dimethylformamide (DMF, 500 mL) and refluxed for 24 h. The mixture was cooled to room temperature and NH_4OH (2 L, 18%) was added, and the resulting solution was filtered. The mixture (filtrate) was extracted with EtOAc (4 × 750 mL) and the organic phase was washed with NH_4OH 18%, de-ionized water, brine, dried with Na_2SO_4, and filtered. The residue was purified through a silica gel plug with CH_2Cl_2/*n*-hexane 2:1, to yield a dark-brown solid (15.7 g, 102 mmol, 42% yield).



The synthesis of 4-amino-3,5-difluorobenzoic acid was conducted by treating 4-amino-3,5-difluorobenzonitrile (14.91 g, 96.7 mmol, 1 eq.) with sodium hydroxide (NaOH 1 *M*, 480 mL). The resulting solution was heated to reflux for 24 h. The reaction was then cooled to room temperature and HCl conc. (60 mL) was added to the reaction mixture dropwise until the reaction turned acidic pH ∼1; the product precipitated as a hydrochloride salt. The salt was then dissolved in ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under vacuum to obtain 4-amino-3,5-difluorobenzoic acid (14.9 g, 81.4 mmol, 84.2%).

To obtain 4-amino-3,5-difluorobenzoate (**II**), 4-amino-3,5-difluorobenzoic acid (14.9 g, 96.7 mmol) was dissolved in

ethanol (300 mL) and H_2SO_4 (6 mL) and refluxed for 10 h. The reaction was neutralized using a saturated solution of sodium bicarbonate, followed by extraction with dichloromethane (DCM, 4 × 300 mL). The organic phase was dried using sodium sulfate (Na_2SO_4), filtered, and concentrated under reduced pressure, yielding the intermediate product (14.99 g, 75 mmol, 77% yield).

To obtain diethyl-4,4′-(2,2′,6,6′-tetrafluoro)azobenzene dicarboxylate (**III**), 4-amino-3,5-difluorobenzoate (12.0 g, 60 mmol, 1 eq.) and sodium iodide (NaI) (18.4 g, 120 mmol, 2 eq.) in Et_2O (400 mL) were added into a 1 L flask. To the reaction mixture, *tert*-butyl hypochlorite (*t*-BuOCl, 14 mL, 4 eq.) was added and the resulting mixture was stirred for 12 h at rt. Thereafter, a freshly prepared solution of 1 *M* Na_2SO_3 (1200 mL) was added, and the mixture was mixed thoroughly. The resulting mixture was washed by DCM (1 × 600 mL) and the organic layer was collected and washed with RO water (3 × 1L) and brine (3 x 750 mL), dried with Na_2SO_4 (anhydrous), filtered, purified through a silica gel plug and evaporated under reduced pressure. The crude product was rinsed with a small amount of EtOAc to yield a reddish precipitate (4.9 g, 12.4 mmol, 21% yield).

Crystallization of all compounds for diffraction studies was performed using the slow evaporation method. All solutions were prepared by dissolving compounds **I**–**III** in DCM (2 mL) and sonicating them for 10 min. Then they were capped with cotton plugs and left in the hood for 4 days. Thereafter transparent plate-like crystals of **I** and **II**, and dark-red needle-like crystals of **III** were obtained.

6. Refinement

Crystal data, data collection and structure refinement details for compounds **I, II**, and **III** are summarized in Table 4. The acidic N–H protons in **I** and **II** were localized from the residual electron-density map and refined freely. All other H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(C-methyl).

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Synthesis, molecular and crystal structures of 4-amino-3,5-difluorobenzonitrile, ethyl 4-amino-3,5-difluorobenzoate, and diethyl 4,4′-(diazene-1,2-diyl)bis(3,5-difluorobenzoate)

Egor M. Novikov, Jesus Guillen Campos, Javier Read de Alaniz, Marina S. Fonari and Tatiana V. Timofeeva

Computing details

4-Amino-3,5-difluorobenzonitrile (I)

Crystal data

$C_7H_4F_2N_2$
M_r = 154.12
Monoclinic, $P2_1/n$
a = 3.7283 (4) Å
b = 10.5275 (12) Å
c = 16.9073 (19) Å
β = 94.604 (2)°
V = 661.46 (13) Å^3
Z = 4
$F(000)$ = 312
D_x = 1.548 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4913 reflections
θ = 2.3–31.2°
μ = 0.14 mm^{-1}
T = 100 K
Block, clear colourless
0.36 × 0.22 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube, EIGENMANN GmbH
Graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.661, T_{max} = 0.746
11242 measured reflections
2140 independent reflections
1775 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 31.7°, θ_{min} = 2.3°
$h = -5 \rightarrow 5$
$k = -14 \rightarrow 15$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.130
S = 1.09
2140 reflections
108 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.2291P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.8337 (2)	0.47654 (7)	0.39927 (5)	0.0311 (2)
F2	0.3651 (2)	0.80481 (8)	0.23493 (4)	0.0314 (2)
N2	0.6762 (3)	0.56770 (11)	0.24999 (7)	0.0276 (3)
N1	0.2518 (4)	0.89360 (14)	0.57454 (7)	0.0379 (3)
C6	0.4379 (3)	0.75726 (11)	0.30925 (7)	0.0206 (2)
C4	0.6741 (3)	0.59252 (11)	0.39189 (7)	0.0207 (2)
C5	0.6003 (3)	0.63732 (11)	0.31445 (6)	0.0194 (2)
C2	0.4317 (3)	0.77685 (12)	0.44923 (7)	0.0217 (2)
C7	0.3518 (3)	0.82791 (11)	0.37357 (7)	0.0215 (2)
H7	0.241446	0.908931	0.366727	0.026*
C3	0.5960 (3)	0.65780 (12)	0.45866 (7)	0.0224 (2)
H3	0.652163	0.622977	0.509999	0.027*
C1	0.3337 (4)	0.84385 (13)	0.51849 (8)	0.0267 (3)
H2A	0.671 (6)	0.602 (2)	0.2066 (14)	0.047 (6)*
H2B	0.814 (5)	0.500 (2)	0.2560 (12)	0.036 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0404 (5)	0.0221 (4)	0.0309 (4)	0.0075 (3)	0.0035 (3)	0.0050 (3)
F2	0.0466 (5)	0.0272 (4)	0.0199 (4)	0.0021 (3)	−0.0008 (3)	0.0057 (3)
N2	0.0384 (6)	0.0244 (5)	0.0208 (5)	0.0015 (5)	0.0065 (4)	−0.0020 (4)
N1	0.0425 (7)	0.0426 (7)	0.0299 (6)	−0.0056 (6)	0.0099 (5)	−0.0095 (5)
C6	0.0227 (5)	0.0204 (5)	0.0185 (5)	−0.0036 (4)	0.0008 (4)	0.0032 (4)
C4	0.0214 (5)	0.0173 (5)	0.0236 (5)	−0.0008 (4)	0.0025 (4)	0.0022 (4)
C5	0.0190 (5)	0.0192 (5)	0.0202 (5)	−0.0045 (4)	0.0034 (4)	−0.0001 (4)
C2	0.0201 (5)	0.0240 (6)	0.0213 (5)	−0.0049 (4)	0.0040 (4)	−0.0031 (4)
C7	0.0208 (5)	0.0185 (5)	0.0252 (5)	−0.0011 (4)	0.0023 (4)	−0.0008 (4)
C3	0.0231 (5)	0.0256 (6)	0.0187 (5)	−0.0037 (4)	0.0017 (4)	0.0029 (4)
C1	0.0267 (6)	0.0286 (6)	0.0253 (6)	−0.0056 (5)	0.0046 (4)	−0.0034 (5)

Geometric parameters (Å, º)

F1—C4	1.3596 (14)	C4—C5	1.3982 (16)
F2—C6	1.3596 (13)	C4—C3	1.3726 (16)
N2—C5	1.3617 (15)	C2—C7	1.3975 (17)
N2—H2A	0.82 (2)	C2—C3	1.3984 (17)
N2—H2B	0.88 (2)	C2—C1	1.4390 (17)
N1—C1	1.1455 (18)	C7—H7	0.9500

C6—C5	1.4000 (16)	C3—H3	0.9500
C6—C7	1.3765 (16)		

C5—N2—H2A	119.3 (15)	C4—C5—C6	114.49 (10)
C5—N2—H2B	120.1 (13)	C7—C2—C3	120.55 (11)
H2A—N2—H2B	115.7 (19)	C7—C2—C1	120.46 (11)
F2—C6—C5	116.31 (10)	C3—C2—C1	118.95 (11)
F2—C6—C7	119.29 (11)	C6—C7—C2	117.98 (11)
C7—C6—C5	124.39 (11)	C6—C7—H7	121.0
F1—C4—C5	116.14 (10)	C2—C7—H7	121.0
F1—C4—C3	119.63 (10)	C4—C3—C2	118.35 (10)
C3—C4—C5	124.23 (11)	C4—C3—H3	120.8
N2—C5—C6	123.49 (11)	C2—C3—H3	120.8
N2—C5—C4	122.01 (11)	N1—C1—C2	177.81 (15)

F1—C4—C5—N2	1.45 (17)	C7—C6—C5—N2	178.51 (12)
F1—C4—C5—C6	−179.65 (10)	C7—C6—C5—C4	−0.36 (17)
F1—C4—C3—C2	−179.98 (10)	C7—C2—C3—C4	−0.41 (17)
F2—C6—C5—N2	−1.79 (17)	C3—C4—C5—N2	−178.59 (12)
F2—C6—C5—C4	179.34 (10)	C3—C4—C5—C6	0.31 (17)
F2—C6—C7—C2	−179.65 (10)	C3—C2—C7—C6	0.36 (17)
C5—C6—C7—C2	0.04 (18)	C1—C2—C7—C6	−177.28 (11)
C5—C4—C3—C2	0.06 (18)	C1—C2—C3—C4	177.26 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1^{i}	0.82 (2)	2.28 (2)	3.0297 (17)	153 (2)
N2—H2*B*···F2^{ii}	0.88 (2)	2.38 (2)	3.2526 (15)	173.9 (19)

Symmetry codes: (i) x+1/2, −y+3/2, z−1/2; (ii) −x+3/2, y−1/2, −z+1/2.

Ethyl 4-amino-3,5-difluorobenzoate (II)

Crystal data

$C_9H_9F_2NO_2$
M_r = 201.17
Orthorhombic, *Pbcn*
a = 14.877 (3) Å
b = 8.9995 (18) Å
c = 13.635 (3) Å
V = 1825.6 (6) Å^3
Z = 8
F(000) = 832
D_x = 1.464 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3255 reflections
θ = 2.7–23.4°
μ = 0.13 mm^{-1}
T = 100 K
Block, clear colourless
0.21 × 0.13 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube, EIGENMANN GmbH
Graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.973, T_{max} = 0.986

29363 measured reflections
1665 independent reflections
1265 reflections with $I > 2\sigma(I)$
$R_{int} = 0.114$
$\theta_{max} = 25.3°$, $\theta_{min} = 2.7°$
$h = -17 \rightarrow 17$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.131$
$S = 1.21$
1665 reflections
136 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 3.0535P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
F1	0.54938 (12)	0.31169 (18)	0.35054 (15)	0.0396 (5)
F2	0.26856 (12)	0.4861 (2)	0.45376 (15)	0.0403 (5)
O2	0.58679 (14)	0.8516 (2)	0.34897 (17)	0.0327 (6)
O1	0.45423 (15)	0.9500 (2)	0.39457 (17)	0.0365 (6)
N1	0.3767 (2)	0.2502 (3)	0.4064 (2)	0.0374 (8)
C6	0.35426 (19)	0.5153 (3)	0.4228 (2)	0.0284 (7)
C1	0.4077 (2)	0.3925 (3)	0.4014 (2)	0.0275 (7)
C4	0.4707 (2)	0.6876 (3)	0.3866 (2)	0.0253 (7)
C2	0.4942 (2)	0.4276 (3)	0.3721 (2)	0.0274 (7)
C7	0.5012 (2)	0.8429 (3)	0.3781 (2)	0.0278 (7)
C3	0.5275 (2)	0.5693 (3)	0.3645 (2)	0.0279 (7)
H3	0.587797	0.586326	0.344706	0.033*
C5	0.3829 (2)	0.6589 (3)	0.4160 (2)	0.0279 (7)
H5	0.343351	0.738484	0.431279	0.034*
C8	0.6241 (2)	1.0007 (3)	0.3392 (3)	0.0350 (8)
H8A	0.625203	1.051356	0.403614	0.042*
H8B	0.587471	1.060564	0.293261	0.042*
C9	0.7174 (2)	0.9825 (4)	0.3006 (3)	0.0468 (10)
H9A	0.715460	0.928930	0.238005	0.070*
H9B	0.753448	0.926045	0.347797	0.070*
H9C	0.744541	1.080539	0.290498	0.070*
H1A	0.414 (2)	0.179 (4)	0.399 (3)	0.043 (11)*
H1B	0.326 (3)	0.237 (4)	0.435 (3)	0.045 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0434 (11)	0.0199 (9)	0.0556 (13)	0.0081 (8)	0.0050 (10)	−0.0026 (9)
F2	0.0312 (10)	0.0295 (10)	0.0603 (13)	−0.0029 (8)	0.0050 (9)	0.0013 (9)
O2	0.0363 (13)	0.0176 (10)	0.0442 (14)	−0.0032 (9)	0.0032 (10)	0.0027 (10)
O1	0.0390 (13)	0.0195 (11)	0.0512 (16)	0.0044 (10)	−0.0015 (11)	−0.0011 (10)
N1	0.0405 (19)	0.0169 (14)	0.055 (2)	−0.0022 (14)	0.0048 (16)	0.0004 (13)
C6	0.0250 (16)	0.0267 (17)	0.0335 (18)	−0.0001 (13)	−0.0012 (14)	0.0017 (14)
C1	0.0352 (18)	0.0190 (15)	0.0284 (18)	−0.0012 (13)	−0.0053 (14)	0.0001 (13)
C4	0.0285 (17)	0.0198 (15)	0.0276 (17)	−0.0003 (12)	−0.0048 (13)	0.0021 (12)
C2	0.0293 (17)	0.0194 (15)	0.0336 (18)	0.0084 (13)	−0.0008 (14)	−0.0018 (13)
C7	0.0329 (18)	0.0240 (16)	0.0264 (17)	0.0015 (14)	−0.0049 (14)	−0.0017 (14)
C3	0.0302 (18)	0.0236 (16)	0.0299 (18)	0.0021 (13)	0.0002 (13)	−0.0011 (13)
C5	0.0326 (18)	0.0191 (15)	0.0321 (18)	0.0082 (13)	−0.0054 (14)	−0.0014 (13)
C8	0.044 (2)	0.0182 (15)	0.043 (2)	−0.0047 (15)	−0.0021 (16)	0.0007 (14)
C9	0.045 (2)	0.035 (2)	0.060 (3)	−0.0108 (17)	0.0055 (19)	0.0014 (18)

Geometric parameters (Å, º)

F1—C2	1.360 (3)	C4—C3	1.392 (4)
F2—C6	1.368 (3)	C4—C5	1.390 (4)
O2—C7	1.336 (4)	C2—C3	1.372 (4)
O2—C8	1.458 (4)	C3—H3	0.9500
O1—C7	1.212 (4)	C5—H5	0.9500
N1—C1	1.363 (4)	C8—H8A	0.9900
N1—H1A	0.86 (4)	C8—H8B	0.9900
N1—H1B	0.86 (4)	C8—C9	1.493 (5)
C6—C1	1.392 (4)	C9—H9A	0.9800
C6—C5	1.365 (4)	C9—H9B	0.9800
C1—C2	1.385 (4)	C9—H9C	0.9800
C4—C7	1.474 (4)		
C7—O2—C8	116.4 (2)	C4—C3—H3	120.8
C1—N1—H1A	118 (2)	C2—C3—C4	118.4 (3)
C1—N1—H1B	117 (2)	C2—C3—H3	120.8
H1A—N1—H1B	122 (3)	C6—C5—C4	119.3 (3)
F2—C6—C1	116.4 (3)	C6—C5—H5	120.4
C5—C6—F2	119.6 (3)	C4—C5—H5	120.4
C5—C6—C1	124.0 (3)	O2—C8—H8A	110.4
N1—C1—C6	122.9 (3)	O2—C8—H8B	110.4
N1—C1—C2	122.9 (3)	O2—C8—C9	106.6 (3)
C2—C1—C6	114.2 (3)	H8A—C8—H8B	108.6
C3—C4—C7	121.4 (3)	C9—C8—H8A	110.4
C5—C4—C7	119.2 (3)	C9—C8—H8B	110.4
C5—C4—C3	119.4 (3)	C8—C9—H9A	109.5
F1—C2—C1	116.7 (3)	C8—C9—H9B	109.5
F1—C2—C3	118.7 (3)	C8—C9—H9C	109.5

C3—C2—C1	124.7 (3)	H9A—C9—H9B	109.5
O2—C7—C4	111.9 (3)	H9A—C9—H9C	109.5
O1—C7—O2	123.9 (3)	H9B—C9—H9C	109.5
O1—C7—C4	124.2 (3)		

F1—C2—C3—C4	179.9 (3)	C7—C4—C5—C6	179.2 (3)
F2—C6—C1—N1	2.6 (5)	C3—C4—C7—O2	−0.8 (4)
F2—C6—C1—C2	−178.9 (3)	C3—C4—C7—O1	178.6 (3)
F2—C6—C5—C4	178.6 (3)	C3—C4—C5—C6	0.1 (5)
N1—C1—C2—F1	−1.7 (5)	C5—C6—C1—N1	−178.3 (3)
N1—C1—C2—C3	178.9 (3)	C5—C6—C1—C2	0.2 (5)
C6—C1—C2—F1	179.8 (3)	C5—C4—C7—O2	−179.9 (3)
C6—C1—C2—C3	0.4 (5)	C5—C4—C7—O1	−0.5 (5)
C1—C6—C5—C4	−0.4 (5)	C5—C4—C3—C2	0.4 (5)
C1—C2—C3—C4	−0.7 (5)	C8—O2—C7—O1	1.3 (4)
C7—O2—C8—C9	−176.7 (3)	C8—O2—C7—C4	−179.3 (3)
C7—C4—C3—C2	−178.7 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{i}	0.85 (3)	2.15 (4)	2.942 (3)	155 (3)
C8—H8*B*···F1^{ii}	0.99	2.46	3.015 (3)	115

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, *y*+1, *z*.

Diethyl 4,4′-(diazene-1,2-diyl)bis(3,5-difluorobenzoate) (III)

Crystal data

$C_{18}H_{14}F_4N_2O_4$
M_r = 398.31
Triclinic, $P\overline{1}$
a = 4.6106 (17) Å
b = 8.839 (3) Å
c = 10.969 (4) Å
α = 99.330 (8)°
β = 99.431 (8)°
γ = 96.442 (7)°
V = 430.7 (3) Å^3
Z = 1
F(000) = 204
D_x = 1.536 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1029 reflections
θ = 2.4–27.2°
μ = 0.14 mm^{-1}
T = 100 K
Needle, dark brown
0.57 × 0.13 × 0.1 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: sealed X-ray tube, EIGENMANN GmbH
Graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.926, T_{max} = 0.986
3269 measured reflections
1913 independent reflections
1414 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°, θ_{min} = 1.9°
h = −5→5
k = −11→11
l = −12→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.150$
$S = 1.01$
1913 reflections
132 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
F1	0.3292 (3)	0.83917 (13)	0.96263 (11)	0.0332 (3)
F2	0.2359 (3)	0.43669 (13)	1.19462 (11)	0.0352 (3)
O1	−0.2904 (3)	0.84303 (16)	1.39751 (13)	0.0308 (4)
O2	−0.1813 (3)	1.04412 (15)	1.30209 (12)	0.0261 (3)
N1	0.4466 (3)	0.55792 (18)	0.98505 (15)	0.0256 (4)
C1	0.2996 (4)	0.6346 (2)	1.07526 (16)	0.0206 (4)
C2	0.2364 (4)	0.7829 (2)	1.05820 (17)	0.0235 (4)
C3	0.0879 (4)	0.8714 (2)	1.13506 (17)	0.0229 (4)
C4	−0.0091 (4)	0.8109 (2)	1.23300 (17)	0.0212 (4)
C5	0.0423 (4)	0.6636 (2)	1.25239 (17)	0.0232 (4)
H5	−0.028030	0.621698	1.318322	0.028*
C6	0.1961 (4)	0.5799 (2)	1.17490 (17)	0.0223 (4)
C7	−0.1761 (4)	0.8990 (2)	1.32022 (17)	0.0223 (4)
C8	−0.3390 (4)	1.1407 (2)	1.38246 (19)	0.0277 (4)
H8A	−0.296123	1.121791	1.469698	0.033*
H8B	−0.556011	1.116299	1.351234	0.033*
C9	−0.2333 (5)	1.3059 (2)	1.3787 (2)	0.0347 (5)
H9A	−0.274544	1.322754	1.291824	0.052*
H9B	−0.018988	1.329046	1.411153	0.052*
H9C	−0.337013	1.374039	1.430782	0.052*
H3	0.060 (4)	0.969 (2)	1.117 (2)	0.027 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0480 (7)	0.0331 (6)	0.0279 (7)	0.0169 (5)	0.0208 (5)	0.0111 (5)
F2	0.0462 (7)	0.0308 (6)	0.0397 (7)	0.0187 (5)	0.0220 (6)	0.0152 (5)
O1	0.0320 (7)	0.0348 (8)	0.0301 (8)	0.0085 (6)	0.0151 (6)	0.0072 (6)
O2	0.0271 (7)	0.0277 (7)	0.0256 (7)	0.0089 (5)	0.0108 (5)	0.0016 (6)

N1	0.0250 (8)	0.0295 (8)	0.0239 (8)	0.0092 (6)	0.0078 (6)	0.0028 (7)
C1	0.0174 (8)	0.0253 (9)	0.0183 (9)	0.0055 (6)	0.0029 (7)	0.0005 (7)
C2	0.0243 (9)	0.0293 (10)	0.0180 (9)	0.0056 (7)	0.0050 (7)	0.0056 (7)
C3	0.0246 (9)	0.0241 (9)	0.0210 (9)	0.0075 (7)	0.0039 (7)	0.0047 (7)
C4	0.0155 (8)	0.0270 (9)	0.0190 (9)	0.0031 (6)	0.0016 (7)	−0.0005 (7)
C5	0.0198 (8)	0.0297 (10)	0.0201 (9)	0.0036 (7)	0.0038 (7)	0.0042 (7)
C6	0.0214 (8)	0.0224 (9)	0.0233 (10)	0.0061 (7)	0.0018 (7)	0.0050 (7)
C7	0.0186 (8)	0.0279 (9)	0.0185 (9)	0.0036 (7)	0.0010 (7)	0.0010 (7)
C8	0.0258 (9)	0.0299 (10)	0.0283 (10)	0.0093 (7)	0.0117 (8)	−0.0026 (8)
C9	0.0398 (11)	0.0325 (11)	0.0329 (11)	0.0114 (9)	0.0109 (9)	0.0009 (9)

Geometric parameters (Å, º)

F1—C2	1.341 (2)	C3—H3	0.94 (2)
F2—C6	1.345 (2)	C4—C5	1.392 (3)
O1—C7	1.211 (2)	C4—C7	1.500 (2)
O2—C7	1.332 (2)	C5—H5	0.9500
O2—C8	1.463 (2)	C5—C6	1.373 (3)
N1—N1^{i}	1.252 (3)	C8—H8A	0.9900
N1—C1	1.415 (2)	C8—H8B	0.9900
C1—C2	1.409 (3)	C8—C9	1.496 (3)
C1—C6	1.395 (3)	C9—H9A	0.9800
C2—C3	1.373 (3)	C9—H9B	0.9800
C3—C4	1.389 (3)	C9—H9C	0.9800
C7—O2—C8	116.47 (14)	F2—C6—C5	117.43 (16)
N1^{i}—N1—C1	114.4 (2)	C5—C6—C1	122.86 (17)
C2—C1—N1	115.52 (16)	O1—C7—O2	124.89 (17)
C6—C1—N1	128.64 (16)	O1—C7—C4	123.19 (18)
C6—C1—C2	115.76 (16)	O2—C7—C4	111.91 (16)
F1—C2—C1	117.69 (16)	O2—C8—H8A	110.3
F1—C2—C3	119.19 (16)	O2—C8—H8B	110.3
C3—C2—C1	123.11 (17)	O2—C8—C9	107.28 (15)
C2—C3—C4	118.52 (17)	H8A—C8—H8B	108.5
C2—C3—H3	116.6 (13)	C9—C8—H8A	110.3
C4—C3—H3	124.9 (13)	C9—C8—H8B	110.3
C3—C4—C5	120.65 (17)	C8—C9—H9A	109.5
C3—C4—C7	121.92 (17)	C8—C9—H9B	109.5
C5—C4—C7	117.42 (17)	C8—C9—H9C	109.5
C4—C5—H5	120.5	H9A—C9—H9B	109.5
C6—C5—C4	119.07 (17)	H9A—C9—H9C	109.5
C6—C5—H5	120.5	H9B—C9—H9C	109.5
F2—C6—C1	119.66 (16)		
F1—C2—C3—C4	179.45 (15)	C3—C4—C7—O1	171.84 (16)
N1^{i}—N1—C1—C2	166.37 (19)	C3—C4—C7—O2	−8.3 (2)
N1^{i}—N1—C1—C6	−17.2 (3)	C4—C5—C6—F2	−178.54 (14)
N1—C1—C2—F1	−2.4 (2)	C4—C5—C6—C1	−1.2 (3)

N1—C1—C2—C3	178.22 (15)	C5—C4—C7—O1	−7.2 (3)
N1—C1—C6—F2	0.7 (3)	C5—C4—C7—O2	172.65 (14)
N1—C1—C6—C5	−176.52 (16)	C6—C1—C2—F1	−179.32 (14)
C1—C2—C3—C4	−1.1 (3)	C6—C1—C2—C3	1.3 (3)
C2—C1—C6—F2	177.21 (15)	C7—O2—C8—C9	161.06 (16)
C2—C1—C6—C5	−0.1 (3)	C7—C4—C5—C6	−179.59 (14)
C2—C3—C4—C5	−0.2 (3)	C8—O2—C7—O1	−0.2 (3)
C2—C3—C4—C7	−179.22 (14)	C8—O2—C7—C4	179.99 (13)
C3—C4—C5—C6	1.4 (3)		

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