# Crystal structure of (E)-1,2-bis(4-bromo-2,6-difluorophenyl)diazene

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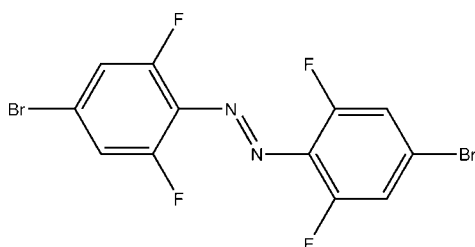
In the crystal, molecules of the centrosymmetric title compound, $C_{12}H_4Br_2F_4N_2$, are linked into strands along [011] by weak C—H···F contacts. Furthermore, the molecules are π–π stacked with perpendicular ring distances of 3.4530 (9) Å.

## 1. Related literature

For background on azobenzenes, see: Mitscherlich (1834); Fehrentz *et al.* (2011); Banghart *et al.* (2004); Levitz *et al.* (2013); Broichhagen *et al.* (2014); Velema *et al.* (2013); Bléger *et al.* (2012). For the synthesis, see: Bléger *et al.* (2012). For related structures, see: Wragg *et al.* (2011); Gabe *et al.* (1981); Crispini *et al.* (1998); Elder & Vargas-Baca (2012); Komeyama *et al.* (1973); Ferguson *et al.* (1998); Reichenbächer *et al.* (2007).



## 2. Experimental

### 2.1. Crystal data

$C_{12}H_4Br_2F_4N_2$
$M_r = 411.98$

Monoclinic, $P2_1/c$
$a = 10.3274$ (5) Å
$b = 4.5667$ (2) Å
$c = 13.1039$ (6) Å
$\beta = 90.340$ (3)°
$V = 618.00$ (5) Å$^3$
$Z = 2$

Mo $K\alpha$ radiation
$\mu = 6.60$ mm$^{-1}$
$T = 173$ K
$0.14 \times 0.07 \times 0.02$ mm

### 2.2. Data collection

Bruker D8 Quest diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
$T_{min} = 0.572$, $T_{max} = 0.746$

9803 measured reflections
1523 independent reflections
1218 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.055$
$S = 1.02$
1523 reflections

91 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.36$ e Å$^{-3}$
$\Delta\rho_{min} = -0.30$ e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C5—H5···F2$^i$ | 0.95 | 2.53 | 3.190 (3) | 126 |

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

Data collection: *Bruker Instrument Service* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP*-III (Burnett & Johnson, 1996); software used to prepare material for publication: *PLATON* (Spek, 2009).

## Acknowledgements

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# supporting information

## Crystal structure of (*E*)-1,2-bis(4-bromo-2,6-difluorophenyl)diazene

**Johannes Broichhagen, David H. Woodmansee, Dirk Trauner and Peter Mayer**

### S1. Comment

Azobenzenes, first discovered in 1834 [Mitscherlich (1834)], are experiencing a renaissance in the last decade for the photocontrol of biological function [Fehrentz *et al.* (2011)]. They offer *cis*-/*trans*-isomerism upon irradiation with discrete and orthogonal wavelengths of light. When attached to a pharmacophore, this conformational change has an impact on binding affinities to its biological target. Therefore, a wide variety of transmembrane proteins, such as ion-channels [Banghart *et al.* (2004)] and metabotropic receptors [Levitz *et al.* (2013)], as well as enzymatic activity [Broichhagen *et al.* (2014)] and cell survival [Velema *et al.* (2013)] has been manipulated with azobenzene-based molecular structures. With our ongoing research in photopharmacology, we aimed to synthesize tetrafluoro-azobenzenes, which are characterized by their bistability once isomerized [Bléger *et al.* (2012)]. During our synthetic studies, we obtained (*E*)-1,2-bis(4-bromo-2,6-difluorophenyl)diazene (1) in a crystalline form, which we are reporting herein. This symmetric molecule serves as a precursor for further functionalization and implementation in photopharmacological studies, which will be described in a separate publication.

The molecular structure of the title compound is depicted in Figure 1. There are several structures containing (*E*)-1,2-bis(phenyl)diazene derivatives with at least one halogen substituent in 2-, 4- or 6-position reported in the literature, *e.g.* Wragg *et al.* (2011), Gabe *et al.* (1981), Crispini *et al.* (1998), Elder & Vargas-Baca (2012) and Komeyama *et al.* (1973). Furthermore there are two structures reported which contain the 4-bromo-2,6-difluorophenyl moiety [Ferguson *et al.* (1998), Reichenbächer *et al.* (2007)]. Due to centrosymmetry the phenyl rings are exactly coplanar, however, the entire molecule deviates significantly from exact planarity. The bond of the azo group forms an angle of 4.04 (16)° with the least-square plane of the phenyl ring while it is much larger with 13.21 (12)° in a related structure [Crispini *et al.* (1998)]. The C4–Br1 bond encloses an angle of 2.95 (10)° with the least-square plane of the phenyl ring which is quite close to the angle of 0.2 (3)° in a reported 4-bromo-2,6-difluorophenyl derivative [Ferguson *et al.* (1998)]. The 4-bromo-2,6-di-fluorophenyl derivative reported of Reichenbächer *et al.* (2007) is suitable for the comparison of bond lengths with the title compound since both compounds have been investigated at 173 K. In the title compound, the C–Br bond distance is 1.888 (2) Å which is almost in the same range of distances found in the reported structure: 1.889 (5), 1.883 (6) and 1.882 (6) Å. The C–F distances are 1.345 (3) and 1.335 (3) Å in the title compound and in the range of 1.336 (7) to 1.353 (7) Å in the related derivative [Reichenbächer *et al.* (2007)].

The packing of the title compound is dominated by weak C–H···F contacts, Br-*π* contacts and *π*-stacking. Strands along [011] are formed by C–H···F contacts (see Figure 2 and Table 1 for details). The *π*-stacking is well visible in Figure 3. The molecules are arranged staggered by what the azo group and the Br substituent of adjacent molecules are located above or below a phenyl ring. The centre of gravity of the phenyl ring (coordinates $x = 0.28683$, $y = 0.5321$, $z = 0.56133$) is in a distance of 3.412 and 3.459 Å from the N-atoms of the azo group (N1[ii] with [ii] = $x,1 + y,z$ and N1[iii] with [iii] = 1 - $x,2 - y,-z$ resp.) and 3.573 (1) Å from an adjacent Br substituent (Br1[iv] with [iv] = $x,-1 + y,z$). The perpendicular distances of phenyl rings interacting by *π*-contacts are in a narrow range of 3.4528 (9) and 3.4532 (9) Å with a *Cg*–*Cg* distance of

4.5665 (14) Å. Besides the $\pi$ contact the Br substituent forms weak contacts to two adjacent Br substituents in a distance of 3.6817 (4) Å each (Br1$^v$ and Br1$^{vi}$ with $^v$ = -x,1/2 + y,1/2 - z and $^{vi}$ = -x,-1/2 + y,1/2 - z).

## S2. Experimental

(*E*)-1,2-bis(4-bromo-2,6-difluorophenyl)diazene (1) was synthesized as reported before and the spectral data matched the previously reported data [Bléger *et al.* (2012)]. Crystals suitable for X-Ray diffractometry were obtained as deep-red needles by slow evaporization from chloroform.

## S3. Refinement

All H atoms were found in difference maps. C-bonded H atoms were positioned in ideal geometry (C—H = 0.95 Å) and treated as riding on their parent atoms [$U_{iso}$(H) = 1.2$U_{eq}$(C)].
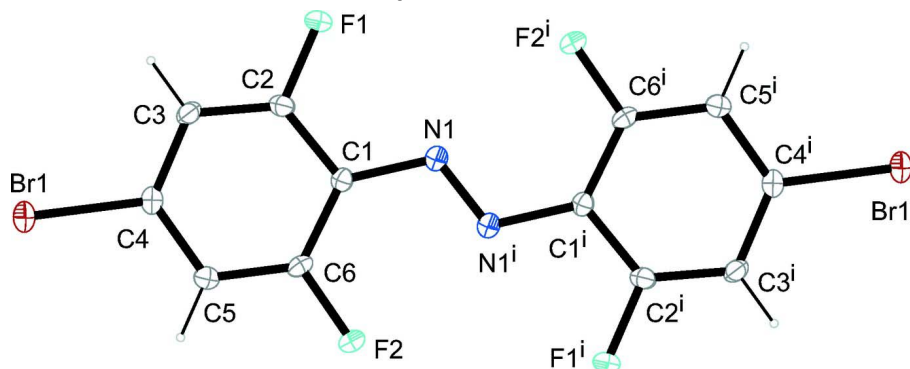


**Figure 1**

The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids (drawn at 30% probability level) for non-H atoms. Symmetry code: (i) 1 - x, 2 - y, 1 - z.
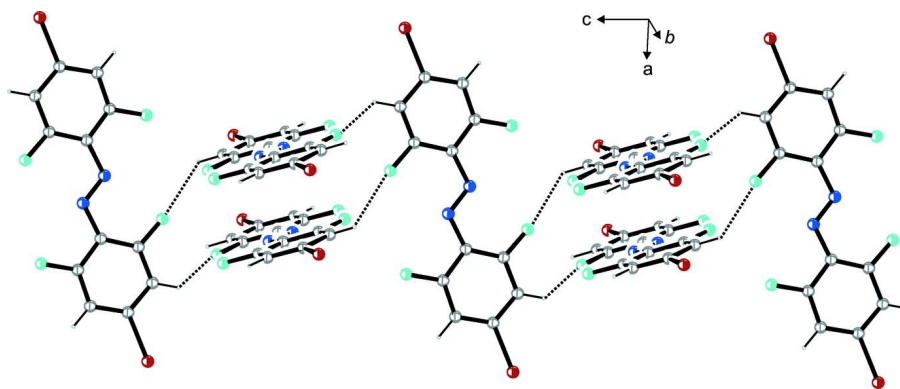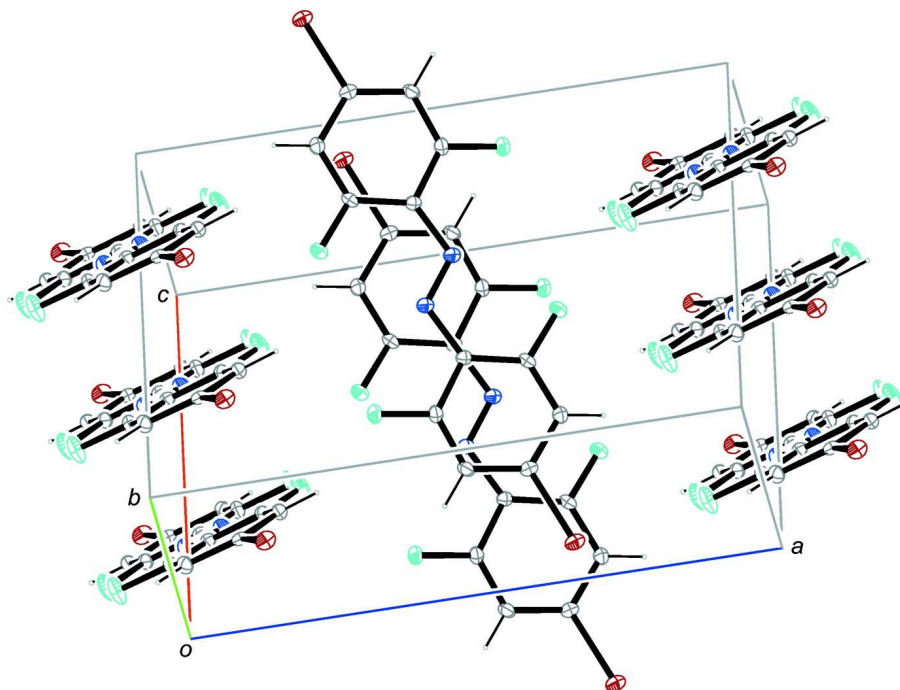


**Figure 2**

Weak C—H⋯F contacts (dotted lines) linking the title compound into strands along [011].

**Figure 3**

The unit cell of the title compound (displacement ellipsoids drawn at 30% probability level).

## (*E*)-1,2-bis(4-bromo-2,6-difluorophenyl)diazene

*Crystal data*

| | |
|---|---|
| $C_{12}H_4Br_2F_4N_2$ | $F(000) = 392$ |
| $M_r = 411.98$ | $D_x = 2.214 (1)$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 95 reflections |
| $a = 10.3274 (5)$ Å | $\theta = 5.4–24.6°$ |
| $b = 4.5667 (2)$ Å | $\mu = 6.60$ mm$^{-1}$ |
| $c = 13.1039 (6)$ Å | $T = 173$ K |
| $\beta = 90.340 (3)°$ | Platelet, orange |
| $V = 618.00 (5)$ Å$^3$ | $0.14 \times 0.07 \times 0.02$ mm |
| $Z = 2$ | |

*Data collection*

| | |
|---|---|
| Bruker D8 Quest diffractometer | $T_{min} = 0.572$, $T_{max} = 0.746$ |
| Radiation source: Microfocus source, Bruker I$\mu$S | 9803 measured reflections |
| | 1523 independent reflections |
| Focusing mirrors monochromator | 1218 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 10.4167 pixels mm$^{-1}$ | $R_{int} = 0.051$ |
| mix of phi and $\omega$ scans | $\theta_{max} = 28.4°$, $\theta_{min} = 3.1°$ |
| Absorption correction: multi-scan | $h = -13\rightarrow13$ |
| (*SADABS*; Bruker, 2012) | $k = -6\rightarrow6$ |
| | $l = -17\rightarrow17$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.055$ | |
| $S = 1.02$ | H-atom parameters constrained |
| 1523 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.2317P]$ |
| 91 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.36$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.30$ e Å$^{-3}$ |

*Special details*

**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 $F^2 > 2\sigma(F^2)$ 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.3771 (2) | 0.7379 (5) | 0.52174 (17) | 0.0188 (5) |
| C2 | 0.2748 (2) | 0.6243 (6) | 0.46388 (18) | 0.0232 (5) |
| C3 | 0.1860 (2) | 0.4296 (6) | 0.49948 (18) | 0.0233 (5) |
| H3 | 0.1179 | 0.3594 | 0.4570 | 0.028* |
| C4 | 0.1983 (2) | 0.3376 (5) | 0.59963 (18) | 0.0197 (5) |
| C5 | 0.2992 (2) | 0.4325 (5) | 0.66162 (18) | 0.0216 (5) |
| H5 | 0.3084 | 0.3629 | 0.7296 | 0.026* |
| C6 | 0.3856 (2) | 0.6304 (5) | 0.62162 (18) | 0.0205 (5) |
| N1 | 0.45691 (19) | 0.9452 (5) | 0.47266 (15) | 0.0234 (4) |
| F1 | 0.26329 (15) | 0.7158 (4) | 0.36666 (10) | 0.0382 (4) |
| F2 | 0.48197 (15) | 0.7201 (4) | 0.68235 (11) | 0.0373 (4) |
| Br1 | 0.07408 (2) | 0.08357 (6) | 0.656884 (19) | 0.02666 (10) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0172 (11) | 0.0184 (13) | 0.0208 (12) | −0.0001 (10) | 0.0014 (9) | −0.0017 (10) |
| C2 | 0.0266 (13) | 0.0257 (14) | 0.0173 (12) | −0.0002 (10) | −0.0020 (9) | 0.0017 (10) |
| C3 | 0.0206 (12) | 0.0262 (14) | 0.0230 (12) | −0.0035 (11) | −0.0047 (9) | −0.0029 (12) |
| C4 | 0.0173 (12) | 0.0150 (12) | 0.0270 (13) | 0.0020 (9) | 0.0046 (9) | −0.0014 (10) |
| C5 | 0.0239 (12) | 0.0215 (13) | 0.0193 (11) | 0.0016 (11) | −0.0011 (9) | 0.0003 (11) |
| C6 | 0.0203 (12) | 0.0199 (13) | 0.0214 (12) | 0.0000 (10) | −0.0052 (9) | −0.0049 (10) |
| N1 | 0.0221 (11) | 0.0239 (11) | 0.0243 (11) | −0.0046 (9) | −0.0016 (8) | 0.0014 (10) |
| F1 | 0.0385 (9) | 0.0555 (11) | 0.0205 (8) | −0.0178 (8) | −0.0093 (6) | 0.0125 (8) |
| F2 | 0.0372 (9) | 0.0479 (10) | 0.0268 (8) | −0.0201 (8) | −0.0142 (7) | 0.0079 (8) |

| Br1 | 0.02328 (14) | 0.02389 (15) | 0.03287 (15) | −0.00452 (11) | 0.00594 (9) | 0.00056 (13) |
|---|---|---|---|---|---|---|

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.397 (3) | C4—C5 | 1.387 (3) |
| C1—C6 | 1.400 (3) | C4—Br1 | 1.888 (2) |
| C1—N1 | 1.412 (3) | C5—C6 | 1.376 (3) |
| C2—F1 | 1.345 (3) | C5—H5 | 0.9500 |
| C2—C3 | 1.362 (3) | C6—F2 | 1.335 (3) |
| C3—C4 | 1.383 (3) | N1—N1$^i$ | 1.244 (4) |
| C3—H3 | 0.9500 | | |
| | | | |
| C2—C1—C6 | 114.8 (2) | C3—C4—Br1 | 120.30 (18) |
| C2—C1—N1 | 116.3 (2) | C5—C4—Br1 | 117.97 (18) |
| C6—C1—N1 | 128.9 (2) | C6—C5—C4 | 117.9 (2) |
| F1—C2—C3 | 118.1 (2) | C6—C5—H5 | 121.0 |
| F1—C2—C1 | 117.5 (2) | C4—C5—H5 | 121.0 |
| C3—C2—C1 | 124.4 (2) | F2—C6—C5 | 117.2 (2) |
| C2—C3—C4 | 117.7 (2) | F2—C6—C1 | 119.4 (2) |
| C2—C3—H3 | 121.2 | C5—C6—C1 | 123.3 (2) |
| C4—C3—H3 | 121.2 | N1$^i$—N1—C1 | 115.1 (2) |
| C3—C4—C5 | 121.7 (2) | | |
| | | | |
| C6—C1—C2—F1 | −178.8 (2) | Br1—C4—C5—C6 | −176.42 (17) |
| N1—C1—C2—F1 | 1.6 (3) | C4—C5—C6—F2 | 179.8 (2) |
| C6—C1—C2—C3 | 1.7 (4) | C4—C5—C6—C1 | −0.5 (4) |
| N1—C1—C2—C3 | −177.9 (2) | C2—C1—C6—F2 | 178.4 (2) |
| F1—C2—C3—C4 | −179.7 (2) | N1—C1—C6—F2 | −2.1 (4) |
| C1—C2—C3—C4 | −0.2 (4) | C2—C1—C6—C5 | −1.2 (4) |
| C2—C3—C4—C5 | −1.7 (4) | N1—C1—C6—C5 | 178.3 (2) |
| C2—C3—C4—Br1 | 176.76 (18) | C2—C1—N1—N1$^i$ | 176.3 (3) |
| C3—C4—C5—C6 | 2.1 (4) | C6—C1—N1—N1$^i$ | −3.2 (4) |

Symmetry code: (i) −x+1, −y+2, −z+1.

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C5—H5···F2$^{ii}$ | 0.95 | 2.53 | 3.190 (3) | 126 |

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