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Dimethyl 4,4′-(diazenediyl)dibenzoate at 100 K

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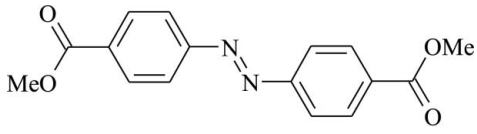
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.147; data-to-parameter ratio = 11.3.

In the asymmetric part of the unit cell of the title compound, $C_{16}H_{14}N_2O_4$, there are two chemically equivalent but crystallographic independent half molecules. The geometric centre of each complete molecule lies on a crystallographic inversion centre. Both molecules are almost planar [mean deviations of atoms in the two molecules are 0.032 (2) and 0.044 (2) Å] and their geometries are similar. In the crystal, molecules are arranged in columns along the a axis. There are no intermolecular donor–acceptor distances shorter than 3.4 Å.

Related literature

For general background to the use of azo compounds as dyes, pigments and advanced materials, see: Allmann (1997); Scott *et al.*, (2002); Maniam *et al.* (2008); Zeitouny *et al.*, (2009). For a related structure, see: Yu & Liu (2009); Niu *et al.* (2011). For related literature, see: Onto *et al.* (1998). For the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_{16}H_{14}N_2O_4$
M_r = 298.29
Triclinic, $P\overline{1}$
a = 3.8146 (8) Å
b = 11.2571 (18) Å
c = 16.904 (3) Å
α = 72.456 (16)°
β = 85.030 (18)°
γ = 84.468 (16)°
V = 687.6 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.35 × 0.17 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
4264 measured reflections
2405 independent reflections
1652 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.147
S = 1.05
2405 reflections
213 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2074).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allmann, R. (1997). *The Chemistry of the Hydrazo, Azo and Azoxy groups*, Vol. 2, edited by S. Patai, pp. 23–52. New York: John Wiley & Sons.
Maniam, S., Cieslinski, M. M., Lincoln, S. F., Onagi, H., Steel, P. J., Willis, A. C. & Easton, C. J. (2008). *Org. Lett.* **10**, 1885–1888.
Niu, Y., Huang, J., Zhao, C., Gao, P. & Yu, Y. (2011). *Acta Cryst.* E**67**, o2671.
Onto, K., Hatakeyama, T., Takeo, M., Uchiito, S., Tokuda, M. & Suginome, H. (1998). *Tetrahedron*, **54**, 8403–8410.
Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Scott, J., Asami, M. & Tanaka, K. (2002). *New J. Chem.* **26**, 1822–1826.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yu, Q.-D. & Liu, Y.-Y. (2009). *Acta Cryst.* E**65**, o2326.
Zeitouny, J., Aurisicchio, C., Bonifazi, D., De Zorzi, R., Geremia, S., Bonini, M., Palma, C.-A., Samori, P., Listorti, A., Belbakra, A. & Armaroli, N. (2009). *J. Mater. Chem.* **19**, 4715–4724.

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Acta Cryst. (2013). E**69**, o1607 [doi:10.1107/S1600536813026846]

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S1. Comment

Azo compounds and its derivatives represent the dominant class of coloured compounds and are used as dyes and pigments (Allmann, 1997). Azobenzenes, due to its efficient and fully reversible photoisomerization and photoinduced anisotropy have widely been investigated as a component in photoresponsive materials (Zeitouny *et al.*, 2009).

There are two chemically equivalent but crystallographic independent molecules in the unit cell (Figure 1), both lie on crystallographic inversion centres. The molecules are almost planar and their geometries are similar; differences do not exceed 0.2 Å for bond lengths, 2° for valence angles and 3° for torsion angles.

All bond distances and angles lie in expected ranges and are in good agreement with the geometry of other *para*-substituted azobenzene derivatives (Yu & Liu, 2009; Niu *et al.*, 2011 and Allen, 2002).

The crystal packing is shown in Fig. 2. The molecules form columns along the *a* axis, the distance between stacked molecules is equal to 3.8146 (8) Å. There are no intermolecular C–H···O/N distances shorter than 3.4 Å.

S2. Experimental

The compound was prepared according to literature procedure, (Onto *et al.*, 1998). Crystals of (I) suitable for X-ray crystal structure analysis was grown from benzene–n-heptane mixture (1:1).

S3. Refinement

Apart from methyl hydrogens all H atoms were positioned geometrically, with C–H = 0.93 Å and U_{iso} (H) = 1.2U_{eq}(C), methyl H atoms were derived from difference Fourier maps and refined as idealized groups with with C–H = 0.96 Å and U_{iso} (H) = 1.5U_{eq}(C). All methyl-H atoms were allowed to rotate but not to tip.

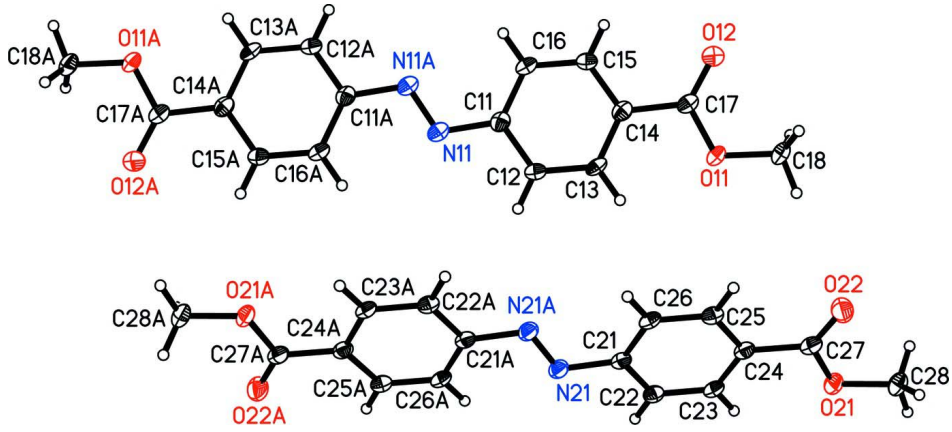

Figure 1

The molecular structure showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). Symmetry code: A = -*x*, -*y*, -*z*.

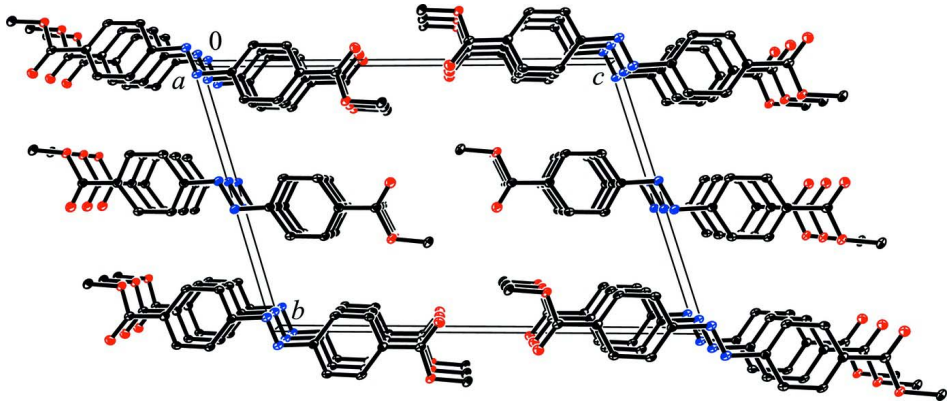

Figure 2

The packing diagram viewed along a-axis.

Dimethyl 4,4′-(diazenediyl)dibenzoate

Crystal data

$C_{16}H_{14}N_2O_4$
$M_r = 298.29$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 3.8146\ (8)$ Å
$b = 11.2571\ (18)$ Å
$c = 16.904\ (3)$ Å
$\alpha = 72.456\ (16)°$
$\beta = 85.030\ (18)°$
$\gamma = 84.468\ (16)°$
$V = 687.6\ (2)$ Å^3
$Z = 2$
$F(000) = 312$
$D_x = 1.441$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4264 reflections
$\theta = 3.6–25.0°$
$\mu = 0.11$ mm^{-1}
$T = 100$ K
Prism, red
0.35 × 0.17 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 1024 x 1024 with blocks 2 x 2 pixels mm^{-1}

ω–scan
4264 measured reflections
2405 independent reflections
1652 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

$\theta_{max} = 25.0°$, $\theta_{min} = 3.6°$
$h = -4 \rightarrow 2$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.147$
$S = 1.05$
2405 reflections
213 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
$w = 1/[\sigma^2(F_o^2) + (0.0791P)^2 + 0.205P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ 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 $F^2 > \sigma(F^2)$ 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}
O11	0.3301 (4)	0.15744 (14)	0.33935 (9)	0.0251 (4)
O12	0.1772 (4)	−0.04021 (15)	0.39802 (10)	0.0296 (4)
N11	0.0393 (5)	0.05005 (17)	0.00495 (12)	0.0216 (5)
C11	0.0777 (6)	0.0436 (2)	0.08962 (14)	0.0191 (5)
C12	0.2050 (6)	0.1480 (2)	0.10194 (14)	0.0196 (5)
H12	0.2585	0.2160	0.0565	0.020 (6)*
C13	0.2522 (5)	0.1511 (2)	0.18173 (14)	0.0191 (5)
H13	0.3387	0.2208	0.1898	0.025 (6)*
C14	0.1695 (5)	0.0493 (2)	0.25002 (14)	0.0194 (5)
C15	0.0372 (6)	−0.0548 (2)	0.23750 (14)	0.0204 (5)
H15	−0.0194	−0.1222	0.2830	0.020 (6)*
C16	−0.0101 (6)	−0.0585 (2)	0.15834 (14)	0.0200 (5)
H16	−0.0992	−0.1278	0.1504	0.028 (7)*
C17	0.2225 (6)	0.0484 (2)	0.33681 (14)	0.0209 (5)
C18	0.3974 (7)	0.1652 (2)	0.42107 (14)	0.0272 (6)
H18A	0.4725	0.2464	0.4158	0.037 (7)*
H18B	0.5788	0.1025	0.4448	0.031 (7)*
H18C	0.1852	0.1519	0.4565	0.038 (8)*
O21	0.6465 (4)	0.65469 (14)	0.35059 (10)	0.0248 (4)
O22	0.8894 (4)	0.45639 (15)	0.38736 (10)	0.0308 (5)

N21	0.4726 (5)	0.55083 (17)	0.00854 (12)	0.0206 (4)
C21	0.5457 (6)	0.5432 (2)	0.09183 (14)	0.0184 (5)
C22	0.4325 (6)	0.6478 (2)	0.11755 (14)	0.0193 (5)
H22	0.3167	0.7168	0.0815	0.034 (7)*
C23	0.4932 (5)	0.6485 (2)	0.19724 (13)	0.0188 (5)
H23	0.4175	0.7183	0.2145	0.027 (7)*
C24	0.6678 (6)	0.5450 (2)	0.25183 (14)	0.0194 (5)
C25	0.7813 (5)	0.4400 (2)	0.22548 (14)	0.0196 (5)
H25	0.8971	0.3710	0.2616	0.023 (6)*
C26	0.7222 (6)	0.4383 (2)	0.14616 (14)	0.0193 (5)
H26	0.7983	0.3686	0.1288	0.027 (7)*
C27	0.7478 (6)	0.5448 (2)	0.33667 (14)	0.0212 (5)
C28	0.7220 (7)	0.6663 (2)	0.43076 (14)	0.0279 (6)
H28A	0.6386	0.7481	0.4340	0.046 (8)*
H28B	0.9720	0.6542	0.4368	0.031 (7)*
H28C	0.6053	0.6044	0.4744	0.039 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0366 (10)	0.0189 (9)	0.0242 (9)	−0.0057 (7)	−0.0049 (7)	−0.0110 (7)
O12	0.0411 (11)	0.0227 (10)	0.0250 (9)	−0.0081 (8)	−0.0030 (8)	−0.0052 (7)
N11	0.0227 (10)	0.0171 (10)	0.0270 (11)	−0.0007 (8)	−0.0018 (8)	−0.0096 (8)
C11	0.0183 (11)	0.0165 (12)	0.0233 (12)	0.0047 (9)	−0.0021 (9)	−0.0089 (9)
C12	0.0205 (11)	0.0136 (12)	0.0239 (13)	−0.0017 (9)	−0.0001 (9)	−0.0047 (9)
C13	0.0184 (11)	0.0133 (11)	0.0289 (13)	−0.0003 (9)	−0.0020 (9)	−0.0114 (10)
C14	0.0163 (11)	0.0185 (12)	0.0253 (13)	0.0014 (9)	−0.0019 (9)	−0.0100 (10)
C15	0.0232 (12)	0.0140 (11)	0.0228 (12)	−0.0005 (9)	−0.0017 (10)	−0.0039 (9)
C16	0.0198 (11)	0.0150 (12)	0.0274 (13)	−0.0027 (9)	−0.0005 (10)	−0.0094 (10)
C17	0.0203 (12)	0.0174 (12)	0.0272 (13)	−0.0014 (9)	−0.0013 (9)	−0.0101 (10)
C18	0.0355 (14)	0.0250 (14)	0.0268 (14)	−0.0061 (11)	−0.0062 (11)	−0.0141 (11)
O21	0.0352 (10)	0.0200 (9)	0.0231 (9)	−0.0018 (7)	−0.0041 (7)	−0.0115 (7)
O22	0.0428 (11)	0.0240 (10)	0.0263 (10)	0.0044 (8)	−0.0080 (8)	−0.0092 (8)
N21	0.0230 (10)	0.0177 (10)	0.0229 (10)	−0.0029 (8)	−0.0008 (8)	−0.0085 (8)
C21	0.0180 (11)	0.0156 (12)	0.0226 (12)	−0.0046 (9)	0.0015 (9)	−0.0069 (9)
C22	0.0188 (11)	0.0143 (11)	0.0245 (13)	−0.0006 (9)	−0.0020 (9)	−0.0055 (9)
C23	0.0189 (11)	0.0141 (11)	0.0255 (13)	−0.0034 (9)	0.0011 (9)	−0.0091 (9)
C24	0.0189 (11)	0.0177 (12)	0.0232 (12)	−0.0057 (9)	0.0017 (9)	−0.0079 (9)
C25	0.0182 (11)	0.0145 (12)	0.0258 (13)	−0.0012 (9)	−0.0017 (9)	−0.0055 (9)
C26	0.0201 (11)	0.0132 (11)	0.0270 (13)	−0.0021 (9)	−0.0003 (9)	−0.0093 (9)
C27	0.0217 (12)	0.0173 (12)	0.0263 (13)	−0.0045 (9)	0.0017 (10)	−0.0088 (10)
C28	0.0368 (14)	0.0263 (14)	0.0264 (14)	−0.0043 (11)	−0.0040 (11)	−0.0153 (11)

Geometric parameters (Å, º)

O11—C17	1.345 (3)	O21—C27	1.342 (3)
O11—C18	1.456 (3)	O21—C28	1.456 (3)
O12—C17	1.215 (3)	O22—C27	1.216 (3)

N11—N11^{i}	1.255 (3)	N21—N21^{ii}	1.257 (4)
N11—C11	1.431 (3)	N21—C21	1.434 (3)
C11—C12	1.391 (3)	C21—C22	1.393 (3)
C11—C16	1.409 (3)	C21—C26	1.411 (3)
C12—C13	1.387 (3)	C22—C23	1.389 (3)
C12—H12	0.9300	C22—H22	0.9300
C13—C14	1.398 (3)	C23—C24	1.401 (3)
C13—H13	0.9300	C23—H23	0.9300
C14—C15	1.398 (3)	C24—C25	1.403 (3)
C14—C17	1.495 (3)	C24—C27	1.491 (3)
C15—C16	1.379 (3)	C25—C26	1.385 (3)
C15—H15	0.9300	C25—H25	0.9300
C16—H16	0.9300	C26—H26	0.9300
C18—H18A	0.9600	C28—H28A	0.9600
C18—H18B	0.9600	C28—H28B	0.9600
C18—H18C	0.9600	C28—H28C	0.9600
C17—O11—C18	116.32 (17)	C27—O21—C28	116.58 (18)
N11^{i}—N11—C11	114.3 (2)	N21^{ii}—N21—C21	114.3 (2)
C12—C11—C16	120.0 (2)	C22—C21—C26	120.4 (2)
C12—C11—N11	115.69 (19)	C22—C21—N21	115.86 (19)
C16—C11—N11	124.25 (19)	C26—C21—N21	123.76 (19)
C13—C12—C11	120.2 (2)	C23—C22—C21	119.7 (2)
C13—C12—H12	119.9	C23—C22—H22	120.2
C11—C12—H12	119.9	C21—C22—H22	120.2
C12—C13—C14	119.88 (19)	C22—C23—C24	120.5 (2)
C12—C13—H13	120.1	C22—C23—H23	119.8
C14—C13—H13	120.1	C24—C23—H23	119.8
C15—C14—C13	119.8 (2)	C23—C24—C25	119.5 (2)
C15—C14—C17	118.83 (19)	C23—C24—C27	121.7 (2)
C13—C14—C17	121.41 (19)	C25—C24—C27	118.8 (2)
C16—C15—C14	120.7 (2)	C26—C25—C24	120.5 (2)
C16—C15—H15	119.7	C26—C25—H25	119.8
C14—C15—H15	119.7	C24—C25—H25	119.8
C15—C16—C11	119.42 (19)	C25—C26—C21	119.4 (2)
C15—C16—H16	120.3	C25—C26—H26	120.3
C11—C16—H16	120.3	C21—C26—H26	120.3
O12—C17—O11	123.6 (2)	O22—C27—O21	123.7 (2)
O12—C17—C14	124.4 (2)	O22—C27—C24	124.4 (2)
O11—C17—C14	111.96 (18)	O21—C27—C24	111.90 (19)
O11—C18—H18A	109.5	O21—C28—H28A	109.5
O11—C18—H18B	109.5	O21—C28—H28B	109.5
H18A—C18—H18B	109.5	H28A—C28—H28B	109.5
O11—C18—H18C	109.5	O21—C28—H28C	109.5
H18A—C18—H18C	109.5	H28A—C28—H28C	109.5
H18B—C18—H18C	109.5	H28B—C28—H28C	109.5
N11^{i}—N11—C11—C12	172.7 (2)	N21^{ii}—N21—C21—C22	−169.5 (2)

N11^{i}—N11—C11—C16	−8.4 (3)	N21^{ii}—N21—C21—C26	10.9 (3)
C16—C11—C12—C13	1.2 (3)	C26—C21—C22—C23	−0.2 (3)
N11—C11—C12—C13	−179.92 (18)	N21—C21—C22—C23	−179.82 (18)
C11—C12—C13—C14	−0.4 (3)	C21—C22—C23—C24	0.1 (3)
C12—C13—C14—C15	−0.4 (3)	C22—C23—C24—C25	0.0 (3)
C12—C13—C14—C17	178.97 (19)	C22—C23—C24—C27	177.82 (19)
C13—C14—C15—C16	0.5 (3)	C23—C24—C25—C26	0.1 (3)
C17—C14—C15—C16	−178.93 (19)	C27—C24—C25—C26	−177.85 (19)
C14—C15—C16—C11	0.3 (3)	C24—C25—C26—C21	−0.1 (3)
C12—C11—C16—C15	−1.1 (3)	C22—C21—C26—C25	0.2 (3)
N11—C11—C16—C15	−179.91 (19)	N21—C21—C26—C25	179.82 (19)
C18—O11—C17—O12	0.8 (3)	C28—O21—C27—O22	1.5 (3)
C18—O11—C17—C14	−178.63 (18)	C28—O21—C27—C24	−178.16 (17)
C15—C14—C17—O12	4.4 (3)	C23—C24—C27—O22	177.8 (2)
C13—C14—C17—O12	−175.0 (2)	C25—C24—C27—O22	−4.3 (3)
C15—C14—C17—O11	−176.20 (18)	C23—C24—C27—O21	−2.5 (3)
C13—C14—C17—O11	4.4 (3)	C25—C24—C27—O21	175.33 (19)

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