organic compounds

(E)-2,3-Bis[(E)-benzylideneamino]but-2-enedinitrile

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The asymmetric unit of the title compound, $C_{18}H_{12}N_4$, consists of a half-molecule, where the two halves of the molecule are related by inversion symmetry. The molecule is effectively planar, with the largest deviation from the 22-atom mean plane, measuring 0.024 (2) Å, exhibited by the *ortho*-C atom of the phenyl ring. The crystal structure exhibits π-stacking, with an interplanar spacing of 3.431 (3) Å.

Related literature

For applications of the title molecule as a semiconductor, see: Tanaka *et al.* (2009). For applications of the title compound and its various derivatives as a dye, see: Neumer (1977); Begland (1976). For the crystal structures of three di(azomethine) dyes with various substituents at the *para* position of the benzene ring of the title compound, see: Matsumoto *et al.* (2004). For a study of the nonlinear optics applications of both the title compound and the mono-condensation product, see: Das *et al.* (2001). For a review of the chemistry and reactions of the diaminomaleonitrile, see: Al-Azmi *et al.* (2003).
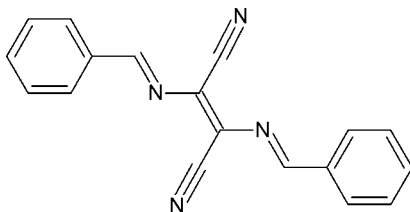
Experimental

Crystal data

$C_{18}H_{12}N_4$	$\gamma = 102.97\ (5)°$
$M_r = 284.32$	$V = 380.6\ (4)\ Å^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 6.389\ (4)$ Å	Mo $K\alpha$ radiation
$b = 7.608\ (5)$ Å	$\mu = 0.08\ mm^{-1}$
$c = 8.311\ (5)$ Å	$T = 295$ K
$\alpha = 103.96\ (5)°$	$0.50 \times 0.20 \times 0.10$ mm
$\beta = 91.67\ (5)°$	

Data collection

Oxford Diffraction Xcalibur 2 CCD diffractometer	2824 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	1498 independent reflections
$T_{min} = 0.963$, $T_{max} = 0.992$	964 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	100 parameters
$wR(F^2) = 0.117$	H-atom parameters constrained
$S = 0.89$	$\Delta\rho_{max} = 0.11$ e Å^{-3}
1498 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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supplementary materials

(*E*)-2,3-Bis[(*E*)-benzylideneamino]but-2-enedinitrile

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Comment

Di(azomethine) compounds derived from diaminomaleonitrile (DAMN) have been extensively studied for their application as dyes, semiconductors and in non-linear optics (Tanaka *et al.*, 2009; Neumer, 1977; Begland, 1976; Matsumoto *et al.*, 2004 and Das *et al.*, 2001). The title compound is interesting in that although it is orientated in a *trans* configuration about the ethylene group of the di(azomethine) linkage the DAMN synthon is exclusively *cis* about this bond. It is proposed that at elevated temperatures during the chemical synthesis an equilibrium is established between the *cis* and *trans* isomers of DAMN in solution. Although it has been shown that the *cis* isomer of DAMN is lower in energy than the *trans* isomer (Al-Azmi *et al.*, 2003) it is likely that non-bonded repulsion between the hydrogen atoms in the *ortho* positions of (1) would result in the *trans* isomer of (1) having a lower energy than the *cis* isomer. The double condensation reaction required to form (1) is therefore more likely to take place with the *trans* isomer of DAMN in solution; the *trans* isomer of (1) would thus be the major product.

 Compound (1) crystallized in the triclinic space group P1̄ with a half molecule in the asymmetric unit. The two halves of the molecule are related by inversion symmetry with an inversion centre at the midpoint of the C═C double bond of the di(azomethine) linkage unit. The molecule is effectively planar with the largest deviations from the 22-atom mean plane exhibited by the *ortho* C-atoms C3 and C5, measuring 0.022 (2) and 0.024 (2) Å, respectively. The structure shows that adjacent molecules are parallel, but are in a staggered configuration. There appear to be *π*-*π* interactions between adjacent molecules with an interplanar spacing of 3.431 (3) Å. The structure shows no genuine hydrogen bonding as all interactions are longer than the sum of their van der Waals radii. The lack of meaningful hydrogen bonds is likely due to a lack of good H-bond donors, as both the cyanide groups and the imine nitrogen atoms are potentially good H-bond acceptors.

Experimental

Benzaldehyde (0.500 g, 4.7 mmol), *cis*-diaminomaleonitrile (0.255 g, 2.4 mmol) and a catalytic amount of piperidine were dissolved in dry toluene (100 ml) and the solution brought to reflux for four hours. Water was continuously removed from the reaction *via* a Dean and Stark apparatus. The solvent was removed by rotary evaporation under reduced pressure and the resulting solid dissolved in a minimum of dichloromethane. The desired product was obtained by column chromatography on silica gel, using dichloromethane as the eluent. Single crystals were grown by slow evaporation of the eluent. Yield (0.413 g, 62%). ^1Ĥ NMR (500 MHz, CD3CN): 7.52 (t, 4H, m-phenyl), 7.60 (t, 2H, p-phenyl), 8.02 (d, 4H, o-phenyl), 8.75 (s, 2H, imine).

Refinement

The positions of all hydrogen atoms were calculated using the standard riding model of *SHELXL97* with C—H(aromatic) distances of 0.93 Å and U_{iso} = 1.2 U_{eq}.

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).
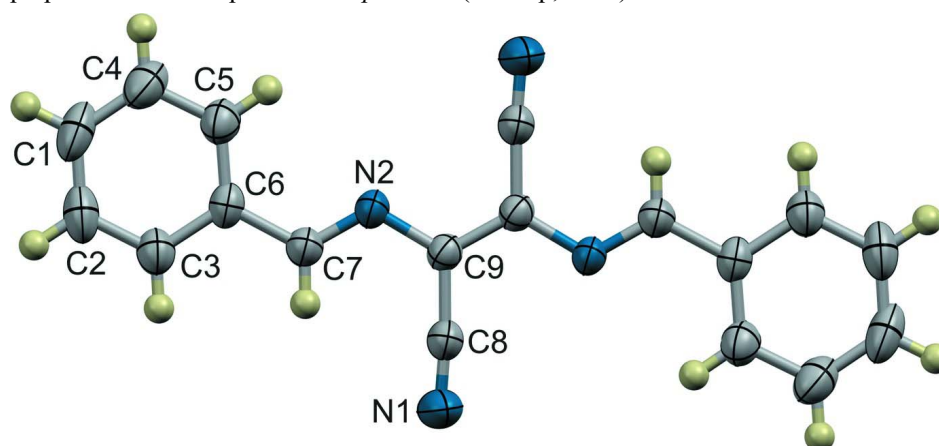

Figure 1

Labelled thermal ellipsoid plot of (1) (50% probability surfaces). Hydrogen atoms have been rendered as spheres of arbitrary radius.

(*E*)-2,3-Bis[(*E*)-benzylideneamino]but-2-enedinitrile

Crystal data

$C_{18}H_{12}N_4$	$Z = 1$
$M_r = 284.32$	$F(000) = 148$
Triclinic, $P\overline{1}$	$D_x = 1.241$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.389$ (4) Å	Cell parameters from 2824 reflections
$b = 7.608$ (5) Å	$\theta = 3.3$–26°
$c = 8.311$ (5) Å	$\mu = 0.08$ mm^{-1}
$\alpha = 103.96$ (5)°	$T = 295$ K
$\beta = 91.67$ (5)°	Needle, yellow
$\gamma = 102.97$ (5)°	$0.50 \times 0.20 \times 0.10$ mm
$V = 380.6$ (4) Å^3	

Data collection

Oxford Diffraction Xcalibur 2 CCD diffractometer	2824 measured reflections
	1498 independent reflections
Radiation source: fine-focus sealed tube	964 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.025$
ω scans at fixed θ angles	$\theta_{max} = 26.1°$, $\theta_{min} = 3.3°$
Absorption correction: multi-scan (Blessing, 1995)	$h = -6 \rightarrow 7$
	$k = -9 \rightarrow 9$
$T_{min} = 0.963$, $T_{max} = 0.992$	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.117$	
$S = 0.89$	H-atom parameters constrained
1498 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$
100 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	$\Delta\rho_{max} = 0.11$ e Å^{-3}
	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Experimental. ^{1}H NMR (500 MHz, CD3CN): 7.52 (t, 4H, m-phenyl), 7.60 (t, 2H, p-phenyl), 8.02 (d, 4H, o-phenyl), 8.75 (s, 2H, imine).

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	−0.8068 (3)	0.8047 (3)	0.9287 (2)	0.0708 (5)
H1	−0.9171	0.8241	0.9965	0.085*
C2	−0.7329 (3)	0.9254 (3)	0.8351 (2)	0.0664 (5)
H2	−0.7932	1.0265	0.8383	0.080*
C3	−0.5686 (2)	0.8984 (2)	0.7353 (2)	0.0547 (4)
H3	−0.5176	0.9818	0.6720	0.066*
C4	−0.7201 (3)	0.6539 (3)	0.9241 (2)	0.0670 (5)
H4	−0.7715	0.5720	0.9887	0.080*
C5	−0.5573 (2)	0.6243 (2)	0.82398 (19)	0.0544 (4)
H5	−0.4998	0.5215	0.8202	0.065*
C6	−0.4787 (2)	0.74650 (19)	0.72903 (16)	0.0436 (4)
C7	−0.3065 (2)	0.72118 (19)	0.62138 (17)	0.0451 (4)
H7	−0.2608	0.8070	0.5592	0.054*
C8	0.0179 (2)	0.7027 (2)	0.40742 (18)	0.0469 (4)
C9	−0.0504 (2)	0.57010 (17)	0.50538 (16)	0.0399 (3)
N1	0.0604 (2)	0.81235 (19)	0.33473 (18)	0.0687 (5)
N2	−0.21601 (17)	0.58581 (15)	0.60912 (13)	0.0412 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0504 (10)	0.1120 (15)	0.0524 (10)	0.0354 (10)	0.0149 (8)	0.0092 (10)
C2	0.0622 (11)	0.0768 (11)	0.0636 (11)	0.0404 (9)	0.0068 (9)	0.0018 (9)
C3	0.0541 (9)	0.0575 (9)	0.0552 (9)	0.0230 (8)	0.0095 (7)	0.0101 (7)

C4	0.0553 (10)	0.0953 (13)	0.0575 (10)	0.0227 (10)	0.0167 (8)	0.0273 (10)
C5	0.0481 (9)	0.0645 (9)	0.0553 (9)	0.0207 (8)	0.0091 (7)	0.0168 (8)
C6	0.0369 (7)	0.0502 (8)	0.0406 (8)	0.0138 (6)	0.0035 (6)	0.0026 (6)
C7	0.0439 (8)	0.0442 (8)	0.0489 (8)	0.0131 (7)	0.0105 (7)	0.0115 (7)
C8	0.0472 (8)	0.0461 (8)	0.0510 (8)	0.0166 (6)	0.0142 (7)	0.0128 (7)
C9	0.0363 (7)	0.0415 (7)	0.0415 (7)	0.0085 (6)	0.0073 (6)	0.0101 (6)
N1	0.0862 (11)	0.0602 (8)	0.0735 (10)	0.0251 (8)	0.0335 (8)	0.0327 (8)
N2	0.0375 (6)	0.0438 (7)	0.0440 (7)	0.0133 (5)	0.0101 (5)	0.0102 (5)

Geometric parameters (Å, º)

C1—C2	1.358 (2)	C5—C6	1.381 (2)
C1—C4	1.375 (2)	C5—H5	0.9300
C1—H1	0.9300	C6—C7	1.4551 (19)
C2—C3	1.377 (2)	C7—N2	1.2751 (17)
C2—H2	0.9300	C7—H7	0.9300
C3—C6	1.392 (2)	C8—N1	1.1340 (17)
C3—H3	0.9300	C8—C9	1.4456 (19)
C4—C5	1.375 (2)	C9—C9^i	1.352 (2)
C4—H4	0.9300	C9—N2	1.3918 (17)
C2—C1—C4	120.52 (15)	C4—C5—H5	119.9
C2—C1—H1	119.7	C6—C5—H5	119.9
C4—C1—H1	119.7	C5—C6—C3	118.88 (13)
C1—C2—C3	120.11 (15)	C5—C6—C7	122.30 (13)
C1—C2—H2	119.9	C3—C6—C7	118.82 (14)
C3—C2—H2	119.9	N2—C7—C6	122.49 (13)
C2—C3—C6	120.20 (16)	N2—C7—H7	118.8
C2—C3—H3	119.9	C6—C7—H7	118.8
C6—C3—H3	119.9	N1—C8—C9	175.27 (15)
C1—C4—C5	120.00 (17)	C9^i—C9—N2	120.38 (15)
C1—C4—H4	120.0	C9^i—C9—C8	118.58 (14)
C5—C4—H4	120.0	N2—C9—C8	121.04 (11)
C4—C5—C6	120.29 (15)	C7—N2—C9	119.86 (12)
C4—C1—C2—C3	−0.5 (3)	C2—C3—C6—C7	179.53 (14)
C1—C2—C3—C6	0.5 (3)	C5—C6—C7—N2	−0.7 (2)
C2—C1—C4—C5	−0.1 (3)	C3—C6—C7—N2	179.89 (12)
C1—C4—C5—C6	0.7 (3)	C6—C7—N2—C9	−179.29 (12)
C4—C5—C6—C3	−0.6 (2)	C9^i—C9—N2—C7	178.32 (15)
C4—C5—C6—C7	179.93 (14)	C8—C9—N2—C7	−1.5 (2)
C2—C3—C6—C5	0.1 (2)		

Symmetry code: (i) −x, −y+1, −z+1.