

Two polymorphs of N^1, N^4 -bis(5-hydroxypenta-1,3-diynyl)- N^1, N^4 -diphenylbenzene-1,4-diamine

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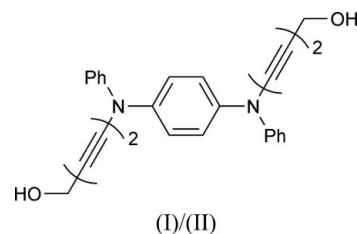
The title compound, $C_{28}H_{20}N_2O_2$, forms two conformational polymorphs, (I) and (II), where the molecular structures are similar except for the orientation of the two hydroxy groups. In (I), which was obtained by slow evaporation from chloroform, the two hydroxy groups have an *anti* conformation. The molecules form a sheet structure within the *ac* plane, where the hydroxy groups form zigzag hydrogen bonds. In (II), which was obtained by slow evaporation from acetonitrile, the two hydroxy groups have a *syn* conformation. The molecules form a double-sheet structure within the *ab* plane, where the hydroxy groups form 4-helix hydrogen bonds.

Comment

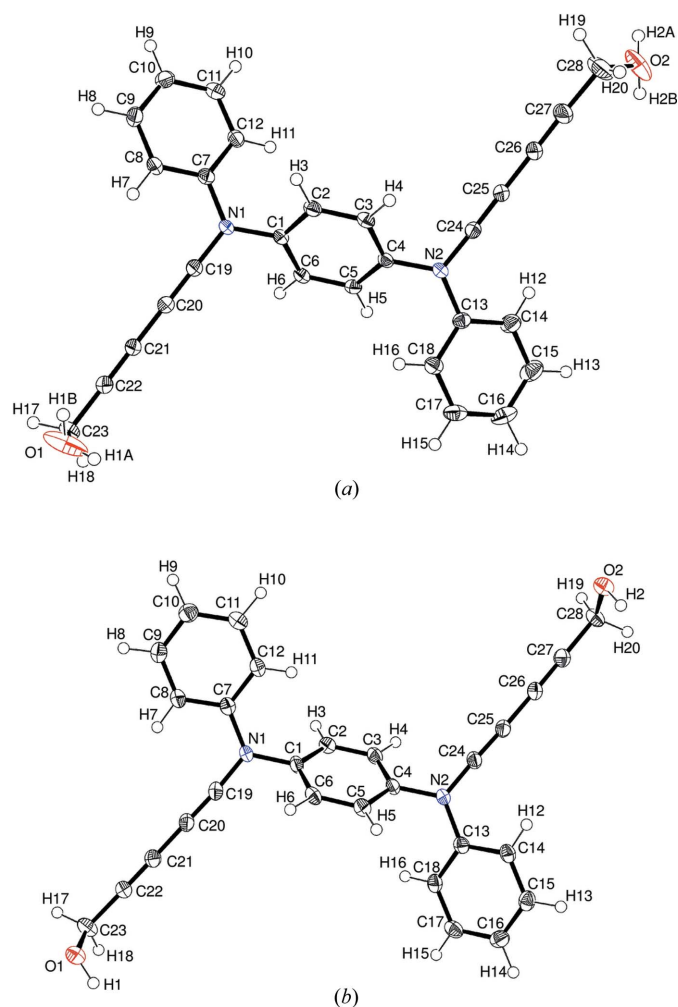
Benzene-1,4-diamines show electron-donating ability and are able to act as π -conjugated linkers. Acetylene derivatives which have amino groups as substituents are named ynamines, and they are known to be unstable because of their high reactivity. In the course of our research into ynamine compounds (Okuno *et al.*, 2006), we succeeded in the preparation and characterization of the title compound, which incorporates an N, N' -diethynylbenzene-1,4-diamine skeleton. The molecule is a key unit in the formation of two-leg ladder polydiacetylenes by solid-state polymerization. We also found conformational polymorphism (Bernstein, 2002) dependant on the recrystallization solvent of the title compound, shown in the orientation of the hydroxy groups. Either crystal could be obtained independently, as judged by powder X-ray diffraction. In order to clarify the difference in the hydrogen-bonding patterns and crystal packings caused by the different hydroxy-group orientations, the crystal structures of the two polymorphs, (I) and (II), were determined.

Displacement ellipsoid plots of the two polymorphs are shown in Fig. 1. The bond lengths and angles of both polymorphs are almost similar (Tables 1 and 3). These structural geometries are consistent with those of the reported ynamines (Galli *et al.*, 1988, 1989; Mayerle & Flandera, 1978; Okuno *et al.*, 2006).

In (I), the structures around the N atoms, *viz.* the N1/C1/C7/C19 (r.m.s. deviation = 0.010 Å) and N2/C4/C13/C24 planes (r.m.s. deviation = 0.003 Å), are planar. The dihedral angles between the plane of the C1–C6 ring and the N1/C1/C7/C19 and N2/C4/C13/C24 planes are 49.15 (8) and 31.92 (8)°, respectively. A large residual density of 0.65 e Å⁻³ is located near atom C28, which has rather elongated displacement ellipsoids. This is presumably due to thermal motion of the hydroxymethyl group.



In (II), the structures around the N atoms, *viz.* the N1/C1/C7/C19 (r.m.s. deviation = 0.045 Å) and N2/C4/C13/


Figure 1

The asymmetric units of (a) polymorph (I) and (b) polymorph (II) of the title compound, showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level. The disordered H atoms in polymorph (I) are identified by suffixes A and B.

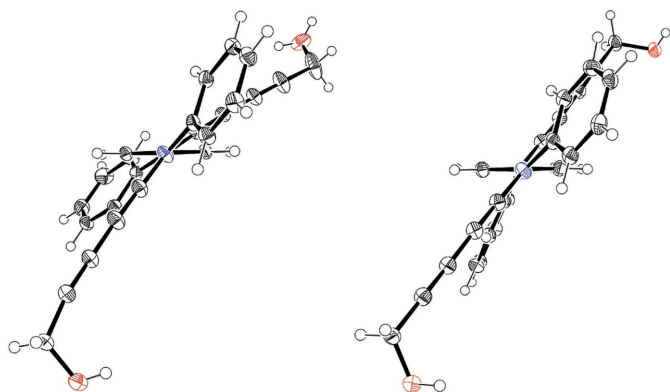


Figure 2
Views of (a) polymorph (I) and (b) polymorph (II), projected along the $N1 \cdots N2$ direction, with the benzene rings horizontal.

C24 planes (r.m.s. deviation = 0.007 \AA), are planar. The dihedral angles between the C1–C6 ring and the N1/C1/C7/C19 and N2/C4/C13/C24 planes are $57.36(8)$ and $46.98(8)^\circ$, respectively.

In both polymorphs, intramolecular conjugation between the two diacetylene units, *i.e.* overlap of *p*- or π -orbitals, is estimated by the value of $\cos^2\theta$, where θ is the torsion angle between the two orbitals. Even in the case of the smallest $\cos^2\theta$ with $\theta = 57.36^\circ$ in (II), the value is 0.29, suggesting the two diacetylene units are conjugated effectively.

We now discuss the differences between the molecular structures in the two polymorphs. A significant difference between the structures of (I) and (II) is the orientation of the hydroxy groups to the C23/N1/N2/C28 planes. The hydroxy groups in (I) have an *anti* conformation, while those in (II) have a *syn* conformation (Fig. 2), affording different types of intermolecular hydrogen bonds and different molecular packing structures. There are no significant π – π or C–H \cdots π interactions.

The molecules in (I) and (II) form similar sheet structures, which are parallel to the *ac* and *ab* planes, respectively. In (I),

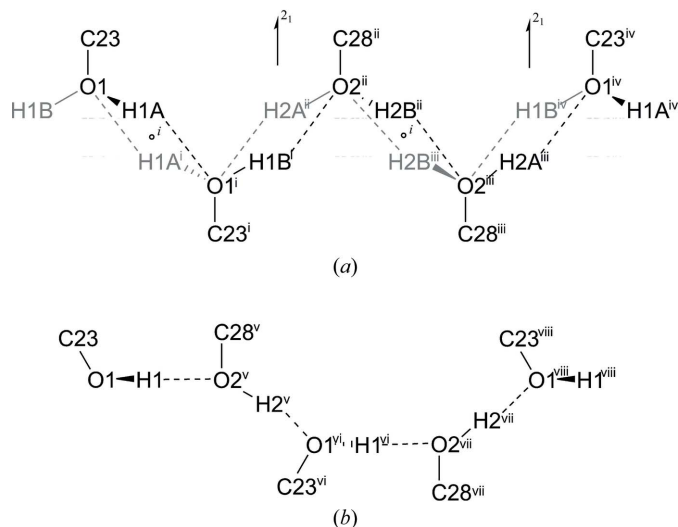


Figure 4
Schematic presentations of (a) the zigzag hydrogen-bonding network of (I) and (b) the 4-helix hydrogen-bonding network of (II). The hydrogen bonds involving the disordered H atoms of (I) are identified by black and grey lines. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x - 1, y, z$; (v) $x + 1, y + 1, z$; (vi) $-x + 3, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + 2, y + \frac{3}{2}, -z + \frac{1}{2}$; (viii) $x, y + 1, z$.]

the hydrogen bonds connect two sheets above and below (Fig. 3) to give zigzag intermolecular hydrogen bonds. The H atoms of both hydroxy groups are disordered and there are four types of O–H \cdots O hydrogen bonds (Table 2). Therefore, two kinds of zigzag intermolecular hydrogen bonds are observed, which are distinguished by black and grey lines in Fig. 4. When the structure of (I) was solved in the $P2_1/c$ space group without disorder, the distances between the O-bound H atoms became too close, because the hydrogen-bonded pair of molecules are related by inversion symmetry. The remaining peaks around the O atoms were also high, indicating the existence of disorder. The possibility of solving the structure in the space group $P2_1$ was examined carefully, but the disorder

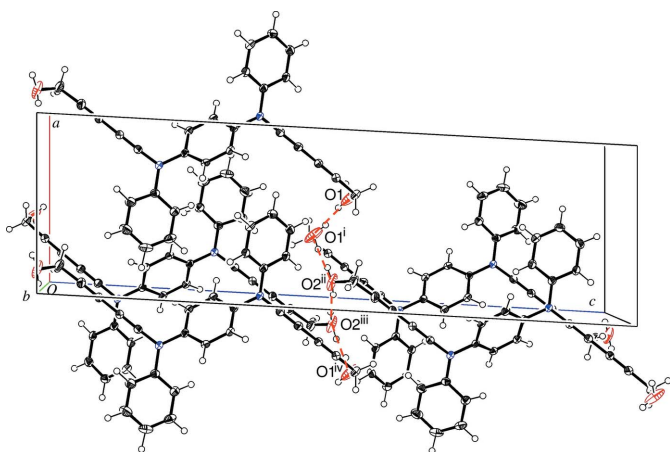


Figure 3
A view of the hydrogen-bonding interactions in (I) (dashed lines). [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x - 1, y, z$.]

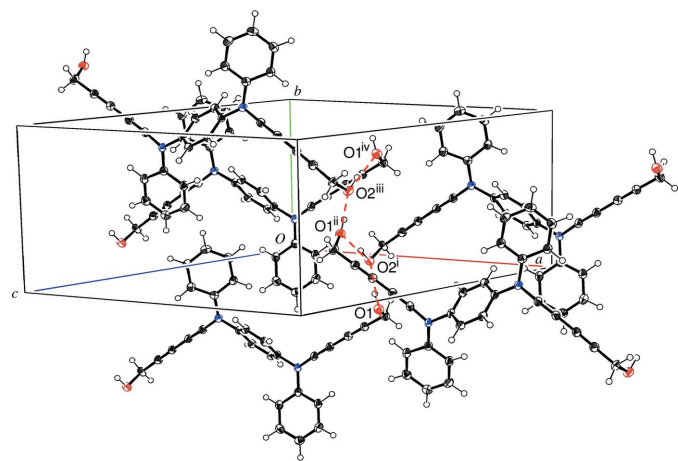


Figure 5
A view of the hydrogen-bonding interactions in (II) (dashed lines). [Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $-x + 3, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 2, y + \frac{3}{2}, -z + \frac{1}{2}$; (iv) $x, y + 1, z$.]

was still present, as indicated by large peaks around the O atoms.

In (II), intermolecular hydrogen bonds are limited within two sheets (Table 4), giving double-sheet structures (Fig. 5). The hydrogen-bonding pattern was classified as a 4-helix (Fig. 4) (Taylor & Macrae, 2001).

In spite of the difference in sheet packing, (I) and (II) have almost the same unit-cell volume and calculated densities of 1.304 and 1.309 Mg m⁻³, respectively.

Experimental

The title compound was prepared according to the method of Tabata *et al.* (2012). A suspension of copper(I) chloride (0.81 g, 7.8 mmol) in acetone (15 ml) was degassed by argon bubbling for 30 min, and then tetramethylethylenediamine (TMEDA; 400 µl, 2.6 mmol) was added and the suspension stirred for 30 min. The supernatant solution containing the CuCl-TMEDA catalyst was transferred to a mixture of N¹,N⁴-diethynyl-N¹,N⁴-diphenylbenzene-1,4-diamine (1.00 g, 3.24 mmol) and 2-propyn-1-ol (2.7 ml, 45 mmol) in acetone (63 ml) at 253 K. The solution was stirred for 2 d under an oxygen atmosphere. The solvent was evaporated and the residue extracted with dichloromethane (200 ml). The solution was washed with 5% ammonium hydroxide (300 ml) and the water layer was extracted twice with dichloromethane (200 ml). The combined organic layer was washed with water (300 ml) and dried over anhydrous sodium sulfate. After the solvent had evaporated, the residue was purified by gel permeation chromatography to give the title compound as a white powder (yield 0.68 g, yield 50%). Slow evaporation from solutions in chloroform or acetonitrile gave polymorphs (I) and (II), respectively.

Polymorph (I)

Crystal data

C ₂₈ H ₂₀ N ₂ O ₂	V = 2121.9 (7) Å ³
M _r = 416.46	Z = 4
Monoclinic, P2 ₁ /c	Mo Kα radiation
a = 9.0669 (18) Å	μ = 0.08 mm ⁻¹
b = 7.7778 (16) Å	T = 100 K
c = 30.135 (6) Å	0.49 × 0.16 × 0.05 mm
β = 93.148 (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	11823 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	4842 independent reflections
T _{min} = 0.961, T _{max} = 0.996	3703 reflections with I > 2σ(I)
	R _{int} = 0.030

Table 1

Selected geometric parameters (Å, °) for polymorph (I).

N1—C19	1.341 (2)	N2—C24	1.346 (2)
C19—C20	1.200 (2)	C24—C25	1.199 (2)
C20—C21	1.373 (2)	C25—C26	1.375 (2)
C21—C22	1.200 (2)	C26—C27	1.195 (3)
C22—C23	1.466 (2)	C27—C28	1.465 (3)
N1—C19—C20	179.4 (2)	N2—C24—C25	178.16 (18)
C19—C20—C21	177.1 (2)	C24—C25—C26	175.7 (2)
C22—C21—C20	179.7 (2)	C27—C26—C25	178.5 (2)
C21—C22—C23	170.6 (2)	C26—C27—C28	178.0 (2)

Refinement

R[F ² > 2σ(F ²)] = 0.051
wR(F ²) = 0.133
S = 1.06
4842 reflections
358 parameters
81 restraints

H atoms treated by a mixture of independent and constrained refinement
 Δρ_{max} = 0.65 e Å⁻³
 Δρ_{min} = -0.53 e Å⁻³

Polymorph (II)

Crystal data

C ₂₈ H ₂₀ N ₂ O ₂	V = 2113.0 (9) Å ³
M _r = 416.46	Z = 4
Monoclinic, P2 ₁ /c	Mo Kα radiation
a = 15.530 (4) Å	μ = 0.08 mm ⁻¹
b = 8.831 (2) Å	T = 100 K
c = 17.108 (4) Å	0.22 × 0.18 × 0.05 mm
β = 115.766 (3)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	11897 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	4826 independent reflections
T _{min} = 0.982, T _{max} = 0.996	3150 reflections with F ² > 2σ(F ²)
	R _{int} = 0.046

Refinement

R[F ² > 2σ(F ²)] = 0.048
wR(F ²) = 0.111
S = 1.05
4826 reflections
366 parameters

H atoms treated by a mixture of independent and constrained refinement
 Δρ_{max} = 0.24 e Å⁻³
 Δρ_{min} = -0.24 e Å⁻³

In polymorph (I), the C-bound H atoms, except for those on atoms C23 and C28, were obtained from a difference Fourier map and refined isotropically. The H atoms on C23 and C28 were placed in idealized locations (C—H = 0.99 Å) and were refined as riding on their parent C atoms, with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H

Table 2

Hydrogen-bond geometry (Å, °) for polymorph (I).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1A...O1 ⁱ	0.82 (1)	1.97 (2)	2.771 (3)	169 (1)
O1—H1B...O2 ⁱⁱ	0.82 (3)	1.94 (3)	2.753 (3)	173 (5)
O2—H2A...O1 ⁱⁱⁱ	0.82 (2)	1.94 (2)	2.753 (3)	173 (2)
O2—H2B...O2 ^{iv}	0.82 (2)	1.94 (2)	2.756 (3)	173 (2)

Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) -x + 2, y - 1/2, -z + 1/2; (iii) -x + 2, y + 1/2, -z + 1/2; (iv) -x + 2, -y + 2, -z.

Table 3

Selected geometric parameters (Å, °) for polymorph (II).

N1—C19	1.348 (3)	N2—C24	1.346 (3)
C19—C20	1.198 (3)	C24—C25	1.195 (3)
C20—C21	1.377 (3)	C25—C26	1.375 (3)
C21—C22	1.194 (3)	C26—C27	1.199 (3)
C22—C23	1.463 (3)	C27—C28	1.462 (3)
N1—C19—C20	176.1 (2)	N2—C24—C25	177.9 (2)
C19—C20—C21	179.0 (2)	C24—C25—C26	177.73 (18)
C20—C21—C22	179.1 (2)	C25—C26—C27	178.6 (3)
C21—C22—C23	178.83 (17)	C26—C27—C28	179.63 (19)

Table 4

Hydrogen-bond geometry (Å, °) for polymorph (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots O2^i$	0.90 (3)	1.93 (3)	2.821 (2)	168 (3)
$O2-H2\cdots O1^{ii}$	0.92 (3)	1.86 (3)	2.777 (2)	172 (3)

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

atoms were obtained from a difference Fourier map and found to be disordered. The occupancies of these H atoms were fixed at 0.5. The O-bound H-atom positions were refined with the restraint $O-H = 0.84 (2) \text{ \AA}$ (DFIX instruction in *SHELXL97*; Sheldrick, 2008), with $U_{iso}(H) = 1.2U_{eq}(O1 \text{ and } O2)$. Similar U restraints (SIMU instruction in *SHELXL97*) and approximately isotropic restraints (ISOR instruction in *SHELXL97*) were applied to atoms C22, C23, C27, C28, O1 and O2, with an effective s.u. of 0.005 \AA^2 . Restraints (SADI instruction in *SHELXL97*) were applied to the C \cdots H distances $C23\cdots H1A/H1B$ and $C28\cdots H2A/H2B$, the O—H bond lengths $O1-H1A/H1B$ and $O2-H2A/H2B$, and the C—O bond lengths $C23-O1$ and $C28-O2$, with an effective s.u. of 0.004 \AA . A planarity restraint (FLAT instruction in *SHELXL97*) was applied to the groups C23/O1/H1A/O1ⁱ [symmetry code: (i) $-x + 1, -y + 1, -z + 1$], C23/O1/H1B/O2ⁱⁱ [symmetry code: (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$], C28/O2/H2A/O1ⁱⁱⁱ [symmetry code: (iii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$] and C28/O2/H2B/O2^{iv} [symmetry code: (iv) $-x + 2, -y + 2, -z$].

In polymorph (II), the H atoms were obtained from a difference Fourier map. All H atoms, except H4, H6 and H14, were refined isotropically. The positions of H4, H6 and H14 were refined, although their $U_{iso}(H)$ values were fixed at $1.2U_{eq}(C)$.

For both compounds, data collection: *APEX2* (Bruker, 2010); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004);

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: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3036). Services for accessing these data are described at the back of the journal.

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