[2,5-Bis(dipropylamino)-4-(hydroxymethyl)phenyl]-methanol

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The centrosymmetric title compound, $C_{22}H_{36}N_2O_2$, was prepared in five steps from diethyl succinate. The dipropylamino groups are almost orthogonal to the central phenylenedimethanol ring [dihedral angle = 87.62 (9)°]. In the crystal, the molecules are connected by O—H⋯N hydrogen bonds, forming (101) layers separated by the propyl chains.

3D view

Chemical scheme
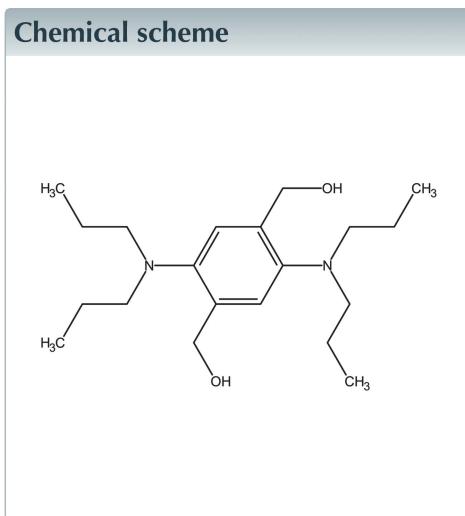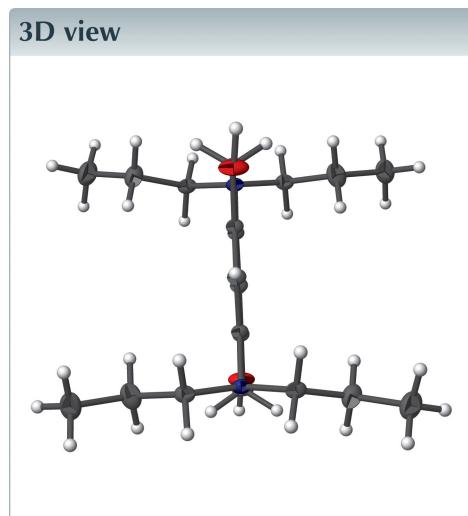
Structure description

In a project focusing on acidochromic oligophenylenevinylenes (Detert *et al.*, 2004; Detert & Sugiono, 2004, 2005), the title compound, $C_{22}H_{36}N_2O_2$, was prepared as an intermediate for fluorophores with a central *p*-aminoaniline unit (Detert & Schmitt, 2004, 2006; Schmitt *et al.*, 2008).

The complete molecule is generated by a crystallographic centre of symmetry (Fig. 1) and two centrosymmetric molecules occupy the monoclinic unit cell. The molecules are composed of an almost planar aromatic ring flanked by prolate dipropylamino groups. The mean planes of the ring and the dipropylamino unit enclose a dihedral angle of 87.62 (9)°. This orientation and torsion angles of −118.97 (11)° (C1—C2—N1—C4) and 0.8 (2)° (O1—C10—C1—C3_a) lead to an H-shape for the molecule.

In the extended structure, slightly bent O—H⋯N hydrogen bonds (Table 1, Fig. 2) connect each molecule with four neighbours, thus forming a slightly undulating network with an angle of 19.9° between the mean planes of the aromatic rings of adjacent molecules. This network lies parallel to (101) and the propyl groups act as spacers between the planes.
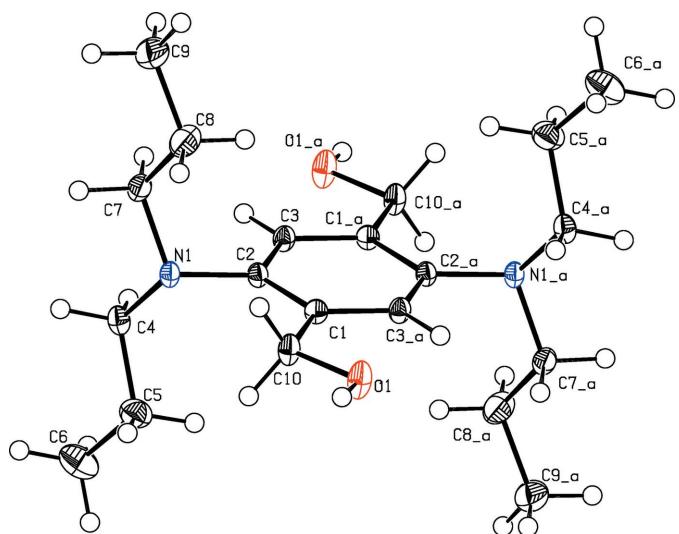
Figure 1
The molecular structure with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (a) $1 - x, 1 - y, -z$.

Synthesis and crystallization

The title compound was prepared from succinoyl succinate (Fehling, 1844) *via* condensation with propyl amine (Liebermann, 1914; Ulbricht *et al.*, 1979), refluxing of the diamine with propionyl chloride for 3 h followed by aqueous work-up and recrystallization of the diamide from toluene solution with *ca* 10% ethyl acetate. The amide (14 g, 0.033 mol) was added slowly to a stirred and boiling suspension of lithium aluminium hydride (3.8 g, 0.1 mol) in 200 ml of ether. After refluxing for 3 h, excess hydride was destroyed by addition of first ethyl acetate, and then aqueous sodium hydroxide (40%) to the stirred solution until clotting occurred. Suction filtration and digesting of the filter cake with ether, and washing of the combined organic phases with brine gave, after concentration and crystallization, 2.4 g (22%) of the diamine. Recrystallization from acetonitrile solution resulted in 2.4 g (22%) of
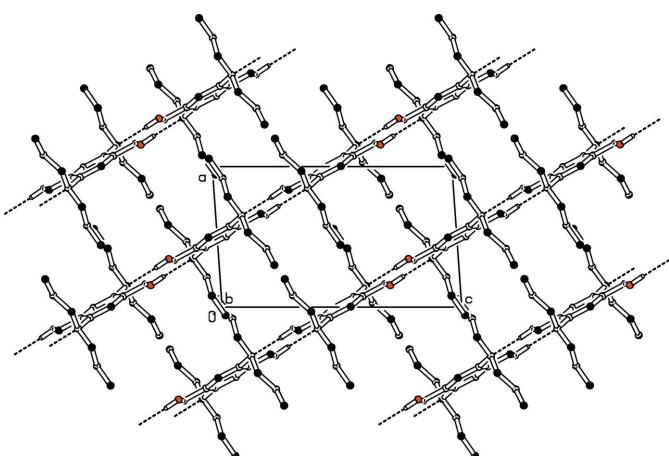

Figure 2
Partial packing diagram viewed along the *b*-axis direction. Hydrogen bonds are shown as dashed lines.

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1—H1⋯N1$^\text{i}$	0.88 (2)	2.05 (2)	2.9269 (13)	171.7 (18)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{36}N_2O_2$
M_r	336.51
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	8.2294 (4), 8.4573 (5), 14.0115 (7)
β (°)	93.974 (4)
V (Å^3)	972.83 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	$0.25 \times 0.20 \times 0.16$
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5278, 2318, 1995
R_int	0.019
$(\sin\theta/\lambda)_\text{max}$ (Å^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.112, 1.05
No. of reflections	2318
No. of parameters	172
H-atom treatment	All H-atom parameters refined
$\Delta\rho_\text{max}, \Delta\rho_\text{min}$ (e Å^{-3})	0.43, −0.16

Computer programs: *X-AREA WinXpose*, *Recipe* and *Integrate* (Stoe & Cie, 2019), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

slightly yellowish cuboid crystals with m.p. = 400–401 K. ^{1}H-NMR (400 MHz, CDCl$_3$): 6.93 (*s*, 2 H ar); 4.75 (*s*, 4 H, benzylic), 2.83 (*m*, 8 H, N—CH2); 1.45 (*m*, 8 H), 0.85 (*t*, 12 H, CH$_3$); ^{13}C-NMR (100 MHz, CDCl$_3$) 146.2 (C-2,5), 136.2 (C-1,4), 122.2 (C3,6), 64.8 (CH$_2$OH), 57.0 (NCH$_2$), 20.3 (CH$_2$), 11.5 (CH$_3$); FD—MS: *m/z* = 336.2 (100%, M^+); IR (CDCl$_3$, cm^{-1}): 3370, 2960, 2940, 2870, 1630, 1500, 1455, 1410, 1285, 1255, 1140, 1055.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were located in difference Fourier maps and refined with isotropic displacement parameters.

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full crystallographic data

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Crystal data

$C_{20}H_{36}N_2O_2$

$M_r = 336.51$

Monoclinic, $P2_1/n$

$a = 8.2294$ (4) Å

$b = 8.4573$ (5) Å

$c = 14.0115$ (7) Å

$\beta = 93.974$ (4)°

$V = 972.83$ (9) Å^3

$Z = 2$

$F(000) = 372$

$D_x = 1.149$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7030 reflections

$\theta = 2.4–28.4°$

$\mu = 0.07$ mm^{-1}

$T = 120$ K

Block, colourless

$0.25 \times 0.20 \times 0.16$ mm

Data collection

STOE IPDS 2T
   diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4
   mm long-fine focus

Detector resolution: 6.67 pixels mm^{-1}

rotation method, ω scans

5278 measured reflections

2318 independent reflections

1995 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$

$\theta_{max} = 27.9°$, $\theta_{min} = 2.8°$

$h = -9 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.112$

$S = 1.05$

2318 reflections

172 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.4938P]$
   where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.43$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ 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	$U_{iso}*/U_{eq}$
O1	0.65711 (12)	0.27293 (10)	0.20873 (7)	0.0244 (2)

H1	0.717 (3)	0.257 (2)	0.2627 (16)	0.046 (5)*
N1	0.65180 (12)	0.75248 (11)	0.10757 (7)	0.0148 (2)
C1	0.57794 (13)	0.47022 (13)	0.09097 (8)	0.0146 (2)
C2	0.57352 (13)	0.62308 (13)	0.05321 (8)	0.0141 (2)
C3	0.49620 (14)	0.65103 (13)	−0.03682 (8)	0.0151 (2)
H3	0.4942 (17)	0.7560 (16)	−0.0625 (10)	0.014 (3)*
C4	0.53162 (15)	0.87545 (14)	0.12965 (8)	0.0179 (2)
H4A	0.4663 (18)	0.9151 (18)	0.0694 (10)	0.018 (2)*
H4B	0.5946 (18)	0.9662 (18)	0.1557 (10)	0.018 (2)*
C5	0.41498 (18)	0.81758 (17)	0.20128 (10)	0.0268 (3)
H5A	0.478 (2)	0.779 (2)	0.2577 (13)	0.033 (3)*
H5B	0.354 (2)	0.728 (2)	0.1733 (13)	0.033 (3)*
C6	0.3000 (2)	0.9476 (2)	0.23025 (12)	0.0369 (4)
H6A	0.227 (3)	0.908 (3)	0.2782 (15)	0.053 (3)*
H6B	0.231 (3)	0.985 (2)	0.1760 (16)	0.053 (3)*
H6C	0.365 (3)	1.039 (3)	0.2574 (15)	0.053 (3)*
C7	0.78539 (15)	0.82069 (14)	0.05542 (8)	0.0186 (3)
H7A	0.8328 (19)	0.9104 (19)	0.0947 (10)	0.020 (3)*
H7B	0.7429 (18)	0.8668 (17)	−0.0069 (11)	0.020 (3)*
C8	0.91847 (17)	0.70094 (17)	0.03952 (11)	0.0285 (3)
H8A	0.870 (2)	0.613 (2)	0.0016 (13)	0.042 (4)*
H8B	0.959 (2)	0.658 (2)	0.1023 (14)	0.042 (4)*
C9	1.05723 (19)	0.77308 (19)	−0.01183 (12)	0.0327 (3)
H9A	1.142 (3)	0.698 (2)	−0.0227 (14)	0.045 (3)*
H9B	1.106 (2)	0.864 (2)	0.0248 (14)	0.045 (3)*
H9C	1.013 (2)	0.821 (2)	−0.0742 (15)	0.045 (3)*
C10	0.66429 (16)	0.43700 (14)	0.18745 (8)	0.0186 (3)
H10A	0.777 (2)	0.4729 (19)	0.1861 (11)	0.024 (3)*
H10B	0.6141 (19)	0.4995 (19)	0.2383 (11)	0.024 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0380 (5)	0.0142 (4)	0.0190 (4)	−0.0034 (4)	−0.0123 (4)	0.0048 (3)
N1	0.0182 (5)	0.0116 (4)	0.0141 (4)	−0.0019 (4)	−0.0016 (3)	−0.0011 (3)
C1	0.0168 (5)	0.0139 (5)	0.0129 (5)	0.0001 (4)	−0.0010 (4)	0.0010 (4)
C2	0.0160 (5)	0.0127 (5)	0.0134 (5)	−0.0011 (4)	−0.0008 (4)	−0.0015 (4)
C3	0.0190 (5)	0.0117 (5)	0.0144 (5)	−0.0004 (4)	−0.0012 (4)	0.0015 (4)
C4	0.0229 (6)	0.0135 (5)	0.0170 (5)	0.0012 (4)	−0.0019 (4)	−0.0015 (4)
C5	0.0304 (7)	0.0249 (7)	0.0260 (6)	0.0042 (5)	0.0079 (5)	0.0005 (5)
C6	0.0368 (8)	0.0409 (9)	0.0340 (8)	0.0107 (7)	0.0087 (7)	−0.0052 (7)
C7	0.0211 (6)	0.0166 (5)	0.0177 (5)	−0.0042 (4)	−0.0005 (4)	0.0005 (4)
C8	0.0241 (6)	0.0219 (6)	0.0401 (8)	−0.0012 (5)	0.0062 (6)	0.0024 (6)
C9	0.0269 (7)	0.0320 (8)	0.0404 (8)	−0.0047 (6)	0.0098 (6)	−0.0032 (6)
C10	0.0269 (6)	0.0126 (5)	0.0152 (5)	−0.0020 (5)	−0.0062 (4)	0.0016 (4)

Geometric parameters (Å, º)

O1—C10	1.4214 (14)	C5—H5B	0.977 (18)
O1—H1	0.88 (2)	C6—H6A	0.99 (2)
N1—C2	1.4577 (13)	C6—H6B	0.97 (2)
N1—C7	1.4787 (15)	C6—H6C	1.00 (2)
N1—C4	1.4825 (15)	C7—C8	1.5194 (18)
C1—C3ⁱ	1.3912 (15)	C7—H7A	1.001 (16)
C1—C2	1.3964 (15)	C7—H7B	0.997 (15)
C1—C10	1.5094 (15)	C8—C9	1.5191 (19)
C2—C3	1.3931 (15)	C8—H8A	0.99 (2)
C3—H3	0.958 (14)	C8—H8B	0.99 (2)
C4—C5	1.5171 (18)	C9—H9A	0.97 (2)
C4—H4A	1.025 (15)	C9—H9B	0.99 (2)
C4—H4B	0.982 (15)	C9—H9C	1.01 (2)
C5—C6	1.524 (2)	C10—H10A	0.980 (16)
C5—H5A	0.970 (19)	C10—H10B	0.999 (16)
C10—O1—H1	107.6 (13)	C5—C6—H6C	109.6 (12)
C2—N1—C7	110.57 (9)	H6A—C6—H6C	109.8 (17)
C2—N1—C4	111.02 (9)	H6B—C6—H6C	108.3 (17)
C7—N1—C4	111.04 (9)	N1—C7—C8	112.37 (10)
C3ⁱ—C1—C2	118.48 (10)	N1—C7—H7A	107.4 (9)
C3ⁱ—C1—C10	120.84 (10)	C8—C7—H7A	109.2 (9)
C2—C1—C10	120.66 (10)	N1—C7—H7B	110.9 (9)
C3—C2—C1	119.90 (10)	C8—C7—H7B	110.2 (9)
C3—C2—N1	120.22 (10)	H7A—C7—H7B	106.6 (12)
C1—C2—N1	119.88 (9)	C9—C8—C7	112.02 (12)
C1ⁱ—C3—C2	121.62 (10)	C9—C8—H8A	109.9 (11)
C1ⁱ—C3—H3	118.9 (8)	C7—C8—H8A	108.2 (11)
C2—C3—H3	119.5 (8)	C9—C8—H8B	110.7 (11)
N1—C4—C5	111.94 (10)	C7—C8—H8B	108.4 (11)
N1—C4—H4A	112.2 (8)	H8A—C8—H8B	107.5 (15)
C5—C4—H4A	109.3 (8)	C8—C9—H9A	112.8 (12)
N1—C4—H4B	106.4 (9)	C8—C9—H9B	111.0 (11)
C5—C4—H4B	110.4 (9)	H9A—C9—H9B	108.4 (16)
H4A—C4—H4B	106.4 (12)	C8—C9—H9C	109.4 (11)
C4—C5—C6	112.13 (12)	H9A—C9—H9C	110.4 (16)
C4—C5—H5A	108.8 (10)	H9B—C9—H9C	104.5 (16)
C6—C5—H5A	109.3 (10)	O1—C10—C1	110.23 (9)
C4—C5—H5B	108.5 (10)	O1—C10—H10A	111.1 (9)
C6—C5—H5B	110.8 (10)	C1—C10—H10A	108.3 (9)
H5A—C5—H5B	107.2 (15)	O1—C10—H10B	110.0 (9)
C5—C6—H6A	110.6 (13)	C1—C10—H10B	110.4 (9)
C5—C6—H6B	111.6 (12)	H10A—C10—H10B	106.9 (13)
H6A—C6—H6B	106.9 (17)		
C3ⁱ—C1—C2—C3	−0.09 (18)	N1—C2—C3—C1ⁱ	179.23 (10)

C10—C1—C2—C3	178.66 (11)	C2—N1—C4—C5	69.20 (12)
C3^i—C1—C2—N1	−179.23 (10)	C7—N1—C4—C5	−167.35 (10)
C10—C1—C2—N1	−0.48 (16)	N1—C4—C5—C6	175.43 (12)
C7—N1—C2—C3	−61.82 (13)	C2—N1—C7—C8	−61.45 (13)
C4—N1—C2—C3	61.89 (13)	C4—N1—C7—C8	174.85 (10)
C7—N1—C2—C1	117.32 (11)	N1—C7—C8—C9	−178.53 (11)
C4—N1—C2—C1	−118.97 (11)	C3^i—C1—C10—O1	0.79 (16)
C1—C2—C3—C1^i	0.09 (19)	C2—C1—C10—O1	−177.92 (10)

Symmetry code: (i) −x+1, −y+1, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1^{ii}	0.88 (2)	2.05 (2)	2.9269 (13)	171.7 (18)

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