Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4,4′-({[(Pyridine-2,6-diyl)bis(methylene)]-bis(oxy)}bis(methylene))dibenzonitrile

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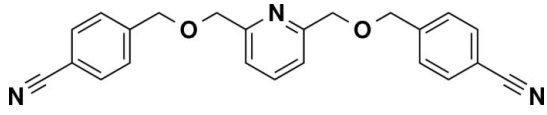
Received 3 January 2014; accepted 6 January 2014

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.106; data-to-parameter ratio = 14.3.

The complete title molecule, $C_{23}H_{19}N_3O_2$, is generated by a twofold axis passing through the central ring. The two oxymethylbenzonitrile arms are attached at the *meta* positions of the central pyridine ring. The dihedral angle between the pyridine ring and benzene ring of both arms is 84.55 (6)° while the benzene rings make a dihedral angle of 46.07 (7)°. In the crystal, weak C—H···π interactions link the molecules sheets parallel to the *ac* plane.

Related literature

For bond-length data, see: Allen *et al.* (1987). For related structures, see: Lima *et al.* (2011); Wang & Zhao (2008): Zhao (2008); Xiao & Zhao (2008).



Experimental

Crystal data

$C_{23}H_{19}N_3O_2$
M_r = 369.41
Monoclinic, $C2/c$
a = 14.1838 (7) Å
b = 7.5493 (4) Å
c = 18.4619 (12) Å
β = 107.837 (2)°
V = 1881.83 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.49 × 0.44 × 0.34 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.960, T_{max} = 0.972
21611 measured reflections
1846 independent reflections
1519 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.05
1846 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

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

Cg is the centroid of the N1/C1–C3/C2′/C3′ ring.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···Cg^{i}	0.93	2.87	3.7180 (15)	152

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

Data collection: *SMART* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; 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: *SHELXTL* and *PLATON* (Spek, 2009).

The authors would like to thank Universiti Kebangsaan Malaysia and the Ministry of Higher Education, Malaysia, for research grants GGPM-2012–016 and DIP-2012–11, respectively. Research facilities provided by the Centre of Research and Instrumentation (CRIM) are very much appreciated.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HG5373).

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supporting information

Acta Cryst. (2014). E**70**, o132 [doi:10.1107/S1600536814000245]

4,4′-({[(Pyridine-2,6-diyl)bis(methylene)]bis(oxy)}bis(methylene))dibenzonitrile

Bohari M. Yamin, Nurul A. Kamalulazmy and Nurul I. Hassan

S1. Comment

Despite the wide application of dibenzonitrile compounds in the area of chemical synthesis and industrial, the structural study of dibenzonitrile derivatives are less reported. Thiadiazole dibenzonitrile (Wang & Zhao, 2008) and naphthalene dibenzonitrile (Lima *et al.*, 2011) are some examples of dibenzonitrile derivatives. On the other hand, 4,4′-{[1,1′-Methylenebis (naphthalene-2,1-diyl)]bis(oxymethylene)}dibenzonitrile (Zhao, 2008) and 4,4′-(Oxydimethylene)dibenzonitrile (Xiao & Zhao, 2008) are few examples of bis(oxymethylene)dibenzonitriles. The title compound is a bis(methylene)bis(-oxy) bis(methylene)dibenzonitrile in which the oxymtheylenedibenzonitrile arms are connected by 2,6-pyridine linkager at *meta* position (Figure 1) making the whole molecule, a bird like structure. The dihedral angle between the two benzene rings [(C6/C7/C8/C9/C10/C11), (C6a/C7a/C8a/C9a/C10*a*/C11*a*)] and the central pyridine (C1/C2/C3/C2a/C3a/N1) is 84.55 (6)°. The maximum deviation of the two planes is 0.005 (1) Å for C2 atom from the least square plane of the pyridine ring. The bond lengths are in normal ranges (Allen *et al.*,1987). In the structure, no intermolecular hydrogen bonds were observed except the presence of C8—H8···π bonds with the pyridine ring (H8—centroid *Cg* distance of 2.87 Å, and *X*—H···centroid angle = 152°).

S2. Experimental

NaH (10.72 g, 17.8 mmol) was carefully added to a solution of 2,6-pyridine dimethanol (1.0 g, 7.2 mmol) in dry THF (35 ml). The resulting mixture was refluxed for 1.5 h and allowed to cool to room temperature. Next, 4-bromomethyl benzonitrile (3.0 g, 15.3 mmol) was added and continued to reflux for another 24 h at 75°C. Water was slowly added to quench the reaction. The organic layers were extracted into ethyl acetate. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting residue was purified using column chromatography (Hexane:Ethyl acetate) to furnish a colorless powder. Single crystals were obtained from the solution of Hexane:Ethyl acetate after one day of evaporation (yield 87%, m.p 378.8–380 K). ^{1}H NMR (300.1 MHz, $CDCl_3$): 7.75 (1*H*, t, $3J_{HH}$ 7.7 Hz; ArH), 7.65 (4*H*, d, $3J_{HH}$ 8.4 Hz;4 *x* ArH),7.49 (4*H*, d, $3J_{HH}$ 8.6 Hz; 4 *x* ArH), 7.40 (2*H*, d, $3J_{HH}$ 7.8 Hz; 2 *x* ArH), 4.71 (4*H*, s; 2 *x* CH_2), 4.70 (4*H*, s; 2 *x* CH_2);^{13}C NMR (75.5 MHz, $CDCl_3$):*C* 157.6 (ArC), 143.6 (ArC), 137.6 (ArCH), 132.4 (ArCH), 127.9 (ArCH), 120.4 (ArCH), 118.9 (CN), 111.6 (ArC),73.7 (CH_2), 72.1 (CH_2); MS (CI^+) m/*z* 239.0 (27), 370.2 ([*M*+H]$^+$, 100); HRMS (CI^+) m/*z* calculated for $C_{23}H_{20}N_3O_2$ [*M*+H]$^+$ 370.1556, found 370.1563.

S3. Refinement

After their location in the difference map, the H-atoms attached to the C and N atoms were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C—H = 0.93 Å, with U_{iso}(H)=1.2U_{eq}(C).

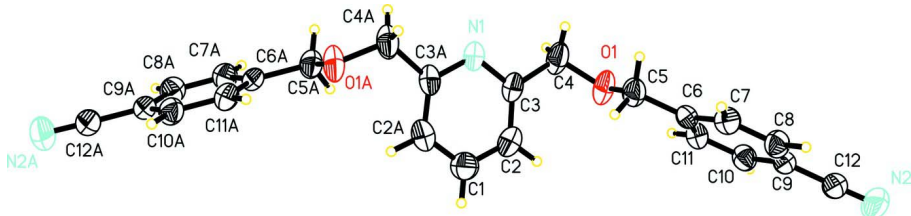

Figure 1

Molecular structure of (I) with 50% probability displacement ellipsoids. Symmetry code A: (-x + 2, y, -z + 1/2).

4,4′-({[(Pyridine-2,6-diyl)bis(methylene)]bis(oxy)}bis(methylene))dibenzonitrile

Crystal data

$C_{23}H_{19}N_3O_2$
M_r = 369.41
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 14.1838 (7) Å
b = 7.5493 (4) Å
c = 18.4619 (12) Å
β = 107.837 (2)°
V = 1881.83 (18) Å^3
Z = 4
F(000) = 776
D_x = 1.304 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 8925 reflections
θ = 3.0–26.0°
μ = 0.09 mm^{-1}
T = 296 K
Block, colourless
0.49 × 0.44 × 0.34 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 83.66 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.960, T_{max} = 0.972
21611 measured reflections
1846 independent reflections
1519 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 26.0°, θ_{min} = 3.1°
h = −17→17
k = −9→9
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.05
1846 reflections
129 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
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.9538P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0196 (14)

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}
O1	0.73355 (7)	0.39554 (16)	0.18488 (6)	0.0547 (3)
N1	1.0000	0.4615 (2)	0.2500	0.0416 (4)
N2	0.25164 (10)	0.0851 (2)	−0.08574 (9)	0.0706 (5)
C1	1.0000	0.0946 (3)	0.2500	0.0530 (6)
H1	1.0000	−0.0286	0.2500	0.064*
C2	0.91206 (10)	0.1866 (2)	0.23419 (8)	0.0495 (4)
H2	0.8519	0.1269	0.2230	0.059*
C3	0.91523 (9)	0.3697 (2)	0.23533 (7)	0.0415 (4)
C4	0.82379 (10)	0.4813 (2)	0.22471 (10)	0.0560 (4)
H4A	0.8206	0.5169	0.2744	0.067*
H4B	0.8300	0.5880	0.1973	0.067*
C5	0.71745 (10)	0.3882 (2)	0.10575 (8)	0.0463 (4)
H5A	0.7659	0.3102	0.0951	0.056*
H5B	0.7257	0.5054	0.0870	0.056*
C6	0.61510 (9)	0.32139 (17)	0.06575 (8)	0.0369 (3)
C7	0.58164 (10)	0.3218 (2)	−0.01320 (8)	0.0429 (4)
H7	0.6225	0.3645	−0.0402	0.052*
C8	0.48871 (11)	0.2599 (2)	−0.05204 (8)	0.0452 (4)
H8	0.4672	0.2599	−0.1050	0.054*
C9	0.42703 (10)	0.19725 (18)	−0.01217 (8)	0.0403 (3)
C10	0.45942 (10)	0.19748 (19)	0.06662 (8)	0.0443 (4)
H10	0.4182	0.1562	0.0936	0.053*
C11	0.55300 (10)	0.25913 (19)	0.10512 (8)	0.0422 (4)
H11	0.5746	0.2588	0.1580	0.051*
C12	0.32950 (11)	0.1331 (2)	−0.05269 (9)	0.0496 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0282 (5)	0.0835 (9)	0.0491 (6)	−0.0047 (5)	0.0069 (4)	−0.0156 (5)
N1	0.0293 (8)	0.0550 (10)	0.0369 (8)	0.000	0.0050 (6)	0.000
N2	0.0447 (8)	0.0701 (10)	0.0859 (11)	−0.0081 (7)	0.0035 (7)	−0.0136 (8)
C1	0.0554 (13)	0.0502 (13)	0.0511 (12)	0.000	0.0130 (10)	0.000
C2	0.0393 (8)	0.0624 (10)	0.0446 (8)	−0.0113 (7)	0.0095 (6)	−0.0047 (7)
C3	0.0302 (7)	0.0592 (9)	0.0329 (7)	−0.0029 (6)	0.0063 (5)	−0.0071 (6)
C4	0.0297 (7)	0.0736 (11)	0.0599 (9)	−0.0005 (7)	0.0065 (6)	−0.0220 (8)

C5	0.0327 (7)	0.0542 (9)	0.0498 (8)	0.0018 (6)	0.0095 (6)	−0.0016 (7)
C6	0.0302 (6)	0.0342 (7)	0.0442 (7)	0.0066 (5)	0.0084 (5)	−0.0003 (6)
C7	0.0403 (7)	0.0467 (8)	0.0441 (8)	0.0014 (6)	0.0164 (6)	−0.0001 (6)
C8	0.0469 (8)	0.0485 (8)	0.0368 (7)	0.0028 (7)	0.0080 (6)	−0.0030 (6)
C9	0.0343 (7)	0.0344 (7)	0.0478 (8)	0.0030 (5)	0.0061 (6)	−0.0013 (6)
C10	0.0368 (7)	0.0469 (8)	0.0500 (8)	0.0009 (6)	0.0142 (6)	0.0073 (6)
C11	0.0381 (7)	0.0480 (8)	0.0376 (7)	0.0046 (6)	0.0071 (6)	0.0040 (6)
C12	0.0419 (8)	0.0432 (8)	0.0588 (9)	0.0025 (7)	0.0080 (7)	−0.0039 (7)

Geometric parameters (Å, º)

O1—C5	1.4088 (18)	C5—H5A	0.9700
O1—C4	1.4217 (17)	C5—H5B	0.9700
N1—C3^{i}	1.3417 (16)	C6—C11	1.3846 (19)
N1—C3	1.3417 (16)	C6—C7	1.3879 (19)
N2—C12	1.1449 (19)	C7—C8	1.3751 (19)
C1—C2	1.3786 (19)	C7—H7	0.9300
C1—C2^{i}	1.3786 (19)	C8—C9	1.387 (2)
C1—H1	0.9300	C8—H8	0.9300
C2—C3	1.382 (2)	C9—C10	1.3847 (19)
C2—H2	0.9300	C9—C12	1.4400 (19)
C3—C4	1.508 (2)	C10—C11	1.3804 (19)
C4—H4A	0.9700	C10—H10	0.9300
C4—H4B	0.9700	C11—H11	0.9300
C5—C6	1.5001 (18)		
C5—O1—C4	112.87 (12)	C6—C5—H5B	109.6
C3^{i}—N1—C3	117.77 (18)	H5A—C5—H5B	108.1
C2—C1—C2^{i}	119.5 (2)	C11—C6—C7	118.96 (12)
C2—C1—H1	120.3	C11—C6—C5	122.07 (12)
C2^{i}—C1—H1	120.3	C7—C6—C5	118.97 (12)
C1—C2—C3	118.50 (14)	C8—C7—C6	120.77 (13)
C1—C2—H2	120.8	C8—C7—H7	119.6
C3—C2—H2	120.8	C6—C7—H7	119.6
N1—C3—C2	122.86 (14)	C7—C8—C9	119.92 (13)
N1—C3—C4	114.79 (14)	C7—C8—H8	120.0
C2—C3—C4	122.25 (13)	C9—C8—H8	120.0
O1—C4—C3	114.53 (13)	C10—C9—C8	119.77 (12)
O1—C4—H4A	108.6	C10—C9—C12	120.20 (13)
C3—C4—H4A	108.6	C8—C9—C12	120.03 (13)
O1—C4—H4B	108.6	C11—C10—C9	119.91 (13)
C3—C4—H4B	108.6	C11—C10—H10	120.0
H4A—C4—H4B	107.6	C9—C10—H10	120.0
O1—C5—C6	110.41 (11)	C10—C11—C6	120.67 (13)
O1—C5—H5A	109.6	C10—C11—H11	119.7
C6—C5—H5A	109.6	C6—C11—H11	119.7
O1—C5—H5B	109.6	N2—C12—C9	178.67 (19)

C2^{i}—C1—C2—C3	−0.50 (9)	C11—C6—C7—C8	−0.7 (2)
C3^{i}—N1—C3—C2	−0.54 (10)	C5—C6—C7—C8	179.27 (13)
C3^{i}—N1—C3—C4	175.99 (14)	C6—C7—C8—C9	0.5 (2)
C1—C2—C3—N1	1.1 (2)	C7—C8—C9—C10	0.0 (2)
C1—C2—C3—C4	−175.22 (11)	C7—C8—C9—C12	179.68 (14)
C5—O1—C4—C3	−76.99 (18)	C8—C9—C10—C11	−0.3 (2)
N1—C3—C4—O1	159.71 (12)	C12—C9—C10—C11	180.00 (13)
C2—C3—C4—O1	−23.7 (2)	C9—C10—C11—C6	0.1 (2)
C4—O1—C5—C6	−171.60 (12)	C7—C6—C11—C10	0.3 (2)
O1—C5—C6—C11	−6.58 (19)	C5—C6—C11—C10	−179.59 (13)
O1—C5—C6—C7	173.49 (12)		

Symmetry code: (i) −*x*+2, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the N1/C1–C3/C2′/C3′ ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O1	0.93	2.39	2.735 (2)	102
C8—H8···*Cg*^{ii}	0.93	2.87	3.7180 (15)	152

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