

Crystal structure of *N,N'*-bis[(pyridin-4-yl)methyl]naphthalene diimide

Mariana Nicolas-Gomez, Diego Martínez-Otero and Alejandro Dorazco-González*

Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Instituto de Química, Universidad Nacional Autónoma de México, Carretera Toluca-Atacomulco Km 14.5 CP 50200 Toluca, Estado de México, México. *Correspondence e-mail: adg@unam.mx

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In the centrosymmetric title compound, $C_{26}H_{16}N_4O_4$ {systematic name: 6,13-bis[(pyridin-4-yl)methyl]-6,13-diazatetracyclo[6.6.2.0^{4,16}.0^{11,15}]hexadeca-1,3,8,10,15-pentaene-5,7,12,14-tetrone}, the central ring system is essentially planar [maximum deviation = 0.0234 (8) Å] and approximately perpendicular to the terminal pyridine ring [dihedral angle = 84.38 (3)°]. The molecule displays a *trans* conformation with the (pyridin-4-yl)methyl groups on both sides of the central naphthalene diimide plane. In the crystal, molecules are linked by π - π stacking between parallel pyridine rings [centroid-centroid distances = 3.7014 (8) and 3.8553 (8) Å] and weak C—H \cdots O hydrogen bonds, forming a three-dimensional supramolecular architecture.

Keywords: crystal structure; naphthalene diimide; transistors; organic supramolecular solids; hydrogen bonding; π - π stacking.

CCDC reference: 1017799

1. Related literature

For crystal structures of related compounds, see: Xu *et al.* (2011); Reczek *et al.* (2006); Li *et al.* (2009). For colorimetric applications and nanoscale properties, see: Pandeeswar *et al.* (2014); Trivedi *et al.* (2009); Matsunaga *et al.* (2014); Pantoş *et al.* (2007). For the design of transistors, see: Jung *et al.* (2009); Oh *et al.* (2010). For organic supramolecular solids, see: Cheney *et al.* (2007). For the design and synthesis of one-dimensional coordination polymers, see: Li *et al.* (2011, 2012).

2. Experimental

2.1. Crystal data

$C_{26}H_{16}N_4O_4$	$\gamma = 87.590$ (4)°
$M_r = 448.43$	$V = 489.37$ (6) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.5891$ (4) Å	Cu $K\alpha$ radiation
$b = 7.5232$ (5) Å	$\mu = 0.87$ mm ⁻¹
$c = 11.9525$ (8) Å	$T = 296$ K
$\alpha = 77.093$ (3)°	$0.34 \times 0.13 \times 0.08$ mm
$\beta = 88.445$ (4)°	

2.2. Data collection

Bruker APEXII CCD diffractometer	14032 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	1748 independent reflections
$T_{\min} = 0.555$, $T_{\max} = 0.753$	1643 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	154 parameters
$wR(F^2) = 0.106$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.19$ e Å ⁻³
1748 reflections	$\Delta\rho_{\text{min}} = -0.19$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 \cdots O1 ⁱ	0.93	2.59	3.5014 (15)	165
C13—H13 \cdots O2 ⁱⁱ	0.93	2.51	3.3242 (15)	146

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *S SAINT* (Bruker, 2008); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5806).

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supporting information

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S1. Comment

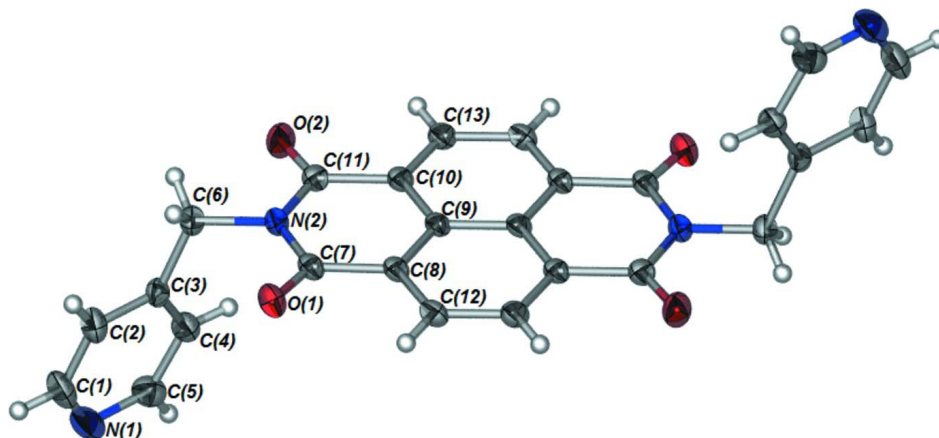
The assembly of organic molecules in solid state has attracted much attention in supramolecular chemistry, especially in crystal engineering and materials science (Cheney *et al.*, 2007). The study and understanding of intermolecular interactions in a crystal is a central topic for design and synthesis of functional organic materials with desirable optical, electronic and structural properties (Pandeewar *et al.*, 2014). Herein we report the crystal structure of the title compound, which was prepared from 1,4,5,8-naphthalene dianhydride and 4-aminomethyl-pyridine under reflux in dry DMF. Suitable single-crystals for X-ray diffraction, were obtained directly from reaction mixture after of 12 h. The compound with methanol solvate (1:1) has been reported (Li *et al.*, 2009) and was obtained as by-product during preparation of transition polymeric complexes in a mixture (methanol:chloroform) under solvothermal conditions, structurally this solvated is similar to compound reported here, both *trans* conformation of *N*-(4-pyridylmethyl) groups as to the dihedral angles between central ring and pyridil groups (86.34°). The title compound has also been studied as a semi-rigid ditopic ligand to the synthesis of one-dimensional coordination polymers with Zn(II), Mn(II), Co(II), Cd(II) where the ligand plays the key role to determine the final conformation of the polymeric structures (Li *et al.*, 2011, 2012). The coordination of (I) to the salts of ZnCl₂, Zn(ClO₄)₂, Zn(CF₃SO₃)₂ generates one-dimensional polymeric structures where *trans* conformation of (I) is maintained and not significant structural changes observed. A series of one-dimensional metal-organic frameworks of Mn(SCN)₂, Co(SCN)₂ and Cd(SCN)₂ with (I) have been reported, in all cases (I) shows a *Z* mode conformation and links up two metal centers such that one-dimensional chains are formed with π - π stacking interactions (centroid-centroid distances = 3.92–4.14 Å).

S2. Experimental

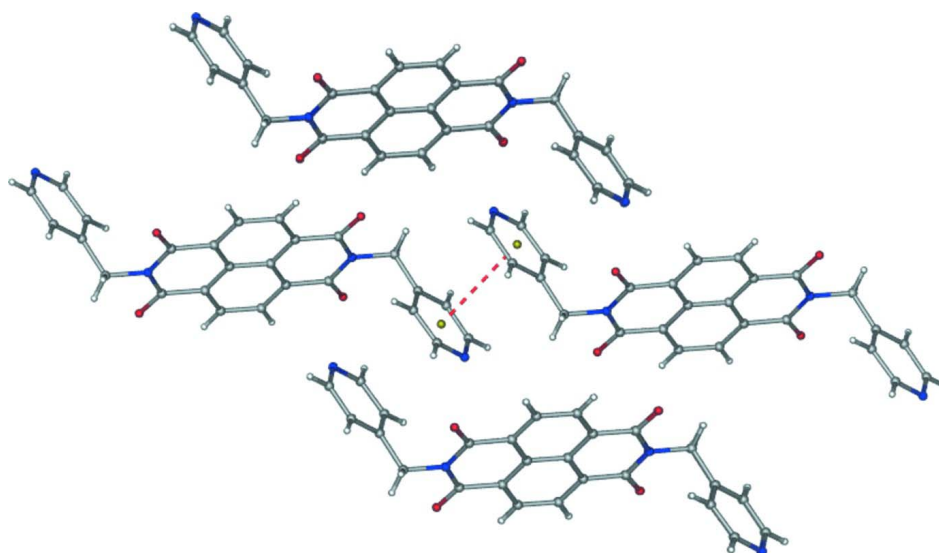
All chemicals were acquired commercially and were used without further purification. A mixture of 1,4,5,8-naphthalene dianhydride (1.0 g, 0.005 mol) and 4-aminomethyl-pyridine (1.08 g, 0.01 mol) in dry DMF (35 ml) was heated under reflux in atmosphere of dinitrogen and stirring for 2 h. Afterwards the resulting yellow solution was cooling and pallid yellow crystals were obtained on the wall of the flask directly from the mixture which corresponds to the compound I pure according to ¹H NMR in DMSO-d₆. Yield: 95%. Elemental analysis calculated (%) for C₂₆H₁₆N₄O₄; C, 69.64; H, 3.60; N, 12.49; found: C, 69.60; H, 3.62; N, 12.45.

S3. Refinement

H atoms were placed in calculated positions with C—H = 0.93–0.97 Å, and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

The structure with displacement ellipsoids drawn at the 30% probability level and H atoms as small sphere of arbitrary radii.

**Figure 2**

View *p*-stacking interactions in the crystal.

6,13-Bis[(pyridin-4-yl)methyl]-6,13-diazatetracyclo[6.6.2.0^{4,16}.0^{11,15}]hexadeca-1,3,8,10,15-pentaene-5,7,12,14-tetrone

Crystal data

C₂₆H₁₆N₄O₄

M_r = 448.43

Triclinic, *P*1̄

a = 5.5891 (4) Å

b = 7.5232 (5) Å

c = 11.9525 (8) Å

α = 77.093 (3)°

β = 88.445 (4)°

γ = 87.590 (4)°

V = 489.37 (6) Å³

Z = 1

F(000) = 232

D_x = 1.522 Mg m⁻³

Cu *Kα* radiation, λ = 1.54178 Å

Cell parameters from 9981 reflections

θ = 3.8–68.3°

μ = 0.87 mm⁻¹

T = 296 K

Plate, colourless

0.34 × 0.13 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer	14032 measured reflections
Radiation source: Incoatec ImuS	1748 independent reflections
Mirrors monochromator	1643 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.045$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$\theta_{\text{max}} = 68.3^\circ$, $\theta_{\text{min}} = 3.8^\circ$
$T_{\text{min}} = 0.555$, $T_{\text{max}} = 0.753$	$h = -5 \rightarrow 6$
	$k = -9 \rightarrow 9$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 0.0799P]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1748 reflections	$\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
154 parameters	$\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{\AA}^{-3}$
0 restraints	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.43898 (16)	0.61174 (13)	0.75255 (7)	0.0471 (3)
N1	-0.0333 (2)	0.68325 (18)	1.12186 (9)	0.0587 (3)
C1	0.1698 (3)	0.7665 (2)	1.09030 (12)	0.0600 (4)
H1	0.2727	0.7785	1.1478	0.072*
O2	-0.21818 (18)	0.96340 (12)	0.62202 (8)	0.0540 (3)
N2	0.10767 (18)	0.78494 (13)	0.68880 (8)	0.0375 (3)
C2	0.2394 (2)	0.83681 (19)	0.97785 (11)	0.0482 (3)
H2	0.3847	0.8938	0.9613	0.058*
C6	0.1602 (2)	0.90343 (17)	0.76740 (10)	0.0425 (3)
H6A	0.0742	1.0198	0.7428	0.051*
H6B	0.3301	0.9262	0.7628	0.051*
C3	0.0913 (2)	0.82151 (15)	0.89059 (9)	0.0372 (3)
C5	-0.1744 (3)	0.66899 (19)	1.03678 (12)	0.0511 (3)
H5	-0.3183	0.6110	1.0560	0.061*
C4	-0.1216 (2)	0.73457 (17)	0.92155 (10)	0.0435 (3)
H4	-0.2276	0.7204	0.8658	0.052*
C7	0.2667 (2)	0.63581 (16)	0.69075 (9)	0.0360 (3)
C8	0.2169 (2)	0.51409 (15)	0.61294 (9)	0.0337 (3)
C9	0.02134 (19)	0.55699 (14)	0.53820 (8)	0.0315 (3)
C10	-0.1324 (2)	0.71073 (15)	0.53795 (9)	0.0340 (3)
C11	-0.0899 (2)	0.83074 (15)	0.61813 (9)	0.0376 (3)

C12	0.3627 (2)	0.36316 (16)	0.61186 (9)	0.0383 (3)
H12	0.4906	0.3354	0.6618	0.046*
C13	-0.3204 (2)	0.74975 (16)	0.46403 (10)	0.0384 (3)
H13	-0.4206	0.8516	0.4641	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0449 (5)	0.0592 (6)	0.0403 (5)	-0.0028 (4)	-0.0085 (4)	-0.0169 (4)
N1	0.0686 (8)	0.0691 (8)	0.0368 (6)	0.0111 (6)	0.0030 (5)	-0.0118 (5)
C1	0.0676 (10)	0.0771 (10)	0.0401 (7)	0.0099 (7)	-0.0136 (6)	-0.0243 (7)
O2	0.0626 (6)	0.0463 (5)	0.0580 (6)	0.0133 (4)	-0.0097 (4)	-0.0237 (4)
N2	0.0465 (6)	0.0387 (5)	0.0292 (5)	-0.0039 (4)	0.0003 (4)	-0.0113 (4)
C2	0.0479 (8)	0.0572 (8)	0.0454 (7)	0.0002 (5)	-0.0060 (5)	-0.0234 (6)
C6	0.0530 (7)	0.0405 (6)	0.0372 (6)	-0.0087 (5)	0.0007 (5)	-0.0143 (5)
C3	0.0436 (6)	0.0356 (6)	0.0358 (6)	0.0031 (4)	-0.0018 (4)	-0.0156 (4)
C5	0.0508 (8)	0.0541 (7)	0.0456 (7)	0.0033 (6)	0.0064 (6)	-0.0074 (6)
C4	0.0454 (7)	0.0467 (7)	0.0391 (6)	-0.0006 (5)	-0.0036 (5)	-0.0108 (5)
C7	0.0376 (6)	0.0437 (6)	0.0264 (5)	-0.0056 (4)	0.0017 (4)	-0.0069 (4)
C8	0.0368 (6)	0.0388 (6)	0.0249 (5)	-0.0027 (4)	0.0023 (4)	-0.0060 (4)
C9	0.0349 (6)	0.0351 (6)	0.0235 (5)	-0.0026 (4)	0.0032 (4)	-0.0044 (4)
C10	0.0384 (6)	0.0356 (6)	0.0272 (5)	-0.0012 (4)	0.0026 (4)	-0.0055 (4)
C11	0.0436 (7)	0.0364 (6)	0.0325 (6)	-0.0003 (5)	0.0021 (4)	-0.0077 (4)
C12	0.0376 (6)	0.0453 (6)	0.0304 (6)	0.0027 (5)	-0.0051 (4)	-0.0055 (5)
C13	0.0420 (6)	0.0376 (6)	0.0346 (6)	0.0061 (5)	-0.0002 (4)	-0.0071 (4)

Geometric parameters (Å, °)

N1—C1	1.325 (2)	C5—H5	0.9300
N1—C5	1.3293 (19)	C6—H6A	0.9700
N2—C11	1.3931 (16)	C6—H6B	0.9700
N2—C7	1.3982 (16)	C7—C8	1.4823 (16)
N2—C6	1.4746 (14)	C8—C12	1.3718 (16)
O1—C7	1.2123 (14)	C8—C9	1.4110 (16)
O2—C11	1.2127 (15)	C9—C10	1.4113 (16)
C1—C2	1.382 (2)	C9—C9 ⁱ	1.416 (2)
C1—H1	0.9300	C10—C13	1.3708 (17)
C2—C3	1.3766 (17)	C10—C11	1.4855 (16)
C2—H2	0.9300	C12—C13 ⁱ	1.4046 (17)
C3—C4	1.3836 (18)	C12—H12	0.9300
C3—C6	1.5100 (16)	C13—C12 ⁱ	1.4046 (17)
C4—C5	1.3834 (18)	C13—H13	0.9300
C4—H4	0.9300		
C1—N1—C5	115.61 (12)	C3—C6—H6B	109.0
C11—N2—C7	125.48 (10)	H6A—C6—H6B	107.8
C11—N2—C6	118.44 (10)	O1—C7—N2	120.35 (10)
C7—N2—C6	116.06 (10)	O1—C7—C8	122.58 (11)

N1—C1—C2	124.53 (13)	N2—C7—C8	117.06 (10)
N1—C1—H1	117.7	C12—C8—C9	120.29 (11)
C2—C1—H1	117.7	C12—C8—C7	120.26 (11)
C3—C2—C1	119.25 (13)	C9—C8—C7	119.44 (10)
C3—C2—H2	120.4	C8—C9—C10	121.50 (11)
C1—C2—H2	120.4	C8—C9—C9 ⁱ	119.18 (13)
C2—C3—C4	117.23 (11)	C10—C9—C9 ⁱ	119.32 (13)
C2—C3—C6	120.00 (11)	C13—C10—C9	120.29 (11)
C4—C3—C6	122.74 (11)	C13—C10—C11	119.95 (10)
C5—C4—C3	118.95 (12)	C9—C10—C11	119.77 (11)
C5—C4—H4	120.5	O2—C11—N2	120.98 (11)
C3—C4—H4	120.5	O2—C11—C10	122.31 (11)
N1—C5—C4	124.44 (13)	N2—C11—C10	116.70 (10)
N1—C5—H5	117.8	C8—C12—C13 ⁱ	120.51 (11)
C4—C5—H5	117.8	C8—C12—H12	119.7
N2—C6—C3	112.85 (9)	C13 ⁱ —C12—H12	119.7
N2—C6—H6A	109.0	C10—C13—C12 ⁱ	120.41 (10)
C3—C6—H6A	109.0	C10—C13—H13	119.8
N2—C6—H6B	109.0	C12 ⁱ —C13—H13	119.8
C5—N1—C1—C2	0.1 (2)	C12—C8—C9—C10	179.61 (9)
N1—C1—C2—C3	0.0 (2)	C7—C8—C9—C10	-1.78 (16)
C11—N2—C6—C3	104.43 (12)	C12—C8—C9—C9 ⁱ	-0.36 (19)
C7—N2—C6—C3	-76.70 (13)	C7—C8—C9—C9 ⁱ	178.25 (10)
C1—C2—C3—C4	-0.20 (18)	C8—C9—C10—C13	179.67 (9)
C1—C2—C3—C6	177.80 (12)	C9 ⁱ —C9—C10—C13	-0.36 (19)
N2—C6—C3—C2	139.13 (11)	C8—C9—C10—C11	-0.25 (17)
N2—C6—C3—C4	-42.99 (16)	C9 ⁱ —C9—C10—C11	179.72 (10)
C1—N1—C5—C4	-0.1 (2)	C7—N2—C11—O2	-179.77 (10)
N1—C5—C4—C3	0.0 (2)	C6—N2—C11—O2	-1.01 (17)
C2—C3—C4—C5	0.19 (17)	C7—N2—C11—C10	-0.43 (17)
C6—C3—C4—C5	-177.75 (11)	C6—N2—C11—C10	178.33 (9)
C11—N2—C7—O1	177.16 (10)	C13—C10—C11—O2	0.79 (18)
C6—N2—C7—O1	-1.63 (16)	C9—C10—C11—O2	-179.29 (10)
C11—N2—C7—C8	-1.55 (16)	C13—C10—C11—N2	-178.55 (9)
C6—N2—C7—C8	179.67 (8)	C9—C10—C11—N2	1.38 (16)
O1—C7—C8—C12	2.58 (17)	C9—C8—C12—C13 ⁱ	0.44 (17)
N2—C7—C8—C12	-178.75 (9)	C7—C8—C12—C13 ⁱ	-178.16 (9)
O1—C7—C8—C9	-176.03 (10)	C9—C10—C13—C12 ⁱ	0.29 (18)
N2—C7—C8—C9	2.64 (15)	C11—C10—C13—C12 ⁱ	-179.78 (10)

Symmetry code: (i) $-x, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 \cdots O1 ⁱⁱ	0.93	2.59	3.5014 (15)	165

C13—H13 \cdots O2 ⁱⁱⁱ	0.93	2.51	3.3242 (15)	146
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Symmetry codes: (ii) $x-1, y, z$; (iii) $-x-1, -y+2, -z+1$.