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Key indicatorsSingle-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.038
 wR factor = 0.100
Data-to-parameter ratio = 12.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**1,9,26-Triazahexacyclo[17.6.1.1^{3,7}.1^{9,16}.0^{10,15}.0^{20,25}]-pentacos-3,5,7(26),10(15),11,13,16(27),17,19(28),-20(25),21,23-dodecaene**

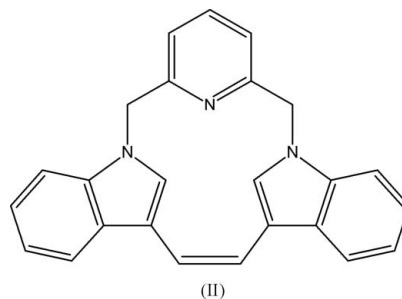
The title compound, $\text{C}_{25}\text{H}_{19}\text{N}_3$, has one half-molecule in the asymmetric unit, with the other half generated by a crystallographic twofold axis of symmetry. The dihedral angle between the two symmetry-related indole ring systems is $46.79(2)^\circ$. The pyridine ring forms a dihedral angle of $80.56(2)^\circ$ with the plane of each indole ring system. Molecules related by a center of inversion are linked *via* intermolecular $\text{C}-\text{H}\cdots\pi$ interactions to form chains along the c axis.

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Comment

Indole-based cyclophanes (Bodwell *et al.*, 1999) are of interest because they are infrequently encountered systems (Ortner *et al.*, 2001), but their synthesis has recently been reported (Bodwell & Li, 2002; Black *et al.*, 2002). These molecules have the ability to form complexes with metals such as cobalt (Gibe *et al.*, 2003). The design and synthesis of cyclophanes possessing rigidly defined cavities and shape-persistent structures of molecular dimensions is of interest for the formation of molecular hosts in the areas of host-guest and electron donor-acceptor complexation (Tobe *et al.*, 2000). Previously, we have reported the crystal structure of an indole-based cyclophane, namely, 1,9-diazahexacyclo[17.6.1.1^{3,7}.1^{9,16}.0^{10,15}.0^{20,25}]hexacos-3,5,7(26),10(15),11,13,16(27),17,19(28),20(25),21,23-dodecaene, (I) (Senthil Kumar *et al.*, 2006), and we report here the crystal structure of the title compound, (II), in which the macrocycle benzene ring of (I) has been replaced by pyridine.



The asymmetric unit of compound (II) contains one half-molecule, with the other half generated by a crystallographic twofold axis of symmetry (Fig. 1). The twofold axis passes through C12, H12, N2 and the mid-point of the C13–C13ⁱ bond [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. The indole ring system is essentially planar. Atom N1 deviates slightly [0.102 (1) Å] from the plane through C1, C8 and C9, as observed in phenylsulfonyl indole derivatives (Beddoes *et al.*, 1986).

The geometric parameters in the indole ring system (Table 1) are comparable to those observed in (I) (Senthil Kumar *et al.*, 2006). The two symmetry-related indole systems

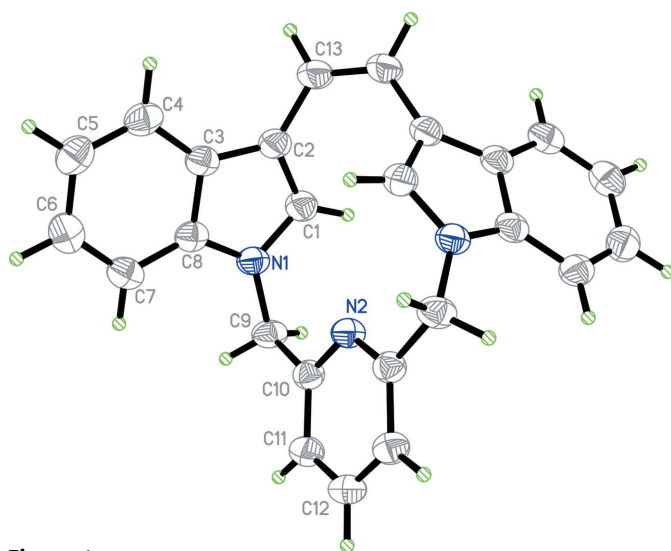


Figure 1
The structure of (II), showing 30% probability displacement ellipsoids and the atom numbering. Unlabeled atoms are related to labeled atoms by the symmetry operation $(-x, y, \frac{1}{2} - z)$.

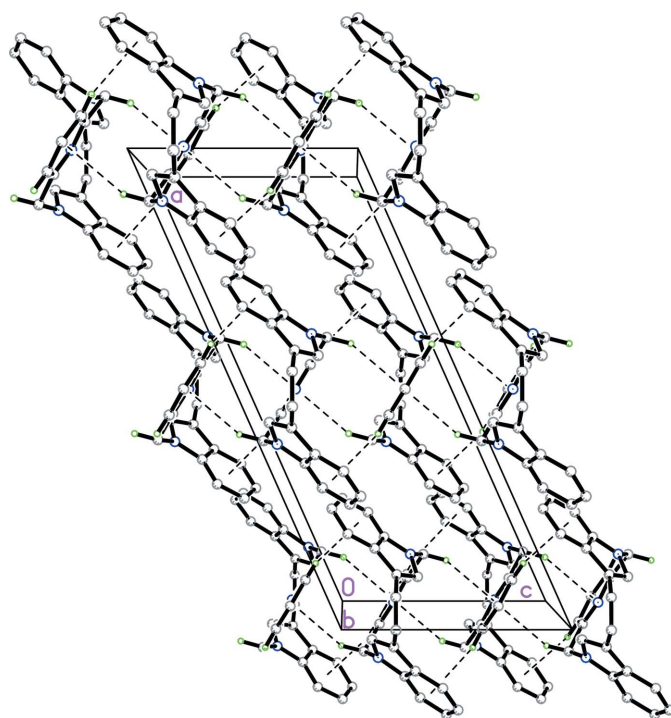


Figure 2
Crystal packing of (II), showing the C—H... π hydrogen-bonded (dashed lines) chains. Only the H atoms involved in hydrogen bonding are shown.

are inclined at an angle of $46.79(2)^\circ$. The pyridine ring is oriented at an angle of $80.56(2)^\circ$ with respect to the plane of each indole ring system.

The crystal packing reveals that molecules related by centers of inversion are linked *via* intermolecular C—H... π interactions (Table 2) involving the N2/C10—C12/C10ⁱ/C11ⁱ pyridine ring (centroid Cg1) and the C3—C8 benzene ring (centroid Cg2) to form chains along the *c* axis (Fig. 2).

A superimposed fit of the non-H atoms of (II) and the corresponding atoms in (I) (Senthil Kumar *et al.*, 2006) gives

an r.m.s. deviation of 0.115 \AA . This indicates that the conformation of the cyclophane is not very much altered by replacing the benzene ring in (I) by a pyridine ring. The pattern of the intermolecular C—H... π hydrogen bonding involving the methylene H atom is identical in the crystal structures of (I) and (II).

Experimental

TiCl₄ (2.55 mmol), Zn (5.08 mmol) and a few drops of pyridine were added to tetrahydrofuran (THF, 200 ml). The mixture was refluxed for 45 min and 1-[(6-((3-formyl-1*H*-indol-1-yl)methyl)pyridin-2-yl)methyl]-1*H*-indole-3-carbaldehyde (127 mmol) was added. The reaction mixture was refluxed overnight, cooled, quenched with K₂CO₃ and filtered, and the THF was removed *in vacuo*. The residue was extracted with chloroform ($3 \times 100 \text{ ml}$), washed with water ($2 \times 100 \text{ ml}$) and brine (150 ml), and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo* and the residue was subjected to column chromatography (SiO₂) using hexane and chloroform (3:2). The compound was recrystallized from chloroform by slow evaporation.

Crystal data

C₂₅H₁₉N₃
M_r = 361.43
Monoclinic, C2/*c*
a = 19.9027 (7) Å
b = 11.3107 (3) Å
c = 8.7157 (5) Å
 β = 113.994 (3)[°]
V = 1792.48 (13) Å³

Z = 4
D_x = 1.339 Mg m⁻³
Mo K α radiation
 μ = 0.08 mm⁻¹
T = 100.0 (1) K
Needle, colorless
0.61 × 0.18 × 0.18 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2005)
T_{min} = 0.917, *T_{max}* = 0.986

24681 measured reflections
2064 independent reflections
1927 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
 θ_{max} = 27.5[°]

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)]$ = 0.038
 $wR(F^2)$ = 0.100
S = 1.07
2064 reflections
166 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 1.0129P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.26 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.31 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------------|-------------|--------------------------|-------------|
| N1—C1 | 1.3748 (13) | C3—C4 | 1.4037 (14) |
| N1—C8 | 1.3773 (12) | C3—C8 | 1.4197 (13) |
| N1—C9 | 1.4494 (12) | C4—C5 | 1.3858 (15) |
| N2—C10 | 1.3366 (11) | C5—C6 | 1.4098 (15) |
| N2—C10 ⁱ | 1.3366 (11) | C6—C7 | 1.3827 (15) |
| C1—C2 | 1.3698 (14) | C7—C8 | 1.3963 (14) |
| C2—C3 | 1.4383 (13) | C13—C13 ⁱ | 1.340 (2) |
| C1—N1—C8 | 108.28 (8) | N2—C10—C11 | 122.69 (9) |
| C1—N1—C9 | 124.37 (9) | N2—C10—C9 | 115.81 (9) |
| C8—N1—C9 | 125.74 (8) | C13 ⁱ —C13—C2 | 123.73 (5) |

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

Table 2
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|------------|-------------|-------------|---------------|
| $C9-H9B\cdots Cg1^{ii}$ | 1.000 (13) | 2.804 (15) | 3.7233 (11) | 153 (1) |
| $C9-H9B\cdots Cg1^{iii}$ | 1.000 (13) | 2.804 (15) | 3.7233 (11) | 153 (1) |
| $C11-H11\cdots Cg2^{iii}$ | 0.967 (13) | 2.728 (13) | 3.6732 (11) | 166 (1) |

Symmetry codes: (ii) $-x, -y, -z$; (iii) $x, -y, z - \frac{1}{2}$. Cg1 is the centroid of the N2/C10-C12/C10'/C11' pyridine ring and Cg2 is the centroid of the C3-C8 benzene ring.

All H atoms were located in a difference map and were refined isotropically. The C-H distances lie in the range 0.965 (14)-1.005 (13) Å.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

- Beddoes, R. L., Dalton, L., Joule, J. A., Mills, O. S., Street, J. D. & Watt, C. I. F. (1986). *J. Chem. Soc. Perkin Trans. 2*, pp. 787-797.
- Black, D. StC., Craig, D. C. & Rezaie, R. (2002). *Chem. Commun.* pp. 810-811.
- Bodwell, G. J. & Li, J. (2002). *Org. Lett.* **4**, 127-130.
- Bodwell, G. J., Li, J. & Miller, D. O. (1999). *Tetrahedron*, **55**, 12939-12956.
- Bruker (2005). *APEX2* (Version 1.27), *SAINT* (Version 7.12A) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Gibe, R., Green, J. R. & Davidson, G. (2003). *Org. Lett.* **5**, 1003-1005.
- Ortner, B., Waibel, R. & Gmeiner, P. (2001). *Angew. Chem. Int. Ed.* **40**, 1283-1285.
- Senthil Kumar, G., Chinnakali, K., Swaroop, M. G., Rajakumar, P. & Fun, H.-K. (2006). *Acta Cryst. E* **62**, o1809-o1811.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7-13.
- Tobe, Y., Nagano, A., Kawabata, K., Sonoda, M. & Naemara, K. (2000). *Org. Lett.* **2**, 3265-3268.