

**1,9-Diazahehexacyclo[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****G. Senthil Kumar,^a
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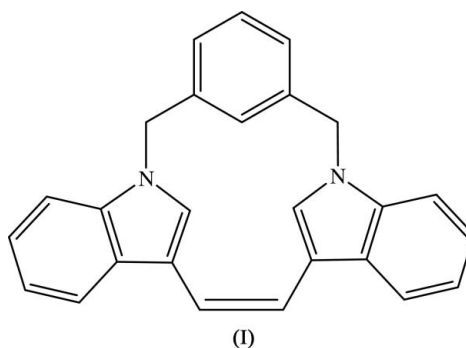
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Key indicatorsSingle-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.051
 wR factor = 0.154
Data-to-parameter ratio = 22.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{26}\text{H}_{20}\text{N}_2$, has one half-molecule in the asymmetric unit. The molecular twofold rotational symmetry is preserved on crystallization. The dihedral angle between the two symmetry-related indole ring systems is $49.65(4)^\circ$. The benzene ring is oriented almost perpendicular [dihedral angle $86.02(3)^\circ$] to the planes of both indole ring systems. Molecules related by a centre of inversion are linked *via* intermolecular $\text{C}-\text{H}\cdots\pi$ interactions to form chains along the c axis.

Comment

The indole system is present in a number of natural products (Yu *et al.*, 2003) and is known to be a bioactive nucleus (Nussbaum, 2003). Indole-based cyclophanes (Bodwell *et al.*, 1999) are of interest because they are infrequently encountered systems (Ortner *et al.*, 2001). The synthesis of indole-based cyclophanes has recently been reported (Bodwell & Li, 2002; Black *et al.*, 2002) and these compounds 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). We report here the crystal structure of the title compound, (I), a cyclophane containing two indole units.



The asymmetric unit of compound (I) contains one half-molecule, with the other half generated by a crystallographic twofold axis of symmetry (Fig. 1). The twofold axis passes through atoms C12, H12, C13 and H13 and the mid-point of the C14–C14ⁱ bond [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. The indole ring system is planar, with a maximum deviation of $0.024(1)\text{ \AA}$ for atom N1. Atom N1 deviates by $0.147(2)\text{ \AA}$ from the plane through atoms C1, C8 and C9, and the sum of the angles around N1 is 356.7° . This slight pyramidalization behaviour is also observed in phenylsulfonyl indole derivatives (Beddoes *et al.*, 1986).

Received 24 March 2006
Accepted 25 March 2006

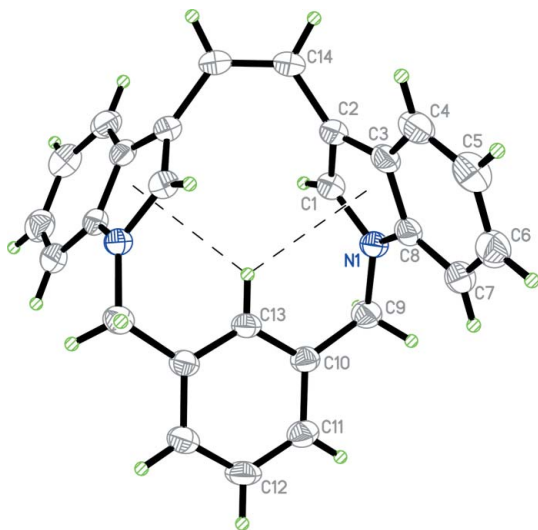


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering scheme. Unlabelled atoms are related to labelled atoms by the symmetry operation $(1-x, y, \frac{1}{2}-z)$. Dashed lines represent C—H... π interactions.

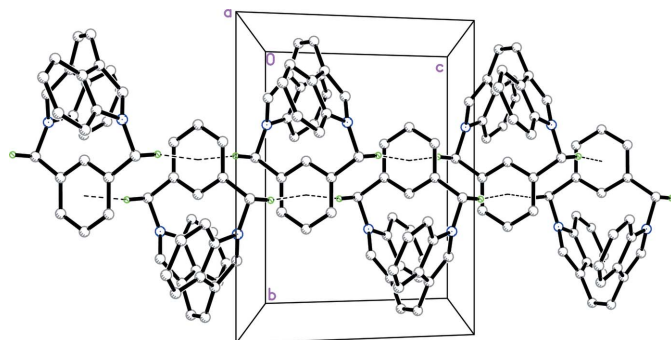


Figure 2
Part of the crystal packing of (I), showing a C—H... π hydrogen-bonded (dashed lines) chain. Only H atoms involved in the hydrogen bonding are shown.

The geometric parameters in the indole ring systems of (I) are comparable with those observed in 2-(2-acetamido-5-methylbenzoyl)-1*H*-indole (Ravishankar *et al.*, 2005). The two symmetry-related indole ring systems are inclined at an angle of $49.65(4)^\circ$. The benzene ring is oriented almost perpendicular [dihedral angle $86.02(3)^\circ$] to the planes of both indole ring systems. This orientation is influenced by intramolecular C—H... π interactions, namely C13—H13...Cg1 and C13—H13...Cg1ⁱ (symmetry code as in Table 2), where Cg1 is the centroid of the N1/C1—C3/C8 ring. Additional C—H... π interactions involving the six-membered C10—C13/C10ⁱ/C11ⁱ ring of which Cg2 is the centroid are also observed (Table 2). These interactions link molecules into chains along the *c* axis (Fig. 2).

Experimental

Tetrahydrofuran (THF) (200 ml) was placed in a three-necked round-bottomed flask, and TiCl₄ (2.55 mmol), Zn (5.08 mmol) and a few drops of pyridine were added. The mixture was refluxed for 45 min and then 1-[3-(3-formyl-3a,7a-dihydroindol-1-ylmethyl)benzyl]-1*H*-

indole-3-carbaldehyde (127 mmol) was added. The reaction mixture was refluxed overnight and then cooled, quenched with K₂CO₃ and filtered, and the THF was removed using a rotary evaporator. The residue was extracted with chloroform (3 × 100 ml), washed with water (2 × 100 ml) and brine (150 ml), and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo* and the residue subjected to column chromatography (SiO₂) using hexane–chloroform (3:2). The compound was recrystallized from chloroform by slow evaporation.

Crystal data

C₂₆H₂₀N₂
M_r = 360.44
 Monoclinic, C2/c
a = 19.6434 (9) Å
b = 11.2843 (5) Å
c = 9.0441 (3) Å
 β = $112.635(4)^\circ$
V = 1850.32 (13) Å³
Z = 4

D_x = 1.294 Mg m⁻³
 Mo K α radiation
 Cell parameters from 1440 reflections
 θ = 2.3–21.2°
 μ = 0.08 mm⁻¹
T = 293 (2) K
 Needle, colourless
 0.57 × 0.16 × 0.10 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
T_{min} = 0.762, *T_{max}* = 0.993
 13509 measured reflections

2891 independent reflections
 1316 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
 θ_{\max} = 30.8°
h = −28 → 28
k = −16 → 15
l = −12 → 12

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.051
wR(*F*²) = 0.154
S = 0.97
 2891 reflections
 129 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
 Extinction correction: SHELXTL (Sheldrick, 1998)
 Extinction coefficient: 0.0035 (9)

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.378 (2)	C3—C8	1.412 (2)
N1—C8	1.379 (2)	C4—C5	1.377 (2)
N1—C9	1.459 (2)	C5—C6	1.398 (3)
C1—C2	1.363 (2)	C6—C7	1.368 (2)
C2—C3	1.435 (2)	C7—C8	1.388 (2)
C2—C14	1.470 (2)	C14—C14 ⁱ	1.329 (3)
C3—C4	1.399 (2)		
C1—N1—C8	107.73 (13)	N1—C9—C10	112.33 (13)
C1—N1—C9	124.46 (14)	C14 ⁱ —C14—C2	124.63 (9)
C8—N1—C9	124.52 (14)		

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

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the rings N1/C1—C3/C8 and C10—C13/C10ⁱ/C11ⁱ, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C9—H9B...Cg2 ⁱⁱ	0.97	2.82	3.7184 (19)	154
C9—H9B...Cg2 ⁱⁱⁱ	0.97	2.82	3.7184 (19)	154
C13—H13...Cg1	0.93	2.62	3.2625 (18)	127
C13—H13...Cg1 ⁱ	0.93	2.62	3.2625 (18)	127

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

H atoms were positioned geometrically and treated as riding on their parent C atoms, with C–H distances of 0.93 (aromatic) and 0.97 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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

HKF thanks the Malaysian Government and the Universiti Sains Malaysia for Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/653003/A118 and USM short-term grant No. 304/PFIZIK/635028.

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