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1,2-Bis(3,5-dimethylpyrazol-1-yl)-*anti*-[2.2]paracyclonaphthane

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Key indicators

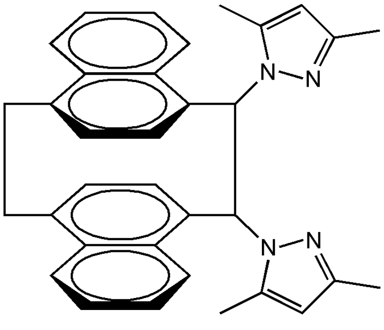
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.145
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{34}H_{33}N_4$, is a new 3,5-dimethylpyrazole-substituted paracyclonaphthane. Each of the two symmetry-independent molecules in the asymmetric unit occupies a special position on a twofold axis and exhibits an intramolecular π–π stacking interaction between the naphthalene moieties. The geometry of both molecules is essentially the same, the bridged rings of the naphthalene nuclei being deformed into a boat shape.

Comment

Paracyclophanes have long been the focus of extensive structural studies. A number of interesting paracyclophane derivatives have been documented in recent years, among them such compounds as dibenzo[2.2]paracyclophane (Chan & Wong, 1988), poly(9-hydroxyl[2.2]paracyclophan-l-ene) (Miao & Bazan, 1994), octafluoro[2,2]*p*-cyclophanes (Alfonso *et al.*, 2001) and 4,7,12,15-tetra(4-dihexylaminostyryl)[2.2]-paracyclophane (Bartholomew & Bazan, 2002). The crystal structures of the *anti* and *syn* isomers of [2,2]paracyclonaphthane (Fratini *et al.*, 1995) and substituted derivatives of *anti*-[2.2]paracylonaphthanes (Gleiter *et al.*, 1997) have also been reported.



(I)

We have synthesized a series of derivatives of *anti*-[2.2]-paracyclonaphthane and report here the crystal structure of the title compound, (I).

The crystal structure of (I) has two symmetry-independent molecules in the asymmetric unit, each occupying a special position on a twofold axis. The geometry of both molecules is essentially the same; the structures of the two molecules are shown in Fig. 1. As in other paracyclophanes, there is intramolecular π–π stacking between the two naphthalene rings. A peculiar structural feature is the deformation of the bridged rings of the naphthalene systems into a boat shape, the

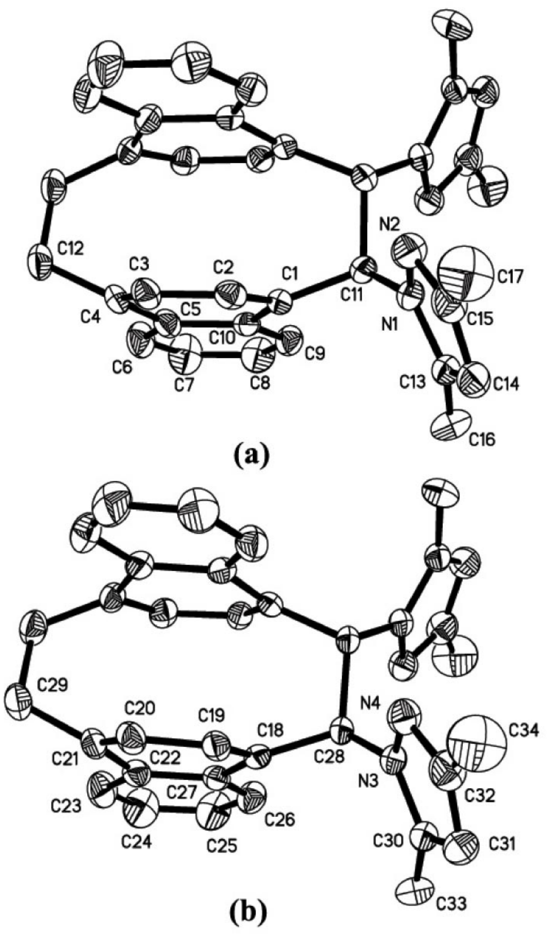


Figure 1
The structures of the two independent molecules of the title compound, showing 35% probability displacement ellipsoids and the atom-numbering scheme; H atoms have been omitted.

distortions from ideal geometries being attributed to intramolecular effects. Indeed, in the first independent molecule, atoms C1 and C4 are displaced towards the second naphthalene system of this molecule by 0.145 (4) and 0.159 (5) Å, respectively, from the plane formed by atoms C2, C3, C5 and C10. The dihedral angles between the latter plane and the planes defined by C1/C2/C10 and C3/C4/C5 are 11.7 (2) and 12.7 (2)°, respectively. In the second molecule, atoms C18 and C21 exhibit similar displacements of 0.147 (4) and 0.164 (5) Å, respectively, from the C19/C20/C22/C27 plane; the dihedral angles between the C19/C20/C22/C27 plane and C18/C19/C27 and C20/C21/C22 are 12.0 (2) and 13.1 (2)°, respectively.

Experimental

The synthesis of the title compound was carried out under a nitrogen atmosphere. A tetrahydrofuran (THF) solution of pyrazole (10 g, 0.147 mmol) was added to a suspension of oil-free sodium hydride (7.56 g, 2.94 mmol) in an ice-bath and the mixture was stirred for 1 h at room temperature. A THF solution (100 ml) of 1,4-bis(bromomethyl)naphthalene (16 g, 0.05 mol) was added dropwise and the mixture was stirred for 24 h at 333 K. The solvent was removed using a rotary evaporator and water (100 ml) was added to the residue. The solution was extracted with CH_2Cl_2; the dichloromethane phase was dried with anhydrous $MgSO_4$ and the solvent was removed. The solid residue was chromatographed on silica gel with petroleum ether and ethyl acetate as the eluant (yield: 15%). Calculated for $C_{34}H_{33}N_4$: C 80.79, H 6.54, N 12.67%; found: C 80.70, H 6.48, N 12.71%. ^{1}H NMR: δ 8.29 (*d*, 2H), 7.69 (*d*, 2H), 7.52 (*d*, 2H), 7.41 (*t*, 2H), 6.46 (*t*, 2H,), 5.73 (*s*, 2H,), 5.49 (*d*, 2H), 3.65 (*m*, 2H), 2.82 (*m*, 2H), 2.28 (*s*, 6H), 2.17 (*s*, 6H).

Crystal data

$C_{34}H_{32}N_4$
$M_r = 496.64$
Orthorhombic, *Ibca*
$a = 16.6732$ (18) Å
$b = 16.674$ (2) Å
$c = 39.267$ (8) Å
$V = 10916$ (3) Å^3
$Z = 16$
$D_x = 1.209$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 938 reflections
$\theta = 2.8$–26.4°
$\mu = 0.07$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.32 × 0.26 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
30 541 measured reflections
5619 independent reflections

3521 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.060$
$\theta_{\rm max} = 26.4°$
$h = -13 \rightarrow 20$
$k = -20 \rightarrow 20$
$l = -46 \rightarrow 49$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.145$
$S = 1.06$
5619 reflections
347 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 3.9798P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00047 (8)

Table 1
Selected geometric parameters (Å, °).

N1—C11	1.462 (4)	C12—C12$^{\rm i}$	1.565 (8)
N3—C28	1.457 (4)	C18—C28	1.517 (4)
C1—C11	1.526 (4)	C21—C29	1.507 (4)
C4—C12	1.515 (4)	C28—C28$^{\rm ii}$	1.578 (6)
C11—C11$^{\rm i}$	1.582 (6)	C29—C29$^{\rm ii}$	1.586 (8)
C1—C11—C11$^{\rm i}$	111.83 (17)	C18—C28—C28$^{\rm ii}$	111.67 (17)
C4—C12—C12$^{\rm i}$	111.7 (2)	C21—C29—C29$^{\rm ii}$	111.4 (2)

Symmetry codes: (i) $1 - x, \frac{3}{2} - y, z$; (ii) $1 - x, \frac{1}{2} - y, z$.

Even though the *a* and *b* axis lengths are essentially identical and an approximate diagonal mirror symmetry pattern is observed in the reflection intensities $[I(h, k, l) \simeq I(k, h, l)]$, numerous attempts to solve the structure in one of the possible tetragonal space groups proved to be unsuccessful. However, we managed to obtain a plausible model in the orthorhombic space group *Ibca*, which, nevertheless, could not be refined to an *R* value of less than 0.13. At this point, we considered that a twinned orthorhombic crystal with *a* and *b* equal in length might emulate tetragonal symmetry as a result of exchange of the two axes. This twin model was successfully applied, dramatically reducing the *R* value. *PLATON* (Spek, 2003) was used to check the geometric consistency of the structure and did not reveal any problems or overlooked symmetry. H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å, and included in the

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final cycles of refinement in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ of the carrier atom [1.5$U_{\rm eq}$(C) for methyl H atoms].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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