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1-(*p*-Biphenyl)-4′-(2-naphthyl)cubane

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In the title compound, $C_{30}H_{22}$, the biphenyl and naphthyl substituents are each planar to within 0.03 Å. They extend from the cubane like the wings of a butterfly, with a slight dihedral angle of 9.4 (2)° between their planes. In the crystal structure, the naphthyl groups form close-packed stacks, with cubyls and biphenyls extending alternately to the right and the left.

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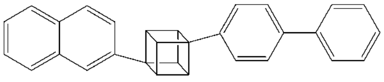
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.008 Å
R factor = 0.062
wR factor = 0.168
Data-to-parameter ratio = 7.3

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

Comment

The title molecule, (I), was synthesized by Eaton *et al.* (1999) along with 1-(*p*-biphenyl)-4′-(2-naphthyl)-*p*-[2]cubyl, and a series of other polycubyl molecules, to study the properties of cubanes that are linked together at the 1 and 4 positions. As poly-1,4-cubanes are semi-rigid rod-like structures, the distances between two terminal substituents are fixed, even in solution, making them useful for studying the distance dependence of intramolecular electron-transfer reactions. Paulson *et al.* (1993) studied the electron-transfer reaction of the title compound by irradiating the molecules (in solution) with high-energy electrons and photometrically observing electron transfer in the anionic form of (I). They found that using cubane as a spacer enhanced the electron-transfer rate between the biphenyl and naphthyl groups. Compared to the electron transfer between the same substituents on cyclohexane spacers, the rate of transfer was measured to be 10±3 times larger for the cubane compound. Stronger bond-to-bond couplings and a larger number of pathways are offered as explanations for the enhanced coupling through cubane spacers. Increasing the distance by doubling or tripling the number of cubyl or cyclohexyl spacers leads to an exponential decline in transfer rate with distance; the fall-off with distance is similar for both types of spacer.


(I)

The biphenyl groups of (I) are nearly planar, with all C atoms fitting a least-squares plane to within ±0.031 Å (Fig. 1 and Table 1). The torsion angle of the biphenyl linkage is 2.1°, *versus* an average of 23.4° for 772 similar biphenyl linkages (all those with four H atoms adjacent to the central linkage bond) found in the Cambridge Structural Database (Version 5.24; Allen, 2002). The naphthyl groups are even more closely planar; their C atoms fit a least-squares plane to within 0.007 Å.

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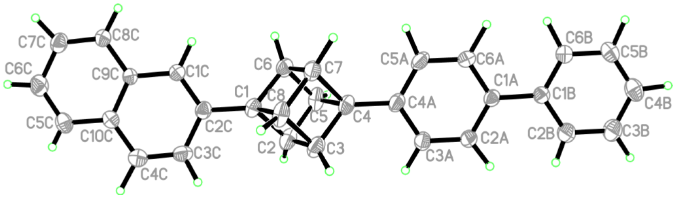

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 25% probability level.

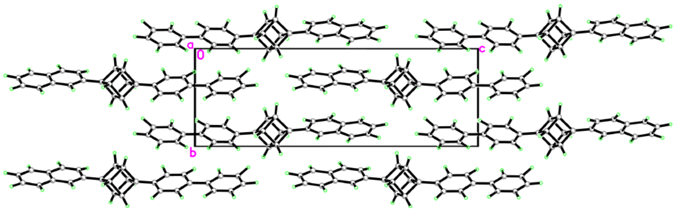

Figure 2
A packing diagram of (I), looking down the short *a* axis, illustrating the close-packed naphthyl groups and the intercalated biphenyl groups.

The title molecule, (I), has a complex supramolecular assembly. Looking down the *a* axis (Fig. 2), one can see stacks of intercalated biphenyl groups at the ends of the cell, and a close-packed stack of naphthyl substituents in the center of the cell. There is a twofold screw axis along *b*, which goes through the central naphthyl stack. Fig. 3 illustrates an end-on view of a naphthyl stack, showing that it is actually a herring-bone stack, not a stack wherein all planes are parallel. Despite the presence of the close-packed naphthyl stacks and slightly looser biphenyl stacks, there are no intermolecular contacts that are significantly less than the sum of van der Waals radii.

Experimental

The crystals were provided by Philip Eaton and Todd Emrick of the University of Chicago. Details of the synthesis of the title molecule, (I), from 1,4-diiodocubane, *p*-biphenyllithium and naphthalene-1,4-oxide were reported by Eaton *et al.* (1999). Crystals were grown by slow evaporation from an *n*-octane solution.

Crystal data

$C_{30}H_{22}$
$M_r = 382.48$
Monoclinic, $P2_1$
$a = 5.9788$ (4) Å
$b = 7.579$ (1) Å
$c = 22.044$ (1) Å
$\beta = 94.570$ (8)°
$V = 995.71$ (15) Å^3
$Z = 2$
$D_x = 1.276$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 22 reflections
$\theta = 6.2$–42.2°
$\mu = 0.55$ mm^{-1}
$T = 294$ (2) K
Thin lath, colorless
0.52 × 0.16 × 0.02 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: by integration (Wuensch & Prewitt, 1965) $T_{\min} = 0.847$, $T_{\max} = 0.988$
2001 measured reflections
2001 independent reflections
1271 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 68.8°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 1$
$l = 0 \rightarrow 26$
3 standard reflections every 97 reflections intensity decay: none

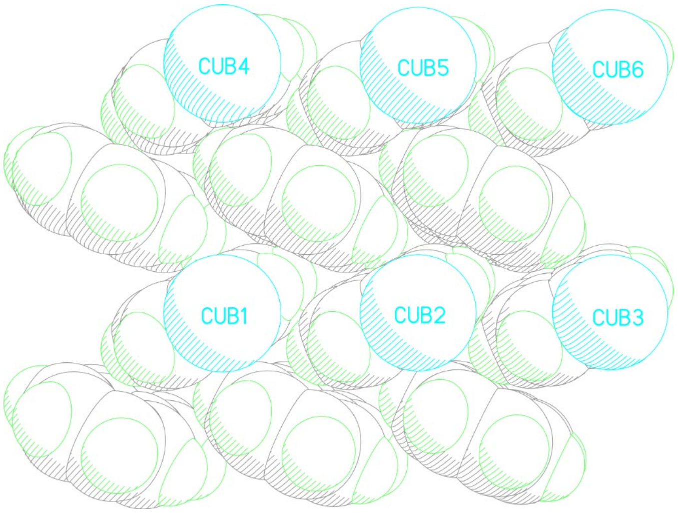

Figure 3
A space-filled diagram, illustrating an edge-on view of the close-packed stacks of naphthyl groups. The biphenyl rings have been omitted for clarity and the cubanes are represented by large labeled spheres.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.168$
$S = 1.08$
2001 reflections
273 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.2164P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0034 (7)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.559 (9)	C3—C4	1.559 (8)
C1—C6	1.560 (8)	C4—C5	1.558 (9)
C1—C8	1.566 (9)	C4—C7	1.573 (9)
C2—C3	1.535 (9)	C5—C6	1.540 (10)
C2—C5	1.549 (10)	C6—C7	1.542 (10)
C3—C8	1.546 (9)	C7—C8	1.553 (9)
C2*A*—C1*A*—C1*B*—C2*B*	−2.2 (10)	C6*A*—C1*A*—C1*B*—C6*B*	−2.0 (10)

Although the space group is non-centrosymmetric, with Cu *Kα* radiation and only carbon and hydrogen atoms present there is no basis for determining the absolute configuration. Friedel pairs were merged, and the 'handedness' displayed by the structure (if any) is purely arbitrary. The Flack (1983) parameter, before merging, refined to a value of 2 (5). All H atoms were found in a difference Fourier map, but during the refinement they were placed at ideal tetrahedral or trigonal positions. They were riding on their bonded neighbors during the refinement (C—H distances = 0.98 and 0.93 Å for the cubane and naphthyl/biphenyl moieties, respectively), with periodic reidealization, and their displacement parameters were set to be isotropic, with a value equal to $1.2U_{\rm eq}$ of the neighboring C atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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