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r-1,*c*-2,*t*-3,*t*-4-1-(2-Benzoxazolyl)-2-biphenyl-4-phenyl-3-pyridinylcyclobutane

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.115
Data-to-parameter ratio = 13.5

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

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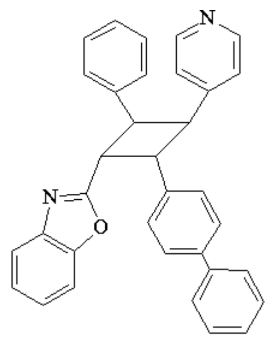
The title compound, $C_{34}H_{26}N_2O$, (I), was synthesized by intermolecular [2+2] photocycloaddition of *trans*-2-(2-phenylethenyl)benzoxazole and *trans*-4-(2-biphenylethenyl)pyridine in sulfuric acid solution. Compound (I), with an *rctt* stereostructure, is the only crossed photocycloadduct in which the two heteroaryl groups are situated opposite each other, which reveals that the cross-photodimerization process is a head-to-tail reaction rather than a head-to-head one. In (I), the cyclobutane ring shows a puckered conformation and the two dihedral angles between the two triangles defined by diagonal lines of the cyclobutane ring are 19.7 (2) and 19.8 (2)°. The four single bonds of the cyclobutane ring are 1.558 (4), 1.545 (4), 1.572 (4) and 1.566 (4) Å.

Comment

The conformation of cyclobutane in the crystalline state has been determined by X-ray diffraction; however, owing to the distortion and weak molecular interaction, its structure can not be determined precisely, even at very low temperature, and the dihedral angle was deduced to be 31 (2)° (Stein *et al.*, 1992). The molecular structures in crystals of *rctt*-1,2,3,4-tetraphenylcyclobutane (TPCB) and octachlorocyclobutane (OCCB) were also determined. The cyclobutane ring of TPCB is planar, while that of OCCB is non-planar, with a dihedral angle of about 19° (Margulis, 1965). Most of the tetraarylcyclobutanes synthesized by photodimerization are centrosymmetric. However, the conformation of the cyclobutane ring is strongly dependent on the nature of the substituents. Some derivatives have a puckered conformation, such as *rctt*-1,3-bis(4-R-phenyl)-2,4-di(4-pyridyl)cyclobutane [R = Cl (II*a*), CH_3 (II*b*), and C_6H_5 (II*c*)], in which the average dihedral angles of the cyclobutane ring are 19.2 (1), 24.6 (2) and 16.4 (2)°, respectively (Busetti *et al.*, 1980; Zhang *et al.*, 1998, 2000). Other derivatives have rigorously planar cyclobutane rings, such as *rctt*-1,2,3,4-tetrakis(5-phenyloxazol-2-yl)cyclobutane (Zhang *et al.*, 1996) and *rctt*-1,3-bis(4-methoxylphenyl)-2,4-bis(5-phenyl-1,3,4-oxadiazol-2-yl)cyclobutane (Zheng *et al.*, 2001). The complex of *rctt*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane with palladium chloride also shows a planar cyclobutane ring (Bianchini *et al.*, 2000). To the best of our knowledge, the title compound, (I), is the first example in which the cyclobutane ring is substituted with four different aryl groups. It is interesting to study the molecular structure and its conformation.

The C—C—C bond angles in the cyclobutane ring of (I) are in the range 88.2 (2)–89.6 (2)°. Though these angles are nearly rectangular, the cyclobutane ring has a puckered conformation (Fig. 1 and Table 1). The dihedral angle between the C1/C2/C3 and C1/C4/C3 planes is 19.7 (2)° and that between the

C2/C1/C4 and C2/C3/C4 planes is 19.8 (2)°; they are similar to those of (II*a*) (Busetti *et al.*, 1980). The C1—C2, C2—C3, C3—C4 and C4—C1 bond distances of the cyclobutane ring are 1.558 (4), 1.545 (4), 1.572 (4) and 1.566 (4) Å, respectively, and the corresponding values for (II*a*) are 1.573 (7), 1.536 (7), 1.574 (7) and 1.567 (7) Å, respectively.



(I)

The benzoxazolyl group is planar, while the biphenyl group is twisted. The dihedral angle between the two phenyl planes of the biphenyl is 33 (2)°, which is in good agreement with that of 31 (3)° in 3-chlorobiphenyl-4-carbonitrile (Sutherland & Rawas, 1984). The angle between the phenyl and pyridyl planes, which are situated on the same side of the cyclobutane ring, is 61.6 (4)°, while that between the benzoxazolyl and the first phenyl ring of the biphenyl moiety is 64 (2)°. The title molecule is chiral, and there are two enantiomers in the unit cell (Fig. 2).

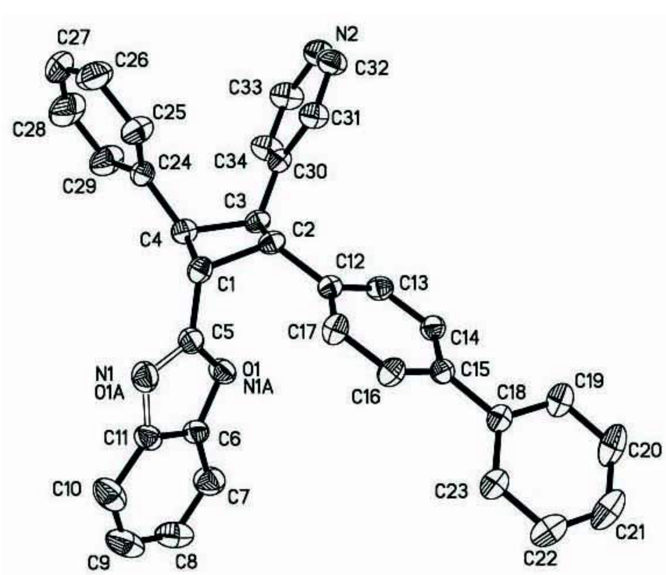


Figure 1
The molecular structure of (I), drawn with 30% probability ellipsoids. Atoms O1 and N1 are shared between the two possible orientations of the benzoxazolyl moiety.

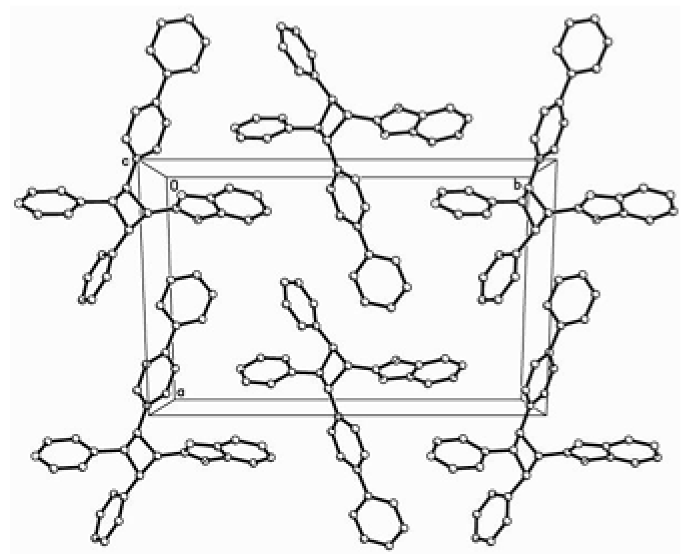


Figure 2
The crystal structure of (I), viewed along *c*.

Experimental

The monomers *trans*-2-(2-phenylethenyl)benzoxazole (BOEP) and *trans*-4-(2-biphenylethenyl)pyridine (BPEPy) were synthesized according to the literature method of Zhang *et al.* (2001). 221 mg (1 mmol) BOEP and 257 mg (1 mmol) BPEPy were dissolved in 10 ml concentrated sulfuric acid. This solution was then added to 80 ml 50% hot sulfuric acid to give a transparent yellow solution. After being irradiated with a water-cooled 300 W medium-pressure mercury lamp for 5 h, the reaction mixture was poured into 300 ml water and neutralized with aqueous ammonia. The precipitate was filtered off and separated by column chromatography, eluting with petroleum ether–ethyl acetate (*v*/*v* = 3:2) to give the title compound, (I). Recrystallization of (I) from ethanol gave single crystals suitable for the X-ray analysis. M.p. 470–471 K. IR (KBr): 3058 (*w*), 3030 (*m*), 2946 (*w*), 1599 (*s*), 1567 (*s*), 1489 (*s*), 1455 (*s*), 1416 (*m*), 1244 (*s*), 1139 (*m*), 1006 (*m*), 827 (*m*), 749 (*s*), 698 (*s*) cm^{-1}. ^{1}H NMR ($CDCl_3$, p.p.m.): 8.36 (2H, *d*), 7.70 (1H, *d*), 7.44 (2H, *d*), 7.39–7.15 (15, *m*), 6.97 (2H, *d*), 4.99 (1H, *t*), 4.85–4.75 (2H, *m*), 4.56 (H, *d*); ^{13}C NMR ($CDCl_3$, p.p.m.): 166.15, 151.13, 149.61, 148.81, 141.12, 140.64, 140.02, 138.42, 137.66, 128.86, 128.74, 128.29, 127.66, 127.42, 127.24, 127.14, 127.07, 124.88, 124.35, 123.17, 119.82, 110.48, 46.23, 45.97, 45.58, 42.83. MS (70 eV, EI): *m*/*z* (%) 478 (M^+, 1), 296 (8), 258 (BPEPy+H$^+$, 25), 257 (BPEPy$^+$, 100), 221 (BOEP$^+$,37), 220 (BOEP–H$^+$, 64), 180 (5), 91 (5).

Crystal data

$C_{34}H_{26}N_2O$
M_r = 478.57
Monoclinic, $P2_1/c$
a = 12.661 (5) Å
b = 19.247 (7) Å
c = 11.010 (4) Å
β = 107.273 (7)°
V = 2561.8 (16) Å^3
Z = 4

D_x = 1.241 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 93 reflections
θ = 2.3–24.7°
μ = 0.08 mm^{-1}
T = 293 (2) K
Plate, colorless
0.35 × 0.25 × 0.15 mm

Data collection

Bruker CCD area-detector diffractometer	4517 independent reflections
φ and ω scans	1891 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$R_{int} = 0.082$
$T_{min} = 0.974$, $T_{max} = 0.989$	$\theta_{max} = 25.0°$
10446 measured reflections	$h = -15 \rightarrow 14$
	$k = -22 \rightarrow 20$
	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.115$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
$S = 0.98$	$\Delta\rho_{min} = -0.16$ e Å^{-3}
4517 reflections	Extinction correction: *SHELXL*97
335 parameters	Extinction coefficient: 0.0023 (4)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.329 (3)	C2—C12	1.502 (4)
O1—C6	1.384 (3)	C2—C3	1.545 (4)
N1—C5	1.310 (3)	C3—C30	1.491 (4)
N1—C11	1.392 (3)	C3—C4	1.572 (4)
C1—C5	1.462 (4)	C4—C24	1.491 (4)
C1—C2	1.558 (4)	C6—C11	1.360 (4)
C1—C4	1.566 (4)		
C5—O1—C6	104.3 (3)	C24—C4—C3	118.1 (2)
C5—N1—C11	105.1 (3)	C1—C4—C3	88.2 (2)
C5—C1—C2	117.8 (3)	N1—C5—O1	114.5 (3)
C5—C1—C4	112.3 (2)	N1—C5—C1	123.0 (3)
C2—C1—C4	89.4 (2)	O1—C5—C1	122.1 (3)
C12—C2—C3	118.7 (2)	C11—C6—C7	121.2 (3)
C12—C2—C1	120.4 (2)	C11—C6—O1	108.6 (3)
C3—C2—C1	89.4 (2)	C7—C6—O1	130.2 (3)
C30—C3—C2	121.6 (3)	C6—C11—C10	121.5 (4)
C30—C3—C4	119.4 (2)	C6—C11—N1	107.5 (3)
C2—C3—C4	89.6 (2)	C10—C11—N1	130.9 (4)
C24—C4—C1	118.2 (2)		

The benzoxazolyl group shows orientational disorder. It was assumed that atoms O1 and N1*A*, and atoms O1*A* and N1, share the same positional and atomic displacement parameters. Equal occupancy was assumed for atoms O1 and N1 in each position.

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

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References

Bianchini, C., Lee, H. M., Meli, A., Oberhauser, W., Vizza, F., Bruggeller, P., Haid, R. & Langes, C. (2000). *Chem. Commun.* pp. 777–778.

Bruker (1997). *SADABS, SMART, SAINT* and *SHELXTL.* Versions 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Busetti, V., Valle, G., Zanotti, G. & Galiazzo, G. (1980). *Acta Cryst.* B**36**, 894–897.

Margulis, T. N. (1965). *Acta Cryst.* **19**, 857–859.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Stein, A., Lehmann, C. W. & Luger, P. (1992). *J. Am. Chem. Soc.* **114**, 7684–7687.

Sutherland, H. H. & Rawas, A. (1984). *Acta Cryst.* C**40**, 830–832.

Zhang, W. Q., Wang, M. Z. & Wang, H. G. (1996). *Sci. China Ser. B*, **39**, 105–112.

Zhang, W. Q., Zhang, M. J., Wang, J. X., Yang, X. R., Wang, S. L., Jiang, Q. & An, Y. (1998). *Acta Chim. Sin.* **56**, 612–617.

Zhang, W. Q., Zhang, Z. M., Zhen, Y., Wang, S. L. & Zhao, S. N. (2000). *Acta Phys. Chim. Sin.* **16**, 207–213.

Zhang, W. Q., Zhuang, J. P., Li, C. B., Sun, H. & Yuan, X. N. (2001). *Chin. J. Chem.* **19**, 695–701.

Zheng, Y., Zhuang, J. P., Zhang, W. Q., Leng, X. B. & Weng, L. H. (2001). *Acta Cryst.* E**57**, o1029–o1031.