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r-1,*c*-2,*t*-3,*t*-4-1,3-Bis(4-methoxyphenyl)-2,4-bis(5-phenyl-1,3,4-oxadiazol-2-yl)cyclobutane 1,4-dioxane solvate

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The asymmetric unit of the crystal structure of $C_{34}H_{28}N_4O_4.C_4H_8O_2$, which is a 1:1 inclusion complex, consists of half a molecule of the title compound *t*-DPC and half a molecule of 1,4-dioxane. The structure shows that *t*-DPC is centrosymmetric; its cyclobutane ring has an exactly planar conformation, and is nearly square. The four C—C single bonds are of equal length [1.569 (4) Å] and the bond angles are 91.6 (2) and 88.4 (2)°. The major photodimerization process is a head-to-tail reaction rather than a head-to-head one.

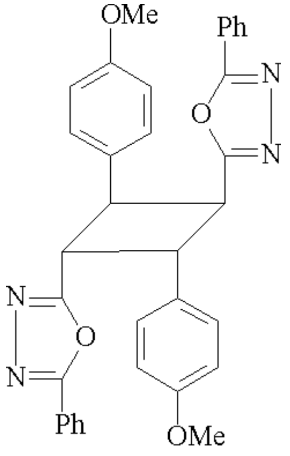
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.068
wR factor = 0.167
Data-to-parameter ratio = 12.6

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

Comment

The cyclobutane rings for most tetraarylcyclobutanes have a puckered conformation, such as in *r*-1,*c*-2,*t*-3,*t*-4-1,3-bis[2-(4-*R*-phenyl)]-2,4-di-(4-pyridyl)cyclobutane (*R* = Cl, CH_3, C_6H_5). The average dihedral angles of the cyclobutane ring are 19.2, 24.6 and 16.4°, respectively, in the three structures (Busetti *et al.*, 1980; Zhang *et al.*, 1998; Zhang, Zhang *et al.*, 2000). However, it is very interesting that some tetraoxazolyl-substituted cyclobutanes have planar four-membered rings, as found in *r*-1,*c*-2,*t*-3,*t*-4-tetrakis[2-(5-phenyl-oxazolyl)]cyclobutane (Zhang *et al.*, 1996), *r*-1,*c*-2,*t*-3,*t*-4-tetrakis[2-benzoxazolyl]cyclobutane (Zhang, Li *et al.*, 2000) and *r*-1,*c*-2,*t*-3,*t*-4-tetrakis[2-(6,7-dimethylbenzoxazolyl)]cyclobutane (Kao *et al.*, 1989). This interesting phenomenon prompted us to generate a new heteroaryl-substituted cyclobutane in order to study the effect of the substituent on the conformation of the cyclobutane ring. We report here for the first time that a diphenyl-diphenyloxadiazolyl-substituted cyclobutane (*t*-DPC) has a planar conformation.



t-DPC

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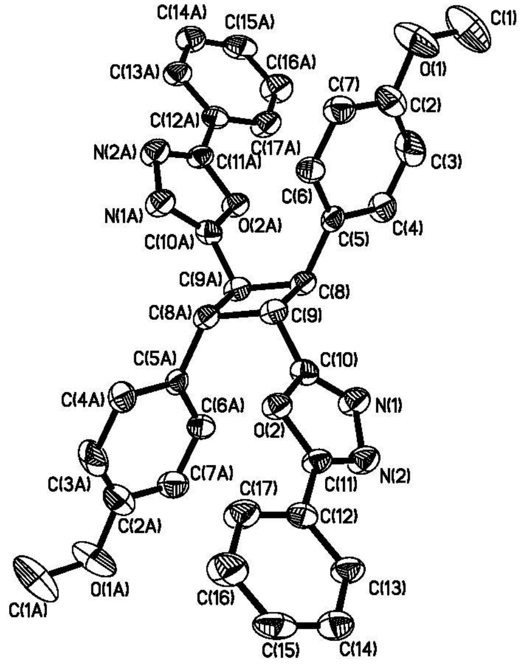

Figure 1

View of *t*-DPC with 30% probability ellipsoids.

The X-ray diffraction results clearly show that there are one *t*-DPC molecule and one 1,4-dioxane molecule in the unit cell and the molecules are exactly centrosymmetric, demonstrating that a head-to-tail photodimerization process has occurred. The cyclobutane ring of *t*-DPC is planar, just as in tetraoxazolylcyclobutanes. It appears that the substituents in these compounds, lacking an α–H atom, have a relatively small steric requirement, allowing a planar four-membered ring.

The two independent pairs of C—C bonds of the cyclobutane ring are equal in length [1.569 (4) Å] and are longer than a normal C—C single bond. However, this elongation is common for cyclobutanes. The bond angles C8—C9—C8^{i} and C9—C8—C9^{i} are 91.6 (2) and 88.4 (2)° respectively, so that the cyclobutane ring is almost a square. The dihedral angle between the phenyloxadiazolyl plane and the 4-methoxyphenyl plane situated on the same side of the cyclobutane ring is 50.4 (3)°, intermediate between parallel and perpendicular.

For the five bonds in the oxadiazolyl ring, the C—O single bonds are shorter than that (1.365 Å) of 2,5-di(4-pyridyl)-1,3,4-oxadiazole (DPO), but the N—N single bond is much longer than that (1.409 Å) of DPO (Stockhause *et al.*, 2001).

The bond angle C1—O1—C2 is 118.0 (4)°, which is quite large compared with that of common aliphatic ethers, and atoms C1 and O1 are almost coplanar with the benzene ring plane [the torsion angles C1—O2—C2—C3 and C1—O2—C2—C3 are −3.1 (7) and 178.6 (4)°, respectively], which means that O1 is an *sp*^{2} hybridized atom and there exists an *n*-π conjugation between O1 and the benzene ring. Because of the non-bonding repulsion between the methyl group and H3*a* (on C3), the bond angle C3—C2—O1 is increased to 125.0 (4)°, whereas the C7—C2—O1 angle is reduced to 114.7 (4)°.

Experimental

trans-1-(4-Methoxyphenyl)-2-[2-(5-phenyl-1,3,4-oxadiazolyl)]ethene (PDE) was synthesized by condensing 4-methoxybenzaledhyde and 2-methyl-5-phenyl-1,3,4-oxadiazole in DMF with KOH catalysis at 348 K; m.p. 403–404 K. UV (1,4-dioxane): λ_{max} 338 (logε 4.58) nm; IR (KBr): 3056 (*w*), 1640 (*m*), 1606 (*vs*), 1528 (*vs*), 1246 (*vs*), 1176 (*vs*), 1012 (*m*), 960 (*m*) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 8.14–8.08 (4H, *m*), 7.60–7.47 (12H, *m*), 6.96–6.89 (6H, *m*), 4.10 (4H, *t*), 2.00 (4H, *m*) p.p.m. 1.0 g PDE was dissolved in 200 ml acetonitrile and irradiated with a 300 W medium-pressure mercury lamp for 70 h. Then 200 ml of water was added, the precipitate was filtered and recrystallized from ethanol to give 123 mg *t*-DPC; m.p. 504–505 K. λ_{max} 255 (logε 4.58) nm; IR (KBr): 3037 (*w*), 2958 (*w*), 1612 (*s*), 1563 (*s*), 1515 (*vs*), 1251 (*vs*), 1181 (*s*), 1037 (*s*), 829 (*s*), 775 (*s*) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.81 (4H, *d*), 7.47 (6H, *m*), 7.26 (4H, *d*), 6.77 (4H, *d*), 4.89 (2H, *t*), 4.80 (2H, *t*), 3.66 (6H, *s*) p.p.m. ^{13}C NMR (CDCl$_3$): δ 165.65, 165.40, 159.19, 131.77, 129.37, 129.11, 128.60, 126.96, 123.97, 114.36, 55.39, 43.70, 39.93 p.p.m. A single-crystal of the title compound was grown in 1,4-dioxane by slow evaporation of the solvent.

Crystal data

$C_{34}H_{28}N_4O_4 \cdot C_4H_8O_2$
$M_r = 644.71$
Triclinic, $P\bar{1}$
$a = 5.995$ (2) Å
$b = 10.242$ (4) Å
$c = 14.292$ (5) Å
$\alpha = 93.370$ (6)°
$\beta = 90.595$ (6)°
$\gamma = 103.557$ (6)°
$V = 851.4$ (5) Å^3
$Z = 1$
$D_x = 1.257$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2713 reflections
$\theta = 2.6$–21.3°
$\mu = 0.09$ mm^{-1}
$T = 298$ (2) K
Plate, colorless
0.30 × 0.25 × 0.20 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
3275 measured reflections
2746 independent reflections
1195 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 25.0$°
$h = -7 \rightarrow 6$
$k = -12 \rightarrow 7$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.167$
$S = 0.97$
2746 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.023 (4)

Table 1

Selected geometric parameters (Å, °).

C1—O1	1.405 (5)	C8—C9^{i}	1.569 (4)
O2—C10	1.352 (3)	C9—C10	1.472 (4)
O2—C11	1.354 (3)	C10—N1	1.298 (4)
O1—C2	1.394 (5)	N1—N2	1.422 (3)
C5—C8	1.504 (4)	N2—C11	1.281 (4)
C8—C9	1.569 (4)	C11—C12	1.463 (4)
C10—O2—C11	102.9 (3)	C8—C9—C8^{i}	91.6 (2)
C2—O1—C1	118.0 (4)	N1—C10—O2	112.7 (3)
C3—C2—O1	125.0 (4)	C10—N1—N2	105.3 (3)
C7—C2—O1	114.7 (4)	C11—N2—N1	105.9 (3)
C9—C8—C9^{i}	88.4 (2)	N2—C11—O2	113.1 (3)

Symmetry code: (i) $-x, -y, 1-z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* and *SHELXTL* (Bruker, 1998); 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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