

***r*-1,*c*-2,*t*-3,*t*-4-1,2-Bis(4-methoxyphenyl)-3,4-bis(5-phenyl-1,3,4-oxadiazol-2-yl)-cyclobutane****Jun-Peng Zhuang and Yan Zheng\***

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**Key indicators**

Single-crystal X-ray study

 $T = 298\text{ K}$ Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$  $R$  factor = 0.044 $wR$  factor = 0.133

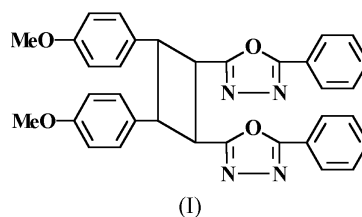
Data-to-parameter ratio = 13.1

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

The title compound,  $\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_4$ , is a derivative of diphenyl-oxadiazolylcyclobutane (*s*-DPC), and although it is a *syn*-head-to-head photodimer, it does not display molecular mirror symmetry in the crystalline state. The cyclobutane ring has a puckered conformation, with a dihedral angle of  $30^\circ$ , which is the largest among tetraaryl-substituted cyclobutanes reported so far. The four C—C single bonds of the cyclobutane ring differ from each other. One is the same length as a typical C—C single bond, while the others are longer. The photodimerization of the corresponding monomer yields only 1% of *s*-DPC, suggesting that the head-to-head reaction is a minor photodimerization process.

**Comment**

The average dihedral angle of the cyclobutane ring in tetraaryl-cyclobutanes which 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, with  $R = \text{Cl}$ ,  $\text{CH}_3$  and  $\text{C}_6\text{H}_5$ , is  $19.2$ ,  $24.6$  and  $16.4^\circ$ , respectively (Busetti *et al.*, 1980; Zhang *et al.*, 1998; Zhang, Zhang *et al.*, 2000). However, the ring is planar in some tetraheteroaryl- and diphenylbisheteroaryl-substituted cyclobutanes reported recently by us, such as *r*-1,*c*-2,*t*-3,*t*-4-tetrakis[2-(5-phenyloxazolyl)]cyclobutane (Zhang *et al.*, 1996), *r*-1,*c*-2,*t*-3,*t*-4-tetrakis[2-benzoxazolyl]cyclobutane (Zhang, Li *et al.*, 2000), *r*-1,*c*-2,*t*-3,*t*-4-tetrakis[2-(6,7-dimethylbenzoxazolyl)]cyclobutane (Kao *et al.*, 1989), *r*-1,*c*-2,*t*-3,*t*-4-1,3-bis(5-methylbenzoxazolyl)-2,4-bis(4-methoxyphenyl)cyclobutane (Zhang *et al.*, 2001) and *r*-1,*c*-2,*t*-3,*t*-4-1,3-bis(4-methoxyphenyl)-2,4-bis[2-(5-phenyl-1,3,4-oxadiazolyl)]cyclobutane (*t*-PDC; Zheng *et al.*, 2001). The cyclobutane ring in *t*-DPC, a stereo-isomer of *s*-DPC, is planar and has a head-to-tail structure, while the ring in the present compound is puckered, with a dihedral angle of  $30^\circ$ , which is the largest angle reported so far (angle between planes C1/C2/C3 and C1/C4/C3 and angle between planes C2/C1/C4 and C2/C3/C4).

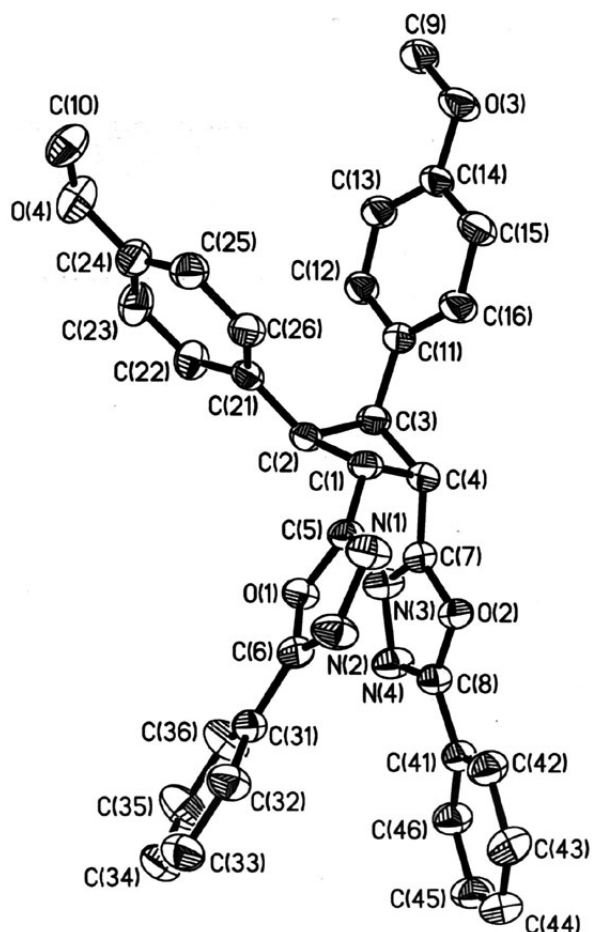


The two methoxyphenyl rings have four  $\alpha$ -H atoms and the steric hindrance between the two methoxyphenyl rings causes the large puckering of the cyclobutane ring. This feature is the same as in structures with pyridyl substituents. The angle between the two oxadiazolyl planes (N1/N2/C6/O1/C5 and N3/

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**Figure 1**  
View of *s*-DPC, drawn with 30% probability ellipsoids

N4/C8/O2/C7) is 31.8° and that between the two methoxyphenyl planes is 50.2°.

In the dimerization process, it was supposed that there exists an excimer formed from an excited singlet molecule with an unexcited singlet molecule, and the excimer can reduce the reaction activity energy. Of the two kinds of photodimers isolated, *t*-DPC is observed to be more stable than *s*-DPC. This is attributed to the dipolar attraction of the phenyl group and the oxadiazolyl group in the *syn*-head-to-tail excimer.

Of the four C—C single bonds of the cyclobutane ring, the C2—C3 single bond between the two phenyl groups is the longest, which indicates that there is an interaction between the two phenyl groups. The distance from atom H16a to H4a is 2.052 Å, which constitutes a very short non-bonding distance.

For the two oxadiazolyl rings, the C—O single bonds are in the range 1.3621 (19)—1.369 (2) Å, C=N double bonds are in the range 1.276 (2)—1.286 (2) Å, and N—N single bonds are 1.411 (2) and 1.412 (2) Å, respectively, all similar to the distances found in 2,5-di(4-pyridyl)-1,3,4-oxadiazole (C—O 1.365, C=N 1.29 and N—N 1.409 Å; Stockhause *et al.*, 2001).

The bond angles C9—O3—C14 and C10—O4—C24 are 117.95 (16) and 125.1 (3)°, respectively, and the methoxy groups are almost coplanar with their attached benzene-ring

plane, which means that atoms O3 and O4 are both  $sp^2$ -hybridized and there is  $n$ - $\pi$  conjugation between these atoms and the benzene rings.

## Experimental

Single crystals of *s*-DPC were separated manually from the mother liquor of *t*-DPC (Zheng *et al.*, 2001) after two weeks storage, in a yield of 1%; m.p. 438–439 K. UV (1,4-dioxane):  $\lambda_{\max}$  249 nm; IR (KBr): 2958 (*w*), 1611 (*m*), 1552 (*m*), 1516 (*vs*), 1255 (*vs*), 1183 (*m*), 1030 (*m*), 842 (*m*), 774 (*s*), 692 (*s*)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.82 (4H, *d*,  $J = 7.6$  Hz), 7.42 (2H, *t*), 7.35 (4H, *m*), 7.02 (4H, *d*,  $J = 7.6$  Hz), 6.74 (4H, *d*,  $J = 7.6$  Hz), 4.89 (2H, *s*), 4.73 (2H, *s*), 3.75 (6H, *s*) p.p.m.

## Crystal data

$\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_4$	$Z = 2$
$M_r = 556.60$	$D_x = 1.280 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.1746$ (8) Å	Cell parameters from 5978 reflections
$b = 11.3853$ (10) Å	$\theta = 1.5$ – $25.0^\circ$
$c = 14.5431$ (12) Å	$\mu = 0.09 \text{ mm}^{-1}$
$\alpha = 91.648$ (2)°	$T = 298$ (2) K
$\beta = 107.925$ (2)°	Plate, colorless
$\gamma = 91.642$ (2)°	$0.35 \times 0.30 \times 0.30 \text{ mm}$
$V = 1443.6$ (2) Å <sup>3</sup>	

## Data collection

Bruker SMART CCD area-detector diffractometer	3382 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.012$
Absorption correction: none	$\theta_{\max} = 25.0^\circ$
6052 measured reflections	$h = -10 \rightarrow 7$
5079 independent reflections	$k = -13 \rightarrow 13$
	$l = -17 \rightarrow 17$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0766P)^2 + 0.0284P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.00$	$\Delta\rho_{\max} = 0.13 \text{ e \AA}^{-3}$
5079 reflections	$\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
388 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

C1—C5	1.475 (2)	O3—C9	1.408 (2)
C1—C2	1.538 (2)	C3—C11	1.503 (2)
C1—C4	1.572 (3)	C3—C4	1.552 (2)
C2—C21	1.497 (2)	C4—C7	1.476 (2)
C2—C3	1.579 (2)	O4—C24	1.362 (3)
O3—C14	1.368 (2)	O4—C10	1.378 (5)
C2—C1—C4	88.40 (13)	C24—O4—C10	125.1 (3)
C1—C2—C3	88.14 (13)	C13—C14—O3	125.08 (17)
C14—O3—C9	117.95 (16)	O3—C14—C15	115.90 (18)
C4—C3—C2	87.64 (13)	O4—C24—C25	120.5 (2)
C3—C4—C1	87.89 (13)	O4—C24—C23	120.1 (2)

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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