

**(*E,E*)-2,5-Dimethoxy-1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene**

Christophe M. L. Vande Velde, Herman J. Geise and Frank Blockhuys\*

Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium

Correspondence e-mail: frank.blockhuys@ua.ac.be

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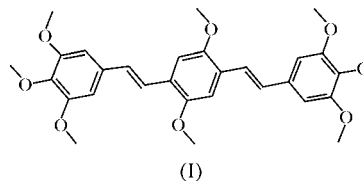
In the title compound,  $C_{30}H_{34}O_8$ , molecular symmetry is coincident with crystallographic inversion symmetry. A three-dimensional network is generated containing both  $C-H \cdots \pi$  and  $C-H \cdots n(O)$  interactions. A comparison of the geometry of this molecule and the structure of a number of 2,4,6-trimethoxy-substituted analogues is provided.

**Comment**

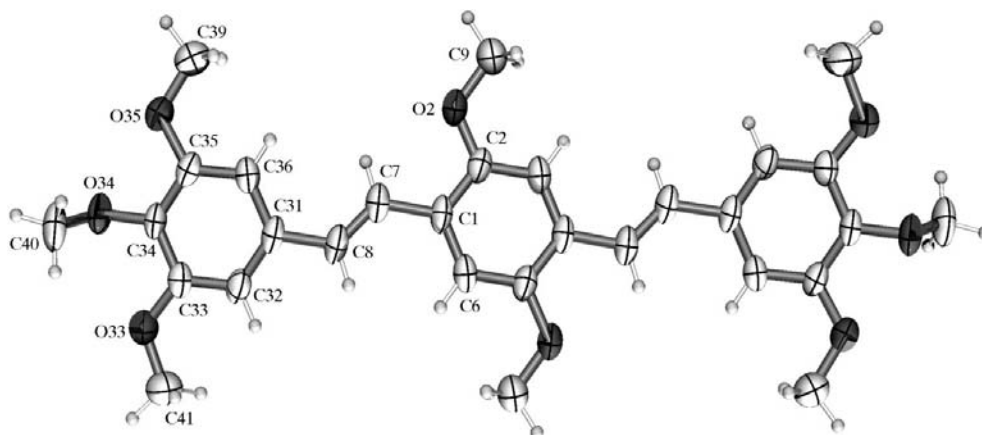
The title compound, (I) (Fig. 1), is a PPV [poly(*p*-phenylenevinylene)] oligomer that can be used as the electroactive material in conductimetric gas sensors (De Wit *et al.*, 1998; Vanneste *et al.*, 1998). A recent study of the crystal packing of a series of 2,4,6-trimethoxy-substituted PPV oligomers (Vande Velde *et al.*, 2004) prompted us to investigate further the crystal structure of (I) in order to establish whether its packing would be comparable with that of these analogues or rather more similar to the previously published 3,4,5-trimethoxy-substituted derivative lacking the methoxy groups on the central ring [Cambridge Structural Database (CSD; Allen, 2002) refcode JACBIY; Verbruggen *et al.*, 1988].

Compound (I) forms crystals in which crystallographic inversion symmetry is coincident with molecular symmetry. Bond distances and angles are normal, and no profound effects due to libration or substitution can be identified. The molecule displays a peculiar *Z* shape, which is obvious from Fig. 2. This shape can be expressed most conveniently *via* the relative orientations of the central and peripheral rings and the C31–C8 and C7–C8 bonds. The least-squares (LS) plane of the peripheral ring makes an angle of 18.2 (3)° with the LS plane of the central ring. The C31–C8 and C7–C8 bonds make angles of 6.5 (5) and 2.1 (5)°, respectively, with the LS plane of the central ring, and of 5.6 (5) and 16.2 (5)°, respectively, with the peripheral ring. The related 3,4,5-trimethoxy-substituted PPV oligomer, CSD refcode JACBIY, which lacks the methoxy groups on the central ring, displays a similar *Z* shape (Verbruggen *et al.*, 1988).

In addition, the molecules in JACBIY are packed edge-to-face, with a few stabilizing  $C-H \cdots n(O)$  contacts, which is fairly standard for distyrylbenzenes (Bartholomew *et al.*, 2000). In contrast, the packing of (I) displays a large number of intermolecular close contacts, some of which can also be observed in the structures of the 2,4,6-substituted analogues (Vande Velde *et al.*, 2004). These will now be discussed in detail.



As can be seen in Fig. 3, there are  $OCH_3 \cdots \pi$  contacts (shown as dashed lines), where each molecule is donor in the interactions with two other molecules and acceptor in those with two different ones, and the four of them are related to the first *via* glide planes. Thus, and in contrast with what was observed for the 2,4,6-analogues, these contacts are not reciprocated by their recipients and thus cannot be the reason for the observed layering in the stacking. The contacts can be designated  $C9-H9A \cdots CgA^i$  [symmetry code: (i)  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ ], with  $C \cdots CgA = 2.84$  (2) Å,  $C-H \cdots CgA = 111.8$  (15)°

**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

and  $\text{perp} = 3.375(9) \text{ \AA}$ , where  $C_gA$  is the centroid of the peripheral ring  $A$ , and 'perp' is the distance of the H atom to the LS plane of the ring. All contacts given in this discussion, unless specifically noted, use the coordinates of the H atoms from the CIF, which are not normalized to  $1.083 \text{ \AA}$ . These contacts also give rise to the close contacts of atom H9A with atoms C35 and C36, given by  $\text{H9A} \cdots \text{C35}^i = 2.76(2) \text{ \AA}$  and  $\text{C9-H9A} \cdots \text{C35}^i = 127.5(16)^\circ$ , and  $\text{H9A} \cdots \text{C36}^i = 2.66(2) \text{ \AA}$  and  $\text{C9-H9A} \cdots \text{C36}^i = 139.7(17)^\circ$ , which are not shown in Fig. 3.

The observed layered stacking of (I) is due to the interactions detailed in Fig. 4, given by  $\text{O2} \cdots \text{H40C}^{ii} = 2.67(2) \text{ \AA}$  and  $\text{C9-O2} \cdots \text{H40C}^{ii} = 118.3(6)^\circ$  [symmetry code: (ii)  $1+x, y, z$ ], and  $\text{C8} \cdots \text{C8}^{iii} = 3.325(9) \text{ \AA}$  and  $\text{C7-C8} \cdots \text{C8}^{iii} = 104.1(4)^\circ$  [symmetry code: (iii)  $-x, -y, -z$ ]. The first of these contacts, which can be labelled  $\text{C-H} \cdots n(\text{O})$ , links the molecules into strings with overlapping backbones. It is quite interesting to note that the above-mentioned Z shape of the molecule seems to originate specifically from the latter two interactions. This suggests that they play a rather important role in the determination of the packing mode. The methoxy groups that are involved are bent out of the plane of the ring to which they are attached, possibly to relieve steric strain.

There are more of these  $\text{C-H} \cdots n(\text{O})$  interactions present in the structure of (I), also indicated by dotted lines in Fig. 4, and these are given by  $\text{O33} \cdots \text{H39A}^{iv} = 2.67(3) \text{ \AA}$  and  $\text{C41-O33} \cdots \text{H39A}^{iv} = 111.3(7)^\circ$ , and  $\text{O2} \cdots \text{H40B}^{iv} = 2.53(3) \text{ \AA}$  and

$\text{C2-O2} \cdots \text{H40B}^{iv} = 116.5(7)^\circ$  [symmetry code: (iv)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ].

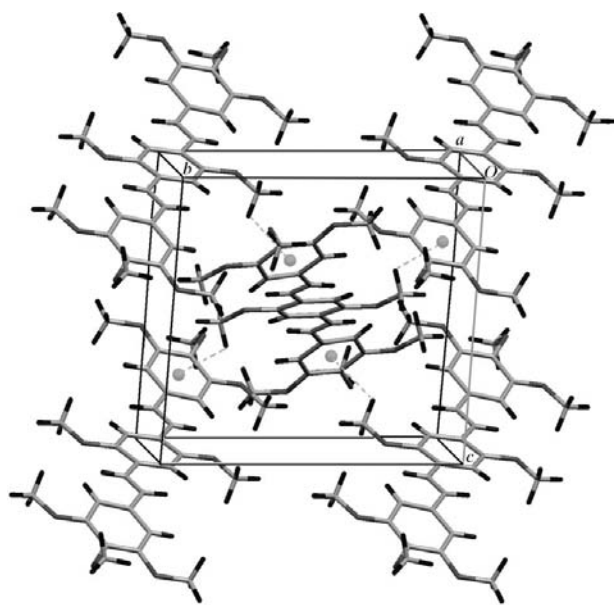
These  $\text{C-H} \cdots n(\text{O})$  contacts link molecules through the central ring of the oligomer and thus diagonally through the unit cell. In this way, they form T-shaped contacts, in which the C39 and C40 methoxy groups exchange intermolecular  $\text{C-H} \cdots n(\text{O})$  interactions with atoms O2 and O33. The  $\text{O2} \cdots \text{H40B}^{iv}$  contact is about  $0.2 \text{ \AA}$  shorter than the sum of the van der Waals radii of the participating atoms, which could explain why only the C40 terminal methoxy groups are bent so far out of the plane of the ring to which they are attached; atom O34 lies  $0.187(4) \text{ \AA}$  out of the LS plane of the ring.

The last remaining short contact in the structure of (I) is given by  $\text{H9B} \cdots \text{H41A}^v = 2.37(5) \text{ \AA}$  and  $\text{C9-H9B} \cdots \text{H41A}^v = 113(2)^\circ$  [symmetry code: (v)  $1+x, \frac{1}{2} - y, \frac{1}{2} + z$ ]. This contact represents yet another way in which the molecules link up by means of their methoxy groups. It is quite likely that this close contact is of purely steric origin.

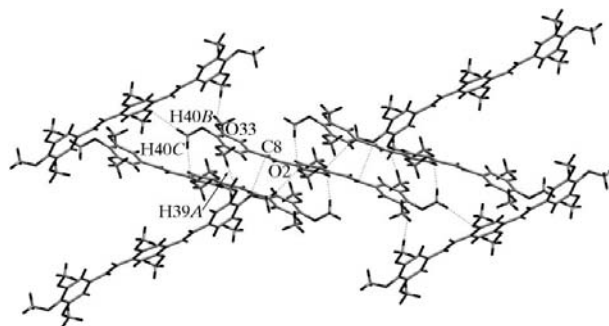
It is instructive to look also at the intramolecular  $\text{C-H} \cdots n(\text{O})$  contacts, which are always present in these types of methoxy-substituted PPV oligomers. We have demonstrated previously that they are attractive contacts and contribute to the observed conformation and planarity of the molecule (Wu *et al.*, 1996). In (I), there is only one *ortho*-methoxy group in the asymmetric unit, so there is only one such contact, given by  $\text{O2} \cdots \text{H7} = 2.3806 \text{ \AA}$  and  $\text{C9-O2} \cdots \text{H7} = 157^\circ$ . After normalization of the C-H distance to  $1.083 \text{ \AA}$ ,  $\text{O2} \cdots \text{H7}$  becomes  $2.344 \text{ \AA}$ . This contact fixes the central ring with respect to the double bond. The lack of this contact for the peripheral 3,4,5-trimethoxy-substituted ring may be a second important contributing factor to the Z shape of the molecule. Indeed, a comparison of the solid-state geometry with that obtained from a density-functional theory B3LYP/6-31G\* calculation (GAUSSIAN98; Frisch *et al.*, 2001) on an isolated molecule reveals that the bond distances and angles are quasi-equal, but that the Z shape has disappeared from the gas-phase structure. Furthermore, examination of the calculated angles between the C31-C8 and C7-C8 bond vectors and the LS plane of the central ring reveals values of  $0.82$  and  $6.06^\circ$ , respectively. The corresponding angles with the peripheral ring are  $0.18$  and  $10.17^\circ$ , respectively. The LS planes of the central and peripheral rings themselves are at an angle of  $20.68^\circ$ .



**Figure 2**  
A view of a molecule of (I), demonstrating its Z shape in the crystal.



**Figure 3**  
A view of the cell of (I), showing the  $\text{OCH}_3 \cdots \pi$  interactions (dashed lines) between the middle-ring methoxy groups and the outer aromatic rings.



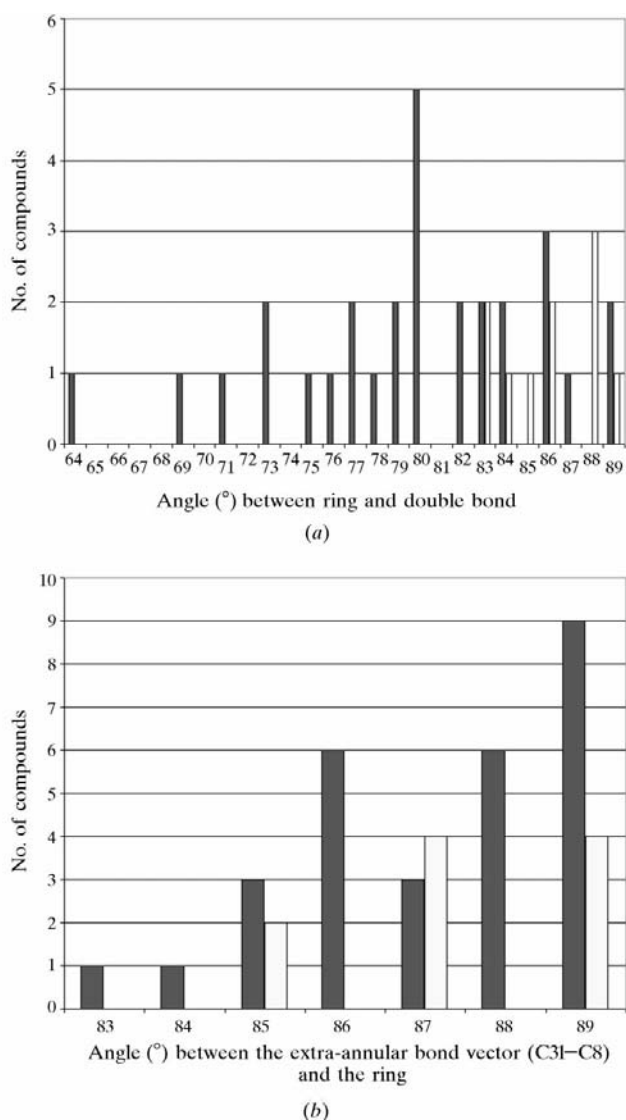
**Figure 4**  
The  $\text{C-H} \cdots n(\text{O})$  interactions (dotted lines) in the structure of (I).

The introduction of 3,4,5-trimethoxy- instead of 2,4,6-trimethoxy substitution on the peripheral rings appears to have a twofold effect. While it allows the peripheral rings to twist about  $20^\circ$  away from a coplanar arrangement, it also increases the end-to-end flexibility of the molecule, and this results in its deformation to the observed Z shape by the packing environment. To support this theory, we carried out a search of the CSD [version 1.6 (Allen, 2002), with the November 2003, and April and July 2004 updates] and found 20 compounds containing 29 different (3,4,5-trimethoxyphenyl)ethenyl moieties, and five compounds containing a (2,4,6-trimethoxyphenyl)ethenyl moiety {ten including our recent data [Vande Velde *et al.* (2004), and unpublished data]}. It is clear that the angle the double-bond vector makes with the plane of the

peripheral ring is generally closer to planar in the 2,4,6-trimethoxy-substituted moieties (mean  $85.7^\circ$ ) than in the 3,4,5-trimethoxy-substituted moieties ( $81.2^\circ$ ) (Fig. 5*a*), further corroborating the attractive nature of the C—H $\cdots$ n(O) interaction and the role it plays in keeping the distyrylbenzene skeleton planar in these highly substituted derivatives. The angle of the C31—C8 bond vector with respect to the ring plane was also evaluated in the same compounds (Fig. 5*b*), but it is in all cases smaller than or equal to  $5^\circ$ , which, combined with the small number of compounds that were evaluated, makes it difficult to draw conclusions. In short, in a 3,4,5-trimethoxy-substituted distyrylbenzene, the peripheral ring is more free to adapt to the other packing needs of the structure, and able to twist up to  $20^\circ$  away from the plane of the double bond, without insurmountable energetic requirements. This favours a C—H $\cdots$ n(O) network instead of a layered OCH<sub>3</sub> $\cdots$  $\pi$  network for (I).

**TLS** tensor analysis (Schomaker & Trueblood, 1968) implemented in *PLATON* (Spek, 2003) shows that the translation and screw components are close to zero, as expected for a structure that is centrosymmetric, and that the libration along the axis parallel to the long axis of the molecule is about one order of magnitude larger than those along the other axes ( $L1 = 20.05^\circ$ ,  $L2 = 0.96^\circ$ ,  $L3 = 0.63^\circ$ ); its orientation deviates only  $2.97^\circ$  from the long axis. In JACBIY (Verbruggen *et al.*, 1988), this same phenomenon was attributed to the large librational motion of the middle ring only, an explanation which is far less likely for (I), as the methoxy groups on the central ring display a number of stabilizing contacts comparable with those on the peripheral rings. Furthermore, the bond distances and angles of the central ring display no unusual deviations. It would be more logical that, in (I), the entire molecule librates along its long axis.

In conclusion, although the packing mode of (I) is similar to that of the previously described 2,4,6-trimethoxy-substituted derivatives, the most important intermolecular interactions in (I) are of the C—H $\cdots$ n(O) type, as also observed by Bartholomew *et al.* (2000), and not of the OCH<sub>3</sub> $\cdots$  $\pi$  type, as observed by us (Vande Velde *et al.*, 2004) in the 2,4,6-trimethoxy derivatives. The reason for this must be found in the competition that exists between these weak interactions, which is fierce in an environment that is entirely controlled by them. Thus, a small difference in stabilization energy can make a very large difference in the resulting packing. The change from 2,4,6-trimethoxyphenyl to 3,4,5-trimethoxyphenyl, apart from steric considerations (in particular, the methoxy group in the 4-position of the peripheral ring being perpendicular to the plane of this ring), has its main effect on the molecular geometry, by twisting the peripheral rings out of the plane formed by the central ring and the ethenyl bonds. This causes the molecule to adopt a Z shape.



**Figure 5**

Graphical representations of the population of known compounds with a trimethoxyphenylethenyl fragment (*a*) versus the angle their outer rings make with the double-bond vector and (*b*) versus the angle between the ring and the extra-annular single-bond vector. Shaded bars indicate data for 3,4,5-trimethoxy-substituted compounds and open bars indicate data for 2,4,6-trimethoxy-substituted compounds.

## Experimental

Compound (I) was prepared by the Wittig reaction between 3,4,5-trimethoxybenzaldehyde and 2,5-dimethoxy-*p*-xylylenebis(triphenylphosphonium bromide), under conditions identical to those

described for the 2,4,6-trimethoxy derivatives (Nowaczyk *et al.*, 2005). Crystals of (I) were grown from a hot ethanol solution, and a single fragment was used for the diffraction experiment.

## Crystal data

$C_{30}H_{34}O_8$	$D_x = 1.321 \text{ Mg m}^{-3}$
$M_r = 522.57$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 8.778 (3) \text{ \AA}$	$\theta = 7.1\text{--}13.6^\circ$
$b = 11.520 (5) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 14.717 (6) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 118.05 (3)^\circ$	Block, yellow
$V = 1313.5 (9) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 2$	

## Data collection

Enraf–Nonius MACH-3 diffractometer	$\theta_{\text{max}} = 25.0^\circ$
Non-profiled $\omega/2\theta$ scans	$h = -10 \rightarrow 0$
5016 measured reflections	$k = -13 \rightarrow 13$
2308 independent reflections	$l = -15 \rightarrow 17$
1149 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.113$	frequency: 60 min
	intensity decay: 2%

## Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2308 reflections	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
180 parameters	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

The H atoms were placed in calculated positions. Methoxy groups were allowed to rotate and the C–H distances to refine, but the angles between the H atoms were kept close to  $109.5^\circ$ . The final range of C–H distances was  $0.9843\text{--}1.0311 \text{ \AA}$  and  $U_{\text{iso}}(\text{H})$  values were constrained to  $1.5U_{\text{eq}}(\text{C})$ . All other H atoms were treated as riding, with C–H =  $0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The crystal is rather weakly diffracting and this causes  $R_{\text{int}}$  to be higher than usual, due to the large amount of weak data. As the other quality indicators are satisfactory, we do not judge this to be truly problematic.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Version 1.64; Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1476). Services for accessing these data are described at the back of the journal.

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