

**(*E,E*)-2,5-Dipropoxy-1,4-bis[2-(2,4,6-trimethoxyphenyl)ethenyl]benzene**

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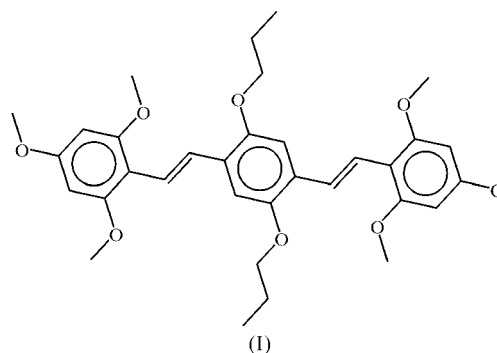
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The title compound, C<sub>30</sub>H<sub>34</sub>O<sub>8</sub>, crystallizes in the space group  $P\bar{1}$  with one-half of a molecule in the asymmetric unit. A three-dimensional network is generated by OCH<sub>3</sub>·· $\pi$  and CH·· $\pi$  interactions. The conformation of the C—C bond exocyclic to the central benzene ring is different from that of every other known derivative. A comparison of the geometry of the title molecule and of its solid-state structure with other 2,4,6-trimethoxy-substituted PPV [*i.e.* poly(*p*-phenylenevinylene)] oligomers, in particular the isopropoxy-substituted compound, is provided.

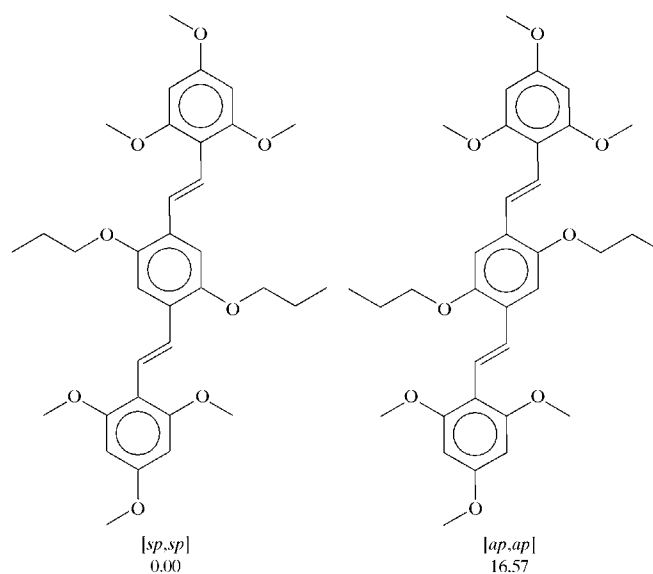
**Comment**

In a recent study on the crystal packings of several 2,4,6-trimethoxy-substituted PPV [*i.e.* poly(*p*-phenylenevinylene)] oligomers with side chains of varying size on the central ring (Vande Velde *et al.*, 2004), the claim was made that most of these compounds crystallize only with great difficulty since their solid-state structures are determined by weak OCH<sub>3</sub>·· $\pi$  interactions, which, owing to the discrete occurrence of methoxy groups and aromatic rings in the molecule, can only form networks spaced at specific intervals. For this to occur, the volume of the side chain on the central ring has to be well matched to the residual space between the molecules in order to generate long-range order. Four of these 2,4,6-trimethoxy-substituted compounds were crystallized and studied (Vande Velde *et al.*, 2004), and four markedly different networks determining the packing in the solid were found. [The vast influence that the particular substitution of the distyrylbenzene skeleton can have on the crystal structure was recently also demonstrated by Vande Velde *et al.* (2005).] One feature the four previous compounds did have in common was the presence of stabilizing intramolecular interactions between the H atoms on the olefinic link and the O atoms in the methoxy groups, in a five-membered ring assembly, designated CH-*n*(O), as explained by Wu *et al.* (1996) and Vande Velde *et al.* (2004) (§3.2 and Table 3). Theoretical calculations indicated that these interactions are stabilizing

(Wu *et al.*, 1996; Vande Velde *et al.*, 2004). In the case of the title compound, (I), the situation is the same (see Table 1). For the isolated molecule, calculations at the DFT/B3LYP/6-31G\* level (Frisch *et al.*, 2001) indicate that the conformer with the ‘correct’ conformation, *viz.* [*sp,sp*], is 16.57 kJ mol<sup>-1</sup> more stable than the [*ap,ap*] conformer (Fig. 1). Nevertheless, in the crystal, the latter less stable form is found. At the moment, the precise reason for this preference is not clear and further research is needed to shed more light on this matter. One possibility, in the context of the role of the volume of the side chain mentioned above, is that the reorientation of the central ring is a requirement for filling the space generated by the OCH<sub>3</sub>·· $\pi$  network in an efficient manner. For now, we limit ourselves mainly to the discussion of the crystal structure of (I), compare it with that of the isopropoxy isomer and only hint at a possible reason for the conformational anomaly.



The title compound (see Fig. 2 for structure and numbering scheme) crystallizes in the space group  $P\bar{1}$ , with one-half of a molecule in the asymmetric unit and one molecule in the unit cell. Bond distances and angles are unremarkable; the aromatic bond distances display their usual slight variations as a result of steric hindrance around the highly substituted



**Figure 1**  
Calculated conformers of (I). IUPAC names and calculated energies are given; see *Comment* for details.

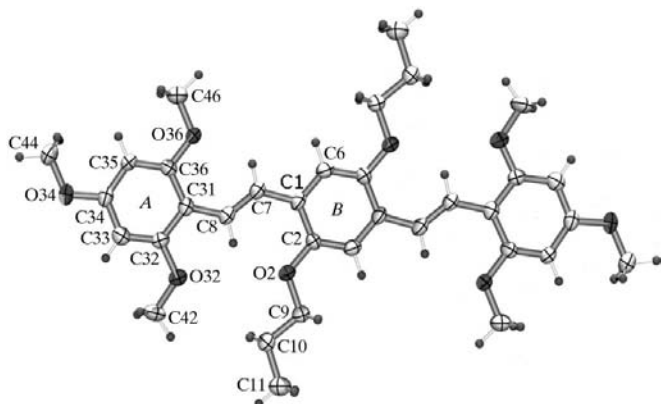
benzene rings. The central and peripheral rings are at an angle of  $6.3(3)^\circ$ , mainly owing to the torsion of the peripheral ring with respect to the double bond [ $\varphi = 6.8(3)^\circ$ ]. The central ring and the double bond vector are in the same plane [ $\varphi = 0.5(4)^\circ$ ].

The crystal structure can be described as flat interconnected sheets of molecules. For views of the structure and the resulting close contacts [ $C42 \cdots H44B^i = 2.84(3) \text{ \AA}$  and  $O32 - C42 \cdots H44B^i = 159.4(8)^\circ$ ,  $H11B \cdots H46B^{ii} = 2.23(5) \text{ \AA}$  and  $C11 - H11B \cdots H46B^{ii} = 144(3)^\circ$ , and  $H42C \cdots H44B^i = 2.35(4) \text{ \AA}$  and  $C42 - H42C \cdots H44B^i = 112(2)^\circ$ ; symmetry codes: (i)  $2 - x, -1 - y, 1 - z$ ; (ii)  $-1 + x, -1 + y, z$ ], see Figs. 3 and 4.

The sheets themselves are connected to one another by  $OCH_3 \cdots \pi$  interactions between the *p*-methoxy groups on the peripheral rings (*A*) and the peripheral rings (*A*) of the next molecule (Fig. 4) [ $C44 - H44C \cdots CgA^{iii}$ :  $2.86(3) \text{ \AA}$  and  $153.0(18)^\circ$ ; symmetry code: (iii)  $2 - x, -y, 1 - z$ ; *CgA* indicates the centroid of ring *A*].

After normalization of the positions of the terminal H atoms to  $1.083 \text{ \AA}$ , the contact becomes  $C44 - H44C \cdots CgA^{iii}$  ( $2.82 \text{ \AA}$  and  $152.6^\circ$ ). This  $OCH_3 \cdots \pi$  interaction is also expressed by the following close contacts (Fig. 3):  $C31 \cdots H44C^{iii} = 2.77(4) \text{ \AA}$  and  $C8 - C31 \cdots H44C^{iii} = 101.9(7)^\circ$ ;  $C36 \cdots H44C^{iii} = 2.88(3) \text{ \AA}$  and  $O36 - C36 \cdots H44C^{iii} = 103.7(9)^\circ$ . There is one more  $CH \cdots \pi$  contact that may contribute to the stabilization of the crystal structure, *i.e.* between a  $\beta$ -H atom of a propoxy group and ring *A* of the next molecule along the *a* axis (not shown in Figs. 3 and 4) [ $C10 - H10a \cdots CgA^{iv}$ ;  $2.70(3) \text{ \AA}$  and  $145.1(11)^\circ$ ; symmetry code: (iv)  $x - 1, y, z$ ]. The latter distance becomes  $2.63 \text{ \AA}$  after normalization of the position of the H atom.

The Cambridge Structural Database (Version 5.25, with November 2003 and April and July 2004 updates; Allen, 2002) lists only nine entries that have similar non-terminal  $\beta$ -H atoms of an alkyl group contacting the  $\pi$ -cloud of a methoxy-substituted benzene ring at a distance shorter than that in (I); in all cases but one, the alkyl group is a substituent on a ring system. The fact that this type of contact is so rare leaves two possible interpretations. The first is that this particular contact



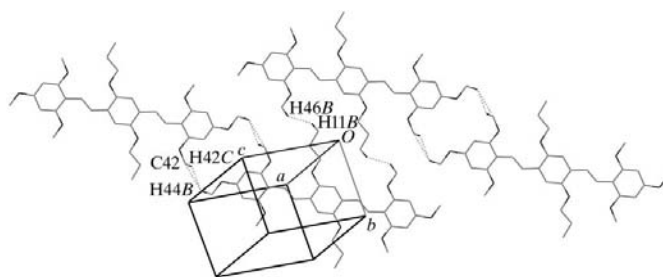
**Figure 2**

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

is remarkably strong and contributes to the stabilization of the crystal structure. The second is that its occurrence is purely coincidental, and other interactions force it this close; in this case it is repulsive. No conclusive evidence for either of the two possibilities could be found here.

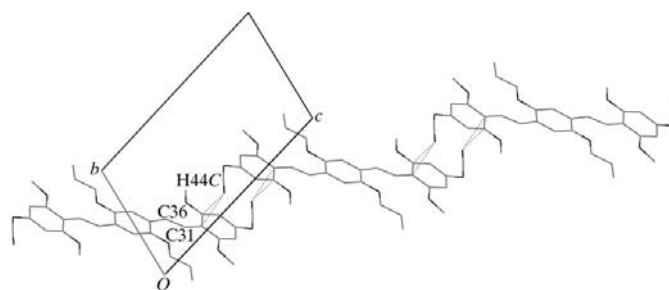
As mentioned before, the  $OCH_3 \cdots \pi$  network is different from what was observed in the isopropoxy analogue (Vande Velde *et al.*, 2004). In that structure, there are eight  $OCH_3 \cdots \pi$  interactions per molecule, four between the *p*-methoxy groups of the peripheral rings (*A*) and the central rings (*B*), and four more between the *o*-methoxy groups on rings *A* and rings *A* [for a detailed description and figures, see Vande Velde *et al.* (2004)]. Additionally, all contact distances are shorter than the  $C44 - H44 \cdots CgA$  contact observed in (I). The latter distance actually bears more similarity to that found for the compound with hexoxy substituents on the middle ring (Vande Velde *et al.*, 2004), where a (weaker) contact exists between the *o*-methoxy groups of rings *A* and rings *A*. For (I), the backbones of the molecules have apparently shifted even further over one another, bringing the *p*-methoxy group of ring *A* into contact with ring *A*.

In the previous study (Vande Velde *et al.*, 2004), we also compared two physical properties of the compounds in relation to the number and strength of the  $OCH_3 \cdots \pi$  interactions present. Firstly, the melting point of (I) ( $441\text{--}442 \text{ K}$ ) fits nicely in the set of the four earlier compounds, since it is nearly



**Figure 3**

A view of one sheet making up the structure of (I) and the resulting close contacts. Symmetry operations that relate the depicted molecules to the lower central molecule are, from left to right,  $(x + 1, y - 2, z + 1)$ ,  $(x - 1, y - 1, z)$  and  $(x - 2, y + 1, z - 1)$ .



**Figure 4**

A view of the structure along the *a* axis. The stacking of the sheets has the molecules of (I) displaced in a parallel manner over their long axis by two phenylethenyl moieties, with the contacts between the sheets indicated. Symmetry operations that relate the depicted molecules to the central molecule on the left are  $(x + 1, y - 1, z + 1)$  and  $(x + 2, y - 2, z + 2)$ .

identical to that of the hexoxy compound (437–439 K). The number of  $\text{OCH}_3 \cdots \pi$  interactions is indeed identical for both compounds without taking the  $\text{CH} \cdots \pi$  contact of the propoxy group into account. Secondly, (I) has the highest density of all the 2,4,6-trimethoxy-substituted PPV oligomers we have measured so far ( $1.29 \text{ Mg m}^{-3}$ ). Being an isomer of the isopropoxy compound, comparison of the cell volumes and packing efficiency can be made directly; the cell volume of (I) is  $744.0 (4) \text{ \AA}^3$ , with a filled volume of 70.5%, while for the isopropoxy derivative, these values are  $776.8 (7) \text{ \AA}^3$  and 67.6%, respectively. This remarkably high packing efficiency may be a result of the flipping over of the central ring (B) with respect to the equilibrium (gas-phase) conformation. This results in the presence of the less stable [ap,ap] conformer in the crystal; apparently, the energy required to force the molecules into the energetically less favourable conformer is provided by the van der Waals contact stabilization. It is likely that the solid-state structure of the [sp,sp] conformer displays a large number of destabilizing interactions as a result of steric hindrance between the side chains of neighbouring molecules. As mentioned above, further research is necessary in order to investigate these issues to a greater extent. Unfortunately, the presence of the [ap,ap] conformer makes treating the density as a function of the number of  $\text{OCH}_3 \cdots \pi$  contacts impossible.

Finally, a TLS analysis (Schomaker & Trueblood, 1968) with the PLATON software (Spek, 2003) shows that the largest librational movement is along the long axis of the molecule, as is customary for this type of compound. The difference between the different directions is quite small for (I) ( $L1 = 4.28^\circ$ ) and lies along an axis making an angle of  $4.07^\circ$  with the long axis of the molecule;  $L2$  and  $L3$  are  $1.18$  and  $0.63^\circ$ , respectively.

In conclusion, (I) crystallizes in small clustered crystals, which display a hitherto unobserved packing based on  $\text{OCH}_3 \cdots \pi$  and  $\text{CH} \cdots \pi$  interactions. In effect, the compound is a spectacular demonstration of how the moving of one methyl group in a large molecule can make a remarkable difference in the crystal packing of compounds in which good crystal synthons are absent and the main interactions available for forming the crystal structure are weak.

## Experimental

Compound (I) was prepared by the Wittig reaction of 2,4,6-trimethoxybenzaldehyde with 2,5-dimethoxy-*p*-xylylenebis(triphenylphosphonium bromide), as described by Nowaczyk *et al.* (2005). Small crystal clusters were grown from hot ethanol solution and a single fragment was used for the diffraction experiment.

### Crystal data

$\text{C}_{34}\text{H}_{42}\text{O}_8$	$Z = 1$
$M_r = 578.68$	$D_x = 1.292 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.842 (3) \text{ \AA}$	Cell parameters from 25
$b = 8.026 (2) \text{ \AA}$	reflections
$c = 14.215 (3) \text{ \AA}$	$\theta = 4\text{--}12^\circ$
$\alpha = 73.99 (2)^\circ$	$\mu = 0.09 \text{ mm}^{-1}$
$\beta = 82.82 (3)^\circ$	$T = 293 (2) \text{ K}$
$\gamma = 86.17 (3)^\circ$	Block, yellow
$V = 744.0 (4) \text{ \AA}^3$	$0.1 \times 0.1 \times 0.1 \text{ mm}$

### Data collection

Enraf–Nonius MACH3	$\theta_{\text{max}} = 25.0^\circ$
diffractometer	$h = 0 \rightarrow 8$
$\omega/2\theta$ scans	$k = -9 \rightarrow 9$
2854 measured reflections	$l = -16 \rightarrow 16$
2613 independent reflections	3 standard reflections
1135 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{\text{int}} = 0.045$	intensity decay: 6%

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.1376P)^2]$
$wR(F^2) = 0.272$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2613 reflections	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
212 parameters	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$

**Table 1**

Experimental (XRD, X-ray diffraction) and calculated (DFT, density functional theory) CH–*n*(O) distances,  $r$  (Å), between the H atoms on the olefinic link and the O atoms of the methoxy groups, and angles,  $\alpha$  ( $^\circ$ ), between the olefinic C–H bond and the O atom of the nearest methoxy group for the [ap,ap] conformer of (I).

Method	C7–H7···O36		C8–H8···O32		C8–H8···O2	
	$r$	$\alpha$	$r$	$\alpha$	$r$	$\alpha$
XRD	2.169	121.17	2.198	102.55	2.030	126.30
DFT	2.166	118.78	2.224	104.41	2.260	121.88

Note: original values of  $r$  and  $\alpha$  were corrected by a normalization of the C–H bond lengths to  $1.083 \text{ \AA}$ .

The low number of observed data and the low precision on the bond distances are a result of the crystal being small and weakly diffracting. The H atoms were placed at calculated positions and constrained with the SHELXL97 (Sheldrick, 1997) commands AFIX 44 for aromatic and ethenyl H atoms, and AFIX 24 for methylene H atoms, which allow the H distances to refine, and AFIX 138 for methoxy groups, which allows the methyl group to rotate and the H distances to refine but which keeps the angles between the H atoms close to  $109.5^\circ$ . The filled volumes were calculated with PLATON (Spek, 2003).

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1999) and MERCURY (Bruno *et al.*, 2002); software used to prepare material for publication: WinGX (Farrugia, 1997) and PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1163). Services for accessing these data are described at the back of the journal.

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