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1,2,3-Trimethoxy-4-[(*E*)-2-phenylvinyl]benzene and (*E*,*E*)-1,4-bis(2,3,4-trimethoxyphenyl)buta-1,3-diene

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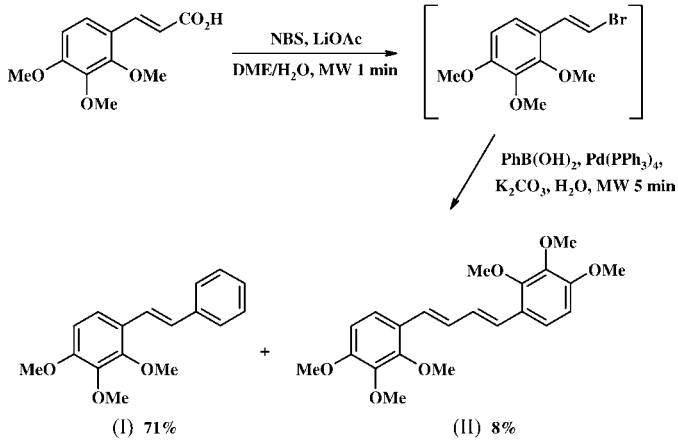
The stilbene derivative 1,2,3-trimethoxy-4-[(*E*)-2-phenylvinyl]-benzene, $C_{17}H_{18}O_3$, (I), and its homocoupling co-product (*E*,*E*)-1,4-bis(2,3,4-trimethoxyphenyl)buta-1,3-diene, $C_{22}H_{26}O_6$, (II), both have double bonds in *trans* conformations in their conjugated linkages. In the structure of stilbene (I), the aromatic rings deviate significantly from coplanarity, in contrast with coproduct (II), the core of which is rigorously planar. The deviation in stilbene (I) seems to be driven by intermolecular electrostatic interactions. Diene (II) sits on a crystallographic inversion centre, which bisects the conjugated linkage.

Comment

Stilbenes are important core structures and their photochemical (photooxygenation; Kwon *et al.*, 1989) and photophysical properties [photoisomerization (Waldeck, 1991), fluorescence (Chaudhuri & Ganguly, 1969; Singh & Kanvah, 2001) and photochromic activity (Irie *et al.*, 1994; Lucas *et al.*, 1998)] have been widely studied in connection with π–π^* electronic transitions of the C═C double bond. Stilbenes can exist as two possible isomers, *viz.* *trans*-stilbene and *cis*-stilbene. The *cis* series, for example, is involved in combretastatin derivatives, which display cytotoxic activities against a wide range of human cancers (Pettit *et al.*, 2005). Stilbenes are not only used as dyes and in optics (lasers), but are also of interest from a medical point of view (Heynekamp *et al.*, 2006; Sanoh *et al.*, 2006; Vander Jagt & Deck, 2007).

Other natural products derived from *trans*-stilbenes, such as resveratrol and its analogues, exhibit important biological activities. Indeed, *trans*-resveratrol is known to possess antioxidant and anti-inflammatory properties and is antiproliferative with pro-apoptotic effects (Baur & Sinclair, 2006).

We have previously reported a synthesis of *trans*-1,2-diarylethenes (*trans*-stilbenes), compounds having potential photoprotective properties. They were synthesized from *trans*-cinnamic acids using a strategy combining Hunsdiecker-type bromodecarboxylation and the Suzuki cross-coupling reaction under microwave heating (Bazin *et al.*, 2007). Bromodecarboxylation starting from 2,3,4-trimethoxycinnamic acid gave the corresponding β-bromostyrene intermediate, which allowed the Suzuki cross-coupling reaction with phenylboronic acid. The desired stilbene, (I), was obtained in 71% yield and we also observed 1,4-diarylbuta-1,3-diene (II) as an unexpected homocoupling by-product (8% yield).



The asymmetric unit of (I) (Fig. 1*a*) contains one molecule and that of (II) (Fig. 1*c*) contains one half-molecule, the remainder of (II) being generated by the symmetry centre situated at the mid-point of C8—C8^{i} in the conjugated linkage [symmetry code: (i) $-x$, $-y$, $-z$].

For both compounds, the double bonds in the conjugated linkage are in the *trans* configuration. Futhermore, the observed double bonds are longer and the single bonds shorter (Tables 1 and 2) than the theoretical values (1.32 Å for double bonds and 1.51 Å for single bonds; Glusker *et al.*, 1994), indicating the formation of a weak conjugated π-electron system.

In the structure of stilbene (I), the aromatic rings deviate significantly from a coplanar arrangement, with a dihedral angle of 16.92 (3)° between the planes. The origin of this deviation seems to be an intermolecular interaction occurring between neighbouring molecules rather than internal steric hindrance. A contact is observed between the benzene C11—H11 group and atom O3^{ii} of the methoxy group of a neighbouring molecule [symmetry code: (iii) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$], with H11···O3^{iii} = 2.473 (12) Å, C11···O3^{iii} = 2.4570 (8) Å and C11—H11···O3^{iii} = 173.6 (9)°. Among the three methoxy substituents of each aromatic ring, only that at C4 is approximately coplanar with the attached ring; the other two, at C5 and C6, are oriented towards opposite sides of the attached ring (Fig. 1*b*).

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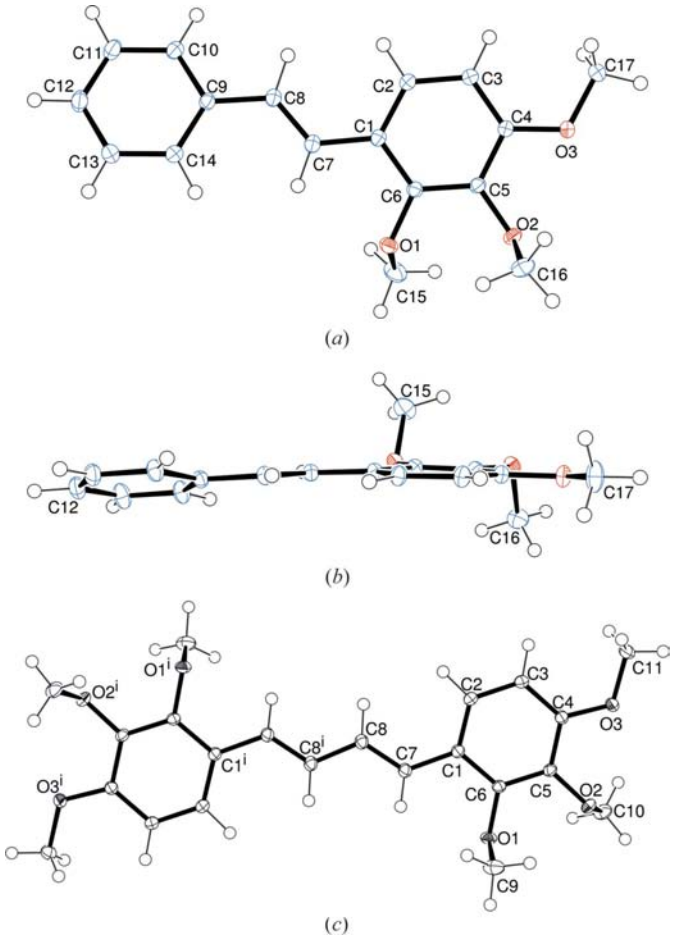

Figure 1
(*a*), (*b*) Mutually perpendicular views of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii. (*c*) The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x, -y, -z$.]

The core of the structure of co-product (II) is rigorously planar, as the two halves are related by a symmetry centre. As in compound (I), only one of the three methoxy substituents is approximately coplanar with the aromatic ring. The other two are again out of the plane on opposite sides.

In stilbene (I) there are two nearly edge-on (or T-shaped) stacking contacts (Fig. 2), one involving each of the two aromatic rings. Atom H14 of the unsubstituted phenyl ring is oriented toward the centroid $Cg1^{ii}$ of its neighbour [$Cg1$ is the centroid of the C9–C14 ring; symmetry code: (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$], with H14$\cdots Cg1^{ii}$ = 2.765 (11) Å and C14—H14$\cdots Cg1^{ii}$ = 136.2 (9)°. The second contact, between atom H8 of the double-bonded fragment and the substituted aromatic ring of a neighbour, is weak but appears to be directed; H8$\cdots Cg2^{iv}$ = 3.23 (13) Å and C8—H8$\cdots Cg2^{iv}$ = 166.7 (10)° [$Cg2$ is the centroid of the C1–C6 ring; symmetry code: (iv) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. As we have already described, a weak electrostatic H11$\cdots$O3^{iii} interaction is also present.

In the extended structure of co-product (II), only one significant contact was found, which consists of a T-shaped

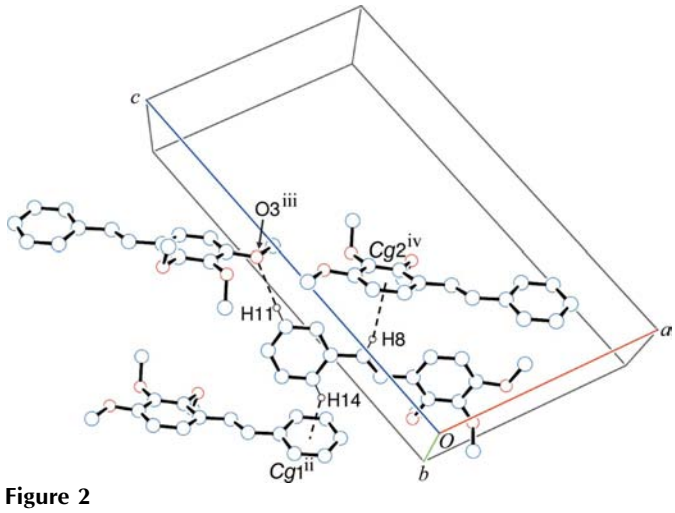

Figure 2
A view of the stacking interactions (dashed lines) in stilbene (I). $Cg1$ and $Cg2$ are the centroids of the C9–C14 and C1–C6 rings, respectively. [Symmetry codes: (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.]

stacking interaction between the aromatic rings. C2—H2 contacts the centroid $Cg1^{iv}$ of a neighbouring ring [$Cg1$ is the centroid of the C1–C6 ring; symmetry code: (iv) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$], with H2$\cdots Cg1^{iv}$ = 2.837 (15) Å and C2—H2$\cdots Cg1^{iv}$ = 154.6 (11)°.

Experimental

Compounds (I) and (II) were prepared according to the literature procedure of Bazin *et al.* (2007). Compound (II) was isolated as the homocoupling by-product. Compound (I) was recrystallized from methanol to afford pure (I) as colourless crystals (m.p. 355 K). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.89 (*s*, 3H, –OMe), 3.90 (*s*, 3H, –OMe), 3.91 (*s*, 3H, –OMe), 6.71 (*d*, 1H, J = 8.8 Hz), 7.03 (*d*, 1H, J = 16.6 Hz), 7.24–7.37 (*m*, 5H), 7.51–7.53 (*m*, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 56.0 (–OMe), 60.9 (–OMe), 61.3 (–OMe), 107.8, 120.7, 122.9, 124.5, 126.4 (2C), 127.2, 127.9, 128.6 (2C), 137.9, 142.4, 151.7, 153.2; MS (ESI): $[M + H]^+$ 271. Compound (II) was recrystallized by slow evaporation of a cyclohexane–ethyl acetate mixture (9:1 *v*/*v*), giving colourless crystals of (II) after 1 or 2 d. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.87, 3.88 and 3.89 (3 *s*, 18H, 6 × –OMe), 6.41–6.54 (*m*, 2H), 6.63–6.70 (*m*, 2H), 6.87–6.90 (*m*, 1H), 7.12–7.23 (*m*, 3H); MS (ESI): $[M + H]^+$ 387.

Compound (I)

Crystal data

$C_{17}H_{18}O_3$
M_r = 270.31
Monoclinic, $P2_1/n$
a = 10.7138 (7) Å
b = 7.1069 (5) Å
c = 19.8033 (13) Å
β = 104.760 (3)°
V = 1458.10 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 296 K
0.52 × 0.37 × 0.25 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
66478 measured reflections
6392 independent reflections
5406 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Table 1
Selected bond lengths (Å) for (I).

C1—C7	1.4667 (8)	C8—C9	1.4673 (8)
C7—C8	1.3445 (8)		

Table 2
Selected bond lengths (Å) for (II).

C1—C7	1.4614 (10)	C8—C8^{i}	1.4441 (14)
C7—C8	1.3511 (11)		

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	253 parameters
$wR(F^2) = 0.122$	All H-atom parameters refined
$S = 1.07$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
6392 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Compound (II)

Crystal data

$C_{22}H_{26}O_6$	$V = 987.76$ (7) Å^3
$M_r = 386.43$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.2899$ (4) Å	$\mu = 0.09$ mm^{-1}
$b = 7.0186$ (3) Å	$T = 296$ K
$c = 13.9897$ (5) Å	0.32 × 0.21 × 0.18 mm
$\beta = 102.138$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	4333 independent reflections
	3409 reflections with $I > 2\sigma(I)$
30080 measured reflections	$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	179 parameters
$wR(F^2) = 0.136$	All H-atom parameters refined
$S = 1.07$	$\Delta\rho_{max} = 0.68$ e Å^{-3}
4333 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}

All H atoms were determined *via* difference Fourier maps and refined with isotropic atomic displacement parameters [C—H = 0.956 (13)–1.028 (17) Å].

For both compounds, data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3186). Services for accessing these data are described at the back of the journal.

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