

**(Z)- $\alpha$ -Chloromethyl-3,3',4,4'-tetramethoxystilbene**

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**Key indicators**

Single-crystal X-ray study  
 $T = 173\text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.038  
 $wR$  factor = 0.113  
 Data-to-parameter ratio = 23.8

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

The title compound,  $\text{C}_{19}\text{H}_{21}\text{ClO}_4$ , adopts a non-planar conformation. The angle between the aromatic ring planes is  $75.74(6)^\circ$ . The angle between the plane of the aromatic ring attached to the C atom carrying the chloromethyl substituent and the plane defined by the ethylene group and the atoms attached to it is  $40.60(6)^\circ$ . The angle between this latter plane and the plane of the second aromatic ring is  $35.29(6)^\circ$ . The arrangement of the molecules in the crystal lattice can be attributed to weak  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonding. Stereoisomers of methyl 2,3-bis(4-acetoxy-3-methoxyphenyl)-2-propenesulfonate are assigned, based on  $^1\text{H}$  NMR spectral comparisons with the title compound and the isomeric *E* form.

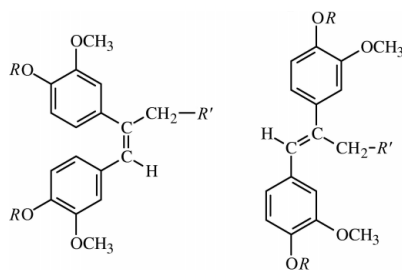
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**Comment**

Stereoisomers of  $\alpha$ -chloromethyl-3,3',4,4'-tetramethoxystilbene, (I), are present in reaction mixtures obtained on refluxing the lignin model 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol with 0.2 *M* hydrogen chloride in dioxane–water 9:1 (Li *et al.*, 1997). The identification of the compounds was based on comparisons with synthetic samples (Li *et al.*, 1997). The applied synthetic method gave a mixture of stereoisomers from which the *Z* isomer, (Ib), could be isolated in crystalline form (Li *et al.*, 1997). The crystalline form of the *E* isomer, (Ia), has been described earlier (Russel & Hunziker, 1969). To verify the assignments of the *E*, (Ia), and *Z*, (Ib), isomers of (I), we have determined the crystal structure of (Ib).



(Ia)  $R = \text{CH}_3$ ,  $R' = \text{Cl}$

(Ib)  $R = \text{CH}_3$ ,  $R' = \text{Cl}$

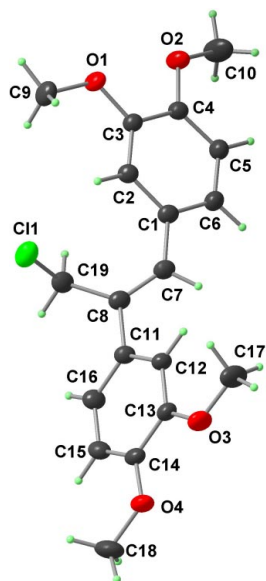
(IIa)  $R = \text{CH}_3$ ,  $R' = \text{OCOCH}_3$

(IIb)  $R = \text{CH}_3$ ,  $R' = \text{OCOCH}_3$

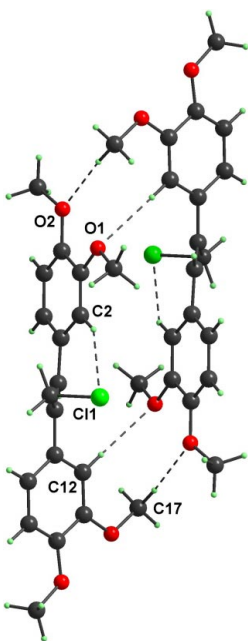
(IIIa)  $R = \text{CH}_3\text{CO}$ ,  $R' = \text{SO}_3\text{CH}_3$

(IIIb)  $R = \text{CH}_3\text{CO}$ ,  $R' = \text{SO}_3\text{CH}_3$

A perspective drawing of (Ib) and the atom-numbering scheme is shown in Fig. 1. In the crystal structure, (Ib) adopts a non-planar conformation. The torsion angles  $\text{C}2-\text{C}1-\text{C}7-\text{C}8$  and  $\text{C}7-\text{C}8-\text{C}11-\text{C}12$  are  $32.84(16)$  and  $41.63(14)^\circ$ , respectively. The angle between the aromatic ring planes is  $75.74(6)^\circ$ . The ethylene group and the atoms attached to it (C1, C11 and C19) are nearly coplanar [maximum deviation



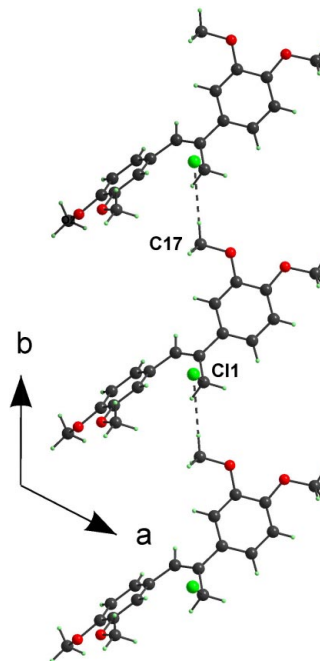
**Figure 1**  
A perspective drawing of (*Ib*), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.



**Figure 2**  
A centrosymmetric dimer of (*Ib*) formed by weak hydrogen bonds, which are shown as dashed lines.

0.028 (1) Å]. The angles between this latter least-squares plane and the aromatic ring planes C1–C6 and C11–C16 are 35.29 (6) and 40.60 (6)°, respectively. The conformations of the  $\alpha$ -substituted stilbenes (*Z*)-2,3-bis(3,4-dimethoxyphenyl)-2-propen-1-ol (Stomberg *et al.*, 1995) and methyl (*E*)-*p*-[2-(2,3-dihydro-3,3-dimethyl-5-benzofuranyl)-1-propenyl]benzoate (Gale *et al.*, 1990) exhibit similarities to that of (*Ib*). Stilbenes with *trans*-orientated aryl groups lacking an  $\alpha$ -substituent, such as (*E*)-4,4'-dimethoxystilbene (Theocharis *et al.*, 1984), are planar or nearly planar.

There are weak C–H···O and C–H···Cl hydrogen bonds present in the crystal structure of (*Ib*) (Table 1). Two types of



**Figure 3**  
A chain of (*Ib*) molecules, related by unit-cell translations in the *b* direction, connected by weak hydrogen bonds, which are shown as dashed lines.

C–H···O hydrogen bonding lead to the formation of dimers of molecules related by an inversion center (Fig. 2). On the first-level graph-set, following Bernstein *et al.* (1995) and Grell *et al.* (1999), the hydrogen bond C12–H12···O1<sup>i</sup> [symmetry code: (i) 1 – *x*, 1 – *y*, –*z*] forms an  $R_2^2(18)$  ring, and the hydrogen bond C17–H17C···O2<sup>i</sup> forms an  $R_2^2(26)$  ring. The intramolecular hydrogen bond C2–H2···Cl1 forms an  $S(7)$  string, while the intermolecular hydrogen bond C17–H17B···Cl1<sup>ii</sup> [symmetry code: (ii) *x*, 1 + *y*, *z*] forms a  $C(9)$  chain, connecting the molecules in the *b* direction (Fig. 3). On the second-level graph-set, rings  $R_2^2(10)$ ,  $R_2^2(22)$ ,  $R_4^4(24)$ ,  $R_4^4(28)$ ,  $R_4^4(36)$  and  $R_4^4(44)$  were recognized. The assignment of graph-set descriptors was performed using *PLUTO*, as described by Motherwell *et al.* (1999).

The methylene group signal is located at  $\delta$  4.44 in the <sup>1</sup>H NMR spectrum of the *E* isomer, (*Ia*), and at  $\delta$  4.65 in the <sup>1</sup>H NMR spectrum of the *Z* isomer, (*Ib*) (Li *et al.*, 1997). The methylene group signal of the *E* isomer, (*IIa*) ( $\delta$  4.89), is also located at higher field than that of the *Z* isomer, (*IIb*) ( $\delta$  5.16) (Li *et al.*, 1997). Stereoisomers of (*III*) have been described by Gellerstedt *et al.* (1976) but steric assignments were not reported. Based on <sup>1</sup>H NMR spectral comparisons with (*I*) and (*II*) it is possible to conclude that the isomer denoted '1. Form' by Gellerstedt *et al.* (1976) is (*IIIb*) (the methylene group signal is located at  $\delta$  4.46) and that the isomer denoted '2. Form' by these authors is (*IIIa*) (the methylene group signal is located at  $\delta$  4.16).

## Experimental

(*Z*)- $\alpha$ -Chloromethyl-3,3',4,4'-tetramethoxystilbene, (*Ib*), was prepared according to the method of Li *et al.* (1997).

## Crystal data

$C_{19}H_{21}ClO_4$   
 $M_r = 348.81$   
 Triclinic,  $P\bar{1}$   
 $a = 9.2561$  (1) Å  
 $b = 10.0669$  (2) Å  
 $c = 11.5351$  (2) Å  
 $\alpha = 104.620$  (1)°  
 $\beta = 108.441$  (1)°  
 $\gamma = 109.692$  (1)°  
 $V = 879.06$  (3) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.318$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5499 reflections  
 $\theta = 2.4$ – $31.5$ °  
 $\mu = 0.24$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Prism, colourless  
 $0.52 \times 0.40 \times 0.18$  mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
 $T_{\min} = 0.887$ ,  $T_{\max} = 0.959$   
 14932 measured reflections

5768 independent reflections  
 4859 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 31.5$ °  
 $h = -13 \rightarrow 13$   
 $k = -14 \rightarrow 14$   
 $l = -16 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.113$   
 $S = 1.02$   
 5768 reflections  
 242 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.1791P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.43$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots C1$	0.95	2.73	3.5800 (10)	150
$C12-H12 \cdots O1^i$	0.95	2.57	3.5130 (13)	170
$C17-H17B \cdots CH^{ii}$	0.98	2.82	3.7947 (12)	173
$C17-H17C \cdots O2^i$	0.98	2.59	3.5640 (16)	174

Symmetry codes: (i)  $1 - x, 1 - y, -z$ ; (ii)  $x, 1 + y, z$ .

H atoms were constrained to the ideal geometry using an appropriate riding model. For methyl groups, the C–H distances (0.98 Å) and C–C–H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine, with the starting position based on the threefold averaged circular Fourier synthesis.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT and SADABS (Sheldrick, 2002); program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2000); software used to prepare material for publication: SHELXTL.

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