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Key indicators

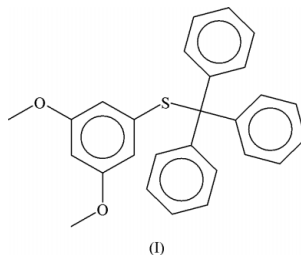
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.039
 wR factor = 0.113
Data-to-parameter ratio = 14.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,3-Dimethoxy-5-(triphenylmethylthio)-
benzene

The title compound, $\text{C}_{27}\text{H}_{24}\text{O}_2\text{S}$, crystallizes in space group $P\bar{1}$ with one molecule in the asymmetric unit. The geometry and intermolecular contacts are described: the rings in the triphenylmethyl moiety show a near-threefold symmetry, and the compound displays $\text{OCH}_3-\pi$ interactions in the methoxy-substituted ring and herringbone interactions between the unsubstituted rings.

Received 28 August 2003
Accepted 8 September 2003
Online 24 September 2003

Comment

The title compound, (I) (Fig. 1), was synthesized as a precursor material for a sulfur-substituted PPV oligomer, which is a possible candidate for a break-junction experiment (Weber *et al.*, 2001). In the course of purification, it crystallized exceedingly easily, which prompted us to perform an X-ray structure determination to verify the identity of the product. The intramolecular distances and angles contain no surprises. The phenyl rings in the triphenylmethyl moiety (TPM) show nearly threefold symmetry, the angles between the planes of the rings being $77.62(9)^\circ$ ($B-C$), $72.60(9)^\circ$ ($B-D$) and $70.77(10)^\circ$ ($C-D$). The packing consists of columns of methoxy-substituted rings, surrounded by areas dominated by TPM groups. There are a number of intermolecular contacts shorter than the sum of the van der Waals radii. The methoxy-substituted rings are loosely connected by weak $\text{OCH}_3-\text{Cg}(A)$ interactions (see Table 1). Another methoxy group, which is directed outside the stack, contacts C24 in ring D of the next molecule in the same stack [$\text{C}24 \cdots \text{C}27^{\text{iv}}$ 3.384 (4) Å, symmetry code: (iv) $-x, 1 - y, -z$]. Two of the phenyl rings in the TPM moiety show herringbone interactions with each other (see Table 1). A close contact also exists between H24 and O5 [$\text{O}5 \cdots \text{H}24^{\text{v}}$ 2.66 (3) Å, symmetry code: (v) $x, 1 + y, z$].



Experimental

3,5-Dimethoxythiophenol (II) was prepared as described by Wolfers *et al.* (1979). $\delta^1\text{H}$ (in p.p.m., relative to TMS, in CDCl_3): 6.42 (d , $J = 2.13\text{ Hz}$, 2H, H2 and H6); 6.25 (t , $J = 2.13\text{ Hz}$, 1H, H4); 3.75 (s , 6H, OCH_3); 3.46 (s , 1H, SH) $\delta^{13}\text{C}$ (in p.p.m., relative to TMS, in CDCl_3): 161.06 (C3), 132.59 (C1), 107.45 (C2), 98.38 (C4), 55.36 (OCH_3). 1,3-Dimethoxy-5-(triphenylmethylthio)benzene (I) was synthesized as follows: 3.5 g (0.0206 mol) of crude (II) was dissolved in 4 ml of

CH_2Cl_2 and carefully added to 36 g (0.0206 mol) of triphenylmethanol dissolved in 36 ml of trifluoroacetic acid (TFA). The orange–black solution was stirred for 1 h at room temperature, then the TFA was distilled off under vacuum. The brown dry residue was carefully neutralized with conc. aqueous sodium bicarbonate and stirred for 1 h, giving rise to a bright orange precipitate. This was extracted three times with chloroform and dried over MgSO_4 . The solvent was evaporated, and the residue recrystallized from methanol/ CH_2Cl_2 ; yield 5.3 g (60%). Crystals suitable for X-ray diffraction were grown by recrystallization from hot methanol. $\delta^1\text{H}$ (in p.p.m., relative to TMS, in CDCl_3): 7.40 (*m*, 6H, aromatic *m*-H); 7.22 (*m*, 9H, aromatic *o*- and *p*-H); 6.22 (*t*, $J = 2.29$ Hz, 1H, H4); 6.15 (*d*, $J = 2.29$ Hz, 2H, H2–H6) 3.48 (*s*, 6H, OCH_3).

Crystal data

$\text{C}_{27}\text{H}_{24}\text{O}_2\text{S}$	$Z = 2$
$M_r = 412.52$	$D_x = 1.286 \text{ Mg m}^{-3}$
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 8.8390$ (12) Å	Cell parameters from 25 reflections
$b = 10.157$ (4) Å	$\theta = 7.7\text{--}19.8^\circ$
$c = 12.672$ (2) Å	$\mu = 0.17 \text{ mm}^{-1}$
$\alpha = 79.37$ (2)°	$T = 293$ (2) K
$\beta = 72.31$ (2)°	Block, colourless
$\gamma = 87.93$ (2)°	$0.40 \times 0.23 \times 0.20 \text{ mm}$
$V = 1065.0$ (5) Å ³	

Data collection

Enraf–Nonius Mach3 diffractometer	$\theta_{\text{max}} = 27.0^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 11$
Absorption correction: none	$k = -12 \rightarrow 12$
4949 measured reflections	$l = -15 \rightarrow 16$
4635 independent reflections	3 standard reflections
3417 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{\text{int}} = 0.018$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.227P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
4635 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
329 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Intermolecular C–H $\cdots\pi$ interactions (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{C13--H13}\cdots\text{Cg}(\text{C}^i)$	0.96 (2)	3.913 (3)	3.09 (2)	144.5 (14)
$\text{C17--H17}\cdots\text{Cg}(\text{B}^{ii})$	0.94 (2)	3.585 (3)	2.78 (3)	143.1 (17)
$\text{C26--H26A}\cdots\text{Cg}(\text{A}^{iii})$	0.99 (2)	3.720 (3)	2.797 (15)	157

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-1, y, z$; (iii) $1-x, 1-y, -z$. Cg is the centre of gravity of ring A.

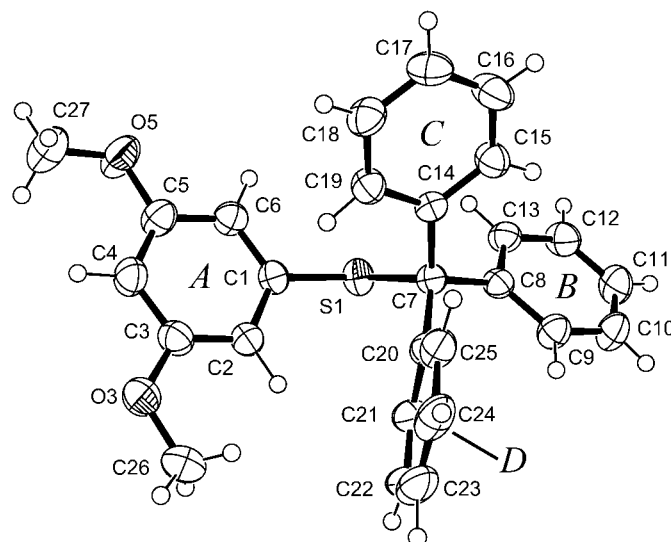


Figure 1 Molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The H atoms on the methoxy groups were constrained, allowing the methyl group to rotate and the distances to refine, but keeping the angles between the H atoms close to 109.5° . All other H atoms were allowed to refine freely.

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: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

CVV thanks the Fund for Scientific Research (FWO Vlaanderen) for a grant as a research assistant. The authors also thank Professor R. Domisse and J. Aerts for recording the NMR spectra.

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