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Bis(3,4-dimethoxybenzyl) Ether and Tetramethoxy-4,4'-(2,3-dimethyltetramethylene)dipyrrocatechol†

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Abstract

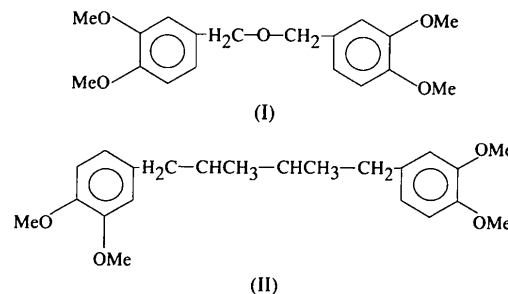
In molecules of both bis(3,4-dimethoxybenzyl) ether, C₁₈H₂₂O₅, (I), and *meso*-tetramethoxy-4,4'-(2,3-dimethyltetramethylene)dipyrrocatechol, C₂₂H₃₀O₄, (II), the methoxy groups are almost coplanar with the attached benzene rings. In (I), the two benzene rings make a dihedral angle of 17.20(5)°, whereas in (II), they are almost perpendicular [94.8(4)°] to one another. The crystal structure is stabilized by van der Waals interactions in both compounds.

† Alternative name: 1,1',2,2'-tetramethoxy-4,4'-(2,3-dimethyltetramethylene)dibenzene.

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Comment

The structure determinations of the title compounds, (I) and (II), represent part of an investigation of a series of methoxybenzenes.



The mean C_{sp²}—O [1.366(2) Å] and C_{sp³}—O [1.423(3) Å] bond distances in the methoxy groups agree with values observed in other methoxybenzene derivatives (Fun, Chinnakali, Sivakumar, Sam & How, 1997; Bryan & White, 1982). The methoxy groups are almost coplanar with the attached benzene rings but significant displacements from their adjacent phenyl rings are observed for C15 (0.120 Å) and C18 (0.239 Å) in (I),

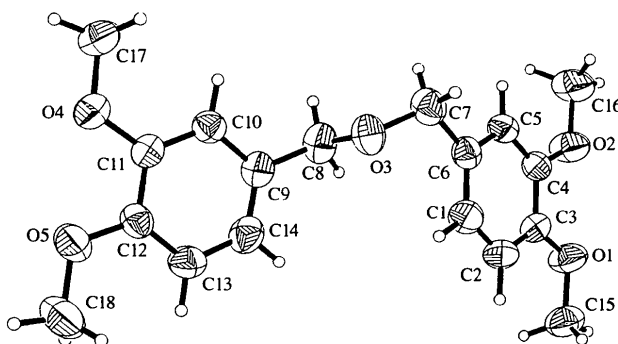


Fig. 1. View of (I) showing the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

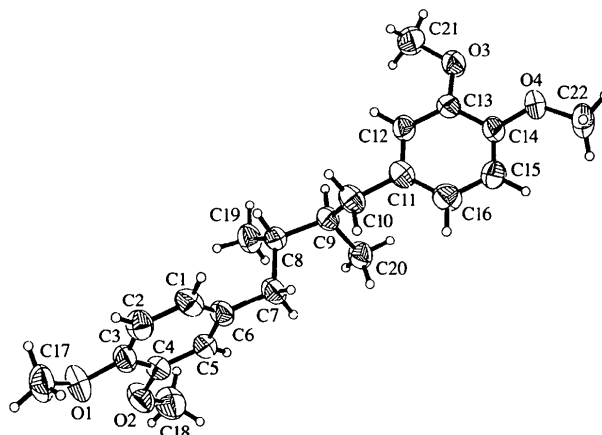


Fig. 2. View of (II) showing the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

and for C17 (0.266 Å) and C22 (0.269 Å) in (II). The dihedral angle between the two benzene ring planes in (I) is 17.20(5)° and these planes are almost normal to that formed by atoms C7, C8 and O3 [dihedral angles 86.89(1) and 87.28(8)°]. The two benzene rings in (II) are almost perpendicular [94.8(4)°] to one another.

The shortest intermolecular contacts observed are C2...O3($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) of 3.368(2) Å and C18...O4($x, y, z - 1$) of 3.395(2) Å in compounds (I) and (II), respectively.

Experimental

Compounds (I) and (II) were prepared from their hydroxy precursors by methylation with dimethyl sulfate in the presence of anhydrous potassium carbonate, using dry acetone as solvent. Single crystals were obtained by slow evaporation from ethyl acetate solutions.

Compound (I)

Crystal data

C ₁₈ H ₂₂ O ₅	Mo K α radiation
$M_r = 318.36$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 52 reflections
$P2_1/n$	$\theta = 2.77\text{--}12.34^\circ$
$a = 10.399(1)$ Å	$\mu = 0.090\text{ mm}^{-1}$
$b = 5.806(1)$ Å	$T = 293(2)$ K
$c = 28.126(2)$ Å	Rectangular
$\beta = 93.02(1)^\circ$	$0.68 \times 0.62 \times 0.26$ mm
$V = 1695.8(2)$ Å ³	Colourless
$Z = 4$	
$D_x = 1.247\text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens P4 diffractometer	$\theta_{\max} = 27.50^\circ$
$\theta/2\theta$ scans	$h = -1 \rightarrow 13$
Absorption correction: none	$k = -1 \rightarrow 7$
5423 measured reflections	$l = -36 \rightarrow 36$
3911 independent reflections	3 standard reflections
2158 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.034$	intensity decay: <3%

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 0.14\text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$\Delta\rho_{\min} = -0.12\text{ e \AA}^{-3}$
$wR(F^2) = 0.110$	Extinction correction:
$S = 0.865$	SHELXL93 (Sheldrick, 1993)
3911 reflections	Extinction coefficient:
297 parameters	0.0216(15)
All H atoms refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)
$(\Delta/\sigma)_{\max} < 0.001$	

Table 1. Selected geometric parameters (Å, °) for (I)

O1—C3	1.362(2)	O4—C11	1.368(2)
O1—C15	1.424(2)	O4—C17	1.421(2)
O2—C4	1.366(2)	O5—C12	1.363(2)

O2—C16	1.422(2)	O5—C18	1.431(2)
O3—C8	1.424(2)	C6—C7	1.509(2)
O3—C7	1.425(2)	C8—C9	1.496(2)
C8—O3—C7	112.47(12)	O3—C7—C6	114.00(14)
O1—C3—C2	125.23(14)	O3—C8—C9	108.15(12)
O2—C4—C5	124.65(14)	O4—C11—C10	125.31(14)
O2—C4—C3	115.38(13)	O5—C12—C13	124.84(14)
C8—O3—C7—C6	−73.3(2)	C7—O3—C8—C9	−177.41(14)
C5—C6—C7—O3	153.05(14)	O3—C8—C9—C10	85.1(2)

Compound (II)

Crystal data

C ₂₂ H ₃₀ O ₄	Mo K α radiation
$M_r = 358.46$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 38 reflections
$P\bar{1}$	$\theta = 5.33\text{--}12.54^\circ$
$a = 6.274(1)$ Å	$\mu = 0.080\text{ mm}^{-1}$
$b = 10.571(1)$ Å	$T = 293(2)$ K
$c = 15.426(1)$ Å	Rectangular
$\alpha = 86.49(1)^\circ$	$0.80 \times 0.70 \times 0.26$ mm
$\beta = 80.78(1)^\circ$	Colourless
$\gamma = 87.72(1)^\circ$	
$V = 1007.5(2)$ Å ³	
$Z = 2$	
$D_x = 1.182\text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens P4 diffractometer	$\theta_{\max} = 27.50^\circ$
$\theta/2\theta$ scans	$h = -1 \rightarrow 8$
Absorption correction: none	$k = -13 \rightarrow 13$
5828 measured reflections	$l = -20 \rightarrow 20$
4591 independent reflections	3 standard reflections
2912 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.019$	intensity decay: <3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{\max} = 0.13\text{ e \AA}^{-3}$
$wR(F^2) = 0.126$	$\Delta\rho_{\min} = -0.22\text{ e \AA}^{-3}$
$S = 0.949$	Extinction correction: none
4591 reflections	Scattering factors from
355 parameters	International Tables for
All H atoms refined	Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 2. Selected geometric parameters (Å, °) for (II)

O1—C3	1.369(2)	C6—C7	1.511(2)
O1—C17	1.413(2)	C7—C8	1.538(2)
O2—C4	1.367(2)	C8—C19	1.515(2)
O2—C18	1.428(2)	C8—C9	1.545(2)
O3—C13	1.366(2)	C9—C20	1.520(2)
O3—C21	1.421(2)	C9—C10	1.534(2)
O4—C14	1.368(2)	C10—C11	1.512(2)
O4—C22	1.424(2)		
O1—C3—C2	125.20(14)	C20—C9—C10	111.12(12)
O2—C4—C5	124.68(14)	C20—C9—C8	113.26(11)
C6—C7—C8	114.79(12)	C11—C10—C9	112.97(11)
C19—C8—C7	111.72(12)	C16—C11—C12	118.05(12)
C19—C8—C9	111.15(12)	O3—C13—C12	125.34(12)
C7—C8—C9	112.18(11)	O4—C14—C15	125.22(12)
C5—C6—C7—C8	97.2(2)	C8—C9—C10—C11	−173.98(12)
C6—C7—C8—C9	−179.90(13)	C9—C10—C11—C16	−109.1(2)
C7—C8—C9—C10	−74.5(2)		

The structures were solved by direct methods and refined by full-matrix least-squares techniques. The H atoms were located from difference Fourier maps and refined isotropically.

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Geometrical calculations: *PARST* (Nardelli, 1983).

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Substituted Methoxybenzene Derivatives:

C₈H₉NO₄, C₉H₁₁NO₅ and C₁₃H₁₈O₄

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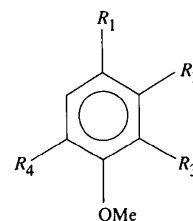
Abstract

The structures of three methoxybenzenes, namely 1,2-dimethoxy-4-nitrobenzene, C₈H₉NO₄, (I), 1,2,3-trimethoxy-5-nitrobenzene, C₉H₁₁NO₅, (II), and 1-(2,4,5-

trimethoxyphenyl)-1-butanone, C₁₃H₁₈O₄, (III), are reported. Molecules of (I) and (III) are planar, but one of the three methoxy groups of (II) is twisted out of the phenyl ring plane as a result of steric hindrance. In all three solids, the molecules are linked to form centrosymmetrically hydrogen-bonded dimers; they are packed in parallel layers in (I) and (II), but in zigzag layers in (III).

Comment

This paper reports an investigation of a series of methoxybenzenes, (I), (II) and (III), which was carried out since such moieties often occur in natural products.



	R ₁	R ₂	R ₃	R ₄
(I)	NO ₂	H	OMe	H
(II)	NO ₂	H	OMe	OMe
(III)	Butanone	OMe	H	OMe

The mean lengths of the C_{sp²}—O [1.361 (3) Å] and O—CH₃ [1.425 (3) Å] bonds in the methoxy groups of these compounds agree with values observed for related structures (Bryan & White, 1982). Molecules of (I) and (III) are essentially planar; the steric interactions of the methoxy groups in (II) cause C8 to deviate by 1.173 (2) Å from the mean plane formed by the remaining non-H atoms.

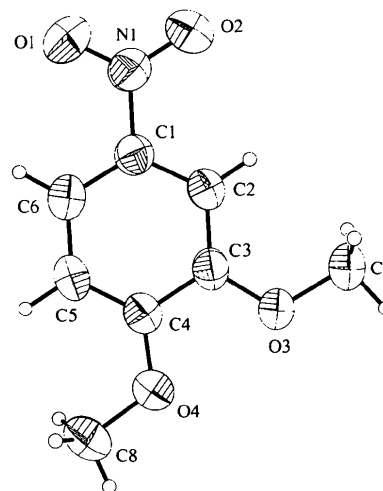


Fig. 1. View of (I) showing the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.