

Stereochemistry of 1-Arylpropane-1,2-diol 2-Aryl Ethers. X-Ray Structures of the Diastereomers of 1-(4-Acetoxy-3,5-dimethoxyphenyl)-2-{2,6-dimethoxy-4-[(*E*)-propenyl]phenoxy}propyl Acetate

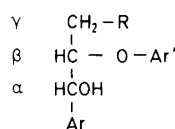
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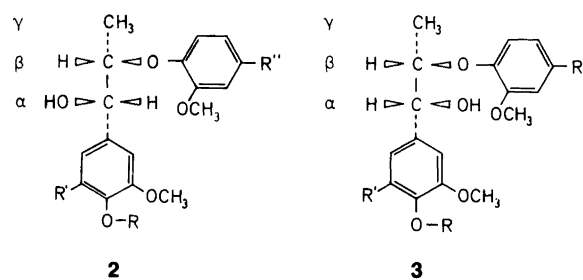
Certain types of 1-arylpropane-1,2-diol 2-aryl ether are often used as lignin model compounds. Some representatives of these types of compound occur in plants (in optically active form); in this context they are classified as neolignans. The crystal structures of the diacetates of two 1-arylpropane-1,2-diol 2-aryl ethers, namely the *threo* (**4a**) and *erythro* (**5a**) forms of 2-{2,6-dimethoxy-4-[(*E*)-propenyl]phenoxy}-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol, have been determined from single-crystal X-ray diffraction data. The structures were solved by direct methods and electron density calculations. The diacetate of **4a** crystallizes in the monoclinic space group $P2_1/a$ with $a = 8.446(4)$, $b = 32.903(3)$, $c = 9.671(2)$ Å, $\beta = 106.44(2)^\circ$ and $Z = 4$. Full-matrix least-squares refinement of 444 structural parameters gave $R = 0.046$ for 2042 observed [$I > 3\sigma(I)$] reflections. The diacetate of **5a** is monoclinic, space group $P2_1/c$, with $a = 11.713(3)$, $b = 12.548(3)$, $c = 17.713(3)$ Å, $\beta = 90.59(2)^\circ$ and $Z = 4$. Full-matrix least-squares refinement of 444 structural parameters gave $R = 0.038$ for 1753 observed [$I > 3\sigma(I)$] reflections. The present work confirms earlier deductions about the structures of **4a** and **5a**. The conformations of the diacetates of **4a** and **5a** are discussed on the basis of crystal structures. An attempt is made to correlate results from conformational considerations with coupling constants and signal positions in the ¹H NMR spectra.

1-Arylglycerol 2-aryl ethers (**1a**) are representative of the most important structures in lignins, in which the arylpropane units are β -O-4 linked. Recent ¹H NMR studies have shown that 30–40 % of the units in a softwood lignin (spruce) and 40–50 % in a hardwood lignin (birch) are joined to adjacent units by these linkages.¹ These estimates are higher if contributions from the arylglycerol β -ether structures derivatized at C- α and C- γ are taken into account.²



1 a; R = OH
b; R = H

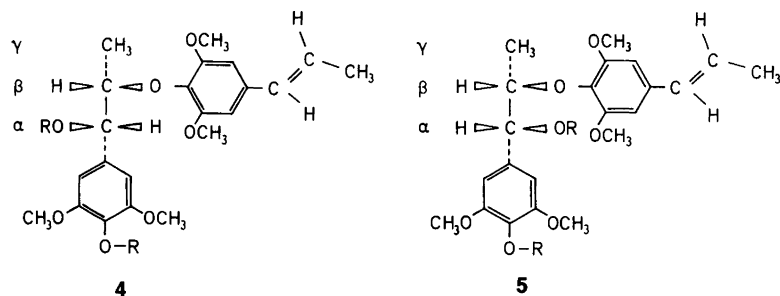
The 1-arylpropane-1,2-diol 2-aryl ethers (**1b**) have often been used as models for studying lignin reactions,^{3–5} because they are easier to prepare and have simpler structures than the γ -oxygenated ethers **1a**. A small family of optically active compounds which occur naturally in plants is also based on the 2-aryl ether skeleton **1b**,⁶ and is classified as



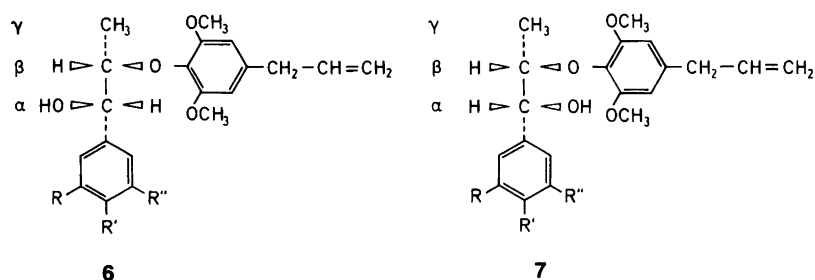
a; R = H, R' = H, R'' = H
b; R = CH₃, R' = H, R'' = H
c; R = H, R' = H, R'' = (*E*)-propenyl
d; R = CH₃, R' = H, R'' = (*E*)-propenyl
e; R = CH₃, R' = OCH₃, R'' = (*E*)-propenyl

neolignans. In addition, the ethers **1b** have been obtained in synthetic studies relating to lignin^{7,8} and neolignans.⁹

Structure **1b** exists in two diastereomeric forms, the *threo* (**2**, **4**, **6**) and the *erythro* (**3**, **5**, **7**) isomers. Described lignin model compounds and neolignans having the structure **1b** have either guaiacyl (**2**, **3**) or syringyl (**4a**, **5a**, **6**, **7**) groups as the β -ether moieties except for a recently isolated neolignan¹⁰ (**5a**, OCH₃ groups replaced by hydrogen atoms).



a; R = H
b; R = CH₃CO



a; R = OCH₃, R' = OH, R'' = H
b; R, R' = OCH₂O, R'' = H
c; R = R' = OCH₃, R'' = OH
d; R, R' = OCH₂O, R'' = OCH₃
e; R = R' = R'' = OCH₃

Assignment of configuration to β -guaiacyl ether isomers **2b** and **3b** followed from their conversion from γ -oxygenated structures determined by paper electrophoresis,³ and was confirmed by crystal-structure analysis.¹¹ Structures **2c** and **3c** were assigned⁷ on the basis of the preponderance of *erythro* products after tetrahydridoborate reduction of α -oxo derivatives.⁴ However, the stereochemical course of the tetrahydridoborate reduction is influenced by a number of factors,¹² which suggests that structural assignments made on that basis should be treated with caution. A structural assignment of the *erythro* isomer **3a** has followed from a recent crystal-structure study.¹³

For the structures **4a** and **5a**, as the tetrahydridoborate reduction of the corresponding α -oxo derivative gave a mixture of isomers, structural assignment was made from the ¹H NMR spectra.⁸ In particular, the chemical shift of the benzylic proton at C- α occurs at lower field for the *threo* isomer (**4a**) than the *erythro* isomer (**5a**), and the coupling constant, $J_{\alpha,\beta}$, is 8.4 Hz for the *threo* and 2.6 Hz for the *erythro* isomer. Zanarotti⁹ prepared a number of analogues of **4a** and **5a** with different C- α substituents, and assigned configuration to the pairs on the basis of ¹H NMR spectra. However, several of the compounds had very bulky substituents, e.g. 2,4,6-trimethoxyphenyl, which renders NMR assignments by comparison with compounds with less-bulky substituents a tenuous process. The crystal-

structure analysis of one such compound with a bulky malonic acid substituent has been briefly alluded to.⁹

Neolignans of type **1b** containing both guaiacyl and syringyl β -ethers and with both *threo* and *erythro* stereochemistry have been described. Shimomura *et al.*¹⁴ found, as constituents of *Machilus thunbergii*, both guaiacyl β -ether isomers **2c** and **3c**, which had previously been prepared by oxidative coupling of (*E*)-isoeugenol.⁷ Two further guaiacyl β -ethers, virolin (**2d**) and surinamensin (**2e**), were isolated from *Virola surinamensis* by Barata *et al.*,¹⁵ and had the *threo* configuration. Assignment of configuration to the neolignans followed from their ¹H NMR spectra, and the correctness of these assignments has been confirmed by the crystal-structure analyses referred to above.

The *erythro* β -syringyl ether **5a**, identical with that prepared previously by oxidative coupling,^{8,9} was isolated from the fruit of *Virola carinata*.¹⁶ A syringyl β -ether neolignan having a basic skeleton **1b** was isolated from *Myristica fragrans* (nutmeg) by Forrest *et al.*¹⁷ The *erythro* configuration (**7b**) was assigned to the compound on the basis of its ¹H NMR spectrum, and after synthesis involving tetrahydridoborate reduction of the α -oxo derivative.¹⁸ Three further β -syringyl ether neolignans, **7a**, **7c** and **7e**, all with *erythro* stereochemistry, were isolated from the same plant (nutmeg and mace).¹⁸ A *threo* isomer **6d** has recently been isolated from *Aristolochia birostris* by Conserva *et al.*¹⁹

Table 1. Crystal and experimental data for the *threo* and *erythro* forms of 1-(4-acetoxy-3,5-dimethoxyphenyl)-2-(2,6-dimethoxy-3-[(*E*)-propenyl]phenoxy)propyl acetate.

	<i>threo</i>	<i>erythro</i>
Crystal data		
Empirical formula	C ₂₆ H ₃₂ O ₉	C ₂₆ H ₃₂ O ₉
Formula weight	488.53	488.53
Crystal colour; habit	Colourless; prism	Colourless; plate
Crystal dimensions (mm)	0.19×0.31×0.37	0.07×0.19×0.51
Crystal system	Monoclinic	Monoclinic
No. of reflections used for unit cell determination (2θ range; °)	25 (34.6–40.0)	24 (20.0–24.1)
Omega scan peak width at half-height	0.34	0.36
Lattice parameters	<i>a</i> = 8.446(4) Å <i>b</i> = 32.903(3) Å <i>c</i> = 9.671(2) Å <i>β</i> = 106.44(2)° <i>V</i> = 2578(1) Å ³	<i>a</i> = 11.713(3) Å <i>b</i> = 12.548(3) Å <i>c</i> = 17.713(3) Å <i>β</i> = 90.59(2)° <i>V</i> = 2603(1) Å ³
Space group	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>Z</i>	4	4
<i>D</i> _{calc} /g cm ⁻³	1.259	1.246
<i>F</i> (000)	1040	1040
<i>μ</i> (Mo <i>K</i> _α)/cm ⁻¹	0.89	0.88
Intensity measurements		
Diffractometer	Rigaku AFC6R	Rigaku AFC6R
Radiation	Mo <i>K</i> _α	Mo <i>K</i> _α
<i>λ</i> /Å	0.71069	0.71069
<i>T</i> /°C	23	23
Take-off angle (°)	6.0	6.0
Detector aperture (mm)	6.0 horizontal 6.0 vertical	6.0 horizontal 6.0 vertical
Crystal to detector distance (cm)	40	40
Scan type	<i>ω</i>	<i>ω</i> -2θ
Scan rate in omega (°/min)	8.0 (4 rescans)	4.0 (4 rescans)
Scan width (°)	0.88 + 0.30 tanθ	1.10 + 0.30 tanθ
2θ _{max} /°	50.0	50.0
No. of reflections measured	Total: 4956 Unique: 4622	Total: 5064 Unique: 4816
Test reflections (change in intensity: %)	$\bar{1} 6 \bar{1}$ (3.6) $1 \bar{3} \bar{2}$ (2.6) $\bar{1} 8 \bar{1}$ (2.6)	$3 3 1$ (2.2) $3 0 4$ (1.2) $4 2 1$ (1.6)
Corrections	Lorentz and polarization	Lorentz and polarization
Structure solution and refinement		
Structure solution	Direct methods; electron density difference maps	
Hydrogen atom treatment	<i>x</i> , <i>y</i> , <i>z</i> , <i>B</i> refined	
Refinement	Full-matrix least-squares	
Function minimized	$\sum w(F_o - F_c)^2$	
Least-squares weights	$w = [\sigma^2(F_o) + p(F_o)^2]^{-1}$	
Anomalous dispersion	All non-hydrogen atoms	
No. of observed independent reflections [<i>I</i> > 3.00σ(<i>I</i>)]	2042	1753
No. of parameters refined	444	444
Reflection/parameter ratio	4.6	4.0
Residuals: <i>R</i>	0.046	0.038
<i>R</i> _w	0.051	0.040
<i>R</i> _w (all unique reflections)	0.068	0.063

(contd.)

Table 1 (contd.).

	<i>threo</i>	<i>erythro</i>
Goodness-of-fit indicator	1.57	1.26
Max. shift/error in final cycle	0.11	0.04
Maximum peak in final electron density difference map (e ⁻ Å ⁻³)	0.21	0.13
Minimum peak in final electron density difference map (e ⁻ Å ⁻³)	-0.16	-0.13

All the configurational assignments for the syringyl β-ethers were determined by comparison of the ¹H NMR data with those reported for the isomers **4a** and **5a**.⁸ For an unequivocal structural assignment to this important class of compounds, we undertook a crystal-structure analysis of the diacetates (**4b** and **5b**) of these two compounds. Results below clearly show that the original assignments given to the compounds were correct. The conformations of the diacetates are discussed on the basis of the crystal structures. An attempt is made to correlate results from conformational considerations with coupling constants and signal positions in the ¹H NMR spectra.

Results and discussion

Atomic fractional coordinates and equivalent isotropic thermal parameters are given in Table 2 for **4b** and in Table 3 for **5b**. Bond distances, bond angles and selected torsion angles are given in Table 4. Figs. 1 and 2 show stereoscopic views of the molecules **4b** and **5b**. The molecules and the atomic numbering are shown in Figs. 3 and 4.

The crystals of **4b** and **5b** consist of monomeric molecules held together by van der Waals forces. The shortest intermolecular contact distance is 2.38(7) Å in **4b** [between O(7) and H1(C19)] and 2.49(5) Å in **5b** [between H(C7) and H2(C21)].

Figs. 1–4 show that **4b** adopts the *threo* and **5b** the *erythro* configuration and that the propenyl side chain has the *E* configuration in both compounds. The crystal structures are thus consistent with earlier deductions made about the stereochemistry of these compounds.⁸

All bond distances and bond angles are normal in both compounds (see Table 4) as are the orientations of the methoxy groups (see Refs. 2, 11, 20). Within the limits of experimental error, the benzene-ring carbon atoms are coplanar in the respective aromatic ring, mean deviations being 0.003–0.011 Å in **4b** and 0.006–0.008 Å in **5b**. The methoxy oxygen atoms are almost coplanar with the respective benzene ring plane; the observed deviations are 0.02–0.07 Å in **4b** and 0.03–0.08 Å in **5b**. The benzylic carbon atoms denoted C(7) in both compounds are slightly twisted out of the benzene ring planes (0.05 Å in both **4b** and **5b**). The oxygen atom in the β-ether linkage is twisted

Table 2. Atomic fractional coordinates and B_{eq} (B_{eq} for H) for *threo*-1-(4-acetoxy-3,5-dimethoxyphenyl)-2-{2,6-dimethoxy-4-[(*E*)-propenyl]phenoxy}propyl acetate, $\text{C}_{26}\text{H}_{32}\text{O}_9$. $T = 296 \text{ K}$.

Atom	x	y	z	B_{eq}^a
C(1)	0.2526(5)	0.09909(13)	-0.0177(4)	3.4(2)
C(2)	0.2572(6)	0.05742(14)	-0.0298(5)	3.9(2)
C(3)	0.2799(6)	0.03303(13)	0.0928(5)	3.8(2)
C(4)	0.2934(5)	0.05138(14)	0.2235(4)	3.4(2)
C(5)	0.2811(5)	0.09324(14)	0.2342(4)	3.4(2)
C(6)	0.2640(6)	0.11670(15)	0.1136(5)	3.6(2)
C(7)	0.2353(6)	0.12654(15)	-0.1480(5)	3.6(2)
C(8)	0.0601(5)	0.13492(14)	-0.2349(5)	3.5(2)
C(9)	-0.0471(8)	0.1496(2)	-0.1452(7)	5.1(3)
C(10)	-0.0662(5)	0.18133(13)	-0.4291(4)	2.9(2)
C(11)	-0.1592(5)	0.16059(12)	-0.5495(4)	3.3(2)
C(12)	-0.2929(6)	0.17940(15)	-0.6458(5)	3.7(2)
C(13)	-0.3366(5)	0.21886(13)	-0.6228(4)	3.2(2)
C(14)	-0.2446(5)	0.23907(14)	-0.5019(5)	3.2(2)
C(15)	-0.1107(5)	0.22090(13)	-0.4055(4)	2.9(2)
C(16)	-0.4741(6)	0.23964(16)	-0.7269(5)	3.6(2)
C(17)	-0.5485(6)	0.22870(16)	-0.8597(5)	4.0(2)
C(18)	-0.6817(8)	0.2520(2)	-0.9624(6)	5.2(3)
C(19)	0.2670(16)	-0.0289(2)	-0.0369(8)	8.1(4)
C(20)	0.2598(9)	0.14974(17)	0.3839(7)	5.2(3)
C(21)	-0.1745(11)	0.1034(2)	-0.7026(7)	6.2(3)
C(22)	-0.0296(9)	0.28261(18)	-0.2732(7)	5.0(3)
C(23)	0.1979(7)	0.01109(16)	0.3829(5)	4.8(2)
C(24)	0.2512(11)	-0.0128(4)	0.5187(9)	8.2(5)
C(25)	0.4850(7)	0.11140(16)	-0.2060(6)	4.7(3)
C(26)	0.5544(11)	0.0904(3)	-0.3100(8)	6.3(4)
O(1)	0.0772(3)	0.16536(8)	-0.3386(3)	3.1(1)
O(2)	0.2971(4)	-0.00784(9)	0.0962(3)	5.5(2)
O(3)	0.3274(4)	0.02813(9)	0.3488(3)	3.9(1)
O(4)	0.2881(4)	0.10755(10)	0.3687(3)	4.9(2)
O(5)	-0.1049(4)	0.12221(9)	-0.5660(3)	4.7(1)
O(6)	-0.0124(4)	0.23970(9)	-0.2856(3)	3.9(1)
O(7)	0.0603(5)	0.01498(14)	0.3097(4)	7.7(2)
O(8)	0.3198(4)	0.10938(9)	-0.2430(3)	4.0(1)
O(9)	0.5634(4)	0.12848(12)	-0.0970(4)	5.9(2)
H(C2)	0.244(5)	0.0447(12)	-0.119(4)	3(1)
H(C6)	0.262(4)	0.1436(11)	0.120(4)	2.3(9)
H(C7)	0.291(5)	0.1526(13)	-0.109(4)	4(1)
H(C8)	0.005(5)	0.1101(12)	-0.293(4)	4(1)
H1(C9)	-0.151(7)	0.1529(15)	-0.208(5)	6(1)
H2(C9)	-0.065(6)	0.1285(16)	-0.082(5)	7(1)
H3(C9)	0.006(10)	0.176(2)	-0.069(8)	16(3)
H(C12)	-0.348(5)	0.1667(13)	-0.724(4)	4(1)
H(C14)	-0.279(4)	0.2638(11)	-0.484(3)	1.9(8)
H(C16)	-0.505(5)	0.2631(12)	-0.695(4)	4(1)
H(C17)	-0.520(5)	0.2046(13)	-0.897(4)	4(1)
H1(C18)	-0.723(7)	0.2751(18)	-0.921(6)	9(2)
H2(C18)	-0.780(7)	0.2337(16)	-1.000(5)	8(2)
H3(C18)	-0.648(6)	0.2635(15)	-1.043(5)	7(1)
H1(C19)	0.151(8)	-0.0204(20)	-0.087(7)	10(2)
H2(C19)	0.276(5)	-0.0547(14)	-0.005(5)	5(1)
H3(C19)	0.333(10)	-0.018(2)	-0.080(8)	12(4)
H1(C20)	0.252(5)	0.1552(13)	0.475(5)	5(1)
H2(C20)	0.348(6)	0.1675(16)	0.361(5)	7(2)
H3(C20)	0.156(6)	0.1598(15)	0.311(5)	6(1)
H1(C21)	-0.289(8)	0.094(2)	-0.707(7)	11(2)
H2(C21)	-0.109(6)	0.0783(17)	-0.699(5)	7(1)
H3(C21)	-0.160(7)	0.1175(17)	-0.775(5)	7(2)
H1(C22)	0.057(5)	0.2907(13)	-0.182(5)	5(1)
H2(C22)	-0.001(6)	0.2970(16)	-0.348(5)	7(2)
H3(C22)	-0.139(7)	0.2903(16)	-0.266(6)	8(2)
H1(C24)	0.246(9)	0.010(2)	0.599(8)	14(3)
H2(C24)	0.354(8)	-0.016(2)	0.546(7)	10(2)

(contd.)

Table 2 (contd.).

Atom	x	y	z	B_{eq}^a
H3(C24)	0.180(8)	-0.0316(18)	0.530(7)	9(2)
H1(C26)	0.462(10)	0.078(2)	-0.377(8)	13(3)
H2(C26)	0.640(8)	0.0742(18)	-0.272(6)	9(2)
H3(C26)	0.596(9)	0.109(2)	-0.354(8)	12(3)

$$^a B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

out of the aromatic ring plane (0.14 Å in **4b** and 0.12 Å in **5b**); this is also the case in previously investigated β -ether model compounds.² The angle between the benzene ring planes is 134° in **4b** and 124° in **5b**. The carbon and oxygen atoms in the acetate groups are coplanar to within 1 σ . In both compounds the plane of the aromatic acetate group is almost perpendicular to the aromatic ring plane (84° in **4b** and 86° in **5b**). In **4b** the plane of the acetate group attached to the benzylic carbon atom C(7) is also almost perpendicular to the benzene-ring plane C(1)–C(6) (87°). The corresponding angle is 132° in **5b**.

The propenyl groups are very similarly orientated in **4b** and **5b**. The vinylic hydrogen atoms H(C16) and H(C17) are, as expected, coplanar with the carbon atoms in the propenyl group in both **4b** and **5b**. The propenyl group plane forms an angle of 15° to the plane of the adjacent benzene ring in both compounds.

Average bond distances in the two compounds are (rms deviations are given in parentheses): C(sp²)–C(sp²) (in the benzene rings) 1.384(7) Å, C(sp²)–C(sp³) 1.493(16) Å, C(sp²)–O 1.366(16) Å, C(sp³)–O 1.428(12) and C(sp²)=O 1.194(11) Å.

Considering the conformations of the compounds, it is noteworthy that the torsion angle C(1)–C(7)–C(8)–O(1) is close to 180° in both compounds (this is also the case in three additional compounds of related structure which are under investigation) which implies that the bulky aryl substituents are as remote as possible from each other. The corresponding torsion angle also approaches 180° in a γ -oxygenated lignin model compound of the β -ether type, *threo*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol.² However, in the crystal structures of two *erythro* isomers of this type of model compound, namely *erythro*-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol¹¹ and *erythro*-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propanediol,²⁰ the corresponding torsion angles are 64 and 71°, respectively. It is possible that hydrogen bonding compensates for the interactions between the aryl substituents in these last cases. Since **4b** and **5b**, together with three additional compounds of the same type under investigation, exhibit a torsion angle C(1)–C(7)–C(8)–O(1) of ca. 180°, we consider it highly probable that this angle corresponds to the most stable conformers of the compounds examined. Therefore we feel

Table 3. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for *erythro*-1-(4-acetoxy-3,5-dimethoxyphenyl)-2-[(*E*)-propenyl]phenoxy propyl acetate, $\text{C}_{26}\text{H}_{32}\text{O}_9$. $T = 296$ K.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
C(1)	0.2548(3)	0.1192(3)	0.8067(2)	3.4(2)
C(2)	0.2279(4)	0.0119(3)	0.7999(2)	3.6(2)
C(3)	0.3108(4)	-0.0645(3)	0.8092(2)	3.6(2)
C(4)	0.4224(4)	-0.0329(3)	0.8239(2)	3.8(2)
C(5)	0.4515(4)	0.0738(3)	0.8289(2)	3.9(2)
C(6)	0.3662(4)	0.1502(4)	0.8207(2)	4.1(2)
C(7)	0.1584(3)	0.1983(3)	0.8025(2)	3.4(2)
C(8)	0.0894(3)	0.2004(4)	0.8747(2)	3.6(2)
C(9)	0.1523(5)	0.2467(5)	0.9415(3)	5.1(3)
C(10)	-0.0827(3)	0.2933(3)	0.9112(2)	3.5(2)
C(11)	-0.1027(4)	0.4019(3)	0.9196(2)	3.8(2)
C(12)	-0.1831(4)	0.4378(4)	0.9709(3)	4.4(3)
C(13)	-0.2419(4)	0.3660(4)	1.0152(2)	4.2(2)
C(14)	-0.2198(4)	0.2586(4)	1.0081(3)	4.4(3)
C(15)	-0.1424(4)	0.2218(3)	0.9561(2)	4.0(2)
C(16)	-0.3308(4)	0.3998(5)	1.0699(3)	5.4(3)
C(17)	-0.3802(5)	0.4895(5)	1.0752(3)	6.4(3)
C(18)	-0.4693(7)	0.5193(7)	1.1322(5)	7.7(4)
C(19)	0.1814(5)	-0.2077(5)	0.7885(5)	6.3(4)
C(20)	0.5957(6)	0.2023(6)	0.8494(5)	7.0(4)
C(21)	-0.0496(6)	0.5777(4)	0.8842(4)	5.6(3)
C(22)	-0.182(1)	0.0386(5)	0.9835(5)	8.3(5)
C(23)	0.5269(4)	-0.1532(4)	0.8980(3)	5.0(3)
C(24)	0.6200(7)	-0.2356(7)	0.8937(5)	7.3(4)
C(25)	0.1561(4)	0.3622(4)	0.7324(3)	4.5(3)
C(26)	0.1935(9)	0.4750(5)	0.7376(5)	6.5(4)
O(1)	-0.0108(2)	0.2611(2)	0.8547(1)	3.9(1)
O(2)	0.2939(2)	-0.1719(2)	0.8062(2)	4.8(2)
O(3)	0.5085(2)	-0.1098(2)	0.8294(2)	4.7(2)
O(4)	0.5639(2)	0.0945(3)	0.8421(2)	5.4(2)
O(5)	-0.0386(3)	0.4664(2)	0.8743(2)	5.0(2)
O(6)	-0.1204(2)	0.1165(2)	0.9416(2)	5.3(2)
O(7)	0.4730(3)	-0.1294(3)	0.9518(2)	7.5(2)
O(8)	0.2005(2)	0.3052(2)	0.7905(2)	4.0(1)
O(9)	0.0972(3)	0.3248(3)	0.6838(2)	6.4(2)
H(C2)	0.151(3)	-0.009(3)	0.791(2)	3.2(9)
H(C6)	0.382(3)	0.221(3)	0.825(2)	3(1)
H(C7)	0.106(2)	0.181(2)	0.761(2)	1.7(7)
H(C8)	0.066(3)	0.123(3)	0.883(2)	2.7(8)
H1(C9)	0.221(4)	0.210(3)	0.950(2)	6(1)
H2(C9)	0.170(4)	0.326(4)	0.930(2)	7(1)
H3(C9)	0.111(3)	0.240(3)	0.990(2)	5(1)
H(C12)	-0.192(2)	0.509(2)	0.974(2)	1.8(8)
H(C14)	-0.264(3)	0.210(3)	1.035(2)	3.2(9)
H(C16)	-0.357(4)	0.352(4)	1.102(3)	8(2)
H(C17)	-0.366(4)	0.545(4)	1.036(3)	9(2)
H1(C18)	-0.441(6)	0.573(6)	1.163(4)	15(3)
H2(C18)	-0.545(6)	0.537(5)	1.108(3)	12(2)
H3(C18)	-0.484(5)	0.454(5)	1.160(3)	10(2)
H1(C19)	0.130(4)	-0.188(4)	0.830(3)	8(2)
H2(C19)	0.157(4)	-0.178(4)	0.741(3)	9(2)
H3(C19)	0.184(4)	-0.287(4)	0.787(3)	9(2)
H1(C20)	0.671(4)	0.206(4)	0.860(3)	8(2)
H2(C20)	0.575(5)	0.247(4)	0.803(3)	11(2)
H3(C20)	0.562(5)	0.235(4)	0.894(3)	10(2)
H1(C21)	-0.026(4)	0.600(3)	0.938(3)	6(1)
H2(C21)	0.003(4)	0.607(3)	0.849(2)	6(1)
H3(C21)	-0.129(4)	0.595(3)	0.869(2)	6(1)
H1(C22)	-0.263(5)	0.044(5)	0.979(3)	10(2)
H2(C22)	-0.146(4)	-0.031(4)	0.961(3)	8(1)
H3(C22)	-0.147(4)	0.051(4)	1.033(3)	6(2)
H1(C24)	0.615(5)	-0.284(6)	0.934(4)	12(2)
H2(C24)	0.601(8)	-0.291(8)	0.860(5)	20(4)

Table 3 (contd.).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
H3(C24)	0.677(5)	-0.203(5)	0.901(4)	10(3)
H1(C26)	0.249(7)	0.480(6)	0.724(5)	14(4)
H2(C26)	0.154(4)	0.515(4)	0.706(3)	7(2)
H3(C26)	0.189(5)	0.503(4)	0.793(3)	11(2)

$$^a B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

justified in assuming that these conformers also predominate in solution. The coupling constant for $\text{H}_\alpha\text{-C-C-H}_\beta$ is 6.8 Hz in the *threo* isomer and 3.5 Hz in the *erythro* isomer.⁸ A larger coupling constant for the *threo* form than for the *erythro* form is expected from the Karplus correlation (in the crystal structures the torsion angle $\text{H}_\alpha\text{-C-C-H}_\beta$ is 169° in the *threo* form **4b** and 68° in the *erythro* form **5b**). In a study of the positions of the signals from terminal methyl groups in diastereomeric phenylpropane derivatives it was found that the signal from the γ -methyl group in *threo* forms was located at higher field than the corresponding signal from *erythro* forms and this was attributed to the shielding effect of the aromatic ring at C- α .²¹ It is notable that this rule is violated in the case of **4a** (δ 1.19) and **5a** (δ 1.13). However the acetate derivatives obey the rule; the γ -methyl group signals are found at δ 1.13 (**4b**, *threo*) and δ 1.28 (**5b**, *erythro*).⁸ Using data from the crystal-structure determination it is possible to estimate ring-current effects on the basis of distances from the centres of the aromatic rings to the individual hydrogen atoms in the γ -methyl groups and angles between the lines connecting the hydrogen atoms with the aromatic ring centres and the aromatic ring planes. Such calculations applied to **4b** and **5b** clearly suggest a shielding of the β -syringyl ether ring as well as the aromatic ring at C- α on the γ -methyl protons. The calculated upfield shift was, however, somewhat larger in the *erythro* case **5b** and this is not in agreement with observed signal positions. We therefore considered the effect of rotation of the aromatic rings around the bond connecting them to the rest of the molecule and found that this influenced the above-mentioned angles. Calculations in which maximum values for these angles are assumed, gave a slightly higher shielding effect in the *threo* case than in the *erythro* case, due mainly to the ring at C- α . In the ¹H NMR spectra of **4b** and **5b**, the benzylic acetate signals are located at δ 1.92 and δ 2.15, respectively. In every acetate of β -syringyl ethers of types **1a** and **1b** examined (Ref. 8 and unpublished data, Ref. 22 and references therein; see also Ref. 1) the signal from the benzylic acetate of the *erythro* form appears at $\delta \approx 2.15$ and the position of the corresponding signal from the *threo* form varies but the signal is always found at δ -values significantly lower than 2.15. According to calculations of ring current effects this might be due to such effects caused by the β -syringyl ether ring together with the aromatic ring attached to C- α .

Table 4. Bond distances (Å) and angles (°) in the *threo* and *erythro* forms of 1-(4-acetoxy-3,5-dimethoxyphenyl)-2-(2,6-dimethoxy-4-[(*E*-propenyl)phenoxy]propyl acetate, C₂₆H₃₂O₉. The average C–H bond distance is 0.95(7) Å in both the *threo* and the *erythro* form.

	<i>threo</i>	<i>erythro</i>		<i>threo</i>	<i>erythro</i>
Distance					
C(1)–C(2)	1.378(6)	1.388(5)	C(11)–O(5)	1.368(5)	1.368(4)
C(1)–C(6)	1.374(6)	1.381(5)	C(12)–C(13)	1.385(6)	1.383(6)
C(1)–C(7)	1.523(6)	1.504(5)	C(13)–C(14)	1.378(6)	1.378(6)
C(2)–C(3)	1.399(6)	1.374(5)	C(13)–C(16)	1.472(6)	1.492(6)
C(3)–C(4)	1.377(6)	1.388(5)	C(14)–C(15)	1.382(5)	1.379(6)
C(3)–O(2)	1.352(5)	1.363(4)	C(15)–O(6)	1.368(4)	1.370(4)
C(4)–C(5)	1.387(6)	1.384(5)	C(16)–C(17)	1.310(6)	1.268(7)
C(4)–O(3)	1.393(5)	1.399(4)	C(17)–C(18)	1.486(7)	1.508(8)
C(5)–C(6)	1.372(6)	1.391(6)	C(19)–O(2)	1.421(8)	1.425(6)
C(5)–O(4)	1.369(5)	1.360(5)	C(20)–O(4)	1.423(6)	1.409(7)
C(7)–C(8)	1.506(6)	1.519(5)	C(21)–O(5)	1.427(6)	1.414(6)
C(7)–O(8)	1.429(5)	1.446(4)	C(22)–O(6)	1.428(6)	1.425(7)
C(8)–C(9)	1.500(7)	1.505(6)	C(23)–C(24)	1.487(8)	1.505(8)
C(8)–O(1)	1.454(5)	1.440(4)	C(23)–O(3)	1.349(5)	1.348(5)
C(10)–C(11)	1.386(5)	1.391(5)	C(23)–O(7)	1.185(5)	1.186(5)
C(10)–C(15)	1.392(6)	1.394(5)	C(25)–C(26)	1.471(8)	1.485(8)
C(10)–O(1)	1.382(4)	1.374(4)	C(25)–O(8)	1.341(5)	1.352(5)
C(11)–C(12)	1.389(6)	1.391(5)	C(25)–O(9)	1.213(6)	1.194(5)
Angle					
C(2)–C(1)–C(6)	120.1(4)	120.2(4)	C(12)–C(11)–O(5)	124.7(4)	124.8(4)
C(2)–C(1)–C(7)	121.2(4)	117.7(4)	C(11)–C(12)–C(13)	120.9(4)	120.3(4)
C(6)–C(1)–C(7)	118.7(4)	122.0(2)	C(12)–C(13)–C(14)	118.5(4)	119.4(4)
C(1)–C(2)–C(3)	120.0(4)	120.5(4)	C(12)–C(13)–C(16)	121.4(4)	122.5(5)
C(2)–C(3)–C(4)	118.8(4)	119.1(4)	C(14)–C(13)–C(16)	120.2(4)	118.1(5)
C(2)–C(3)–O(2)	125.4(4)	125.7(4)	C(13)–C(14)–C(15)	121.4(4)	120.9(4)
C(4)–C(3)–O(2)	115.7(4)	115.1(4)	C(10)–C(15)–C(14)	120.1(4)	120.2(4)
C(3)–C(4)–C(5)	121.0(4)	121.2(4)	C(10)–C(15)–O(6)	115.8(4)	114.7(4)
C(3)–C(4)–O(3)	120.1(4)	119.6(4)	C(14)–C(15)–O(6)	124.1(4)	125.1(4)
C(5)–C(4)–O(3)	118.8(4)	119.1(4)	C(13)–C(16)–C(17)	127.5(5)	128.4(6)
C(4)–C(5)–C(6)	119.2(4)	119.0(4)	C(16)–C(17)–C(18)	125.2(6)	126.1(7)
C(4)–C(5)–O(4)	115.4(4)	115.7(4)	C(24)–C(23)–O(3)	111.8(5)	109.9(5)
C(6)–C(5)–O(4)	125.5(4)	125.4(4)	C(24)–C(23)–O(7)	125.8(6)	127.3(6)
C(1)–C(6)–C(5)	120.8(4)	120.0(4)	O(3)–C(23)–O(7)	122.4(4)	122.8(5)
C(1)–C(7)–C(8)	114.8(4)	112.0(3)	C(26)–C(25)–O(8)	112.4(6)	110.3(5)
C(1)–C(7)–O(8)	110.4(4)	111.2(3)	C(26)–C(25)–O(9)	125.9(6)	125.9(6)
C(8)–C(7)–O(8)	107.7(4)	107.0(3)	O(8)–C(25)–O(9)	121.7(5)	123.8(4)
C(7)–C(8)–C(9)	113.3(4)	114.1(4)	C(8)–O(1)–C(10)	117.3(3)	118.8(3)
C(7)–C(8)–O(1)	103.7(3)	104.0(3)	C(3)–O(2)–C(19)	118.2(4)	117.0(4)
C(9)–C(8)–O(1)	111.8(4)	112.3(4)	C(4)–O(3)–C(23)	117.3(3)	116.7(3)
C(11)–C(10)–C(15)	118.9(4)	119.0(4)	C(5)–O(4)–C(20)	118.0(4)	117.0(4)
C(11)–C(10)–O(1)	122.1(4)	118.1(4)	C(11)–O(5)–C(21)	116.4(4)	117.3(4)
C(15)–C(10)–O(1)	118.7(4)	122.7(4)	C(15)–O(6)–C(22)	117.8(4)	117.8(4)
C(10)–C(11)–C(12)	120.2(4)	120.2(4)	C(7)–O(8)–C(25)	118.7(4)	118.3(3)
C(10)–C(11)–O(5)	115.0(4)	115.0(4)			
Selected torsion angles					
	<i>threo</i>	<i>erythro</i>		<i>threo</i>	<i>erythro</i>
C(1)–C(2)–C(3)–O(2)	–175.5(5)	177.8(4)			
C(1)–C(6)–C(5)–O(4)	–177.8(4)	179.4(4)			
C(1)–C(7)–C(8)–C(9)	51.4(6)	69.3(5)			
C(1)–C(7)–C(8)–O(1)	172.8(4)	–168.0(3)			
C(1)–C(7)–C(8)–H(C8)	–72(2)	–54(2)			
C(1)–C(7)–O(8)–C(25)	–75.4(5)	127.3(4)			
C(2)–C(1)–C(7)–C(8)	87.4(5)	75.4(5)			
C(2)–C(1)–C(7)–O(8)	–34.6(6)	–164.9(3)			
C(2)–C(1)–C(7)–H(C7)	–152(2)	–45(2)			
C(2)–C(3)–C(4)–O(3)	–175.6(4)	–176.5(3)			
C(3)–C(2)–C(1)–C(7)	177.4(4)	–174.8(4)			
C(7)–C(8)–O(1)–C(10)	–175.9(3)	–169.2(3)			
C(8)–O(1)–C(10)–C(11)	–78.8(5)	121.4(4)			

(contd.)

Table 4 (contd.).

	<i>threo</i>	<i>erythro</i>
C(9)–C(8)–C(7)–O(8)	174.8(4)	–52.8(5)
C(9)–C(8)–C(7)–H(C7)	–67(2)	–169(2)
C(9)–C(8)–O(1)–C(10)	–53.5(5)	–45.3(5)
C(10)–O(1)–C(8)–H(C8)	65(2)	80(2)
C(11)–C(12)–C(13)–C(16)	177.7(4)	–178.7(4)
C(12)–C(11)–C(10)–O(1)	–173.3(4)	173.7(4)
C(12)–C(13)–C(16)–C(17)	–14.4(7)	14.0(9)
C(13)–C(12)–C(11)–O(5)	–178.1(4)	–178.7(4)
C(13)–C(14)–C(15)–O(6)	178.4(4)	–175.5(4)
C(13)–C(16)–C(17)–C(18)	–176.9(5)	–179.7(6)
C(25)–O(8)–C(7)–H(C7)	40(2)	6(2)
O(1)–C(8)–C(7)–O(8)	–63.8(4)	69.9(4)
O(1)–C(8)–C(7)–H(C7)	54(2)	–46(2)
O(1)–C(10)–C(11)–O(5)	4.4(6)	–6.0(6)
O(1)–C(10)–C(15)–O(6)	–4.8(5)	2.4(6)
O(8)–C(7)–C(8)–H(C8)	51(2)	–176(2)
H(C7)–C(7)–C(8)–H(C8)	169(3)	68(3)

Fig. 1. Stereoscopic view²⁶ of a molecule of **4b**.

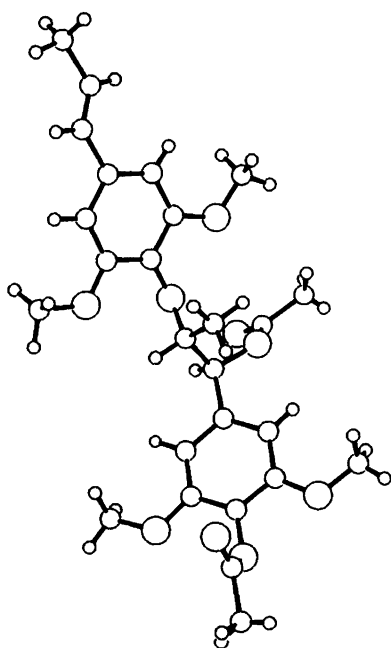
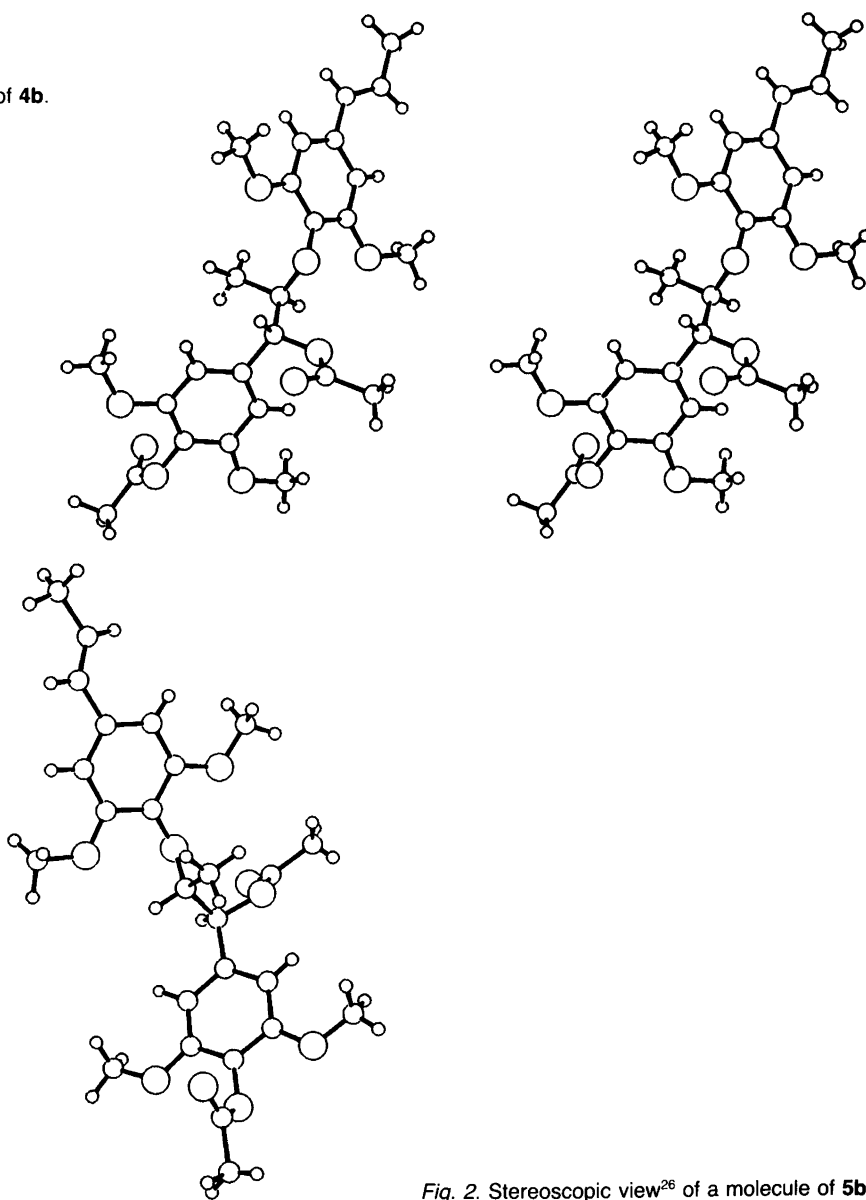
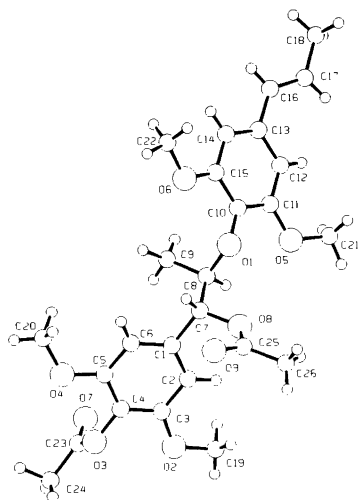


Fig. 2. Stereoscopic view²⁶ of a molecule of **5b**.

Fig. 3. A perspective drawing of the **4b** molecule showing the atomic numbering.

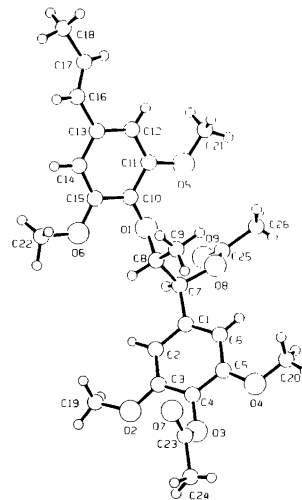


Experimental

Compounds **4b** and **5b** were prepared according to the literature method,⁸ and crystal and experimental data are given in Table 1. Rotation and Weissenberg photographs were taken of **4b** (Cu K_{α} radiation) from which crystal symmetry, conditions for reflections and approximate cell dimensions were obtained. For **5b** a rotation photograph only was taken to check the quality of the crystal. Diffracted intensities were measured for both compounds with a Rigaku AFC6R X-ray diffractometer with graphite-monochromated Mo K_{α} radiation from a RU200 rotating anode source operated at 9kW (50kV; 180 mA). For both compounds the intensities of three representative reflections which were measured after every 150 reflections remained constant throughout the data collection indicating crystal and electronic stability (no decay correction was applied). Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorenz and polarization effects. Cell constants were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections. Omega scans of several intense reflections, made prior to the data collection, had an average width at a half-height of 0.34° for **4b** and of 0.36° for **5b** with a take-off angle of 6.0°. The weak reflections [$I < 10.0 \sigma(I)$] were rescanned (maximum of four rescans for both compounds) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak-counting time to background-counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 40 cm.

The structures were solved by direct methods using the program MITHRIL²³ and by subsequent electron density

Fig. 4. A perspective drawing of the **5b** molecule showing the atomic numbering.



calculations. All hydrogen atomic positions could be located unambiguously from electron density difference maps. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Full-matrix least-squares refinement led to the agreement factors $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.046$ and $R_w = [(\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2} = 0.051$ for **4b**. For **5b** the corresponding values were $R = 0.038$ and $R_w = 0.040$.

The weighting scheme (see Table 1) was based on counting statistics and included a factor ($p = 0.05$) to down-weight the intense reflections. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of index showed no unusual trends.

Some further details concerning the refinement of the structures are summarized in Table 1. Neutral atomic scattering factors as well as $\Delta f'$ and $\Delta f''$ were taken from International Tables for X-Ray Crystallography.²⁴ All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation,²⁵ and structural illustrations were drawn with ORTEP.²⁶

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