

displaced 0.696 (8) and 0.686 (7) Å respectively from the best plane through C5, C6, C8 and C9. The absolute value of the intracycle torsion angles is on average 56.8 (6)°. The dihydropyran ring *C*, which has a double bond in positions 13,14, approximates a half-boat conformation with apex at C16 and total puckering amplitude  $Q = 0.521$  (8) Å; the atom O1 is only 0.189 (4) Å out of the plane formed by the remaining four atoms. The lactone system is planar within the e.s.d. and makes a dihedral angle of 106.8 (3)° with the acetoxy group. The torsion angle O1—C16—C17—C18 is 6(1)° with O1 *cis* to C18 and C15 *gauche* to C25. The molecule has the most extended conformation with the central ethylene group in a nearly *trans* conformation.

The molecular arrangement, shown in Fig. 2, is governed by van der Waals interactions and the shortest intermolecular contacts ( $> 3.0$  Å) involve the lactone ring *D* and the acetyl group.

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## Structures of 2-(2-Methoxyphenyl)-4*H*-1-benzopyran-4-one (1) and 5,7-Dimethoxy-2-(2,4-dimethoxyphenyl)-4*H*-1-benzopyran-4-one (2) (2'-Methoxyflavone and 2',4',5,7-Tetramethoxyflavone)

BY JEAN-CLAUDE WALLET\* AND EMILE M. GAYDOU

Laboratoire de Phytochimie, Ecole Supérieure de Chimie de Marseille, Faculté des Sciences et Techniques de Saint-Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille CEDEX 13, France

JOËL JAUD

CNRS, Laboratoire de Chimie de Coordination, 205, Route de Narbonne, 31077 Toulouse CEDEX, France

AND ANDRÉ BALDY

CNRS UA126, Faculté des Sciences, Centre de Saint-Jérôme, 13397 Marseille CEDEX 13, France

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**Abstract.** Compound (1):  $C_{16}H_{12}O_3$ ,  $M_r = 252.27$ , triclinic,  $P\bar{1}$ ,  $a = 7.245$  (10),  $b = 8.305$  (12),  $c = 10.800$  (14) Å,  $\alpha = 97.7$  (1),  $\beta = 93.1$  (1),  $\gamma = 111.2$  (1)°,  $V = 597$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.4$ ,  $D_x = 1.404$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.904$  cm<sup>-1</sup>,  $F(000) = 264$ ,  $T = 223$  K.  $R = 0.053$  for 2180 reflections. 2'-Methoxyflavone is a predominantly flat molecule (the  $\gamma$ -benzopyrone portion makes an angle of 3° with the phenyl ring). Two intramolecular hydrogen bonds may contribute to the marked planarity of the molecule. Compound

(2):  $C_{19}H_{18}O_6$ ,  $M_r = 342.35$ , monoclinic,  $P2_1/n$ ,  $a = 7.205$  (7),  $b = 12.769$  (4),  $c = 17.567$  (8) Å,  $\beta = 93.27$  (2)°,  $V = 1613$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.412$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.986$  cm<sup>-1</sup>,  $F(000) = 720$ ,  $T = 223$  K.  $R = 0.041$  for 3621 reflections. The dihedral angle between the planar phenyl ring and the slightly puckered  $\gamma$ -benzopyrone portion is 24°. No intramolecular H bonds.

**Introduction.** Flavonoids are used in the treatment of diabetes, cancers, allergies and viral infections. From the structure-activity data in the literature it is clear

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\* Author to whom correspondence should be addressed.

Table 1. *Crystallographic summary for (1) and (2)*

	(1)	(2)
Data collection		
Mode	$\omega/2\theta$	$\omega/2\theta$
Scan range ( $^{\circ}$ )	$0.8 + 0.35\tan\theta$	$1 + 0.35\tan\theta$
Max. $\theta$ ( $^{\circ}$ )	30	30
Range in $h, k, l$ min.	0, -11, -15	0, 0, -24
max.	6, 10, 15	10, 17, 24
Total, unique reflections measured	3239, 2884	4664, 4363
Crystal shape	Parallelepiped	Irregular fragment
Crystal dimensions (mm)	$2 \times 0.3 \times 0.2$	Length 0.4 Section 0.2
Structure refinement		
Reflections used $I > 3\sigma(I)$	2180	3621
$R, wR$ ( $w = 1$ )	0.053, 0.055	0.041, 0.064
Goodness of fit $S$	0.681	1.538
Max. $\Delta/\sigma$	0.01	0.02
$\rho$ in $\Delta F$ map ( $e \text{ \AA}^{-3}$ ) max.	0.25	0.30
min.	-0.26	-0.28

that a particular flavonoid may have different responses, depending on enzyme site. These data suggest that conformations are recognized by enzyme site. A report has recently appeared on that subject (Cody, 1988). Therefore, to obtain an accurate knowledge of conformational properties and details about the structures, single-crystal X-ray experiments were undertaken in our laboratory (Wallet, Gaydou, Fadlane & Baldy, 1988; Wallet, Gaydou & Baldy, 1989). The two compounds studied here are natural products. 2'-Methoxyflavone was isolated from *Pimelea simplex* (Freeman, Murphy, Nemorin & Taylor, 1981) and from *Primula kewensis* (Wollenweber & Mann, 1986). 2',4',5,7-Tetramethoxyflavone was isolated from *Terminalia arjuna* fruits (Nagar, Gujral & Gupta, 1979).

The compounds were prepared by a procedure previously described starting from suitable hydroxyacetophenones and benzoic acids (Gaydou & Bianchini, 1978).

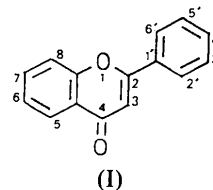
**Experimental.** Single crystals of compound (1) grown from slow evaporation of ethanol and from dimethyl sulfoxide for compound (2).

Enraf-Nonius diffractometer equipped with a graphite monochromator. Data collection and refinement details of both structures in Table 1. For (1), attempts to cut the crystal (to reduce the largest dimension) did not give satisfactory results. No absorption corrections (low absorption factor). Furthermore measurements around the vector of diffusion did not reveal significant changes which proved despite the abnormal size of the crystal that measurements were correct. Unit-cell parameters refined by least squares on  $2(\sin\theta)/\lambda$  values for 25 reflections ( $14 < \theta < 16^{\circ}$ ).

Intensity controls every hour of irradiation revealed no decrease with time. Intensities corrected for polarization and Lorentz effects. Structure solved

by direct methods with *MULTAN* (Main, Woolfson & Germain, 1977) which revealed all non-H atoms. Positional and thermal parameters for all non-H atoms refined by full-matrix least-squares procedures with isotropic and anisotropic temperature factors, using the Enraf-Nonius *SDP* (Frenz, 1985), scattering factors of Cromer & Waber (1974) and anomalous coefficients of Cromer (1974). H atoms located by difference Fourier synthesis. These positions were afterwards theoretically calculated using C—H distances equal to 0.97 Å. To discuss the hydrogen bonds, positions of related H atoms were calculated using C—H distances equal to 1.09 Å as proposed by a referee. Final refinement on  $F$  carried out with isotropic thermal parameters for H and anisotropic for non-H atoms.

**Discussion.** The structures of 2'-methoxyflavone and 2',4',5,7-tetramethoxyflavone are shown in Figs. 1 and 2 with the numbering system used in the tables. Final positional and thermal parameters are presented in Tables 2 and 3.\* Bond distances and angles are given in Table 4. For convenience we give the chemical numbering generally agreed for flavones; we did not use this for the crystallographic approach.



2'-Methoxyflavone is remarkably planar. A least-squares plane fitted to the  $\gamma$ -benzopyrone atoms has a standard deviation of 0.003 Å, with the same deviation for the six phenyl C atoms. The phenyl ring is almost coplanar with the  $\gamma$ -benzopyrone plane  $O(1)C(1)C(10)C(11) = -2.7^{\circ}$ ,  $C(2)C(1)C(10)C(15) = -2.9^{\circ}$ .

Planar configurations of flavonoid structures exist in the case of acacetin and 5,6-benzoflavone (Rossi, Cantrell, Farber, Dyott, Carrell & Glusker, 1980) through hydrogen bonds which stabilize the negative charge on the carbonyl O atom.

In some reports (Wurm & Geres, 1977; Tanaka, Iinuma & Mizuno, 1986) it was suggested that 2'-methoxy-substituted flavones could not form planar structures. At least in the crystalline state, very short hydrogen contacts,  $H(12)\cdots O(3)$  2.043 and

\* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52852 (86 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

H(111)⋯O(1) 2.231 Å, which correspond respectively to distances O(3)H(12)C(2) = 3.132 and O(1)H(111)C(11) = 3.321 Å and angles O(3)H(12)C(2) = 121.5 and O(1)H(111)C(11) = 99.1°, can maintain the phenyl ring nearly coplanar with the  $\gamma$ -benzopyrone plane (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984). These intramolecular bonds are probably destroyed in solution.

2',4',5,7-Tetramethoxyflavone is not planar. The dihedral angle between the phenyl ring and the mean plane of the  $\gamma$ -pyrone portion is O(1)C(1)C(10)C(11) = 24.0°. Moreover, the C(1)C(10) bond makes an angle of 6° with respect to the latter plane. Steric interaction between O(2) and O(6) atoms leads to a deformation of the  $\gamma$ -pyrone ring which is slightly puckered, C(2)C(3)C(4)C(9) = -6.6, C(3)C(4)C(9)-O(1) = 6.6, C(3)C(4)C(9)C(8) = -174.2°. This puckering might contribute to diminish the mesomeric effect between the phenyl ring and the conjugated double bonds C(1)C(2) and C(3)O(2) and allow a rotation by 24° of the phenyl ring. There is no intramolecular hydrogen bond O(1)⋯H(111); O(3)⋯H(12) distances are 2.32 and 3.36 Å, respectively. The structure of a flavone substituted by a methoxy group in position 5 [3',5,5',6-tetramethoxyflavone, found in the literature (Ting, Watson &

Table 2. *Positional parameters and their e.s.d.'s for (1)*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0.2383 (3)	0.3062 (2)	0.4023 (2)	2.17 (3)
O(2)	0.3633 (3)	0.6467 (2)	0.1518 (2)	3.19 (4)
O(3)	0.2963 (3)	0.8098 (2)	0.5732 (2)	2.77 (4)
C(1)	0.2581 (3)	0.4770 (3)	0.4384 (2)	1.76 (4)
C(2)	0.3002 (4)	0.5910 (3)	0.3564 (2)	2.01 (5)
C(3)	0.3257 (4)	0.5427 (3)	0.2266 (2)	2.08 (5)
C(4)	0.3020 (3)	0.3589 (3)	0.1908 (2)	1.95 (5)
C(5)	0.3239 (4)	0.2903 (3)	0.0691 (2)	2.57 (5)
C(6)	0.3031 (4)	0.1180 (4)	0.0401 (3)	3.04 (6)
C(7)	0.2598 (4)	0.0097 (3)	0.1313 (3)	2.96 (6)
C(8)	0.2379 (4)	0.0743 (3)	0.2521 (3)	2.54 (5)
C(9)	0.2599 (4)	0.2493 (3)	0.2806 (2)	1.96 (5)
C(10)	0.2269 (3)	0.5077 (3)	0.5720 (2)	1.81 (5)
C(11)	0.1755 (4)	0.3671 (3)	0.6389 (2)	2.18 (5)
C(12)	0.1482 (4)	0.3870 (3)	0.7649 (2)	2.60 (5)
C(13)	0.1705 (4)	0.5497 (4)	0.8282 (2)	2.69 (6)
C(14)	0.2172 (4)	0.6914 (3)	0.7648 (2)	2.51 (5)
C(15)	0.2462 (4)	0.6726 (3)	0.6382 (2)	2.01 (5)
C(16)	0.2992 (4)	0.9746 (3)	0.6338 (3)	3.18 (6)

Table 3. *Positional parameters and their e.s.d.'s for (2)*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0.2284 (1)	0.13342 (6)	0.48279 (4)	2.31 (1)
O(2)	0.0465 (2)	0.11932 (7)	0.69792 (5)	3.52 (2)
O(3)	0.2399 (1)	0.43007 (6)	0.57463 (5)	2.68 (2)
O(4)	0.2037 (2)	0.57046 (7)	0.32423 (5)	3.60 (2)
O(5)	0.3536 (1)	-0.22922 (6)	0.47123 (6)	3.19 (2)
O(6)	0.1671 (2)	-0.08221 (7)	0.70213 (5)	3.42 (2)
C(1)	0.1757 (2)	0.22239 (8)	0.51959 (6)	2.02 (2)
C(2)	0.1144 (2)	0.21798 (8)	0.59048 (6)	2.19 (2)
C(3)	0.1101 (2)	0.12123 (9)	0.63397 (6)	2.26 (2)
C(4)	0.1832 (2)	0.02889 (8)	0.59528 (6)	2.09 (2)
C(5)	0.2055 (2)	-0.07311 (9)	0.62784 (7)	2.45 (2)
C(6)	0.2649 (2)	-0.15612 (9)	0.58484 (7)	2.77 (2)
C(7)	0.3012 (2)	-0.14141 (9)	0.50805 (7)	2.47 (2)
C(8)	0.2854 (2)	-0.04365 (9)	0.47444 (6)	2.29 (2)
C(9)	0.2303 (2)	0.03907 (8)	0.51963 (6)	1.98 (2)
C(10)	0.1914 (2)	0.31429 (8)	0.46996 (6)	2.08 (2)
C(11)	0.1836 (2)	0.29967 (9)	0.39112 (7)	2.61 (2)
C(12)	0.1912 (2)	0.3817 (1)	0.33959 (7)	2.80 (2)
C(13)	0.2049 (2)	0.48286 (9)	0.36826 (7)	2.53 (2)
C(14)	0.2212 (2)	0.50081 (9)	0.44695 (7)	2.43 (2)
C(15)	0.2174 (2)	0.41764 (8)	0.49765 (6)	2.09 (2)
C(16)	0.2799 (2)	0.5333 (1)	0.60369 (7)	2.96 (2)
C(17)	0.1879 (2)	0.5566 (1)	0.24300 (8)	4.03 (3)
C(18)	0.3864 (2)	-0.2194 (1)	0.39163 (8)	3.24 (2)
C(19)	0.2040 (2)	-0.1812 (1)	0.73844 (8)	3.91 (3)

Dominguez, 1972)] also has a puckered  $\gamma$ -pyrone ring. The reported torsion angle is 28°, not very different from the value found here. At the same temperature, the inter-ring bonds C(1)C(10) are equal confirming that there is no relation between the torsion angle and this bond (Wallet, Gaydou, Fadlane & Baldy, 1988; Cody, 1988). If we compare distances and angles around this torsion angle, we find that there is not much difference between the two molecules. In (1) the methoxy group is oriented

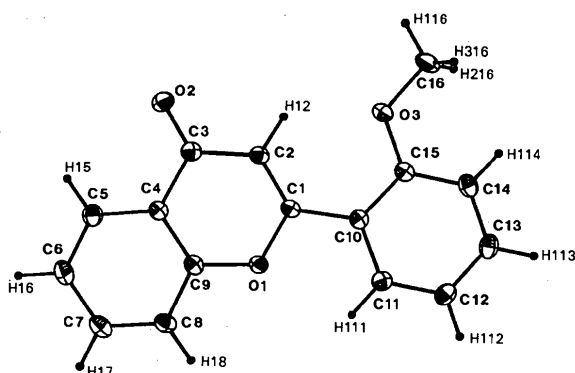


Fig. 1. View of (1) showing atom-numbering scheme.

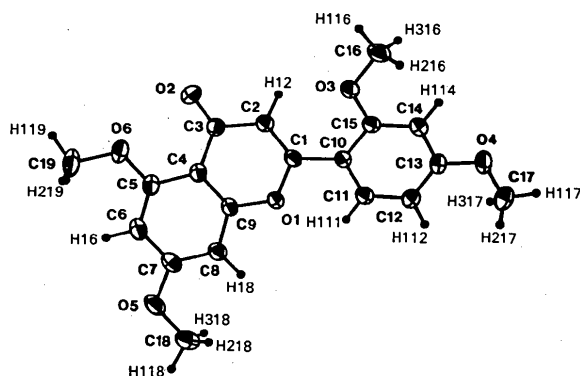


Fig. 2. View of (2) showing atom-numbering scheme.

Table 4. Bond distances (Å) and angles (°) in (1) and (2) with their *e.s.d.*'s in parentheses

	(1)	(2)
O(1)—C(1)	1.372 (3)	1.371 (1)
O(1)—C(9)	1.374 (3)	1.367 (1)
O(2)—C(3)	1.229 (3)	1.237 (2)
O(3)—C(15)	1.366 (4)	1.362 (1)
O(3)—C(16)	1.428 (3)	1.436 (1)
C(1)—C(2)	1.348 (3)	1.346 (2)
C(1)—C(10)	1.475 (3)	1.470 (1)
C(2)—C(3)	1.448 (3)	1.453 (2)
C(3)—C(4)	1.468 (3)	1.473 (2)
C(4)—C(5)	1.402 (3)	1.427 (2)
C(4)—C(9)	1.389 (3)	1.397 (2)
C(5)—C(6)	1.374 (5)	1.384 (2)
C(6)—C(7)	1.394 (4)	1.401 (2)
C(7)—C(8)	1.384 (4)	1.382 (2)
C(8)—C(9)	1.393 (3)	1.392 (2)
C(10)—C(11)	1.402 (3)	1.395 (2)
C(10)—C(15)	1.413 (3)	1.415 (1)
C(11)—C(12)	1.383 (4)	1.387 (2)
C(12)—C(13)	1.379 (4)	1.388 (2)
C(13)—C(14)	1.386 (4)	1.399 (2)
C(14)—C(15)	1.392 (4)	1.387 (2)
O(4)—C(13)		1.359 (1)
O(4)—C(17)		1.436 (2)
O(5)—C(7)		1.359 (1)
O(5)—C(18)		1.436 (2)
O(6)—C(5)		1.354 (2)
O(6)—C(19)		1.433 (2)
C(1)—O(1)—C(9)	119.8 (2)	120.1 (1)
C(15)—O(3)—C(16)	118.6 (3)	118.0 (1)
O(1)—C(1)—C(2)	121.0 (3)	121.0 (1)
O(1)—C(1)—C(10)	110.3 (2)	110.4 (1)
C(2)—C(1)—C(10)	128.6 (2)	128.5 (1)
C(1)—C(2)—C(3)	123.0 (2)	122.7 (2)
O(2)—C(3)—C(2)	122.9 (2)	120.9 (2)
O(2)—C(3)—C(4)	122.5 (2)	124.3 (2)
C(2)—C(3)—C(4)	114.6 (3)	114.7 (1)
C(3)—C(4)—C(5)	122.3 (2)	125.5 (2)
C(3)—C(4)—C(9)	119.2 (3)	118.5 (1)
C(5)—C(4)—C(9)	118.5 (2)	116.1 (1)
C(4)—C(5)—C(6)	120.3 (2)	120.7 (2)
C(5)—C(6)—C(7)	120.4 (3)	120.2 (2)
C(6)—C(7)—C(8)	120.5 (3)	121.2 (2)
C(7)—C(8)—C(9)	118.7 (2)	117.5 (2)
O(1)—C(9)—C(4)	122.4 (3)	122.4 (1)
O(1)—C(9)—C(8)	116.0 (2)	113.2 (1)
C(4)—C(9)—C(8)	121.6 (2)	124.4 (1)
C(1)—C(10)—C(11)	119.1 (3)	118.9 (1)
C(1)—C(10)—C(15)	123.8 (3)	123.7 (1)
C(11)—C(10)—C(15)	117.2 (3)	117.6 (1)
C(10)—C(11)—C(12)	122.2 (2)	123.1 (2)
C(11)—C(12)—C(13)	119.7 (2)	118.1 (2)
C(12)—C(13)—C(14)	119.9 (2)	120.7 (2)
C(13)—C(14)—C(15)	120.8 (2)	120.3 (2)
O(3)—C(15)—C(10)	117.2 (3)	117.1 (1)
O(3)—C(15)—C(14)	122.5 (2)	122.9 (1)
C(10)—C(15)—C(14)	120.3 (2)	120.1 (2)
C(13)—O(4)—C(17)		117.5 (2)
C(7)—O(5)—C(18)		117.2 (1)
C(5)—O(6)—C(19)		117.5 (2)
O(6)—C(5)—C(4)		116.1 (2)
O(6)—C(5)—C(6)		123.2 (2)
O(5)—C(7)—C(6)		114.8 (2)
O(5)—C(7)—C(8)		124.0 (1)
O(4)—C(13)—C(12)		124.1 (2)
O(4)—C(13)—C(14)		115.1 (2)

slightly out of the plane of the phenyl ring with a torsion angle  $C(16)O(3)C(15)C(14) = -6.5^\circ$ . In (2), the methoxy groups at C(5), C(7), C(15) and C(13) lie close to the planes of the respective rings. The

values of torsion angles are  $C(19)O(6)C(5)C(6) = -4.8$ ,  $C(18)O(5)C(7)C(8) = -2.7$ ,  $C(16)O(3)C(15)C(14) = -3.7$  and  $C(17)O(4)C(13)C(12) = -0.3^\circ$ . If we disregard differences ascribed to the repulsion between the carbonyl O atom and the C(5)-substituted methoxy group, bond distances are comparable with the values reported for similar flavonoids (Rossi, Cantrell, Farber, Dyott, Carrell & Glusker, 1980; Kimura, Okuda, Taira, Shoji, Takemoto & Arichi, 1984; Wallet, Gaydou & Baldy, 1989). The short carbonyl bond 1.229 Å is indicative of the lack of any H bonding.

For (1), the methoxy group lies on the side of H(12). This configuration is more favourable compared with the methoxy group near O(1) if we consider the repulsion of the lone pairs of the O atom. Recently the structure of 3-(2-methoxyphenyl)-1*H*-2-benzopyran-1-one has been published (Prince, Miller, Fronczek & Gandour, 1989). This molecule is planar, the dihedral angle between the fused-ring system and the phenyl ring is  $4.7^\circ$  and the methoxy group in this case is on the side of the vinyl proton. The packing of molecules is shown in Figs. 3 and 4. A close-spaced packing occurs between two inversion-related molecules. There are no intermolecular hydrogen bonds. The shortest contacts are between carbonyl O(2) and H(17) (2.53 Å) with

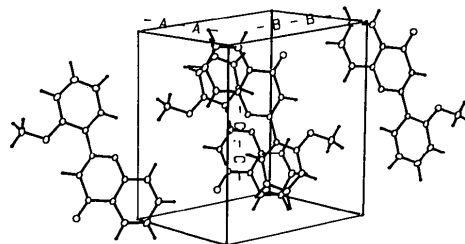


Fig. 3. Molecular packing diagram of (1).

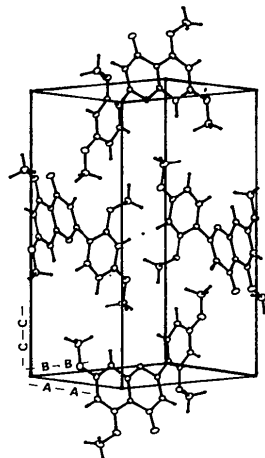


Fig. 4. Molecular packing diagram of (2).

C(7)H(17)O(2) = 147.7° for compound (1) and O(2) and H(217) (2.58 Å) with O(2)H(217)C(17) = 170.5° for compound(2).

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## Structure of 1,1,4,4-Tetrakis(phenylthio)butane

BY GEORGE FERGUSON\* AND BRANKO KAITNER

*Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

AND BRID M. DILWORTH AND M. ANTHONY MCKERVEY

*Department of Chemistry, University College, Cork, Ireland*

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**Abstract.**  $C_{28}H_{26}S_4$ ,  $M_r = 490.8$ , monoclinic,  $P2_1/n$ ,  $a = 9.834$  (2),  $b = 13.692$  (2),  $c = 10.261$  (2) Å,  $\beta = 112.60$  (2)°,  $V = 1275.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.28$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 3.7$  cm<sup>-1</sup>,  $F(000) = 516$ . Final  $R = 0.030$  for 2181 reflections with  $I > 3\sigma(I)$ . The molecule lies on a crystallographic inversion centre with the central S—CH—(CH<sub>2</sub>)<sub>2</sub>—CH—S moiety maximally extended. Mean distances are  $C_{\text{arom}}\text{—S } 1.777$  (2) and  $C_{\text{sp}^3}\text{—S } 1.828$  (2) Å.

**Introduction.** In a recent communication (Cronin, Dilworth & McKerverey, 1986) on new methods of organic synthesis employing  $\alpha$ -chlorosulfides as reaction intermediates we described a convenient procedure whereby an alkyl phenyl sulfide is converted in a two-step sequence into a (phenylthio)acetal. The procedure was also applied to

several  $\alpha\omega$  bis sulfides. In a typical example, 1,4-bis(phenylthio)butane was treated with *N*-chlorosuccinimide to afford the corresponding bis(chlorosulfide) which on exposure to thiophenol with zinc chloride catalysis gave 1,1,4,4-tetrakis(phenylthio)butane (1), a compound previously prepared from 2,5-dimethoxytetrahydrofuran (Cohen, Ritter & Ouellette, 1982). For many years thioacetals and thioketals have been recognized as valuable intermediates in a wide variety of useful synthetic transformations. The crystal and molecular structure of a simple bifunctional thioacetal has not previously been recorded. Accordingly, having isolated good quality crystals of (1), we determined the crystal and molecular structure.

**Experimental.** Colorless crystals of (1),  $C_{28}H_{26}S_4$ , were grown from ethanol. Accurate cell data and orientation matrix were determined on a CAD-4

\* E-mail address: CHMFERG@VM.UOGUELPH.CA