2,5-Dimethoxy-2,5-dihydro-2-furylmethyl Benzoate

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Abstract. $C_{14}H_{16}O_5$, $M_r = 264\cdot28$, monoclinic, $P2_1/c$, $a = 11\cdot491$ (9), $b = 11\cdot197$ (9), $c = 13\cdot200$ (7) Å, $\beta = 127\cdot85$ (4)°, $V = 1341\cdot1$ (18) Å^3, $Z = 4$, $D_x = 1\cdot309$, $D_m = 1\cdot312$ g cm^{-3} (by flotation in bromoform–heptane mixture, 23 °C), μ(Mo $K\alpha$) $= 0\cdot93$ cm^{-1}, m.p. $77\cdot5$ °C. The structure was refined to $R = 0\cdot055$ for 1415 counter reflections. The analysis shows that the methoxy groups adopt a *cis* configuration.

Introduction. $C_{14}H_{16}O_5$ is one of a series of 2,5-dialkoxy-2,5-dihydrofuran compounds first prepared by Kochetkov, Kudryashov, Molodtzov & Khomutova (1961), who showed the existence of two isomers. Only one of these crystallizes at room temperature and was chosen for the X-ray study. Kochetkov *et al.* (1961) assumed this to be the *trans* isomer. However, Achmatowitz, Bukowski, Szechner, Zwierchowska & Zamojski (1971) have shown from NMR studies of related substances that this assignment is uncertain.

A sample was purified by multiple recrystallization (methanol) and dry column chromatography (silica gel–methanol) to a final purity >99·9% and m.p. 77·5 °C.

The colourless crystals are air-stable and do not decompose in X-rays. The space group and preliminary lattice constants were obtained from photographs (Cu $K\alpha$ radiation). Refined cell parameters were obtained from the orientation matrix calculated by the least-squares method (Shoemaker, 1970) from 25 reflections centred on the diffractometer. A crystal 0·5 × 0·3 × 0·2 mm was used for intensity measurements on a Hilger & Watts four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0\cdot71073$ Å). The ω–2θ scan technique was used with a constant scan speed of 0·6° min^{-1} over a range of 2° to measure 2370 independent reflections with $2\theta < 50°$. 955 of these were classified as unobserved on the criterion $I < 2\sigma_1(I)$, where $I = TC - B_1 - B_2$ and $\sigma_1(I) = (TC + B_1 + B_2)^{1/2}$ (TC = total count, B_1 and B_2 = backgrounds measured at the scan limits for half of the scan time). All unobserved reflections were used in the refinement with $F_{unobs} = \frac{1}{2}F_{min}$

and $\sigma_1(F_{unobs}) = 1/\sqrt{12}F_{min}$ (F_{min} = the minimum observable value of $|F|$). The intensities of one standard measured after every ten reflections showed no significant variation. The data were corrected for Lorentz and polarization effects, but not for absorption and extinction.

The structure was solved with the tangent formula (Karle & Hauptman, 1956). Normalized structure factor amplitudes, $|E|$, were calculated, with the scale and overall temperature factor estimated from a Wilson plot. The $|E|$ statistics showed a centric distribution. Three reflections were selected as starting phases and another three to define the origin. Tangent formula refinement was then applied to 220 reflections with $|E| > 1\cdot2$. The resulting E map revealed all 19 non-hydrogen atoms. Refinement was carried out with a local version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$ {derived from $\sigma_2(I) = [\sigma_1(I) + (0\cdot015I)^2]^{1/2}$}. Refinement with isotropic temperature factors converged to $R = 0\cdot119$ and with anisotropic to $R = 0\cdot088$ (for observed reflections). A subsequent difference synthesis revealed the positions of all H atoms. Final refinement was carried out in two blocks: the first block consisted of positional parameters of all atoms, the second of anisotropic temperature parameters of the non-hydrogen and isotropic for H atoms. The final R was 0·055 for the observed and 0·082 for all reflections. The maximum residual electron density in the final difference synthesis was 0·14 e Å^{-3}. Final coordinates are given in Table 1.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on a TESLA 200 computer.

Table 1. *Fractional atomic coordinates*

E.s.d.'s (in parentheses) refer to the last decimal place.

	x	y	z
C(1)	0·8737 (4)	0·6658 (3)	0·0545 (3)
C(2)	1·0100 (5)	0·7385 (3)	0·1382 (4)
C(3)	1·0016 (4)	0·8029 (3)	0·2154 (3)
C(4)	0·8623 (3)	0·7806 (3)	0·1973 (3)
C(5)	0·7617 (4)	0·8883 (3)	0·1571 (3)
C(6)	0·6595 (3)	1·0358 (3)	−0·0058 (3)
C(7)	0·6303 (3)	1·0678 (2)	−0·1288 (3)
C(8)	0·6586 (4)	0·9905 (3)	−0·1930 (3)
C(9)	0·6347 (4)	1·0257 (3)	−0·3059 (3)
C(10)	0·5834 (4)	1·1382 (4)	−0·3527 (4)
C(11)	0·5556 (5)	1·2164 (4)	−0·2899 (4)
C(12)	0·5765 (4)	1·1815 (3)	−0·1789 (3)
C(13)	0·7921 (7)	0·4712 (5)	−0·0304 (5)
C(14)	0·9822 (5)	0·6387 (4)	0·3707 (4)
O(1)	0·7869 (2)	0·6922 (2)	0·0971 (2)
O(2)	0·7275 (2)	0·9299 (2)	0·0385 (2)
O(3)	0·6293 (3)	1·0973 (2)	0·0501 (2)
O(4)	0·9077 (3)	0·5433 (2)	0·0691 (2)
O(5)	0·8807 (2)	0·7375 (2)	0·3074 (2)
H(1)	0·813 (3)	0·686 (3)	−0·040 (3)
H(2)	1·092 (4)	0·733 (3)	0·134 (3)
H(3)	1·072 (4)	0·859 (3)	0·274 (3)
H(5₁)	0·820 (3)	0·948 (3)	0·223 (3)
H(5₂)	0·668 (3)	0·862 (2)	0·146 (3)
H(8)	0·691 (4)	0·913 (3)	−0·161 (3)
H(9)	0·662 (4)	0·972 (3)	−0·350 (4)
H(10)	0·570 (4)	1·168 (3)	−0·434 (3)
H(11)	0·521 (4)	1·291 (3)	−0·320 (3)
H(12)	0·555 (3)	1·237 (3)	−0·132 (3)
H(13₁)	0·832 (5)	0·390 (4)	−0·023 (4)
H(13₂)	0·702 (5)	0·474 (4)	−0·031 (4)
H(13₃)	0·740 (4)	0·501 (3)	−0·114 (4)
H(14₁)	1·076 (5)	0·666 (3)	0·416 (4)
H(14₂)	0·974 (5)	0·605 (4)	0·434 (4)
H(14₃)	0·951 (4)	0·575 (4)	0·305 (4)

Fig. 1. Molecular conformation viewed down the vector (0·29, 0·42, −0·04). The thermal ellipsoids are at the 50% probability level.

Discussion. Fig. 1 shows the molecule as viewed down the vector (0·29, 0·42, −0·04). The equations of some best planes (Blow, 1960) are given in Table 2. The χ^2 value for the 2,5-dihydrofuran ring (plane I) shows that it is not planar. The atoms C(2), C(3), C(4), O(1) are, however, planar (plane II). The displacement of C(1) from this plane is significant at 0·039 Å, which is roughly $10\sigma_\perp$ [$\sigma_\perp$ is the e.s.d. of C(1) in the direction normal to plane II]. The torsion angles of Table 3 (plane I) show that the methoxy groups are *cis* to each other.

The methyl groups exhibit an interesting arrangement. Their positions can be described by torsion angles (Table 3, plane II). These angles differ from the values which correspond to a symmetrical arrangement with respect to the dihydrofuran ring, where the absolute values have to be the same but with opposite signs.

The ester group at C(7) is planar, with the alcohol C(5) *cis* to the C=O group (Table 3, plane III). The conformation about O(2)—C(5) is shown in Fig. 2. The
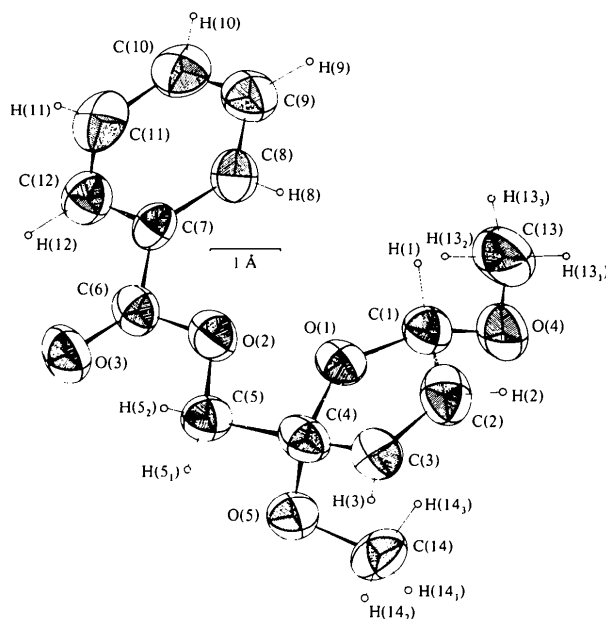
deviation from the ideal staggered arrangement suggested by Mathieson (1965) is significant and can be described as a rotation of the atoms bonded to C(5) by an angle of 10·5°.

The phenyl ring (plane IV) is planar and makes an angle with plane (III) of 6·9° and with (II) of 81·3°.

Table 2. *The best planes through the atoms*

(a) Coefficients of the planes
Each plane is defined by $AX + BY + CZ + D = 0$, where X, Y, Z, D are in Å relative to orthogonal axes parallel to **a**, **b**, **c***.

Plane	A	B	C	D	χ^2
(I)	0·04026	−0·73571	0·67610	4·69924	56·58
(II)	0·03671	−0·72694	0·68572	4·63801	0·17
(III)	0·73953	0·44877	0·50170	−10·81996	7·10
(IV)	0·77155	0·33889	0·53838	−9·71845	8·44

(b) Deviations from planes (in Å ×10³)
The deviations shown in parentheses refer to atoms which were not included in the calculation of the best plane.

Plane	C(1)	C(2)	C(3)	C(4)	O(1)	C(5)	O(4)
(I)	−15	12	−4	−6	13	(1210)	(1108)
(II)	(−39)	−1	1	−1	0	(1195)	(1072)

Plane	O(5)	C(13)	C(14)	H(1)	H(2)	H(3)	
(I)	(1097)	(980)	(2383)	(−850)	(62)	(−37)	
(II)	(1112)	(928)	(2392)	(−882)	(46)	(−23)	

Plane	C(5)	C(6)	C(7)	O(2)	O(3)	H(5₁)	H(5₂)
(III)	−3	−6	0	6	3	(739)	(−922)

Plane	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	
(IV)	4	3	−4	−2	8	−9	

	H(8)	H(9)	H(10)	H(11)	H(12)	
	(−24)	(62)	(38)	(7)	(−20)	

Table 3. *Torsion angles* (°)

Plane (I)

O(5)–C(4)–C(1)–O(4)	−3·44
O(5)–C(4)–C(1)–H(1)	148·34
C(5)–C(4)–C(1)–O(4)	−149·82
C(5)–C(4)–C(1)–H(1)	1·96

Plane (II)

O(1)–C(4)–O(5)–C(14)	68·35
O(1)–C(1)–O(4)–C(13)	80·53

Plane (III)

O(3)–C(6)–O(2)–C(5)	1·53
O(3)–C(6)–C(7)–C(8)	−175·72
O(3)–C(6)–C(7)–C(12)	6·29

Plane (IV)

C(6)–O(2)–C(5)–H(5₁)	−55·44
C(6)–O(2)–C(5)–H(5₂)	71·70
C(6)–O(2)–C(5)–C(4)	−169·49
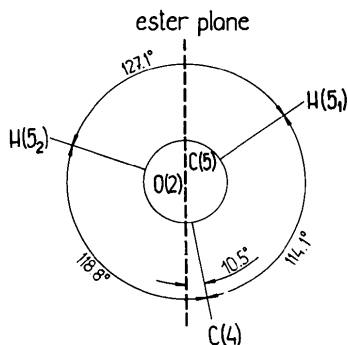
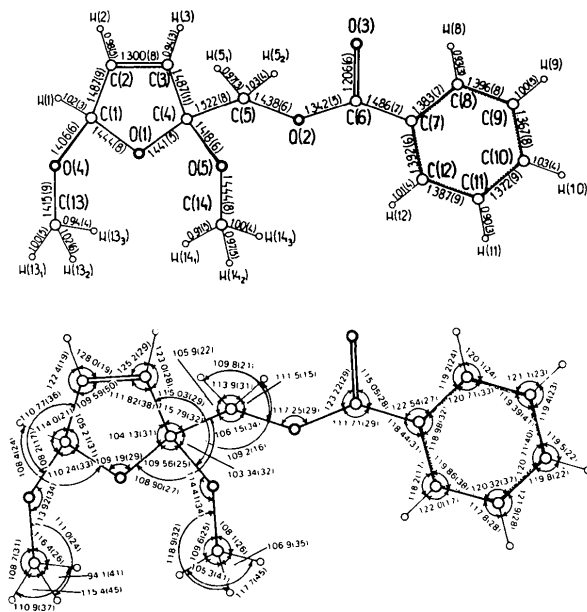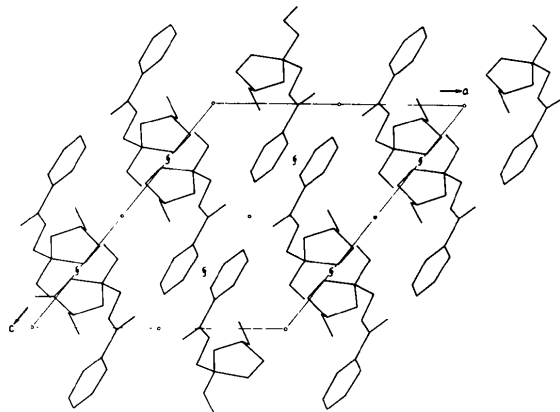
Fig. 2. Projection showing conformation about O(2)–C(5).

Fig. 3. Bond lengths (Å) and angles (°).

Fig. 4. Packing of molecules viewed down **b**.

Bond lengths and angles, uncorrected for thermal motion, are given in Fig. 3. Bond lengths in the phenyl ring and ester group are in agreement with Sutton (1965).

It was found from the χ^2 test that the chemically equivalent bond lengths in the 2,5-dimethoxy-2,5-dihydrofuran moiety do not differ significantly, with the exception of the C—O bonds in the methoxy groups. We tried to explain this by correcting the bond lengths for thermal motion (Busing & Levy, 1964), since C(13) has the largest eigenvalues of the anisotropic temperature factors. However, the corrections were identical and the explanation unsatisfactory. The molecular packing is shown in Fig. 4.

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