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Structure of Diethyl 2,3-*O*-Fluorenylidene-L-tartrate

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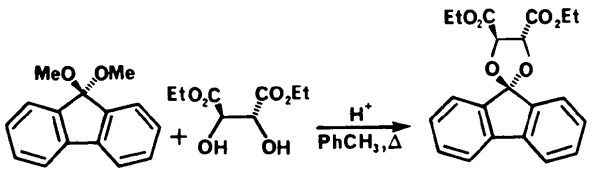
Abstract. $C_{21}H_{20}O_6$, $M_r = 368{\cdot}39$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}669\ (2)$, $b = 14{\cdot}975\ (2)$, $c = 10{\cdot}663\ (2)$ Å, $V = 1863\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}90$ cm^{-1}, $F(000) = 7768$, $T = 203$ K, $R = 0{\cdot}064$ for 1233 unique data with $I > 2\sigma(I)$. The molecular structure is very close to having idealized twofold geometry with the two substituents on the acetal carbon displaced 1·06 and 1·28 Å with respect to the dioxolane ring and the two ethoxycarbonyl groups on the 4 and 5 positions in equatorial positions; the torsional angle about the backbone is 87·4 (6)°.

Introduction. We have synthesized a homochiral dioxolane derived from fluorenone dimethylacetal and diethyl tartrate as part of a program in chiral organometallic reagents. The structure of the dioxolane, reported here, contains several remarkable features important for the study and possible application of homochiral dioxolanes in stereoselective synthesis.



Experimental. The acid-catalyzed reaction of diethyl-L-tartrate with fluorenone dimethylacetal in refluxing toluene gives the title compound. It is isolated as white prisms after purification by column chromatography and recrystallization from acetone/pentane. A colorless block approximately 0·20 × 0·40 × 0·40 mm in size was used for data collection in a thermostated nitrogen cold stream on a Rigaku AFC-6S diffractometer (Mo $K\alpha$ radiation, graphite monochromator, 203 K) using ω–2θ scans with a variable scan width where $\Delta\omega = (1{\cdot}05 + 0{\cdot}30\tan\theta)°$ and a scan rate of 2·0° min^{-1} in ω. Lattice parameters were determined from 25 reflections in the range $25{\cdot}0 < 2\theta < 28{\cdot}1°$. Weak reflections with $I < 10{\cdot}0\sigma(I)$ were rescanned a maximum of three times and counts accumulated. Stationary background counts were recorded at each side of the reflections; the ratio of peak:background counting time was 2:1. Three intensity standards were monitored every 200 reflections; no appreciable decay occurred. The crystal system was confirmed by a check of equivalent reflections and the space group determination was obtained from an analysis (Calabrese, 1972) of systematically absent reflections ($h00$: $h = 2n + 1$; $0k0$: $k = 2n + 1$; $00l$: $l = 2n + 1$) and Laue symmetry. A total of 8499 reflections, to a maximum 2θ of 55·1°, were collected in the range $-12 \le h \le 12$, $-15 \le k \le 15$, $-11 \le l \le 11$. Of 2472 unique reflections ($R_{int} = 0{\cdot}060$), 1233 had $I > 2\sigma(I)$ and were used in the structure solution and refinement. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). H atoms were included in calculated positions with isotropic thermal parameters at 120% of B_{eq} of the neighboring C atom. Full-matrix least-squares refinement of the structure, using the

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Table 1. *Fractional positional and equivalent isotropic thermal parameters*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
O1	0·6331 (3)	0·4497 (2)	0·8259 (4)	5·9 (2)
O2	0·5129 (3)	0·5298 (2)	0·9523 (4)	5·1 (2)
O3	0·7908 (4)	0·5763 (3)	0·7255 (4)	6·5 (2)
O4	0·8966 (3)	0·5123 (4)	0·8734 (5)	8·3 (3)
O5	0·5816 (5)	0·6385 (3)	1·1403 (5)	8·5 (3)
O6	0·7421 (3)	0·6700 (3)	1·0389 (5)	6·7 (2)
C1	0·4362 (7)	0·5450 (4)	0·6688 (7)	7·0 (4)
C2	0·3530 (9)	0·5519 (6)	0·583 (1)	9·3 (5)
C3	0·267 (1)	0·4910 (8)	0·5799 (9)	10·0 (6)
C4	0·2639 (6)	0·4201 (6)	0·6618 (8)	8·0 (4)
C5	0·3175 (6)	0·2704 (5)	0·8815 (8)	6·8 (4)
C6	0·3541 (8)	0·2221 (5)	0·980 (1)	8·6 (5)
C7	0·4470 (8)	0·2483 (4)	1·0472 (8)	7·9 (4)
C8	0·5067 (5)	0·3251 (4)	1·0179 (6)	5·7 (3)
C9	0·5146 (4)	0·4588 (3)	0·8629 (5)	4·5 (3)
C10	0·4371 (5)	0·4757 (4)	0·7529 (6)	5·2 (3)
C11	0·3517 (5)	0·4122 (4)	0·7487 (6)	5·4 (3)
C12	0·3715 (4)	0·3471 (3)	0·8498 (6)	5·1 (3)
C13	0·4684 (4)	0·3741 (3)	0·9182 (5)	4·5 (3)
C14	0·6148 (4)	0·5796 (3)	0·9344 (5)	4·4 (1)
C15	0·7003 (4)	0·5070 (3)	0·9004 (5)	4·3 (1)
C16	0·6423 (5)	0·6319 (4)	1·0510 (7)	5·5 (1)
C17	0·7847 (7)	0·7212 (5)	1·1424 (8)	8·0 (2)
C18	0·9032 (9)	0·7443 (6)	1·119 (1)	10·3 (3)
C19	0·7985 (5)	0·5377 (4)	0·8215 (6)	4·9 (1)
C20	1·0057 (7)	0·5290 (7)	0·801 (1)	9·3 (2)
C21	1·042 (1)	0·6082 (8)	0·845 (1)	13·3 (4)

Table 2. *Intramolecular distances* (Å) *and angles* (°)

O1—C9	1·445 (6)	C5—C6	1·34 (1)
O1—C15	1·407 (6)	C5—C12	1·35 (1)
O2—C9	1·428 (6)	C6—C7	1·36 (1)
O2—C14	1·417 (6)	C7—C8	1·38 (1)
O3—C19	1·179 (7)	C8—C13	1·367 (8)
O4—C19	1·328 (7)	C9—C10	1·502 (8)
O4—C20	1·51 (1)	C9—C13	1·499 (8)
O5—C16	1·192 (8)	C10—C11	1·378 (8)
O6—C16	1·303 (7)	C11—C12	1·472 (9)
O6—C17	1·432 (9)	C12—C13	1·405 (7)
C1—C2	1·34 (1)	C14—C15	1·520 (7)
C1—C10	1·371 (9)	C14—C16	1·504 (9)
C2—C3	1·36 (1)	C15—C19	1·494 (8)
C3—C4	1·38 (1)	C17—C18	1·45 (1)
C4—C11	1·387 (9)	C20—C21	1·34 (1)
C9—O1—C15	108·8 (4)	C4—C11—C12	131·5 (6)
C9—O2—C14	106·8 (4)	C10—C11—C12	108·7 (5)
C19—O4—C20	117·9 (5)	C5—C12—C11	132·2 (6)
C16—O6—C17	118·0 (6)	C5—C12—C13	119·3 (7)
C2—C1—C10	120·8 (8)	C11—C12—C13	108·4 (5)
C1—C2—C3	120·2 (8)	C8—C13—C9	130·0 (5)
C2—C3—C4	121·4 (8)	C8—C13—C12	120·8 (5)
C3—C4—C11	118·1 (8)	C9—C13—C12	109·2 (5)
C6—C5—C12	120·3 (7)	O2—C14—C15	101·9 (4)
C5—C6—C7	120·7 (7)	O2—C14—C16	110·0 (4)
C6—C7—C8	121·6 (7)	C15—C14—C16	115·4 (5)
C7—C8—C13	117·3 (6)	O1—C15—C14	101·8 (4)
O1—C9—O2	105·4 (4)	O1—C15—C19	107·3 (4)
O1—C9—C10	112·3 (5)	C14—C15—C19	114·7 (4)
O1—C9—C13	111·8 (4)	O5—C16—O6	125·0 (6)
O2—C9—C10	112·8 (4)	O5—C16—C14	125·3 (5)
O2—C9—C13	111·2 (4)	O6—C16—C14	109·7 (5)
C10—C9—C13	103·5 (4)	O6—C17—C18	109·2 (8)
C1—C10—C9	130·0 (6)	O3—C19—O4	124·7 (6)
C1—C10—C11	119·7 (6)	O3—C19—C15	125·6 (5)
C9—C10—C11	110·1 (5)	O4—C19—C15	109·7 (5)
C4—C11—C10	119·8 (7)	O4—C20—C21	103 (1)

TEXSAN crystallographic software package (Molecular Structure Corporation, 1985), minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)$, with 203 variables. All O atoms and the C atoms of the fluorene system were refined with anisotropic thermal parameters. A maximum shift/e.s.d. of 0·01 was used to determine convergence. Final $R = 0{\cdot}064$ and $wR = 0{\cdot}093$ and the goodness of fit parameter was 3·18. Maximum positive and negative peaks in the final difference Fourier map of +0·29 and −0·27 e Å^{-3} were observed. Neutral-atom scattering factors for inclusion in F_c, were taken from *International Tables for X-ray Crystallography* (1974).

Atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are given in Table 1.* Bond lengths and angles are presented in Table 2. A drawing of the molecular stucture is given in Fig. 1 and a view of the dioxolane ring and its substituents is presented in Fig. 2.

Discussion. There are now a number of reports of diastereoselective reactions directed by the incorporation of a resolved 1,2-disubstituted vicinal diol in the form of a homochiral dioxolane group generated by acetalization of a carbonyl group. Stereoselection may be achieved as a result of selective cleavage of one of the bonds to the acetal carbon (Alexis, Mangeney, Ghribi, Marek, Sedrani, Guir & Normant, 1988) as in certain nucleophilic substitutions (Solladie-Cavallo, Suffert & Gordon, 1988) and isomerization reactions (Naruse & Yamamoto, 1988). But even in cases when the dioxolane remains formally intact it can still dramatically affect the stereoselection of many reactions with postulated mechanisms including transient ring opening (Castaldi, Cavicchioli, Giordano & Uggeri, 1987), stereoelectronic effects due to the interaction of the lone pairs of the dioxolane ring oxygens with an α,β-unsaturated system (Mash, Nelson & Heidt, 1987; Mori, Arai, Yamamoto, Nakai & Arai, 1986) and actual complexation of a reagent as part of the mechanism (Utaka, Fujii & Takeda, 1986). This final idea has been extended, in the case of dioxolanes with pendant esters, to a powerful strategy involving intramolecular attack of the ester as part of a bromo-lactonization reaction (Suzuki, Kimura & Terashima, 1985).

Despite this diversity, there has been relatively little work done on the critical question of the conformational preferences of the 4 and 5 positions of a

* Lists of H-atom parameters, anisotropic thermal parameters, torsion angles, least-squares planes, intermolecular contacts and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52477 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

4,5-*trans*-disubstituted dioxolane (those that, if equivalent, render the system homochiral), although a fair amount is known about 4,5-*cis*-disubstituted molecules (Willy, Binsch & Eliel, 1970; Bukin, Zakharov & Gren', 1983). This is particularly important because directing strategies do not always work well, as in the complete non-specificity in the addition of chromium tricarbonyl to acetals derived from flourenone (Schlögl & Schölm, 1978; Wink, 1989). In point of fact, as this study suggests, the highly fluxional nature of five-membered heterocycles and of 1,3-dioxolanes in particular (Cremer & Pople, 1975) means that, even where one or another structure may be observed in solution in the solid state, other isomers are almost certainly dynamically accessible in solution.

The molecule reported in this study is unremarkable in an examination of any of the individual bond lengths and angles involved, but it is an extreme in the amount of symmetry present; it has idealized twofold symmetry in solution, and this is very nearly true in the crystal as well. This is shown by a more careful examination of the geometry about the acetal carbon, presented in Fig. 2. Note that, besides consistency in the bond lengths and angles, the two carbons of the fluorenone system are symmetrically disposed with respect to the dioxolane ring plane. The distances of the atoms C10 and C13 to the least-squares plane of the dioxolane are 1·06 and 1·28 Å respectively. Thus, neither half of the flurorenone system is distinguished from the other sterically. Of course, the presence of the homochiral backbone means there are two enantiofaces of the fluorenone system and one would hope to be able to distinguish them in reactions (such as chromium complexation). However, the two directing groups are lying in equatorial positions, with a torsion angle about the dioxolane backbone (C16—C14—C15—C19) of 87·4 (6)°.

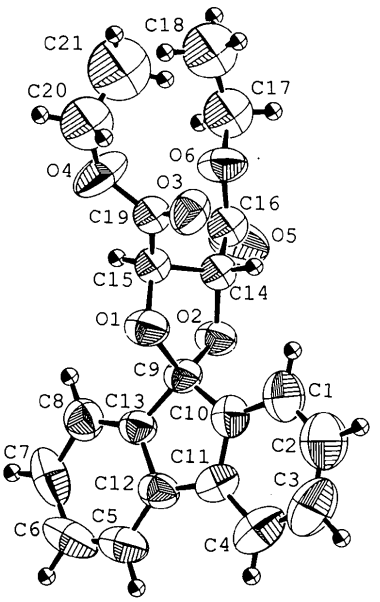

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the compound with thermal ellipsoids given at the 50% probability level.

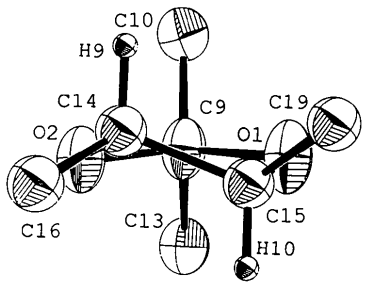

Fig. 2. *ORTEP*II (Johnson, 1976) drawing of the acetal ring and attached atoms with thermal ellipsoids given at the 30% probability level.

One might be tempted to infer a connection between the equatorial substituents and the symmetry about the acetal carbon, but in fact the literature presents two contradictions of this. One report (Bose, Manhas, van der Veen, Bari, Wagle, Hegde & Krishan, 1985) of an isopropylidene acetal of a β-lactam includes an idealized twofold symmetry about the acetal carbon (the two substituents are displaced by 1·22 and 1·27 Å) and two *trans* groups on the diol portion that are in approximately axial positions (the appropriate torsion angle is 145°). Another structure (Franck, Subramaniam, John & Blount, 1984), also of an isopropylidene acetal, has marked asymmetry about the acetal carbon (with subtituents 0·68 and 1·65 Å from the acetal least-squares plane) along with *trans*-equatorial groups on the diol backbone (torsion angle 72·5°).

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Structure of Calcium Tetrasulfinpyrazonate Dihydrate

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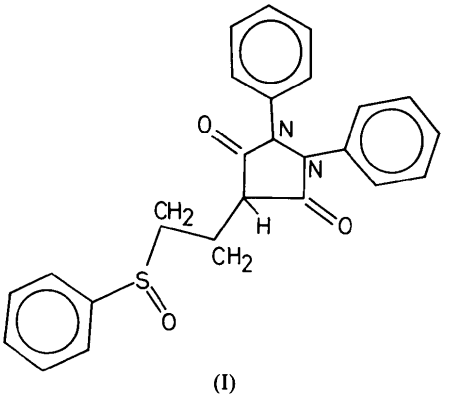
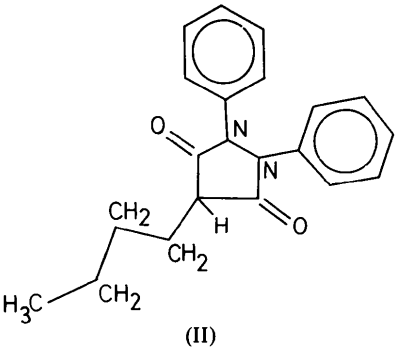
Abstract. Calcium tetrakis{1,2-diphenyl-4-[2-(phenylsulfinyl)ethyl]-3,5-pyrazolidinedionate} dihydrate, $Ca(C_{23}H_{19.5}N_2O_3S)_4.2H_2O$, $M_r = 1615.91$, triclinic, $P\bar{1}$, $a = 11.336$ (2), $b = 13.830$ (4), $c = 14.075$ (11) Å, $\alpha = 76.00$ (5), $\beta = 85.82$ (3), $\gamma = 85.11$ (2)°, $V = 2130$ (2) Å^3, $Z = 1$, $D_m = 1.331$ (5), $D_x = 1.319$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.27$ mm^{-1}, $\mu R = 0.03$, $F(000) = 886$, $T = 298$ K, $R = 0.085$ for 4325 observed reflections with $I \geq 2\sigma(I)$. There are two partly deprotonated sulfinpyrazone molecules, one calcium and one water molecule in the asymmetric part of the unit cell. The conformations of the two crystallographically independent molecules are significantly different. The coordination geometry of the calcium cation is sixfold with octahedral symmetry. The distance of 2.450 (8) Å between the carbonyl O atoms of the crystallographically independent sulfinpyrazone molecules suggests strong hydrogen bonding between them. The crystal structure is stabilized by a network of intermolecular hydrogen bonds, van der Waals interactions and coordination bonds involving the calcium cation.

Introduction. Sulfinpyrazone (I) in which a phenylsulfinylethyl group replaces the butyl side chain of phenylbutazone (II) was synthesized by Pfister & Haflinger (1961). This compound increases the urinary uric acid excretion by inhibiting renal tubular reabsorption of uric acid and thereby reduces the plasma urate concentration and enhances the renal clearance of uric acid (Gutman, 1966). These properties of sulfinpyrazone have led to the intensive therapeutic applications of this compound as a uricosuric agent. The crystal structure of sulfinpyrazone has been reported earlier by Go & Kartha (1984). We have determined the structure of the calcium salt of sulfinpyrazone to elucidate its conformational and electronic properties so that its mechanism of action can be understood.



(I)



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