

References

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2-Methoxymethoxybenzoic Acid, C₉H₁₀O₄*

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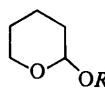
Abstract. $M_r = 182.18$, triclinic, $P\bar{1}$, $a = 4.964$ (1), $b = 7.918$ (2), $c = 11.777$ (3) Å, $\alpha = 99.99$ (2), $\beta = 91.61$ (2), $\gamma = 106.15$ (2)°, $U = 436.5$ Å³, $Z = 2$, $D_x = 1.39$ g cm⁻³, $M_o K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.1$ mm⁻¹, $F(000) = 192$, $T = 293$ K, $R = 0.062$ for 1532 unique reflections. The carboxylic acid groups are paired by hydrogen bonding, as is usual. The crystal structure does not reflect the unusual reactivity of the compound towards acetal hydrolysis.

Introduction. We are interested in correlations between bond length and reactivity. In both axial and equatorial series of tetrahydropyranyl acetals (1) the length of the exocyclic C–OR bond increases with increasing electron withdrawal in the R group (Jones & Kirby, 1979, 1984), and we find a simple linear correlation between the length of the bond and the ease with which it is broken in hydrolysis.

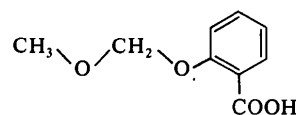
We are currently examining a large number of different systems, and have so far found evidence for variable (C–O and P–O) bond lengths and similar correlations with reactivity in nine out of ten series of compounds (Allen & Kirby, 1984; Jones & Kirby, 1984). Another system of interest is the simplest series of acetals, MeOCH₂OR: we recently reported the crystal structure of methoxymethoxy-2,4-dinitro-

benzene (Jones, Sheldrick, Glenn & Kirby, 1983), and are working on other compounds in this series.

If we can establish relationships between bond length and normal reactivity, it becomes of interest to look at compounds which show abnormal reactivity. One class of particular interest is that of compounds which undergo intramolecular reactions, and we have found linear relationships between reactivity and interatomic distances in two series of sulphonamides and carboxylic esters, which undergo intramolecular nucleophilic and general base catalysis, respectively (Jager, Graafland, Schenk, Kirby & Engberts, 1983). We examine here an acetal which is known to be hydrolysed with intramolecular general acid catalysis. This mode of catalysis is very efficient for derivatives of salicylic acid (Kirby, 1980) – so much so that acetal (1, R = 2-carboxyphenyl) is too reactive to prepare and crystallize (Glenn, 1982). We have therefore examined the more stable acetal (2) (Craze & Kirby, 1974). Colourless rectangular blocks of (2), extremely sensitive to X-rays, were grown by liquid diffusion of hexane into a chloroform solution.



(1)

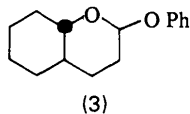


(2)

* Crystal Structures of Acetals. 23. Part 22: Jones, Sheldrick, Kirby & Briggs (1983).

Experimental. 1936 profile-fitted reflections (Clegg, 1981) measured, Stoe four-circle diffractometer, monochromated Mo $K\alpha$ radiation ($2\theta_{\max}$ 50°); 3 standard reflections decreased in intensity by ca 40% and data were scaled accordingly; crystal $0.6 \times 0.35 \times 0.2$ mm; no absorption correction; merging equivalents gave 1532 unique reflections (R_{int} 0.023), of which 1133 with $F > 4\sigma(F)$ were used for all calculations; cell constants refined from 2θ values of 30 reflections in the range $-20 < 2\theta < 24^\circ$; structure solution by routine direct methods; refinement on F to R 0.062, R_w 0.067, $w^{-1} = \sigma^2(F) + 0.0008 F^2$; non-H atoms anisotropic, acidic H refining freely, other H using riding model with C—H 0.96 Å, H—C—H 109.5° , $U(\text{H}) = 1.2 U(\text{C})$; Δ/σ 0.01, 125 parameters, $S = 2.0$; max. and min. heights in final $\Delta\rho$ map $+0.25, -0.31 \text{ e \AA}^{-3}$; calculations performed with *SHELXTL* (Sheldrick, 1978); atomic scattering factors of *SHELXTL* used.*

Discussion. Final atomic coordinates and derived parameters are given in Tables 1 and 2, diagrams of the structure in Figs. 1 and 2. The molecular structure of (2) shows no hint of its unusual reactivity. The conformation about the acetal centre is close to (+*sc*, +*sc*), and the length of the 'bond to the leaving group', C(11)—O(1), is identical, within experimental error, with that in the phenyl acetal (3) — 1.431 (4) compared



with 1.433 (4) Å (Jones, Kennard, Chandrasekhar & Kirby, 1978). This is to be expected, since intramolecular catalysis of hydrolysis involves a key hydrogen-bonding interaction between the phenolic oxygen [O(1)] and the neighbouring carboxyl group. In the crystal, however, the CO_2H group is involved, as usual for a carboxylic acid, in H-bonded dimer formation, with $\text{O}(4)\cdots\text{O}(3')$ 2.67 (1), $\text{O}(4)\cdots\text{H}'$ 1.76 (2) Å (second atoms at $2-x, 1-y, 1-z$). The dihedral angle between the planes of the aromatic ring and the carboxylic acid group is $3(1)^\circ$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39056 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

| | x | y | z | $U_{\text{eq}}/U_{\text{iso}}$ |
|-------|------------|-----------|-----------|--------------------------------|
| C(1) | 3663 (6) | 5760 (3) | 2664 (2) | 42 (1)* |
| C(2) | 5778 (5) | 6793 (3) | 3521 (2) | 39 (1)* |
| C(3) | 6243 (6) | 8639 (3) | 3762 (3) | 50 (1)* |
| C(4) | 4659 (7) | 9468 (4) | 3184 (3) | 57 (1)* |
| C(5) | 2628 (6) | 8427 (4) | 2341 (3) | 56 (1)* |
| C(6) | 2110 (6) | 6600 (4) | 2074 (2) | 52 (1)* |
| C(7) | 7560 (6) | 5988 (3) | 4169 (2) | 41 (1)* |
| C(11) | 738 (7) | 2853 (4) | 1744 (3) | 55 (1)* |
| C(12) | 3180 (8) | 2239 (6) | 111 (4) | 87 (2)* |
| O(1) | 3203 (4) | 3948 (2) | 2452 (2) | 58 (1)* |
| O(2) | 987 (5) | 2884 (3) | 577 (2) | 63 (1)* |
| O(3) | 9356 (4) | 7155 (2) | 4965 (2) | 57 (1)* |
| H | 10297 (89) | 6543 (55) | 5337 (37) | 112 (12) |
| O(4) | 7426 (4) | 4404 (2) | 3989 (2) | 55 (1)* |

* Equivalent isotropic U calculated from anisotropic U by $U_{\text{eq}} = \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 2. Bond lengths (Å), bond angles and torsion angles ($^\circ$)

| | | | |
|-----------------------|------------|----------------------|------------|
| C(1)—C(2) | 1.402 (4) | C(1)—C(6) | 1.391 (6) |
| C(1)—O(1) | 1.365 (4) | C(2)—C(3) | 1.391 (5) |
| C(2)—C(7) | 1.489 (5) | C(3)—C(4) | 1.386 (6) |
| C(4)—C(5) | 1.371 (5) | C(5)—C(6) | 1.373 (5) |
| C(7)—O(3) | 1.312 (4) | C(7)—O(4) | 1.218 (4) |
| C(11)—O(1) | 1.431 (4) | C(11)—O(2) | 1.386 (5) |
| C(12)—O(2) | 1.412 (6) | O(3)—H | 0.91 (5) |
| | | | |
| C(2)—C(1)—C(6) | 119.5 (3) | C(2)—C(1)—O(1) | 117.8 (4) |
| C(6)—C(1)—O(1) | 122.7 (3) | C(1)—C(2)—C(3) | 118.6 (4) |
| C(1)—C(2)—C(7) | 122.4 (3) | C(3)—C(2)—C(7) | 119.0 (3) |
| C(2)—C(3)—C(4) | 121.7 (3) | C(3)—C(4)—C(5) | 118.5 (4) |
| C(4)—C(5)—C(6) | 121.7 (4) | C(1)—C(6)—C(5) | 120.1 (3) |
| C(2)—C(7)—O(3) | 113.7 (3) | C(2)—C(7)—O(4) | 124.4 (3) |
| O(3)—C(7)—O(4) | 121.9 (4) | O(1)—C(11)—O(2) | 112.7 (3) |
| C(1)—O(1)—C(11) | 118.4 (3) | C(11)—O(2)—C(12) | 114.4 (4) |
| | | | |
| C(6)—C(1)—C(2)—C(3) | 0.5 (5) | C(6)—C(1)—C(2)—C(7) | -178.8 (4) |
| O(1)—C(1)—C(2)—C(3) | -178.9 (4) | O(1)—C(1)—C(2)—C(7) | 1.8 (5) |
| C(2)—C(1)—C(6)—C(5) | -0.7 (5) | O(1)—C(11)—C(6)—C(5) | 178.7 (4) |
| C(2)—C(1)—O(1)—C(11) | 168.5 (4) | C(6)—C(1)—O(1)—C(11) | -10.9 (5) |
| C(1)—C(2)—C(3)—C(4) | 0.5 (5) | C(7)—C(2)—C(3)—C(4) | 179.8 (4) |
| C(1)—C(2)—C(7)—O(3) | -177.7 (3) | C(1)—C(2)—C(7)—O(4) | 3.0 (5) |
| C(3)—C(2)—C(7)—O(3) | 3.1 (5) | C(3)—C(2)—C(7)—O(4) | -176.2 (4) |
| C(2)—C(3)—C(4)—C(5) | -1.3 (6) | C(3)—C(4)—C(5)—C(6) | 1.1 (6) |
| C(4)—C(5)—C(6)—C(1) | -0.1 (6) | O(2)—C(11)—O(1)—C(1) | 76.2 (4) |
| O(1)—C(11)—O(2)—C(12) | 61.3 (4) | | |

Sign convention as defined by Klyne & Prelog (1960)

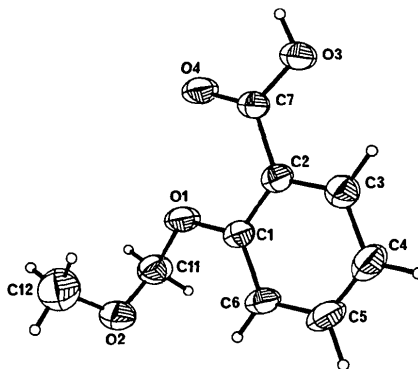


Fig. 1. Thermal ellipsoid plot (50% level) of (2), showing the atom numbering scheme.

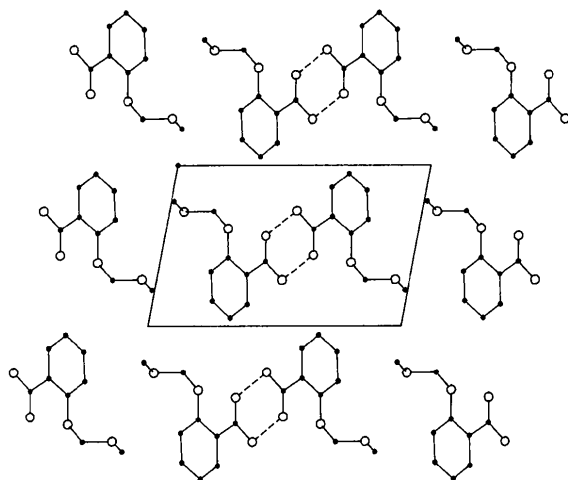


Fig. 2. Packing plot of (2) projected down *a*. Hydrogen bonds are indicated by dashed lines.

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Bis(cyclohexylammonium) Propargyl Phosphate Dihydrate,
 $2C_6H_{14}N^+ \cdot C_3H_3O_4P^{2-} \cdot 2H_2O^*$

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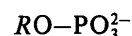
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Abstract. $M_r = 370.43$, monoclinic, $P2_1/c$, $a = 14.186$ (5), $b = 6.355$ (2), $c = 21.417$ (9) Å, $\beta = 105.55$ (5)°, $U = 2034$ Å³, $Z = 4$, $D_x = 1.21$ Mg m⁻³, $F(000) = 808$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.16$ mm⁻¹, room temperature, $R = 0.080$, $R_w = 0.057$ for 1978 unique reflections. The P–OR bond length, 1.626 (4) Å, is appreciably longer than in related ester dianions with $R = \text{Me}$, Et. A complex hydrogen-bonding network links the hydrophilic residues in bands parallel to z .

Introduction. As part of an investigation of correlations between bond length and reactivity, we have determined crystal structures for a large number of acetals (Jones, Sheldrick, Kirby & Briggs, 1984, and references therein). It is important to establish whether the

observed linear correlations (between the length of a bond in the crystal and the free energy of activation for its cleavage in solution) can be extended to related compounds. Our approach is to measure the length of the X–OR bond in a series of compounds in which the effective electronegativity of oxygen is varied by increasing electron demand by the group R . This is the first paper in a series on phosphate monoester dianions (1).



(1)

These compounds are of particular interest because their hydrolysis has many features in common with that of the tetrahydropyranyl acetals (2), for which we first observed a bond-length–reactivity correlation (Jones &

* Phosphate Ester Dianions. 1.