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Bond Length and Reactivity. Structure of 1-Methoxymethoxy-3,5-dinitrobenzene, $C_8H_8N_2O_6^*$

BY PETER G. JONES AND GEORGE M. SHELDRIK

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

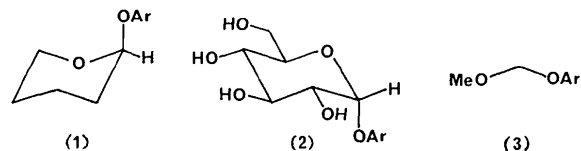
AND ANTHONY J. KIRBY AND ANDREW J. BRIGGS

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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Abstract. $M_r = 228.17$, orthorhombic, $P2_12_12_1$, $a = 5.387$ (2), $b = 11.053$ (2), $c = 16.783$ (3) Å, $V = 999.3$ (5) Å³, $Z = 4$, $D_x = 1.516$ (8) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.0$ cm⁻¹, $F(000) = 472$, $T = 293$ K. $R = 0.041$ for 1654 observed reflections. The C–O bond length to the leaving group (referred to acetal hydrolysis) is 1.431 (3) Å; this forms part of a linear correlation between bond length and reactivity in formaldehyde acetals $\text{MeOCH}_2\text{—OR}$. The conformation about the acetal centre is close to (*-sc*, *-sc*) with torsion angles as expected for an acyclic acetal.

Introduction. Our work on bond length and reactivity in tetrahydropyranyl acetal (1) and glucoside systems (Jones & Kirby, 1984; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984) has shown that there is a very simple relationship between the length of an acetal C–OR bond and the rate at which it is broken hydrolytically: in a given series, the longer the bond, the more easily it is broken. Furthermore, there is some evidence that this generalization also holds for comparisons of acetals from different series. Thus in aryl α -glucosides (2), which are many orders of magnitude less reactive than the parent tetrahydropyranyl acetals (1), the exocyclic acetal C–OAr bond is always substantially shorter than the C–OAr bond of the corresponding axial acetal (1).



As an initial test of the strength of this second generalization, we recently determined the crystal structure of (3, Ar = 2,4-dinitrophenyl) (Jones, Sheldrick, Glenn & Kirby, 1983). The reactivity of this acetal is known to lie between that of the 2,4-dinitrophenyl derivatives of (1) and (2), and a similar relationship was found for the length of the C–OAr bond broken in the reaction.

A more reliable measure of the ease with which a bond can be stretched and, presumably, broken is the sensitivity of its length to the nature of the leaving group. The slope of the (good) linear plot of the length of the C–OAr bond of axial acetals (1) against the pK_a of the conjugate acid (ArOH) of the leaving group, is some 6.5 times greater than that of the corresponding plot for α -glucosides (Briggs *et al.*, 1984), which show very little dependence on Ar. It is thus of interest to measure the sensitivity of the C–OR bond length of a series of formaldehyde acetals, $\text{MeOCH}_2\text{—OR}$, to the nature of the group R. Five structures containing this unit have been reported recently (Jones, Kennard, Kirby & Osborne, 1978; Jones, Kennard, Kirby, Osborne & Malik, 1978; Egert, Cruse & Kennard, 1983; Jones, Sheldrick, Kirby & Briggs, 1984; Jones *et*

* Crystal Structures of Acetals. 24. Part 23: Jones, Sheldrick, Kirby & Briggs (1984).

al., 1983). We here report the crystal structure of a further compound, of intermediate pK_a of ArOH (3, Ar = 3,5-dinitrophenyl), and the sensitivity of the length of the bond C—OR of acetals MeOCH_2OR to the pK_a of ROH.

Experimental. Colourless prisms of 1-methoxymethoxy-3,5-dinitrobenzene (3, Ar = 3,5-dinitrophenyl, prepared from methoxymethoxy chloride and the phenolate) were obtained by the diffusion of diisopropyl ether into a solution in ethyl acetate.

Crystal $0.55 \times 0.4 \times 0.15$ mm. 3482 profile-fitted intensities (Clegg, 1981), recorded on a Stoe—Siemens four-circle diffractometer. Monochromated Mo $K\alpha$ radiation, $2\theta_{\text{max}} 55^\circ$. Three check reflections, no significant intensity change. $R_{\text{int}} 0.022$ for 2273 unique reflections (index ranges after merging: $h -6 \rightarrow +6$, $k 0 \rightarrow 14$, $l 0 \rightarrow 21$), 1654 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*, written by GMS). Cell constants refined from 2θ values of 40 reflections in range $20\text{--}23^\circ$. No absorption correction.

Structure solution by routine direct methods. Refinement on F to $R 0.041$, $wR 0.040$ [all non-H atoms anisotropic; H atoms included using riding model with C—H 0.96 \AA , H—C—H 109.5° , $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$; 149 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0.0002 F^2$, $S = 1.50$, slope of normal probability plot 1.35; extinction correction of the form $F_{\text{corr}} = F_c(1 + xF_c^2/\sin 2\theta)^{-0.25}$ with $x = 1.1(1) \times 10^{-5}$]. No attempt to assign an absolute structure (Jones, 1984). Max. $\Delta/\sigma 0.04$. Max. and min. heights in final $\Delta\rho$ map $+0.29$ and -0.20 e \AA^{-3} . Atomic scattering factors those of *SHELXTL*.

Discussion. Final atomic coordinates are given in Table 1 with derived parameters in Table 2.*

The conformation about the acetal centre (see Fig. 1) is close to ($-sc$, $-sc$), with torsion angles C(12)—O(2)—C(11)—O(1) and O(2)—C(11)—O(1)—C(1) of -70.4 and -64.1° respectively, as expected for an acyclic acetal (Jeffrey, Pople, Binkley & Vishveshwara, 1978). The same conformation is observed for all but one (Egert *et al.*, 1983) of the methoxymethyl acetals for which crystal structures are available, and for tetrahydropyranyl acetals and α -glucosides. Comparisons of bond lengths between the three series of compounds are thus unaffected by conformational differences.

The length of the C—OAr bond in 1-methoxymethoxy-3,5-dinitrobenzene is $1.431(3) \text{ \AA}$, lying between the lengths expected [from the linear correlations

* 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 42264 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

given by Briggs *et al.* (1984)] for the corresponding bonds of an axial tetrahydropyranyl acetal (1.450 \AA) or α -glucoside (1.420 \AA) derived from a phenol of pK_a 6.68 (Martin & Butler, 1939). The plot of the C—OR bond length against the pK_a of ROH for the five organic compounds for which accurate crystal structures are available* (Fig. 2) gives a good straight line (correction

* One compound omitted from the plot, because no value is available for the pK_a of ROH, is the enol of an ester of 2-oxocyclopentene-1-carboxylic acid. The C—OR bond length in 2-methoxymethoxycyclopentene-1-carboxylic acid (Jones, Kennard, Kirby & Osborne, 1978) is $1.445(3) \text{ \AA}$, corresponding to a pK_a of 5.2, according to the bond length— pK_a correlation.

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
C(1)	5299 (4)	2551 (2)	2626 (1)	53 (1)
C(2)	3548 (4)	1681 (2)	2817 (1)	56 (1)
C(3)	1790 (4)	1391 (2)	2252 (1)	53 (1)
C(4)	1625 (4)	1933 (2)	1514 (1)	54 (1)
C(5)	3372 (4)	2811 (1)	1361 (1)	50 (1)
C(6)	5215 (4)	3122 (2)	1888 (1)	52 (1)
N(3)	-74 (4)	465 (2)	2456 (1)	67 (1)
O(31)	-69 (3)	66 (1)	3137 (1)	80 (1)
O(32)	-1529 (4)	154 (2)	1942 (1)	100 (1)
N(5)	3249 (4)	3484 (1)	605 (1)	63 (1)
O(51)	4699 (4)	4307 (1)	498 (1)	84 (1)
O(52)	1688 (4)	3189 (2)	125 (1)	93 (1)
O(1)	7207 (3)	2908 (1)	3107 (1)	72 (1)
C(11)	7263 (4)	2471 (2)	3909 (1)	73 (1)
O(2)	5290 (4)	2869 (1)	4349 (1)	73 (1)
C(12)	5405 (7)	4132 (2)	4526 (2)	98 (1)

* Equivalent isotropic U calculated from anisotropic U .

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

C(1)—C(2)	1.385 (4)	C(1)—C(6)	1.391 (4)
C(1)—O(1)	1.366 (3)	C(2)—C(3)	1.378 (4)
C(3)—C(4)	1.378 (4)	C(3)—N(3)	1.474 (4)
C(4)—C(5)	1.376 (4)	C(5)—C(6)	1.373 (4)
C(5)—N(5)	1.472 (3)	N(3)—O(31)	1.225 (4)
N(3)—O(32)	1.214 (4)	N(5)—O(51)	1.212 (4)
N(5)—O(52)	1.209 (4)	C(11)—O(1)	1.431 (3)
C(11)—O(2)	1.367 (4)	C(12)—O(2)	1.428 (4)
C(2)—C(1)—C(6)	119.9 (3)	C(2)—C(1)—O(1)	125.2 (3)
C(6)—C(1)—O(1)	114.9 (3)	C(1)—C(2)—C(3)	118.1 (3)
C(2)—C(3)—C(4)	124.1 (3)	C(2)—C(3)—N(3)	118.0 (3)
C(4)—C(3)—N(3)	117.8 (3)	C(3)—C(4)—C(5)	115.5 (3)
C(4)—C(5)—C(6)	123.4 (3)	C(4)—C(5)—N(5)	119.2 (3)
C(6)—C(5)—N(5)	117.4 (3)	C(1)—C(6)—C(5)	118.9 (3)
C(3)—N(3)—O(31)	117.7 (3)	C(3)—N(3)—O(32)	118.1 (3)
O(31)—N(3)—O(32)	124.2 (3)	C(5)—N(5)—O(51)	118.5 (3)
O(51)—N(5)—O(52)	117.9 (3)	O(51)—N(5)—O(52)	123.6 (3)
C(1)—O(1)—C(11)	118.4 (3)	O(1)—C(11)—O(2)	112.5 (3)
C(11)—O(2)—C(12)	113.2 (3)		
C(6)—C(1)—C(2)—C(3)	1.4 (4)*	O(1)—C(1)—C(2)—C(3)	-177.6 (3)
C(2)—C(1)—C(6)—C(5)	0.3 (4)	O(1)—C(1)—C(6)—C(5)	179.4 (3)
C(2)—C(1)—O(1)—C(11)	-8.1 (4)	C(6)—C(1)—O(1)—C(11)	172.9 (3)
C(1)—C(2)—C(3)—C(4)	-1.6 (4)	C(1)—C(2)—C(3)—N(3)	-180.0 (3)
C(2)—C(3)—C(4)—C(5)	0.1 (4)	N(3)—C(3)—C(4)—C(5)	178.5 (3)
C(2)—C(3)—N(3)—O(31)	5.1 (4)	C(2)—C(3)—N(3)—O(32)	-175.5 (3)
C(4)—C(3)—N(3)—O(31)	-173.3 (3)	C(4)—C(3)—N(3)—O(32)	6.0 (4)
C(3)—C(4)—C(5)—C(6)	1.7 (4)	C(3)—C(4)—C(5)—N(5)	-176.6 (3)
C(4)—C(5)—C(6)—C(1)	-1.9 (4)	N(5)—C(5)—C(6)—C(1)	176.4 (3)
C(4)—C(5)—N(5)—O(51)	175.4 (3)	C(4)—C(5)—N(5)—O(52)	-4.1 (4)
C(6)—C(5)—N(5)—O(51)	-3.0 (4)	C(6)—C(5)—N(5)—O(52)	177.5 (3)
C(1)—O(1)—C(11)—O(2)	-64.1 (4)	O(1)—C(11)—O(2)—C(12)	-70.4 (3)

* Sign convention as defined by Klyne & Prelog (1960).

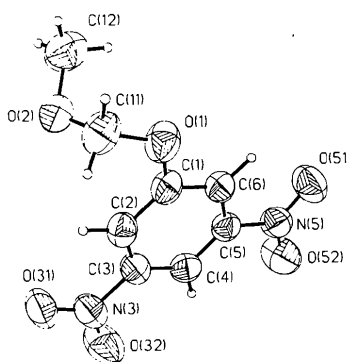


Fig. 1. Thermal ellipsoid plot (50% level) of the molecule of (3, Ar = 3,5-dinitrophenyl), showing the atom-numbering scheme.

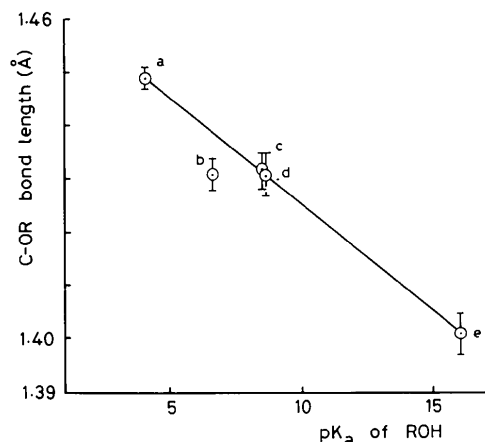


Fig. 2. Plot of the CH_2-OR bond length vs the pK_a of ROH for methoxymethyl acetals $MeOCH_2OR$. Data points are for (a) $R = 2,4$ -dinitrophenyl (Jones *et al.*, 1983); (b) $R = 3,5$ -dinitrophenyl (this paper); (c) $R = 3$ -(but-2-enoic acid) (Jones, Kennard, Kirby, Osborne & Malik, 1978); (d) $R = 2$ -carboxyphenyl (Jones, Sheldrick, Kirby & Briggs, 1984); and (e) a methoxymethoxy derivative of a steroid (Egert *et al.*, 1983). (A second diastereoisomer of this last compound is omitted, because the acetal group has an extended conformation.) pK_a 's used are 4.11 for 2,4-dinitrophenol (Jencks & Regenstein, 1976), 6.68 for 3,5-dinitrophenol (Martin & Butler, 1939), 8.5 for the enol of ethyl acetoacetate (Alcais & Brouillard, 1972), 8.6 for methyl salicylate (Bromilow, Khan & Kirby, 1972), and 16 for the 3-OH group of a steroid. The equation of the least-squares line correlating the five points is given in the text. Omitting point (b) improves the correlation coefficient to 0.9999.

coefficient $r = 0.979$) of slope -3.74×10^{-3} . This slope is a measure of the sensitivity of the length of the C-OR bond to the nature of the leaving group (RO^-), and it too lies between the slopes observed for the corresponding plots for axial tetrahydropyranyl acetals and α -glucosides (6.5×10^{-3} and 1.0×10^{-3} respectively: Briggs *et al.*, 1984).

Thus the length of the C-OR bond (to the more electronegative oxygen atom) in three series of acetals with varying substitution at carbon shows a linear correlation with reactivity as the leaving group OR is varied. Moreover, the sensitivity to the nature of the leaving group RO^- , which is a measure of how easy it is to stretch the C-OR bond in the ground state, is also higher in the more reactive series of compounds.

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