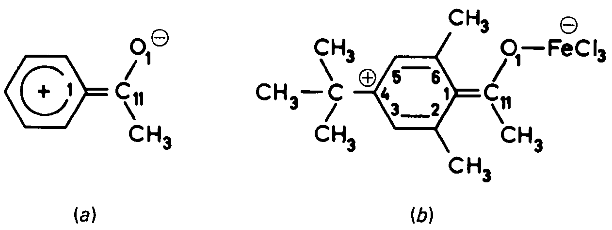
Table 3. *Comparison of relevant bond lengths* (Å), *in connection with conjugation, in acetophenone, in Lig and in Lig.* $FeCl_3$

	Acetophenone	Lig	Lig. $FeCl_3$
C(1)—C(2)	1·389 (2)	1·388 (3)	1·415 (4)
C(2)—C(3)	1·391 (2)	1·398 (5)	1·379 (4)
C(3)—C(4)	1·383 (3)	1·384 (4)	1·392 (4)
C(4)—C(5)	1·382 (3)	1·378 (3)	1·386 (4)
C(5)—C(6)	1·385 (3)	1·400 (5)	1·380 (4)
C(1)—C(6)	1·392 (2)	1·386 (5)	1·406 (4)
C(1)—C(11)	1·494 (2)	1·515 (5)	1·461 (4)
C(11)—O(1)	1·216 (2)	1·202 (5)	1·243 (3)



(*a*) (*b*)

Fig. 2. Resonance structures of (*a*) acetophenone and (*b*) Lig.$FeCl_3$.

Because of the increasing double-bond character, the bond lengths C(2)—C(3), C(5)—C(6) and C(1)—C(11) in Lig.$FeCl_3$ will be shorter than the corresponding values in Lig and, because of the increasing single-bond character, the bond lengths C(1)—C(2), C(3)—C(4), C(4)—C(5), C(6)—C(11) and C(11)—O(1) will be longer. These conjugational effects are confirmed by the distances given in Table 3. Apparently, the resonance structure depicted in Fig. 2(*b*) has an important influence. In acetophenone, without *o*-alkyl substituents, the acetyl moiety coincides with the ring plane (Tanimoto *et al.*, 1973), and strong conjugation is possible. On complexation, more negative charge is available on the carbonyl oxygen atom. Hence, a stronger complexation with $FeCl_3$ can be expected. This may clarify why poisoning of the $FeCl_3$ catalyst, *i.e.* complexation of $FeCl_3$ with the product acetophenones, will be less pronounced in Friedel–Crafts acylations producing *o*-methylacetophenones (Scheele, 1986). It is planned to substantiate this proposal by determining the structure of the $FeCl_3$ complex of *p*-*tert*-butylacetophenone.

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Hydrated Proton Complexes in Methyl 3-Sulfoorsellinate Tetrahydrate*†

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Abstract. $C_9H_{10}O_7S.4H_2O$, $M_r = 334{\cdot}3$, triclinic, $P\bar{1}$, $Z = 2$, Cu $K\alpha_1$, $\lambda = 1{\cdot}54056$ Å, $F(000) = 352$, $T = 293$ K. Form *A*: $a = 7{\cdot}941\ (2)$, $b = 13{\cdot}753\ (2)$, $c = 6{\cdot}935\ (1)$ Å, $\alpha = 99{\cdot}68\ (2)$, $\beta = 91{\cdot}71\ (2)$, $\gamma = 98{\cdot}35\ (2)°$, $V = 737{\cdot}5$ Å^3, $D_x = 1{\cdot}505$ g cm^{-3}, $\mu = 24{\cdot}2$ cm^{-1}, final $R = 0{\cdot}041$ for 1294 unique reflections with $I \geq 3\sigma(I)$. Form *B*: $a = 8{\cdot}099\ (1)$, $b = 13{\cdot}904\ (1)$, $c = 6{\cdot}974\ (1)$ Å, $\alpha = 98{\cdot}95\ (1)$, $\beta = 105{\cdot}80\ (1)$, $\gamma = 82{\cdot}28\ (1)°$, $V = 743{\cdot}0$ Å^3, $D_x = 1{\cdot}494$ g cm^{-3}, $\mu = 24{\cdot}0$ cm^{-1}, final $R = 0{\cdot}031$ for 1965 unique reflections with $I \geq 3\sigma(I)$. In each structure the water molecules and the sulfonic acid oxygen atoms are joined by hydrogen bonds to form continuous sheets. Within these sheets isolated hydrated proton complexes can be recognized. In *A* the complex can be formulated as $H_9O_4^+$, a central oxonium ion joined to three water molecules by bonds of length 2·490 (5), 2·500 (6) and 2·553 (5) Å. In *B* the complex can be formulated as

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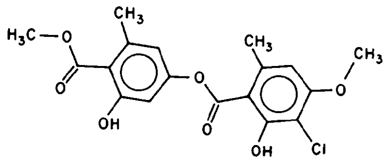
[*] 2,6-Dihydroxy-3-methoxycarbonyl-4-methylbenzenesulfonic acid tetrahydrate.

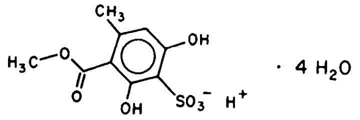
[†] NRCC No. 26527.

$H_{18}O_8^{2+}$, a doubly-protonated centrosymmetrical ring of eight water molecules. The ring includes a pair of nearly-centred hydrogen bonds of length 2·421 (2) Å.

Introduction. The specimen material was obtained as a product from the hydrolysis of wrightiin (I) (Maass & Hanson, 1986) in cold concentrated sulfuric acid. Variations in the subsequent treatment of the product yielded two different crystalline forms of what proved to be the tetrahydrate of methyl 3-sulfoorsellinate (II). The experimental procedures and the significance of the result for structural studies of lichen depsides are presented elsewhere (Maass, 1987). The purpose of the present paper is to describe the hydrated proton complexes which occur. Many such complexes have been reported by Olovssen, Lundgren, and their colleagues at Uppsala (*e.g.* Taesler & Lundgren, 1978). One of the complexes reported here can be formulated as $H_9O_4^+$, and is in the configuration proposed by Eigen (1963). The other can be regarded as a doubly-protonated ring of eight water molecules, $H_{18}O_8^{2+}$.



(I)



(II)

Experimental. Form *A*: tabular crystal [010], 0·07 × 0·15 × 0·17 mm. Picker four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation, θ–2θ scan, $2\theta \leq 130°$, backgrounds for 0·1 times scan time, at each end of scan. Cell constants from 37 reflections, $56 < \theta < 65°$. Absorption correction (Gaussian integration) from 1·18 to 1·46. Max. $\sin\theta/\lambda = 0{\cdot}588$ Å^{-1}, $h = -9$ to 9, $k = 0$ to 16, $l = -8$ to 8. 1 standard reflection (001) measured every 60 reflections, mean intensity 38 400 (414) counts; no indication of specimen decay, 2515 unique reflections scanned, of which 1221 had $I_{\rm net} < 3\sigma(I_{\rm net})$ (σ evaluated from counting statistics). Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refined by block-diagonal least squares, minimizing $\sum w\Delta F^2$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0005F_o^2$. All H atoms located in difference Fourier synthesis. One additional peak was found, about 1 Å from *W*O(1) (Table 1), and at about the right height for an H atom. However, its position was not compatible with those of the (three) other H atoms bonded to *W*O(1). The extraneous peak was regarded as an indication of an alternative position for *W*O(1) in about 10% of structural units, and it was subsequently modelled as an (isotropic) O atom of occupancy ratio 0·1. The occupancy ratio of *W*O(1) was concomitantly reduced to 0·9. Parameters refined were scale factor, extinction coefficient (1·43 × 10³; Larson, 1970), atomic coordinates and temperature factors (anisotropic for non-hydrogen atoms, except as noted above). Final $R = 0{\cdot}041$ [0·10 including reflections with $I_{\rm net} < 3\sigma(I_{\rm net})$]; $wR = 0{\cdot}046$, $S = 1{\cdot}19$. Ratio of the max. shift to e.s.d. in final cycle 0·2. Density in the final difference Fourier synthesis did not exceed $\pm 0{\cdot}2$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer program system described by Larson & Gabe (1978).

Form *B*: as above, except as noted. Tabular crystal [010], 0·11 × 0·18 × 0·43 mm. Cell constants from 43 reflections, $59 < \theta < 65°$. Absorption corrections 1·28 to 1·74, standard reflection 050, mean intensity 25 972 (402) counts. 2541 unique reflections scanned, of which 576 had $I_{\rm net} < 3\sigma(I_{\rm net})$.

An extraneous peak was found in this structure also, about 1 Å from *W*O(2). It was the largest peak in the difference Fourier synthesis (after subtracting the non-hydrogen contribution), and was too large for an H atom. It was attributed to an alternative position for *W*O(2) in about 18% of structural units, and was ultimately modelled as an (isotropic) O atom of occupancy ratio 0·18. [The occupancy ratio of *W*O(2) was reduced to 0·82.] The final extinction coefficient was 7·48 × 10³. Final $R = 0{\cdot}031$ [0·044 including reflections with $I_{\rm net} < 3\sigma(I_{\rm net})$]; $wR = 0{\cdot}042$, $S = 1{\cdot}32$. The structures are defined in Tables 1–3 and in Figs. 1–3.*

Discussion. It must be emphasized that both structures appear to be disordered. In each case one oxygen atom is reasonably assumed to be distributed over a major and a minor site, separated by less than 1 Å. The rest of the structure appears to be unaffected by the disorder, but this can hardly be so. The other atoms must be similarly distributed, but with the major and minor sites too close together to be resolved. (The minor positions of H atoms could probably not be determined, even if spatially resolvable.) The observed positions of these atoms will be some sort of weighted mean of the major and minor positions (and will be substantially closer to the former than to the latter). In the discussion which follows it is assumed that these mean positions, together with the major site of the bimodal atom, provide an

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* Lists of structure factors, H-atom coordinates, thermal parameters, additional bond lengths and angles, and some mean-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43370 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

acceptable description of the major structure. However, it is emphasized that this assumption contains a systematic error not readily evaluated. (The corresponding assumption concerning the *minor* structure contains a substantially greater systematic error. In addition, the precision with which the minor site can be located is unavoidably low. Given these limitations, the distances in Table 3 appear consistent with the proposition that, in each structure, the bonding environment of the minor site is similar to that of the major site.)

Table 1. *Atomic coordinates (e.s.d.'s in parentheses) and equivalent isotropic temperature factors for A (hydrogen atoms not involved in hydrogen bonding are omitted)*

B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid. *W*O(1) and *W*O(1*x*) are assigned occupancy ratios of 0·9 and 0·1 respectively.

	x	*y*	*z*	B_{eq}(Å^2)
*W*O(1)	0·5136 (5)	0·1516 (3)	0·1720 (6)	5·0
*W*O(1*x*)	0·520 (7)	0·084 (4)	0·113 (8)	9·8
*W*O(2)	0·6798 (4)	0·0942 (3)	0·4298 (5)	5·0
*W*O(3)	0·2067 (4)	0·0644 (3)	0·0952 (5)	4·8
*W*O(4)	0·7126 (6)	0·1374 (4)	−0·1005 (7)	9·2
*W*H(1*a*)	0·562 (6)	0·150 (4)	0·091 (7)	6·7
*W*H(1*b*)	0·579 (8)	0·123 (4)	0·287 (9)	10·6
*W*H(1*c*)	0·399 (6)	0·128 (4)	0·127 (7)	7·0
*W*H(2*a*)	0·675 (6)	0·028 (4)	0·430 (7)	6·1
*W*H(2*b*)	0·792 (7)	0·114 (4)	0·444 (8)	8·4
*W*H(3*a*)	0·145 (9)	0·078 (5)	0·197 (11)	13·4
*W*H(3*b*)	0·155 (5)	0·075 (3)	−0·001 (6)	4·3
*W*H(4*a*)	0·733 (8)	0·186 (5)	−0·142 (9)	10·1
*W*H(4*b*)	0·732 (12)	0·100 (7)	−0·096 (13)	19·8
S	0·14145 (14)	0·14817 (9)	0·61143 (18)	3·1
C(1)	0·1155 (5)	0·4445 (3)	0·7305 (6)	2·8
C(2)	0·0777 (5)	0·3408 (3)	0·6901 (6)	2·6
C(3)	0·2037 (5)	0·2786 (3)	0·6671 (6)	2·6
C(4)	0·3750 (5)	0·3244 (3)	0·6858 (7)	3·1
C(5)	0·4120 (5)	0·4270 (3)	0·7249 (7)	3·5
C(6)	0·2906 (6)	0·4891 (3)	0·7476 (7)	3·3
C(7)	0·3530 (6)	0·5999 (4)	0·7847 (8)	4·6
C(8)	−0·0275 (5)	0·5018 (3)	0·7499 (6)	3·2
C(9)	−0·1252 (7)	0·6573 (4)	0·8124 (8)	4·7
O(1)	−0·0859 (4)	0·2924 (2)	0·6716 (5)	3·6
O(2)	0·5077 (4)	0·2732 (2)	0·6694 (5)	4·6
O(3)	−0·1760 (4)	0·4620 (2)	0·7308 (5)	4·6
O(4)	0·0132 (4)	0·5991 (2)	0·7921 (5)	4·2
O(5)	0·3015 (4)	0·1073 (2)	0·5864 (5)	4·6
O(6)	0·0514 (4)	0·1180 (2)	0·7757 (5)	3·9
O(7)	0·0356 (4)	0·1267 (2)	0·4307 (4)	3·6
HO(1)	−0·133 (5)	0·336 (3)	0·675 (6)	4·6
HO(2)	0·466 (7)	0·215 (4)	0·640 (8)	8·3

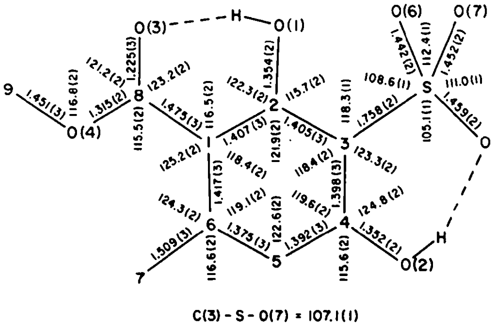


Fig. 1. Bond lengths (Å) and angles (°) of the title compound.

Table 2. *Atomic coordinates (e.s.d.'s in parentheses) and equivalent isotropic temperature factors for B (hydrogen atoms not involved in hydrogen bonding are omitted)*

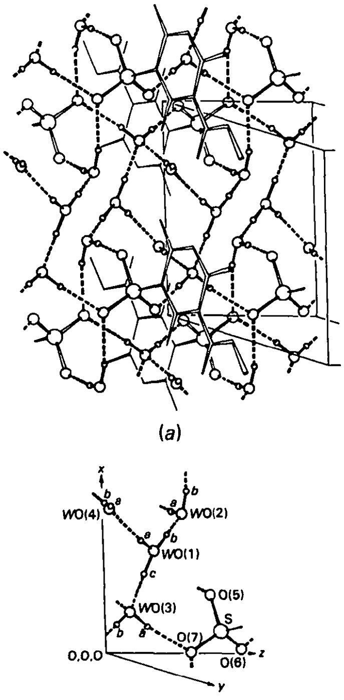
*W*O(2) and *W*O(2*x*) are assigned occupancy ratios of 0·82 and 0·18 respectively.

	x	*y*	*z*	B_{eq}(Å^2)
*W*O(1)	0·2134 (2)	0·06304 (12)	0·6868 (3)	5·1
*W*O(2)	0·5552 (2)	0·05602 (13)	0·8388 (4)	5·1
*W*O(2*x*)	0·5359 (14)	0·0371 (8)	0·7008 (16)	5·9
*W*O(3)	0·7154 (2)	0·17290 (12)	0·7599 (3)	4·9
*W*O(4)	0·7441 (2)	0·14177 (13)	0·3991 (3)	5·5
*W*H(1*a*)	0·170 (4)	0·087 (2)	0·577 (4)	8·7
*W*H(1*b*)	0·166 (3)	0·089 (2)	0·768 (4)	7·3
*W*H(2*a*)	0·587 (3)	0·006 (2)	0·833 (3)	4·9
*W*H(2*b*)	0·430 (4)	0·064 (2)	0·787 (4)	9·4
*W*H(3*a*)	0·723 (3)	0·158 (2)	0·623 (4)	7·0
*W*H(3*b*)	0·825 (4)	0·170 (2)	0·857 (4)	8·3
*W*H(3*c*)	0·637 (6)	0·116 (3)	0·795 (6)	15·6
*W*H(4*a*)	0·775 (3)	0·072 (2)	0·367 (4)	7·0
*W*H(4*b*)	0·803 (4)	0·167 (2)	0·368 (4)	8·3
S	0·14429 (6)	0·17381 (4)	0·18501 (9)	3·6
C(1)	−0·0207 (2)	0·46260 (14)	0·2400 (3)	2·8
C(2)	−0·0107 (2)	0·35975 (14)	0·2142 (3)	2·8
C(3)	0·1466 (2)	0·30166 (14)	0·2232 (3)	3·0
C(4)	0·2967 (2)	0·34838 (15)	0·2605 (3)	3·2
C(5)	0·2866 (3)	0·45011 (15)	0·2858 (3)	3·4
C(6)	0·1336 (3)	0·50782 (14)	0·2770 (3)	3·1
C(7)	0·1433 (3)	0·61698 (16)	0·3101 (4)	4·1
C(8)	−0·1940 (3)	0·51487 (15)	0·2236 (3)	3·2
C(9)	−0·3704 (3)	0·66415 (18)	0·2229 (4)	5·0
O(1)	−0·1516 (2)	0·31043 (10)	0·1774 (2)	3·5
O(2)	0·4567 (2)	0·30185 (11)	0·2765 (2)	4·3
O(3)	−0·3244 (2)	0·47312 (11)	0·1922 (2)	4·3
O(4)	−0·2010 (2)	0·61084 (10)	0·2437 (2)	4·1
O(5)	0·3242 (2)	0·13517 (11)	0·2077 (3)	5·0
O(6)	0·0723 (2)	0·14557 (12)	0·3333 (3)	5·0
O(7)	0·0422 (2)	0·14823 (11)	−0·0186 (2)	4·5
HO(1)	−0·248 (4)	0·362 (2)	0·174 (4)	8·2
HO(2)	0·450 (3)	0·238 (2)	0·273 (3)	5·6

Table 3. *Parameters of hydrogen bonds in Å and ° (e.s.d.'s in parentheses)*

Donor	Proton	Acceptor	O···O	O–H	H···O	O–H···O	Note
Form *A*							
O(1)	HO(1)	O(3)	2·510 (4)	0·75 (4)	1·80 (4)	159 (4)	
O(2)	HO(2)	O(5)	2·576 (4)	0·81 (5)	1·81 (5)	158 (5)	
*W*O(1)	*W*H(1*b*)	*W*O(2)	2·490 (5)	1·10 (6)	1·40 (6)	173 (6)	
*W*O(1)	*W*H(1*c*)	*W*O(3)	2·553 (5)	0·95 (5)	1·63 (5)	163 (5)	
*W*O(1)	*W*H(1*a*)	*W*O(4)	2·500 (6)	0·69 (5)	1·82 (5)	171 (5)	
*W*O(2)	*W*H(2*a*)	O(5)	2·780 (5)	0·91 (5)	1·88 (5)	171 (4)	(*a*)
*W*O(2)	*W*H(2*b*)	O(7)	2·795 (4)	0·89 (5)	1·92 (5)	166 (5)	(*a*)
*W*O(3)	*W*H(3*b*)	O(6)	2·761 (4)	0·82 (4)	1·95 (4)	172 (4)	(*a*)
*W*O(3)	*W*H(3*a*)	O(7)	2·802 (4)	0·88 (7)	1·93 (7)	171 (7)	
*W*O(4)	*W*H(4*b*)	*W*O(3)	2·943 (6)	0·56 (9)	2·38 (9)	175 (11)	(*a*)
*W*O(4)	*W*H(4*b*)	O(6)	2·884 (5)	0·56 (9)	2·70 (9)	103 (10)	(*a,b*)
*W*O(4)	*W*H(4*a*)	O(1)	3·146 (5)	0·77 (6)	2·45 (6)	151 (6)	(*a*)
*W*O(1*x*)	—	*W*O(2)	2·48 (5)				(*c*)
*W*O(1*x*)	—	*W*O(3)	2·46 (5)				(*c*)
*W*O(1*x*)	—	*W*O(4)	2·29 (5)				(*c*)
Form *B*							
O(1)	HO(1)	O(3)	2·498 (2)	0·98 (3)	1·58 (3)	152 (3)	
O(2)	HO(2)	O(5)	2·607 (2)	0·89 (2)	1·80 (2)	150 (2)	
*W*O(1)	*W*H(1*a*)	O(6)	2·774 (2)	0·85 (3)	1·92 (3)	178 (3)	
*W*O(1)	*W*H(1*b*)	O(7)	2·811 (2)	0·78 (3)	2·03 (3)	177 (3)	(*a*)
*W*O(2)	*W*H(2*b*)	*W*O(1)	2·675 (2)	0·98 (3)	1·70 (3)	173 (3)	
*W*O(2)	*W*H(2*a*)	O(5)	2·708 (2)	0·71 (2)	2·00 (2)	175 (2)	(*a*)
*W*O(3)	*W*H(3*c*)	*W*O(2)	2·421 (2)	1·17 (4)	1·25 (4)	178 (4)	
*W*O(3)	*W*H(3*a*)	*W*O(4)	2·554 (3)	0·96 (3)	1·59 (3)	175 (2)	
*W*O(3)	*W*H(3*b*)	O(7)	2·684 (2)	0·96 (3)	1·75 (3)	165 (3)	(*a*)
*W*O(4)	*W*H(4*a*)	*W*O(1)'	2·812 (2)	0·98 (3)	1·85 (3)	167 (2)	(*a*)
*W*O(4)	*W*H(4*b*)	O(6)	2·826 (2)	0·72 (3)	2·23 (3)	140 (3)	(*a*)
*W*O(2*x*)	—	*W*O(1)	2·56 (1)				(*c*)
*W*O(2*x*)	—	*W*O(3)	2·45 (1)				(*c*)
*W*O(2*x*)	—	O(5)	2·60 (1)				(*a,c*)

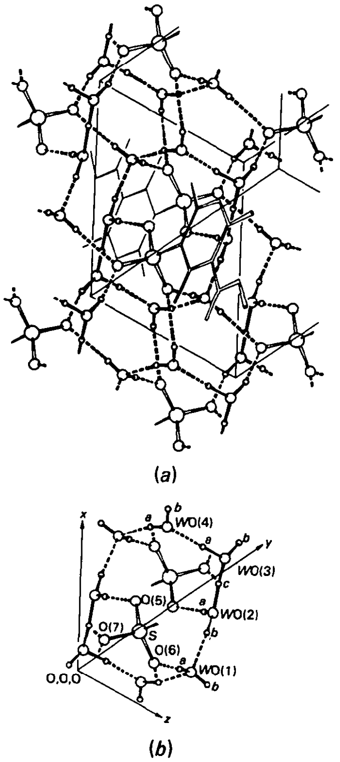
(*a*) 'Acceptor' generated by inversion and/or translation.
(*b*) Probably not a bond (wrong O–H···O angle).
(*c*) 'Donor' at minor site (these distances affected by substantial systematic error).



(a)

(b)

Fig. 2. (a) Crystal packing and (b) details of the hydrated complex of form *A*.



(a)

(b)

Fig. 3. (a) Crystal packing and (b) details of the hydrated complex of form *B*.

The geometry of the methyl 3-sulfoorsellinate ion is unexceptional (Fig. 1). The near equality of the S—O distances confirms the ionic nature of the material. Except for O(6) and O(7), the non-hydrogen skeleton of the ion is essentially planar, a conformation which is stabilized by the intramolecular hydrogen bridges indicated in Fig. 1 and Table 3.

In each of these structures the water molecules and the sulfonic acid groups lie within a region comprising about one third of the total volume, and are linked by hydrogen bonds into infinite sheets parallel to the *xz* plane (Figs. 2, 3). Within these sheets isolated hydrated proton complexes can be recognized. The organic moieties lie perpendicular to the *xz* plane, rooted to the S atoms, and filling the space between successive sheets.

In compound *A* the classification of the hydrated proton complex is unambiguous. An oxonium ion *W*O(1) donates a proton to each of three water molecules, forming strong hydrogen bonds (2·49 to 2·55 Å, Table 3). The resulting complex $H_9O_4^+$ is isolated to the extent that it forms only one rather long (2·94 Å) hydrogen bond to a water molecule of a neighbouring complex. [The criterion suggested by Lundgren (1974) for characterizing an isolated complex is that 'the hydrogen bonds within such a complex are always significantly shorter (≃0·2 Å) than the hydrogen bonds to other water molecules'.] It is of the type proposed by Eigen (1963); *W*O(1) is at the apex of a flattened trigonal pyramid, lying 0·75 Å from the base. [*W*O(1*x*), at the minor site for *W*O(1), lies 0·2 Å from the base, on the opposite side.]

The classification of the hydrated proton complex in *B* is less straightforward, and is to some degree arbitrary. The bond *W*O(2)···*W*O(3) is very short (2·42 Å), and the bridging hydrogen atom, although closer to *W*O(3), is only 0·04 (4) Å from the midpoint. This approximates the geometry of a centred bond, and $H_5O_2^+.2H_2O$ is a possible description of the complex. However, *W*O(2) and *W*O(3) form quite strong bonds to *W*O(1) and *W*O(4) (2·68 and 2·55 Å respectively), and *W*O(4) donates a proton to form a reasonably strong bond (2·81 Å) to *W*O(1)′. None of these bonds is more than 0·13 Å longer than some other, and thus, by the criterion cited above, it seems appropriate to describe the hydrated proton complex as a doubly protonated centrosymmetrical ring of eight water molecules, $H_{18}O_8^{2+}$ (Fig. 3). The ten H atoms not used in maintaining the ring mediate strong bonds to O atoms of the sulfonic acid groups (two of which bridge the ring) but not to any water molecule in a neighbouring ring.

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Bond Length and Reactivity: The Beckmann Rearrangement. 5. Structure of 4-Phenylcyclohexanone Oxime *O*-4-Nitrobenzoate Ester at 290 K

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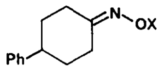
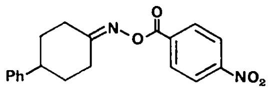
Abstract. $C_{19}H_{18}N_2O_4$, $M_r = 338{\cdot}35$, orthorhombic, $Pbc2_1$ (non-standard $Pca2_1$, No. 29), $a = 5{\cdot}652$ (2), $b = 12{\cdot}584$ (4), $c = 47{\cdot}625$ (18) Å, $V = 3387$ (2) Å^3, $Z = 8$, $D_x = 1{\cdot}327$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}69$ mm^{-1}, $F(000) = 1424$, $T = 290$ K, $R = 0{\cdot}042$ for 3438 reflections. The asymmetric unit contains two independent but structurally similar molecules. The 4-phenyl ring is equatorial on the cyclohexylidene system, and the oxime group is approximately planar, although both carboxylic ester and nitro groups are rotated out of the plane of the benzoate ring.

Introduction. We are looking for correlations between bond length and reactivity (Jones & Kirby, 1984) in ketoxime derivatives known to undergo the Beckmann rearrangement. Data in the literature refer to a random collection of structures, and are too few and too disparate to be a useful source of the kind of trends in which we are interested. So we have set out to apply our 'variable oxygen probe' technique (Jones & Kirby, 1984), measuring structures of a homogeneous series of compounds with varying effective electronegativities of the 'leaving group' oxygen.

After failing to produce suitable crystals in several series, particularly of the most reactive – and therefore the most interesting – oxime arenesulfonate esters, we recently reported structures for two derivatives (1) of 4-phenylcyclohexanone oxime, the 2-naphthalenesulfonate ester (1, X = 2-naphthalenesulfonyl; Jones, Edwards & Kirby, 1986*a*), and the trityl ether (1, X = triphenylmethyl; Jones, Edwards & Kirby, 1986*b*), which have very good ($XO^- = ArSO_3^-$) and very poor (triphenylmethoxide) leaving groups, respectively. The oxime groups of the two compounds show significant differences in geometry. In particular, the N—O bond is very long [1·502 (4) Å] in the sulfonate ester compared with the ether [1·429 (3) Å] – or indeed with any other oxime or derivative for which accurate data are available. We report here the crystal structure of a third derivative in this series, the 4-nitrobenzoate ester (2) of the oxime, which has a leaving group (XO^- = *p*-nitrobenzoate) of intermediate basicity.



(1)



(2)

Experimental. The oxime was acylated using 4-nitrobenzoyl chloride in methylene chloride with pyridine as base. Crystals were grown by diffusing pentane into a solution in methylene chloride. After initial difficulties, a suitable, block-shaped, transparent single crystal was obtained, and was mounted in a 0·5 mm Lindemann capillary in the presence of mother liquor.

Crystal 0·43 × 0·35 × 0·28 mm, Syntex $P2_1$ diffractometer with 200 Å diffracted beam chamber attachment; unit-cell parameters refined from diffractometer angles of 15 centred reflections ($40 < 2\theta < 50°$); 4566

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