Hydrogen Bonding and Stereochemistry of Ring-Hydroxylated Aromatic Aldehyde Oximes. Crystal Structures of Three 4-OH-Substituted Benzaldehyde Oximes

Bodil Jerslev and Sine Larsen

Department of Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 2, DK-2100 Copenhagen, Denmark

Jerslev, B. and Larsen, S., 1991. Hydrogen Bonding and Stereochemistry of Ring-Hydroxylated Aromatic Aldehyde Oximes. Crystal Structures of Three 4-OH-Substituted Benzaldehyde Oximes. Acta Chem. Scand. 45: 285–291.

X-Ray diffraction data have been used to determine the crystal structures of (*E*)-4-hydroxybenzaldehyde oxime monohydrate, of a previous unknown benzene inclusion compound of (*E*)-4-hydroxybenzaldehyde oxime and of (*E*)-4-hydroxy-3-methoxybenzaldehyde oxime (vanillinoxime). The observed geometries of the three oxime molecules are remarkably alike. A common feature of the hydrogen bonding systems in the three crystal structures is the connection between the phenolic OH group in one molecule and the oxime nitrogen atoms in another molecule via an OH group, $OH_{phenol}\cdots OH_{water\ or\ oxime}\cdots N_{oxime}$. It is proposed that (*Z*)-isomers of ring-hydroxylated benzaldehyde oximes undergo a spontaneous, autocatalytic rearrangement to the (*E*)-isomers, caused by protonation of the oxime nitrogen by the phenol. Furthermore it is argued that the slow $Z \rightarrow E$ rearrangement of aromatic aldehyde oximes is a similarly autocatalysed reaction, caused by hydrogen displacement in the hydrogen bonds, $OH_{oxime}\cdots N_{oxime}$, by which the molecules are associated.

It is classical knowledge[1] that aromatic (*Z*)-aldehyde oximes are rearranged to the corresponding *E*-isomers by hydrogen-ion catalysis, and that the opposite rearrangement takes place in strong acid. Likewise it is known that aromatic aldehyde oximes with a phenolic hydroxy group in the molecule are found only in the *E*-form. Finally, aromatic (*Z*)-aldehyde oximes have been found to rearrange very slowly to the *E*-isomer in the crystal. It may take years, but the beginning rearrangement is often noted as a freezing-point depression during a melting-point determination of the *Z*-isomer.

It may be assumed that catalysis by hydrogen ion is important for all these rearrangements, which lead to the more stable isomer by rotation[2] around a $C{=}NH^+$ bond. The non-existence of *Z*-isomers of ring-hydroxylated, aromatic aldehyde oximes can be explained if autocatalysis by the acidic phenolic hydrogen atom promotes their rearrangement to the *E*-isomer. Similarly, the $Z \rightarrow E$ conversion in crystalline aromatic aldehyde oximes may be autocatalysed through systems of hydrogen bonds in the crystal, such as ${=}N\cdots H{-}O{-}N{=}C \rightleftarrows {=}N{-}H^+\cdots {}^-O{-}N{=}C$.

Crystal structure determinations of *ortho*-hydroxylated oximes are known, but no *meta*- or *para*-hydroxylated aromatic aldehyde oxime has previously been structurally characterized. The present crystal structure determinations were undertaken in the hope of obtaining some insight and experimental evidence for the suggested mechanism of the structural rearrangements.

Experimental

Preparation of oximes for X-ray crystal structure determinations. The oximes were synthesized from the corresponding aldehyde, hydroxylamine hydrochloride and sodium carbonate by standard procedures. Suitable crystals for X-ray structure determinations were obtained as described below.

4-Hydroxybenzaldehyde oxime · ½benzene (B). The anhydrous product crystallized from toluene as very thin, soft crystal plates of 4-hydroxybenzaldehyde oxime that were unsuitable for X-ray diffraction, m.p. 112 °C (cap.) (lit.[3] 112 °C). Recrystallizations from a number of organic solvents gave no better results. On crystallization from benzene some soft crystal aggregates were noticed, which rapidly lost the solvent when exposed to the air. However, a benzene solution, which had been left in a glass-stoppered flask for about a year, had evaporated to give a crystalline mass, in which sparkling single crystals were observed. The crystals gave off benzene when exposed to the open air; but a single crystal, rapidly isolated and transferred to the X-ray diffractometer and cooled to 110 K was found to be stable and well suited to an X-ray structure determination.

4-Hydroxybenzaldehyde oxime monohydrate (A). Recrystallization from water of the product obtained from toluene gave well developed, rather flat, needle-shaped crystals, m.p. ca. 67 °C (cap., heating rate 4 °C min^{-1}), (lit.[3] 72–73 °C), one of which was used for structure determination.

By slow heating partial melting of the crystals began at about 67 °C, the compound gradually shrinking, and total melting was observed at 110–112 °C, corresponding to the m.p. of the anhydrous oxime.

Kjær and Rubinstein[4] prepared anhydrous 4-hydroxybenzaldehyde oxime, identified by its m.p. and nitrogen analysis. They stated that 'beautiful crystals' were obtained from benzene. Since our attempts to prepare the oxime from benzene were unsuccessful, the crystallization procedures of Kjær and Rubinstein[4] were repeated on a small scale: anhydrous (*E*)-4-hydroxybenzaldehyde oxime (0.50 g) was dissolved in 10 ml of water, and the solution was extracted by 6+4+4+3 ml of diethyl ether. The ethereal solution was dried over sodium sulfate and the ether was subsequently evaporated, to leave 0.52 g of a brittle crystal mass in which some small glittering crystals were observed; the melting point identified the product as the monohydrate of (*E*)-4-hydroxybenzaldehyde oxime. The crystal mass was extracted with 30 ml of hot benzene; on cooling 0.23 g of small, beautiful crystals were isolated, and a second extraction of the crystal mass with the mother liquid gave further 0.18 g of crystals. The melting point identified both crops as the oxime monohydrate. The monohydrate was found to be practically insoluble in hexane.

4-Hydroxy-3-methoxybenzaldehyde oxime, vanillinoxime (C) was prepared in aqueous solution and recrystallized from water. Hard, rather flat crystals, mostly forming aggregates, were obtained, m.p. 117.5–119 °C (uncorr.), (lit.[5] 121–122.5 °C). The crystals were apparently destroyed on being cooled to 110 K, and the structure did not reform at room temperature.

3-Hydroxybenzaldehyde oxime was prepared as very thin, soft and thread-like crystals. 4-Methoxy-3-hydroxybenzaldehyde oxime crystallized from water in small, very thin flakes. No crystals suitable for X-ray structure determination were obtained from these compounds.

Crystal structure determinations. Photographic methods only were used to characterize A. A CAD-4 diffractometer equipped with a graphite monochromator was used for the characterization of B and C and for data collection for all three compounds. The crystals of A and B were cooled to 110 K by means of an Enraf-Nonius gas-flow low temperature device. The temperature was monitored by a thermocouple placed in the exhaust pipe a few centimetres above the crystal and was constant to within 1 K throughout the data collections. Attempts to collect low-temperature data for C showed that this compound undergoes a phase transition which destroys the crystal during the cooling. As a consequence the data collection for C was performed at room temperature. Owing to the small size of the crystals Cu radiation was chosen for the data collection of B and C.

Table 1. Crystal data and a summary of data collection and refinement results.

Compound	A	B	C
Formula	$C_7H_9NO_3$	$C_{10}H_{10}NO_2$	$C_8H_9NO_3$
Formula weight/g mol^{-1}	155.15	176.20	167.17
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$
Crystal size/mm^3	0.05×0.15×0.55	0.02×0.12×0.37	0.08×0.33×0.40
Temperature/K	110	110	296
Radiation, λ	Mo-K_α 0.71073 Å	Cu-K_α 1.54178 Å	Cu-K_α 1.54178 Å
Linear absorption coefficient, μ/cm^{-1}	1.014	7.316	8.610
a/Å	9.626(3)	5.696(2)	6.3720(3)
b/Å	3.838(3)	6.2559(14)	16.6462(13)
c/Å	10.745(3)	12.651(2)	7.5700(3)
α, β, γ/°	90, 109.17(2), 90	93.33(2), 100.88(2), 97.40(2)	90, 93.930(4), 90
V/Å^3	375.0(5)	437.4(4)	801.1(1)
Z	2	2	4
$d_{calc.}$/g cm^{-3}	1.374	1.338	1.386
θ Range/°	1–33	1–75	1–75
Scan type	ω	ω–2θ	ω–2θ
Scan range, Δω/°	1.5	2.0 + 0.15 tan θ	2.0 + 0.15 tan θ
Max. scan time/s.	60	120	60
Octants measured	$h \pm k \pm l$	$h \pm k \pm l$	$\pm h \pm k \pm l$
Number of independent reflections	1580	1790	1641
Number of observed reflections, *n*	1108	1402	1146
Weights,[a] w^{-1}	$\sigma^2_{CS}(F) + 1.2\times10^{-3}\lvert F\rvert^2$	$\sigma^2_{CS}(F) + 6\times10^{-4}\lvert F\rvert^2$	$\sigma^2_{CS}(F) + 9\times10^{-4}\lvert F\rvert^2$
Number of variables, *m*	99	148	109
R	0.055	0.039	0.053
R_w	0.064	0.054	0.073
Max. shift/error	0.01	0.01	0.01
$S = \Sigma w\Delta F^2/(n-m)$	1.1	1.7	1.7
Δϱ, max. and min. peak/e Å^{-3}	0.5/−0.3	0.2/−0.3	0.2/−0.3

[a] $\sigma_{CS}(F)$ standard deviation calculated from counting statistics.

The unit cell dimensions were determined from a least-squares refinement of 22 reflections ($17° < \theta < 22°$) for A, 20 reflections ($40° < \theta < 49°$) for B and 22 reflections ($37 < \theta < 48°$) for C.

The selections of scan type and range were based on a careful analysis of the reflection profiles. Three standard reflections were monitored after every 10 000 s during the data collection. The orientation of the crystals were controlled after every 300 reflections. These measurements did not reveal any systematic variations. Additional details about the data collection are given in Table 1.

Data reductions included corrections for Lorentz, polarization and background effects; symmetry related reflections were averaged. $R_{int.}(F)$: 0.07 (A), 0.02 (C).

The structures were solved by direct methods by use of the program SHELXS-86[6] which provided initial positions for all non-hydrogen atoms in the structures. The structures were refined by the least-squares methods minimizing $\Sigma w (|F_o|-|F_c|)^2$. The positions of the hydrogen atoms were shown clearly in difference electron densities calculated after anisotropic displacement parameters had been introduced for the non-hydrogen atoms. Only structure B had data of sufficient resolution and quality to make a refinement of the hydrogen parameters reasonable. For the two other structures the carbon-bonded hydrogen atoms were placed in idealized positions. In the structures A and C the positions of the oxygen bonded hydrogen atoms were taken from the difference synthesis.

The SDP-system[7] was used for the crystallographic computations. The atomic scattering factors[8] were used as contained in the programs.

Details about the data collection and the refinement are given in Table 1 together with the final refinement results. Tables 2, 3 and 4 show the positional parameters for the non-hydrogen atoms in the three structures. The numbering of the atoms are shown in Fig. 1.†

Table 2. 4-Hydroxybenzaldehyde oxime monohydrate: positional parameters for the non-hydrogen atoms.

Atom	x	y	z	B_{iso}^{a} [a]
C1	0.2031(2)	0.3309(8)	0.3086(2)	1.03(4)
C2	0.1288(2)	0.4953(9)	0.1890(2)	1.13(4)
C3	−0.0223(3)	0.5374(9)	0.1481(2)	1.17(4)
C4	−0.1009(3)	0.4205(8)	0.2281(2)	1.15(4)
C5	−0.0291(3)	0.2554(9)	0.3474(2)	1.19(4)
C6	0.1219(3)	0.2146(9)	0.3867(2)	1.19(4)
C7	0.3623(3)	0.2737(9)	0.3573(2)	1.23(4)
N8	0.4430(2)	0.3247(9)	0.2857(2)	1.36(4)
O9	0.5916(2)	0.2500000	0.3560(2)	1.92(4)
O10	−0.2505(2)	0.4620(8)	0.1935(2)	1.66(4)
O11	0.3997(2)	0.3317(8)	0.0165(2)	1.79(4)

[a] $B_{iso}^{a} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

† Anisotropic displacement parameters and lists of observed and calculated structure factors are available from the authors.

Table 3. 4-Hydroxybenzaldehyde oxime benzene adduct: positional parameters for the non-hydrogen atoms.

Atom	x	y	z	B_{iso}^{a} [a]
C1	0.5255(2)	−0.0032(2)	0.6874(1)	1.74(2)
C2	0.2941(3)	0.0045(2)	0.6276(1)	2.05(3)
C3	0.1717(3)	0.1751(2)	0.6465(1)	2.02(3)
C4	0.2771(2)	0.3407(2)	0.7258(1)	1.81(2)
C5	0.5050(3)	0.3336(2)	0.7875(1)	1.93(2)
C6	0.6275(2)	0.1623(2)	0.7680(1)	1.86(2)
C7	0.6659(3)	−0.1763(2)	0.6671(1)	1.90(2)
N8	0.5896(2)	−0.3207(2)	0.5881(1)	1.99(2)
O9	0.7575(2)	−0.4670(2)	0.58197(9)	2.39(2)
O10	0.1623(2)	0.5122(2)	0.74696(9)	2.34(2)
C13	0.1759(3)	0.9639(3)	0.9408(1)	2.15(3)
C23	0.0018(3)	0.7945(2)	0.9522(1)	2.11(3)
C33	−0.1740(3)	0.8308(3)	1.0113(1)	2.20(3)

[a] $B_{iso}^{a} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 4. 4-Hydroxy-3-methoxybenzaldehyde oxime: positional parameters for the non-hydrogen atoms.

Atom	x	y	z	B_{iso}^{a} [a]
C1	0.4997(3)	0.5602(1)	0.2310(3)	4.42(4)
C2	0.5782(3)	0.6383(1)	0.2512(3)	3.58(4)
C3	0.4612(3)	0.7026(1)	0.1845(3)	3.32(3)
C4	0.2633(3)	0.6900(1)	0.0972(3)	3.76(4)
C5	0.1852(3)	0.6135(1)	0.0796(4)	5.37(5)
C6	0.3031(4)	0.5490(1)	0.1454(4)	6.09(6)
C7	0.6208(4)	0.4903(1)	0.2965(4)	5.35(5)
N8	0.7955(3)	0.4961(1)	0.3847(3)	4.48(4)
O9	0.8827(3)	0.42024(8)	0.4275(3)	6.19(4)
O10	0.1472(2)	0.75228(8)	0.0285(2)	4.64(3)
O11	0.5217(2)	0.78123(9)	0.1926(2)	4.58(3)
C12	0.7254(3)	0.7989(1)	0.2712(4)	4.83(5)

[a] $B_{iso}^{a} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Descriptions of the structures. Fig. 1 shows ORTEP[9] drawings of the oxime molecules as found for the three structures A, B and C. Apart from the difference in thermal ellipsoids due to different data collection temperatures the three molecular structures are remarkably alike. The dimensions of the molecules and the dihedral angles between the benzene ring and the side-chains do not deviate from the dimensions expected, cf. Ref. 10. Bond lengths and angles are listed in Table 5. The packing of the molecules is described separately for each crystal structure; data on the hydrogen bonds are summarized in Table 6. Fig. 2 shows projections of the structures A, B and C, focusing on the hydrogen bonding systems, and Figs. 3–5 show stereopairs of A, B and C respectively.

A: (E)-*4-Hydroxybenzaldehyde oxime monohydrate.* The molecules form a double layer running parallel to the *ab*-plane and centred around the screw axis in (1/2, *b*, 1/2) as

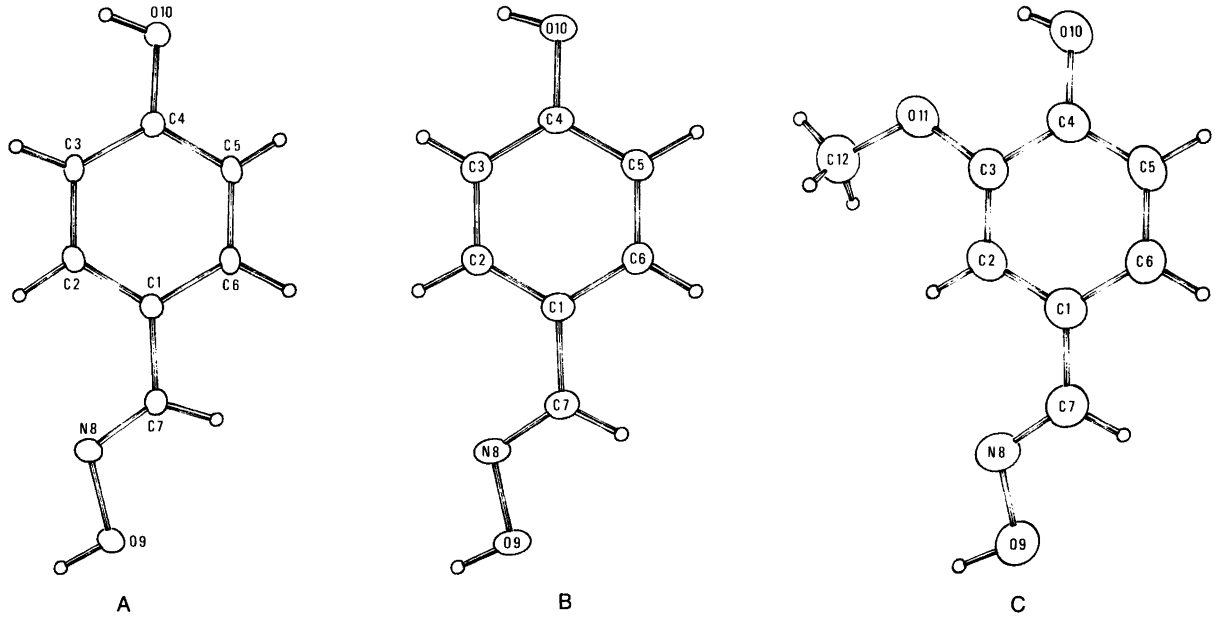

Fig. 1. ORTEP[10] drawing of the oxime molecules as found in the crystal structures A and B at 110 K, and C at 296 K. The ellipsoids are drawn to 50 % probability. The atomic labelling is indicated. Hydrogen atoms are given the same number as the atom to which they are bonded. The atoms of the water molecule in A, 4-hydroxybenzaldehyde oxime monohydrate, are termed O11, H111 and H112. The carbon atoms of benzene in the asymmetric unit of B, 4-hydroxybenzaldehyde oxime · ½benzene, are labelled C13, C23, C33.

shown in Figs. 2 and 3. All distances between atoms in neighbouring layers are longer than the sum of the van der Waals' radii.

A complicated hydrogen bonding scheme connects (1) the phenolic OH group (O_{10}–H_{10}) with the oxygen atom (O_{11}) of a water molecule, in which a hydrogen atom (H_{111}) is bound to an oxime nitrogen atom (N_8); (2) the water molecules (O_{11}) to form chains in the *b*-direction around the screw axis and (3) neighbouring molecules along the surfaces of the double layer by O–H_{oxime}---O_{phenol} bonds.

Table 5. Bond distances and angles with e.s.d.'s in parentheses.[a]

	A	B	C		A	B	C
C1–C6	1.395(3)	1.396(2)	1.383(2)	C2–C1–C6	118.6(2)	118.7(1)	118.8(2)
C6–C5	1.383(4)	1.387(2)	1.383(3)	C1–C6–C5	121.4(3)	121.0(1)	121.1(2)
C5–C4	1.394(4)	1.390(2)	1.370(3)	C6–C5–C4	119.1(2)	119.5(1)	120.1(2)
C4–C3	1.393(3)	1.390(2)	1.399(2)	C5–C4–C3	120.6(2)	120.0(1)	119.7(2)
C3–C2	1.384(4)	1.381(2)	1.380(2)	C4–C3–C2	119.6(2)	120.2(1)	120.2(2)
C2–C1	1.399(4)	1.398(2)	1.399(2)	C3–C2–C1	120.7(2)	120.5(1)	120.1(2)
C1–C7	1.464(3)	1.465(2)	1.463(2)	C6–C1–C7	117.7(2)	118.9(1)	119.5(2)
C7–N8	1.275(3)	1.278(2)	1.262(3)	C2–C1–C7	123.7(2)	122.4(1)	121.7(2)
N8–O9	1.411(3)	1.416(2)	1.409(2)	C1–C7–N8	122.4(2)	121.3(1)	123.0(2)
O9–H9	0.88	0.90	0.94	C7–N8–O9	111.0(2)	111.6(1)	111.9(2)
C4–O10	1.374(3)	1.365(2)	1.357(2)	N8–O9–H9	105(1)	102(1)	98
O10–H10	0.87	0.86	0.78	C5–C4–O10	117.4(2)	117.9(1)	119.3(2)
				C3–C4–O10	122.0(2)	122.1(1)	121.1(2)
				C4–O10–H10	104	105	112
C3–O11			1.365(2)	C4–C3–O11			114.1(2)
O11–C12			1.421(2)	C2–C3–O11			125.7(2)
				C3–O11–C12			117.7(2)
C13–C33		1.390(2)		C13–C23–C33		119.9(2)	
C13–C23		1.388(2)		C13–C33–C23		120.2(2)	
C23–C33		1.391(2)		C23–C13–C33		119.9(2)	

[a]A indicates 4-hydroxybenzaldehyde oxime · H_2O; B indicates 4-hydroxybenzaldehyde oxime · ½ C_6H_6; C indicates 4-hydroxy-3-methoxybenzaldehyde oxime.

Table 6. Hydrogen bonds.

	D---A (Å)		**D–H---A**, (approximate°)
A: 1, O_{10}–H_{10}---$^{a}O_{11}$–H_{111}---$^{a}N_8$	O_{10}---O_{11}	2.654(3)	139
	O_{11}---N_8	2.784(3)	158
2, O_{11}–H_{112}---$^{b}O_{11}$	O_{11}---O_{11}	2.827(3)	151
3, O_9–H_9---$^{c}O_{10}$	O_9---O_{10}	2.785(3)	174
a, (2 + *x*, *y*, *z*); b, (1 − *x*, *y* + 1/2, −*z*); c, (*x* + 1, *y*, *z*)			
B: O_{10}–H_{10}---$^{a}O_9$–H_9---$^{b}N_8$	O_{10}---O_9	2.8251(12)	169(1)
	O_9---N_8	2.7728(14)	155(1)
a, (*x*−1, *y*+1, *z*); b, (1−*x*, −*y*−1, 1 −*z*)			
C: O_{10}–H_{10}---$^{a}O_9$–H_9---$^{b}N_8$	O_{10}---O_9	2.824(2)	136
	O_9---N_8	2.787(2)	162
a, (1−*x*, 1/2+*y*, 1/2−*z*), b (2−*x*, 1−*y*, 1−*z*)			

[a]A indicates 4-hydroxybenzaldehyde oxime · H_2O, B indicates 4-hydroxybenzaldehyde oxime · ½benzene, C indicates 4-hydroxy-3-methoxybenzaldehyde oxime. **D** indicates donor atom, **A** acceptor atom.

B: (E)-*4-Hydroxybenzaldehyde oxime · ½benzene.* The crystal structure is shown in Figs. 2 and 4. The molecules are connected pairwise around the centre of symmetry (1/2, −1/2, 1/2) by bonds $=N_8$---H_9–O_9–$N_8=$; this hydrogen bonding scheme is that usually found in crystal structures of aromatic (*E*)-aldehyde oximes. Furthermore hydrogen bonds O_{10}–H_{10}---O_9 connect molecules that are related by translation one unit in the *b*-direction. The total result is a double layer of molecules, which are linked pairwise across the layer by two hydrogen bonds and connected along the layer by two sets of hydrogen bonds. The oxime molecules are placed between the benzene molecules, which are situated at the corners of the unit cell. None of the distances between the atoms of the double layer of oxime molecules and the surrounding benzene molecules is shorter than the sum of the van der Waals' radii.

C: (E)-*4-Hydroxy-3-methoxybenzaldehyde oxime.* As in the two previously described structures the molecules are packed in a layer structure, see Figs. 2 and 5. Two identical, hydrogen-bonded layers run along the plane series (1,0,−2), the distance between neighbouring planes being 3.35 Å. The molecular layers are displaced one unit in the *a*-direction relative to their neighbours. Dimers of the oxime group are formed around centres of symmetry, and hydrogen bonds O_{10}–H_{10}---O_9 unite the molecules (*x*, *y*, *z*)

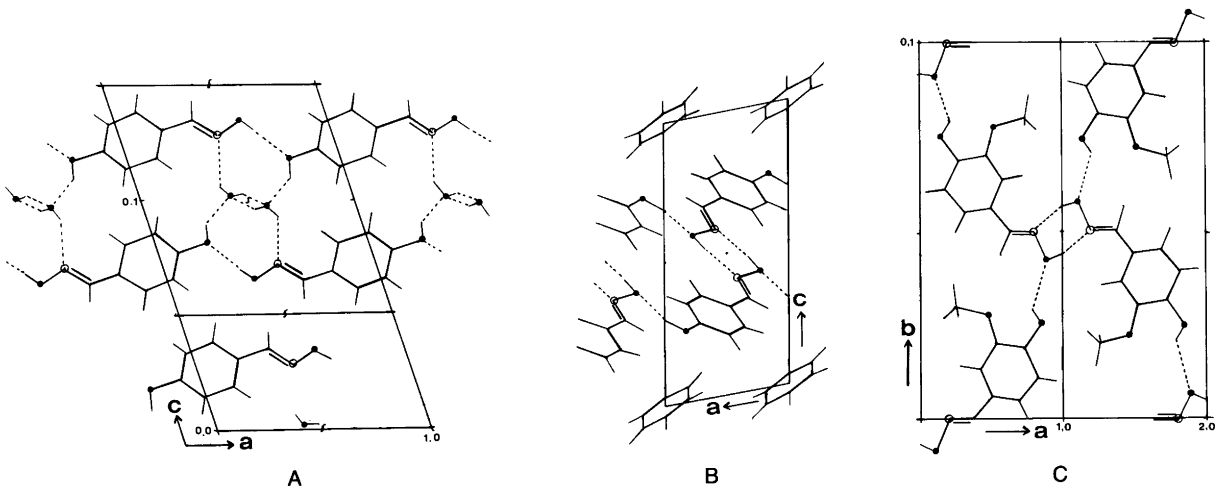

Fig. 2. Projections of the crystal structures A, B and C illustrating the hydrogen bonding schemes: ●, oxygen atoms; ○, nitrogen atoms. The molecules of one double layer in A, (*E*)-4-hydroxybenzaldehyde oxime · H_2O, is shown together with a single molecule of a neighbouring layer. In B, (*E*)-4-hydroxybenzaldehyde oxime · ½benzene, the dimer across the double layer (formed by hydrogen bonds around the centre of symmetry in 1/2, −1/2, 1/2) is shown, as well as the hydrogen bonds along the double layer (connecting molecules *x*, *y*, *z* with molecules *x*+1, *y*−1, *z*). In C, (*E*)-4-hydroxy-3-methoxybenzaldehyde oxime, only one of the layers containing the molecules at *x*, *y*, *z* is shown; parallel layers interspaced between these layers contain the molecules at −*x*, −*y*, −*z*, but are not shown.

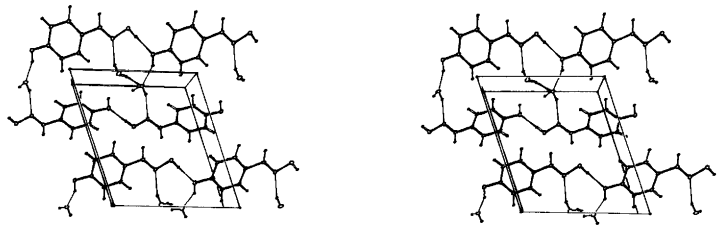

Fig. 3. Stereopair of the structure A viewed along the b^* direction.

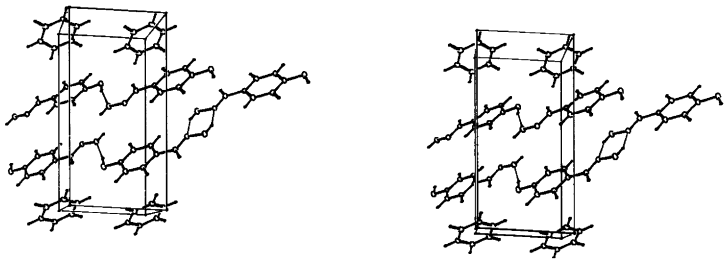

Fig. 4. Stereopair of the structure B viewed along the a^* direction.

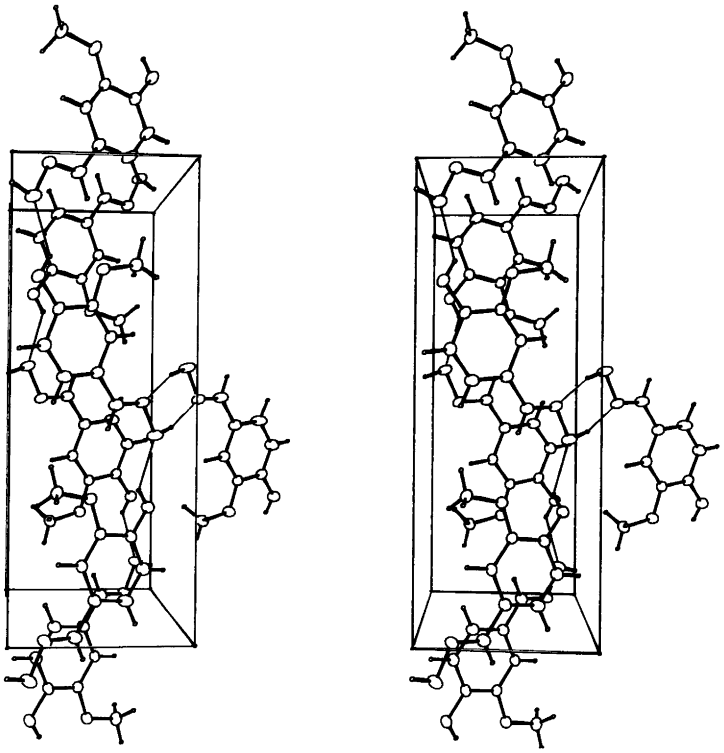

Fig. 5. Stereopair of the structure C viewed along the c^* direction.

and $(1-x, y+1/2, 1/2-z)$. Furthermore a short intramolecular distance, 2.658(2) Å between the phenol oxygen atom O_{10} and the methoxy oxygen atom O_{11} is observed with the angle O_{10}–H_{10}---O_{11} = 113°. This might indicate that H_{10} takes part in a bifurcated hydrogen bond; however, the short distance between O_{10} and O_{11} may also be explained as being due to electrostatic attraction.

Discussion

Three crystal structures of 2-hydroxy-substituted benzaldehyde oximes have been published.[11-13] A chelate, N_{oxime}---H–O_{phenol}, was formed in all of them, as expected. No crystal structure of 3- or 4-hydroxy-substituted benzaldehyde oximes has previously appeared in the literature.

The inclusion compound, (*E*)-4-hydroxybenzaldehyde oxime · ½benzene, has not been described so far. Of the three crystal structures studied here, this compound gave the best X-ray diffraction data, possibly because the layer structure is stabilized by the interstitial benzene molecules; no such stabilization is present in the other two crystal structures.

A hydrate of 4-hydroxybenzaldehyde oxime was mentioned as early as in 1892 by Dollfuss,[14] and in 1914 Brady and Dunn[3] described the compound as a monohydrate, from which the water was not removed by crystallization in non-aqueous media. Confirmation of this statement was obtained by experiments described in the experimental part, which also indicate that the crystalline material obtained by Kjær and Rubinstein[4] was the monohydrate.

The hydrogen bonding schemes in the three crystal structures are interesting. *A priori* it was expected that an *inter*molecular bond between the nitrogen atom and the phenolic hydrogen, N_{oxime}---H–O_{phenol}, would be found by analogy with the *intra*molecular hydrogen bond found in *ortho*-compounds. The geometry of the *para*-hydroxylated oxime molecules apparently prevent the formation of this most favourable hydrogen bonding scheme, so what may be termed the second best scheme unites the nitrogen atom and the phenolic OH-group via a hydrogen-bonded hydroxy group N_{oxime}---H–O_X---H–O_{phenol}, cf. Table 6. A hydrogen-bonded system like this must to some extent react to give N^+_{oxime}–H---O_X–H---O^-_{phenol}; the latter system, and even a chain of hydrogen bonds, N_{oxime}---(H–O_X)$_n$---H–O_{phenol}, may give the nitrogen atom a positive charge – small, but large enough to induce catalytic activity.

It is proposed, that the fact that the *Z*-isomers of ring-hydroxylated, aromatic aldehyde oximes are unknown compounds is due to rearrangement to the *E*-isomers induced by autocatalysis via hydrogen bonding schemes such as those presented above. Similarly, the aromatic *Z*-aldehyde oximes, which associate in chains by means of hydrogen bonds,[15] H–O–H---H–O–N--- are proposed to undergo an autocatalysed $Z \rightarrow E$ rearrangement; since oximes are very weak acids only a very small concentration of the protonated nitrogen atom is formed, and consequently the rearrangement rate is extremely low.

Acknowledgements. The X-ray crystal data were collected by Mr. Flemming Hansen. The diffractometer and low-temperature equipment were provided by the Danish Natural Science Research Council.

References

1. Meisenheimer, J. and Theilacker, W. In: Freudenberg, K., Ed. *Stereochemie,* Franz Deuticke, Leipzig und Wien 1932, Vol. 3, pp. 963–1002.
2. Kessler, H. *Tetrahedron 30* (1974) 184.
3. Brady, O. L. and Dunn, F. P. *J. Chem. Soc. 105* (1914) 821.
4. Kjær, A. and Rubinstein, K. *Acta Chem. Scand. 8* (1954) 598.
5. Ritter, D. M. *J. Am. Chem. Soc. 68* (1946) 2738.
6. Sheldrick, G. M. In: Sheldrick, G. M., Krüger, C. and Goddard, R., Eds., *Crystallographic Computing 3,* SHELX-86, Oxford University Press, Oxford, UK 1985, pp. 179–189.
7. Enraf–Nonius *Structure Determination Package,* Enraf–Nonius, Delft, The Netherlands 1983.
8. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4.
9. Johnson, C. K. ORTEP: Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN 1965.
10. Jerslev, B. *Acta Crystallogr., Sect. C 39* (1983) 1447.
11. Pfluger, C. E. and Harlow, R. L. *Acta Crystallogr. Sect. B 29* (1973) 2608.
12. Simonsen, S. H., Pfluger, C. E. and Thompson, C. M. *Acta Crystallogr. 14* (1961) 269.
13. Pfluger, C. E., Pfluger, M. T. and Brackett, E. B. *Acta Crystallogr., Sect. B 34* (1978) 1017.
14. Dollfuss, W. *Ber. Dtsch. Chem. Ges. 25* (1892) 1908.
15. Jerslev, B. *Acta Chem. Scand., Ser. B 41* (1987) 184.

Received July 9, 1990.