

Crystallizations and Crystal Structure at 122 K of Anhydrous (*E*)-4-Hydroxybenzaldehyde Oxime

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Preparations of anhydrous (*E*)-4-hydroxybenzaldehyde oxime are described, and supplemented with a description of conditions for preparing the solvate: oxime · 1/2 benzene. The crystal structure of the anhydrous oxime was determined at 122 K. It crystallizes in the space group $P2_1/c$, $a = 6.806(2)$, $b = 6.0157(12)$, $c = 15.744(3)$ Å, $\beta = 94.82(2)^\circ$, $Z = 4$. The structure was refined to $R = 0.033$ and $R_w = 0.047$ using 1069 observed reflections collected with Cu K α radiation. The results are compared with the structural data obtained for the solvated oxime · 1/2 benzene. No significant differences between the dimensions of the molecules in the two structures were found, and the intermolecular hydrogen bond pattern is identical in the two structures. The molecular data indicate a similar conjugation of the oxime side chain with the benzene ring in the anhydrous oxime, the benzene solvate and the monohydrate.

In the previous paper¹ we described the crystal structures of three 4-hydroxy-substituted (*E*)-benzaldehyde oximes. It was pointed out that we had not succeeded in preparing suitable crystals of anhydrous (*E*)-4-hydroxybenzaldehyde oxime following Kjær and Rubinstein,² but had obtained only the monohydrate. This prompted Professor Kjær to go back to the laboratory notes for the publication,² and it turned out that a drying procedure with calcium chloride of the intermediate solution in diethyl ether had inadvertently been left out of the publication. Using this information renewed recrystallization of anhydrous (*E*)-4-hydroxybenzaldehyde oxime in analytical grade benzene was undertaken. This resulted in crystals of the anhydrous oxime which corresponded exactly to the description given.²

Additional experiments have furthermore shown that a small amount of the oxime hydrate is usually present in 'anhydrous' oxime which causes a depression of the m.p. of the pure compound to ca. 112°C. The value of 115–116°C given in Ref. 2 must be considered the most accurate m.p. for anhydrous (*E*)-4-hydroxybenzaldehyde oxime.

Crystallization of (*E*)-4-hydroxybenzaldehyde oxime from benzene gave three products, i.e. the anhydrous compound and water or benzene solvates. Some crystallization experiments were performed in order to obtain an understanding of this curious fact.

Experimental

For the following experiments samples from a single preparation of (*E*)-4-hydroxybenzaldehyde oxime crystallized from toluene were used, m.p. (cap., uncorrected) 111–112°C; on heating a few glistening melted drops were observed from 106°C.

Crystallizations from benzene, FERAk, analytical grade, water content < 0.03 %. (*E*)-4-Hydroxybenzaldehyde oxime (0.75 g) was dissolved with heating in 60 ml of the benzene. Slow cooling to room temperature yielded 0.54 g (72 %) of beautiful, pink crystals, which conform exactly to the description given.² One of these crystals was used for the present X-ray studies. M.p. (cap., uncorrected) 111–112°C; at 106°C a few, tiny, melted particles were observed.

In the mother liquor some drops were observed to be adsorbed onto the glass; the drops were not miscible with the liquid, but they dissolved on heating, and on subsequent slow cooling to room temperature 0.06 g of crystals were formed, m.p. (cap., uncorrected) 114–116°C.

FERAK analytical grade benzene (40 ml) was saturated with water on vigorous shaking with approximately 0.02 ml of water, after which the flask was left until the liquid was clear and drops of water had deposited on the glass. (*E*)-4-Hydroxybenzaldehyde oxime (0.25 g) was dissolved in 20 ml of this liquid with heating, and on slow cooling of the solution to room temperature 0.22 g (88 % of the weight of the starting material) of a crystalline product was obtained after filtration and drying in the air. Microscopy showed that crystals of two different shapes had been formed. Melting-point determination (cap.) showed the melting to begin at about 85°C with total melting at about 105–108°C on rapid heating. In another experiment the melting-point tube was inserted at 101°C, and immediate and total melting was observed.

Crystallization from a sample of benzene of unknown purity. Preparation of a sample of (*E*)-4-hydroxybenzaldehyde

Table 1. Positional parameters and isotropic displacement parameters.

Atom	x	y	z	B_{iso}^a
C1	0.5596(2)	0.4618(2)	0.12810(7)	1.24(2)
C2	0.5430(2)	0.2472(2)	0.09351(8)	1.38(2)
C3	0.3790(2)	0.1180(2)	0.10490(7)	1.42(2)
C4	0.2285(2)	0.2003(2)	0.15122(8)	1.38(2)
C5	0.2460(2)	0.4103(2)	0.18831(7)	1.43(2)
C6	0.4110(2)	0.5389(2)	0.17659(7)	1.31(2)
C7	0.7220(2)	0.6111(2)	0.11146(8)	1.44(2)
N8	0.8477(1)	0.5589(2)	0.05941(6)	1.45(2)
O9	0.9857(1)	0.7318(1)	0.04955(6)	1.77(2)
O10	0.0634(1)	0.0804(2)	0.16284(6)	2.08(2)
H2	0.649(2)	0.184(3)	0.060(1)	2.0(3)*
H3	0.363(3)	-0.033(3)	0.081(1)	3.1(4)*
H5	0.142(2)	0.463(3)	0.222(1)	2.4(3)*
H6	0.422(2)	0.685(3)	0.203(1)	1.8(3)*
H7	0.728(3)	0.759(3)	0.141(1)	2.6(4)*
H9	1.072(3)	0.673(4)	0.018(1)	4.6(5)*
H10	0.057(3)	-0.034(4)	0.125(1)	5.5(6)*

*Starred atoms were refined isotropically.

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

oxime · 1/2 benzene and determination of the crystal structure have previously been described.¹ The remainder of the solution used was left in a glass-stoppered Erlenmeyer flask, in which crystals deposited, together with drops of liquid which were immiscible with the bulk of the solvent. After about 5 years, the drops had disappeared, and 1.74 g of largish, approximately cube-shaped, sparkling aggregates of crystals were isolated by suction from the benzene solvent (90 ml). The crystals rapidly gave off benzene, leaving 1.34 g of a slightly coloured, hard substance. On being crushed this gave a pinkish-yellow powder, with m.p. (cap., uncorrected) 112–114 °C. The same value was obtained for the mixed m.p. with the starting oxime. The loss of weight on drying (23.0 %) is within the accuracy of the experiment in accordance with a calculated loss of weight (22.2 %) on drying (*E*)-4-hydroxybenzaldehyde oxime · 1/2 benzene.

Crystallization from benzene dried over sodium thread. (*E*)-4-Hydroxybenzaldehyde oxime (0.30 g) was dissolved in 23 ml of this benzene sample with heating. On slow cooling the liquid was filled with a mass of crystals, which were isolated by suction. The product obtained (0.25 g) immediately lost the smell of benzene and consisted of tiny, pinkish crystals similar to the starting material; undoubtedly the anhydrous oxime had been recrystallized. As in the previous crystallization tiny liquid drops were slowly deposited on the flask under the surface of the solution.

The product isolated in the above experiment was dissolved in 25 ml of the dry benzene, and on slow cooling the liquid was filled with a network of crystals; after two days the network desintegrated when shaken, and a mass of very thin, long crystal needles was observed. A liquid deposit on the glass had also formed. After a further two days a

spontaneous recrystallization to shorter and broader crystals took place. A sample of the bright, sparkling crystals had dimensions of about 1×0.3×0.3 cm; in the air the crystals rapidly became opaque, and the rather strong smell of benzene gradually disappeared. The dimensions of the elementary cell as shown by X-ray investigation was in accordance with those of the oxime benzene solvate.¹

Structure determination of 4-hydroxybenzaldehyde oxime.

Crystal data: $C_7H_7NO_2$. $M_r = 137.14$, monoclinic, $P2_1/c$, $T = 122$ K, $a = 6.806(2)$, $b = 6.0157(12)$, $c = 15.744(3)$ Å, $\beta = 94.82(2)^\circ$, $V = 642.3(7)$ Å³, $Z = 4$, $D_x = 1.418$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, $\mu = 8.38$ cm⁻¹, $F(000) = 288$.

A single crystal, 0.08×0.2×0.4 mm³, was selected for the data collection performed on a CAD4 diffractometer using graphite monochromated Cu K α radiation. The crystal was cooled to 122±0.5 K during the experiment by means of an Enraf-Nonius gas-flow low-temperature device. The unit-cell dimensions were determined from a least-squares refinement of the setting angles for 18 reflections ($30^\circ < \theta < 45^\circ$). Scan type, $\omega-2\theta$, and range, $\Delta\omega = 1.5 + 0.15\tan\theta$, were selected based on a careful analysis of the reflection profiles. The maximum scantime was 60 s. The intensities of three standard reflections were monitored every 10000 s and the orientation of the crystal was checked every 300 reflections. These measurements did not reveal any systematic variations. Data reduction included corrections for background, Lorentz and polarization effects. Symmetry-related reflections were averaged $R_{\text{int}} = 0.023$, to give 1329 independent reflections.

The structure was solved by direct methods. SHELXS-86³ provided starting coordinates for all the non-hydrogen atoms. It was refined by least-squares minimizing, $\Sigma w(|F_o| - |F_c|)^2$.

The positions of the hydrogen atoms were shown clearly in a difference electron-density map calculated after anisotropic displacement parameters had been introduced for the non-hydrogen atoms. The parameters for the hydrogen atoms were also included in the refinement. The weights used in the final refinements follow the expression $w^{-1} = \sigma^2(F) + 6 \times 10^{-4} |F|^2$. 1069 observed reflections [$|F|^2 > 3\sigma(|F|^2)$] were used. The final residuals were $R = 0.033$ and $R_w = 0.047$, the maximum shift 0.01 σ . The difference electron density map was featureless, the maximum and minimum peaks were 0.21 e Å⁻³ and -0.23 e Å⁻³, respectively. The SDP-system⁴ was used for the crystallographic computations. The atomic scattering factors (from Ref. 5) were used as contained in the program.

The final positional parameters are listed in Table 1. Lists of anisotropic displacement parameters and of observed and calculated structure amplitudes may be obtained from the authors.

Discussion

The crystallization experiments indicate that nucleation of anhydrous (*E*)-4-hydroxybenzaldehyde oxime in benzene is

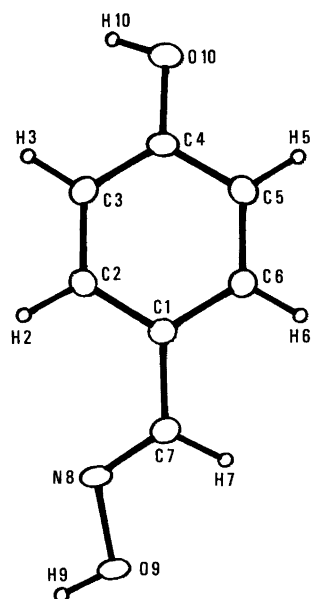


Fig. 1. ORTEP⁷ drawing of the molecule as found in the crystal structure. The ellipsoids are drawn to enclose 50% probability. The atomic labelling is indicated. Hydrogen atoms are drawn as spheres of fixed radius.

greatly influenced by the amount of water present in the solvent. In absolutely dry benzene only very small, soft crystals are formed, which slowly rearrange to the benzene solvate. In analytical grade benzene well developed crystals of the anhydrous oxime are formed, presumably assisted by the presence of a tiny amount of water in the benzene. Since the volume of benzene, used for crystallization is about 60–80 ml per gram of oxime, 0.03% of water in the benzene corresponds roughly to one molecule of water for

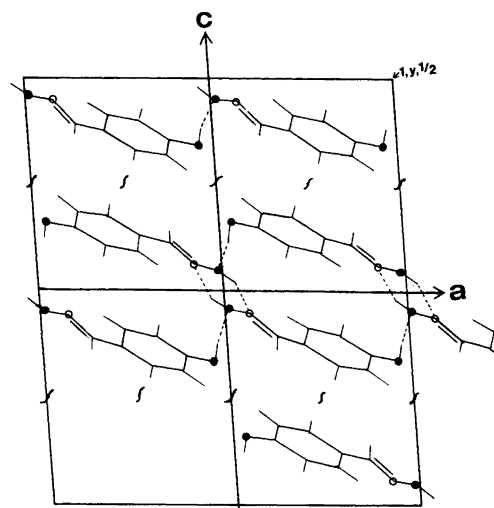


Fig. 2. Projection of the crystal structure illustrating the hydrogen bonding schemes. Oxygen atoms are indicated by black dots, nitrogen atoms by circles. The dimers across the double layer [formed by hydrogen bonds around the centres of symmetry in $(0, -1/2, 0)$ and $(1, 1/2, 0)$] are shown, as well as the hydrogen bonds along the double-layer (connecting the molecules x, y, z with molecules $x-1, y-1, z$).

every 5 molecules of the oxime. Furthermore the affinity of water to the oxime is clearly demonstrated by the observation that the monohydrate can be recrystallized from a number of different organic solvents.¹ Crystallization in water-saturated benzene (0.06% w/w⁶) resulted in a mixture of crystals, which by the characteristic crystal shapes and the behaviour on melting-point determination were identified as the anhydrous oxime and the monohydrate. Apart from this experiment, all the attempts to crystallize

Table 2. Bond distances and angles with esds in parentheses.

	Å	$10^{-3} \Delta \text{Å}$		deg	Δdeg
C1–C6	1.3970(13)	–1	C2–C1–C6	118.67(9)	0
C6–C5	1.3886(14)	–2	C1–C6–C5	121.24(9)	–0.2
C5–C4	1.393(2)	–3	C6–C5–C4	119.40(9)	0.1
C4–C3	1.3969(14)	–7	C5–C4–C3	119.99(9)	0
C3–C2	1.3844(14)	–3	C4–C3–C2	120.22(10)	0
C2–C1	1.4017(14)	–4	C3–C2–C1	120.40(9)	0.1
C1–C7	1.4649(13)	0	C6–C1–C7	119.07(9)	–0.2
C7–N8	1.2731(14)	5	C2–C1–C7	122.18(9)	0.2
N8–O9	1.4181(10)	–2	C1–C7–N8	121.47(9)	–0.2
O9–H9	0.88(2)	(0.02 Å)	C7–N8–O9	112.14(9)	–0.5
C4–O10	1.3607(12)	4	N8–O9–H9	104.3(13)	–2
O10–H10	0.91(2)	(–0.05 Å)	C5–C4–O10	117.82(9)	0.1
			C3–C4–O10	122.17(10)	–0.1
			C4–O10–H10	108.0(13)	–3
Hydrogen bonds:					
H9...N8 ^b	1.95(2)	(–0.02 Å)	O9–H9...N8 ^b	151(2)	4
N8 ^b ...O9	2.7592(13)	14	O10–H10...O9 ^c	168(2)	1
H10...O9 ^c	1.88(2)	(0.10 Å)			
O9 ^c ...O10	2.7750(12)	50			

^a Δ -values indicate $\text{obs.}_{\text{benzene solvate}} - \text{obs.}_{\text{present structure}}$. ^b $(2-x, 1-y, -z)$. ^c $(x-1, y-1, z)$.

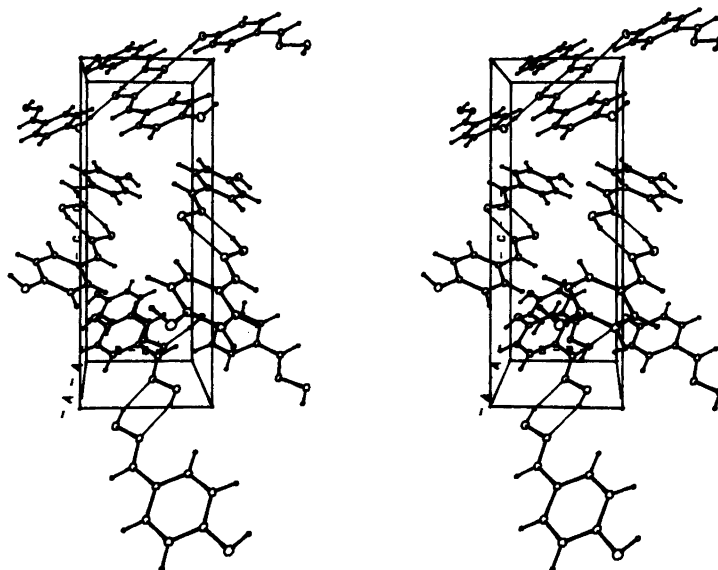


Fig. 3. Stereopair of the structure⁷ viewed along the direction of the *a*-axis. The hydrogen bonds are indicated by thin lines.

the oxime from benzene left a mother liquor with a layer of liquid drops deposited on the glass wall of the flask. From the combined experiments it is inferred that these drops are probably clusters of anhydrous oxime and benzene molecules, which crystallize extremely slowly.

The crystal structure determination of the anhydrous (*E*)-4-hydroxybenzaldehyde oxime has shown, that within the experimental accuracy the bond distances and angles of the oxime (Fig. 1) are virtually identical with those found for the molecule in the benzene solvate,¹ cf. Table 2. The benzene ring is planar in both structures, and the only significant difference in the conformation of the oximes is found in the torsion angle involving C7 (1.2°–3°). Furthermore, in both structures double layers are formed in which the molecules are linked pairwise across the layer and around centres of symmetry by two hydrogen bonds, O9–H9···N8, and in which the molecules are connected along the layer by two sets of hydrogen bonds O10–H10···O9, as shown in Figs. 2 and 3. Another common feature for the packing of the two crystal structures is that no atomic contact shorter than the sum of the van der Waals' radii is observed between the double layers and their surroundings.

Table 3. Deviation of benzene-ring bond lengths in Å × 10⁻³ from their mean value for three (*E*)-4-hydroxybenzaldehyde oximes.^a

	D	B	A		D	B	A
C1–C2	8	8	8	C1–C6	3	6	4
C2–C3	-10	-9	-7	C6–C5	-5	-3	-8
C3–C4	3	0	2	C5–C4	-1	0	3

^aD: oxime, present structure, $\sigma_{\text{bonds}} = 0.001_{3-5}$ Å; B: oxime · 1/2 benzene¹, $\sigma_{\text{bonds}} = 0.001_{5-6}$ Å; A: oxime · H₂O¹, $\sigma_{\text{bonds}} = 0.003_{2-6}$ Å.

While the bond lengths and the valency angles of the oximes in the two structures are virtually identical, the side-chain atoms, C7, N8 and O9 in the present crystal structure are displaced 0.131(1), 0.319(1), and 0.472(1) Å, respectively, from the least-squares plane calculated for the benzene ring atoms as compared with the equivalent values 0.061(2), 0.195(2) and 0.264(2) Å for the benzene solvate.¹ This observation together with some small differences in the geometries of the hydrogen bonds in the two crystal structures (cf. Table 2) may reasonably be ascribed to the differences in the packing conditions for identical molecules in two different crystalline states.

Conjugation between the oxime side chain and the aromatic ring is observed in the present structure as well as in the benzene solvate and the monohydrate of the oxime (Table 3). The bond lengths of the benzene ring in each of the three structures clearly indicate, that the conjugation preferentially involves the part of the ring in the *syn* position relative to the side chain, rather than the part in *anti* position. The same conclusion is obtained from a study of the bond lengths in the benzene rings of two independent molecules of (*E*)-4-hydroxybenzaldehyde.⁸ In contrast with the (*E*)-oximes mentioned above, a study of the benzene bond lengths in crystal structure determinations of (*Z*)-4-methoxybenzaldehyde oxime and the corresponding hydrochloride⁹ indicates a preferred conjugation involving the *anti*-position of the ring relative to the C=N bond.

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