On the Molecular Structures of Aromatic *Z*-Aldoximes and Their *N*-Adducts. Crystal Structures at 105 K of *Z*-4-Methoxybenzaldoxime Hydrochloride and of the Corresponding *Z*-Oxime

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The molecular geometries of the title compounds differ significantly only in the oxime moieties. The dimensions found may be considered as the best estimates at present for the oxime moiety in aromatic *Z*-aldoximes and their *N*-protonated cations. The molecular structures are weakly stabilized by intramolecular chelation $O_{oxime}\cdots H-C_{ortho}$; this is a characteristic feature of molecular structures of aromatic *Z*-aldoximes and their *N*-protonated and *N*-alkylated derivatives. Chains of hydrogen bonds $\cdots N-O-H\cdots N-O-H\cdots$ link the *Z*-4-methoxybenzaldoxime molecules. This association scheme appears to be characteristic for aromatic *Z*-aldoximes, whereas cyclic association of the oxime groups, usually to dimers, appears to be the preferred mode of association of the *E*-forms. The ions in *Z*-4-methoxybenzaldoxime hydrochloride form centrosymmetric pairs by hydrogen bonding $O-H\cdots Cl^-\cdots H-N^+$.

The work reported here is part of a project aimed at providing a better understanding of the stereochemistry of aromatic aldoximes and of their protonated and *N*-alkylated derivatives. An impressive experimental material was accumulated during the early years of organic chemistry, and the literature on oximes up to 1931 is excellently reviewed by Meisenheimer and Theilacker.[1] However, up to now the mechanisms of the isomerization reactions have not been explained, nor are the relative stabilities of the stereoisomers understood. Apparently, the most useful information is obtainable from crystal structure studies. Some general features thus observed for *E*- and *Z*-oximes and for *N*-alkylated oximes have been presented previously,[2] but so far no crystal data on protonated oximes have been published. *Z*-4-Methoxybenzaldoxime hydrochloride is well characterized[3] and was selected for the present study. The crystal structure of the parent oxime has been published previously[4] but the hydrogen positions were not determined; the present structure determination was undertaken in order to obtain comparable data for the oxime and its protonated form. A preliminary account of the structure determination has been given.[5]

Experimental

Z-4-Methoxybenzaldoxime. Crude 4-methoxybenzaldoxime hydrochloride prepared according to Lindemann and Tschang[6] gave, on basification with sodium carbonate, the crude oxime, which upon recrystallization from toluene gave small, needle-shaped crystals, m.p. (cap.) 131–131.5 °C (131.5 °C[3]), used for the structure determination.

Z-4-Methoxybenzaldoxime hydrochloride was prepared in highly concentrated hydrochloric acid following Brady and Dunn,[3] with the only

exception that the starting material was the above crude oxime hydrochloride. The crystals formed were used directly for the structure determination. The somewhat flattened needles or plates had the *b*-direction in the plane of the plate.

Crystal structure determinations. Experimental conditions are summarized in Table 1. The structure of *Z*-4-methoxybenzaldoxime hydrochloride was solved using the MULTAN programme. After least-squares isotropic refinement of the parameters for the non-hydrogen atoms, approximate positional parameters for the hydrogen atoms were obtained by a difference electron density calculation. Further refinement with anisotropic thermal parameters for the non-hydrogen atoms converged with no parameter shifts to give $R = 0.032$, $R_w = 0.042$. The refinement of the structure of *Z*-4-methoxybenzaldoxime started from the coordinates found at room temperature[4] and followed the above scheme, converging with shifts/errors of less than 0.1 (except for B(H10A) ~ 0.8) to give $R = 0.044$, $R_w = 0.052$. Atomic scattering factors were taken from Cromer and Mann,[7] except those for hydrogen which were taken from Stewart, Davidson and Simpson.[8] All computations were performed using the CAD-4 SDP programs.[9]

Crystal data. *Z*-4-Methoxybenzaldoxime, $C_8H_9NO_2$; orthorhombic, space group $Pna2_1$, $a = 7.557(8)$, $b = 11.458(6)$, $c = 17.602(5)$ Å, $V = 1524(1)$ Å^3, $Z = 8$, D_x(105K) = 1.318 g cm^{-3}, $\mu_{Mo} = 0.0894$ mm^{-1}, $F(000) = 640$. *Z*-4-Methoxybenzaldoxime hydrochloride, $C_8H_{10}NO_2Cl$; monoclinic, space group $P2_1/c$, $a = 9.660(10)$, $b = 7.393(1)$, $c = 13.032(10)$ Å, $\beta = 104.87(7)°$, $V = 899(1)$ Å^3, $Z = 4$, D_x(105K) = 1.386 g cm^{-3}, $\mu_{Mo} = 0.381$ mm^{-1}, $F(000) = 392$.

Results

The atomic coordinates in the two crystal structures are given in Tables 2 and 3. The numbering of the atoms is shown in Figs. 1 and 2. Bond distances and angles are presented in Tables 4 and 5.

Z-4-Methoxybenzaldoxime. The equivalent bond angles and bond distances in the two crystallographically independent molecules A and B (Fig. 1) do not deviate significantly. The mean values of the bond lengths and angles of the oxime moiety [C=N = 1.286(2) Å, N–O = 1.394(2) Å, C=N–O = 114.1(2)° and Ar–C=N = 132.4(2)°] agree well with values previously estimated from less accurate structure determinations[2] and may

Table 1. Experimental conditions for the X-ray structure determinations.

	Z-4-Methoxybenzaldoxime	*Z*-4-Methoxybenzaldoxime, HCl
Instrument	Enraf-Nonius CAD-4 diffractometer	
Radiation	Graphite-monochromated Mo($\lambda = 0.71073$ Å)	
Temperature/K	105 ± 5, constant within ±0.5 K	
Scanning mode	$\omega/2\theta$	
Scan interval, $\Delta\omega$/°	$(1 + 0.347 \tan\theta)$	
Background interval	$\Delta\omega \pm 25$ %	
Scan speed/° min^{-1}	5.5 – 0.6	
Max. scan time per reflection/s	150	
Scan range/°	$2 < 2\theta < 76$	
Standard reflections	3 measured every 10 000 s	
Cell dimensions from	18	18
Number of reflections	$(16.37 < \theta < 21.82°)$	$(18.49 < \theta < 22.57°)$
Number of reflections in calculations	2938 ($I_0 > 2\sigma I_0$)	3703 ($I_0 > 3\sigma I_0$)
Reflections/number of parameters refined	10.8	25
h,k,l intervals scanned	0–13, 0–19, 0–30	(–)11–16, 0–12, (–)22–21
Crystal dimensions/mm	0.16×0.25×0.48	0.25×0.25×0.50
Corrections	*Lp*	
Quantity minimized in least-squares calculations	$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
$w = 1/\sigma(F_o)^2 = Lp[\sigma(I_o)^2 + (xI_o)^2]^{-1/2}$	$x = 0.07$	$x = 0.04$

Table 2. Z-4-Methoxybenzaldoxime. Atomic coordinates and isotropic thermal parameters for molecules A and B with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	$B_{eq/iso}$
Molecule A				
C1A	1.0966(2)	0.8972(1)	0.86572(9)	1.17[a]
C2A	0.9741(2)	0.8135(1)	0.8405(1)	1.38[a]
C3A	0.9240(2)	0.8074(2)	0.7643(1)	1.39[a]
C4A	0.9961(2)	0.8846(1)	0.71178(9)	1.29[a]
C5A	1.1204(2)	0.9673(2)	0.7355(1)	1.44[a]
C6A	1.1685(2)	0.9735(1)	0.8111(1)	1.36[a]
C7A	1.1572(2)	0.9132(2)	0.9440(1)	1.56[a]
C8A	0.8092(3)	0.8169(2)	0.6120(1)	2.25[a]
N9A	1.1078(2)	0.8676(2)	1.00740(9)	1.65[a]
O10A	0.9702(2)	0.7880(1)	1.000	1.79[a]
O11A	0.9566(2)	0.8862(1)	0.63633(7)	1.78[a]
H2A	0.914(3)	0.758(2)	0.875(2)	2.0(5)
H3A	0.841(4)	0.757(2)	0.750(2)	2.3(5)
H5A	1.169(4)	1.023(2)	0.700(2)	2.0(5)
H6A	1.251(3)	1.032(2)	0.829(2)	2.3(5)
H7A	1.263(4)	0.956(2)	0.949(2)	3.0(6)
H81A	0.704(3)	0.841(2)	0.639(2)	1.9(5)
H82A	0.838(3)	0.740(2)	0.615(1)	1.7(5)
H83A	0.804(4)	0.839(2)	0.561(2)	2.8(6)
H10A	0.941(6)	0.761(4)	1.045(3)	7(1)
Molecule B				
C1B	0.9523(2)	0.6742(1)	0.28132(9)	1.16[a]
C2B	0.8760(2)	0.5671(1)	0.3011(1)	1.26[a]
C3B	0.8678(2)	0.5325(1)	0.3772(1)	1.30[a]
C4B	0.9368(2)	0.6036(2)	0.43383(9)	1.32[a]
C5B	1.0149(2)	0.7102(2)	0.4147(1)	1.42[a]
C6B	1.0229(2)	0.7445(2)	0.3397(1)	1.35[a]
C7B	0.9666(2)	0.7235(1)	0.2046(1)	1.42[a]
C8B	0.8336(3)	0.4807(2)	0.5334(1)	2.17[a]
N9B	0.8937(2)	0.6962(1)	0.14108(9)	1.55[a]
O10B	0.7838(2)	0.5981(1)	0.14425(8)	1.65[a]
O11B	0.9379(2)	0.5780(1)	0.50928(7)	1.83[a]
H2B	0.833(3)	0.513(2)	0.263(1)	1.4(4)
H3B	0.811(3)	0.457(2)	0.388(1)	1.7(5)
H5B	1.065(4)	0.761(2)	0.453(1)	2.0(5)
H6B	1.073(3)	0.814(2)	0.327(1)	1.7(5)
H7B	1.045(4)	0.792(2)	0.197(2)	2.5(6)
H81B	0.710(3)	0.491(2)	0.526(2)	2.2(5)
H82B	0.845(4)	0.476(2)	0.582(2)	2.7(6)
H83B	0.878(4)	0.411(2)	0.510(2)	2.7(6)
H10B	0.729(5)	0.605(3)	0.101(2)	4.2(7)

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j b_{ij}\,\mathbf{a}_i\mathbf{a}_j$

be regarded as the best estimate at present of the geometry in benzenoid *Z*-aldoximes. The benzene rings with the attached hydrogen atoms are planar, but C7 and O11 in both molecules are slightly displaced from the calculated least-squares planes C1–C6: C7A −0.023(2), C7B −0.036(2), O11A −0.010(1) and O11B 0.010(1) Å. The oxime side chain is planar in molecule A, whereas in molecule B the hydrogen atom H10B deviates 0.21 Å from the least-squares plane

Table 3. *Z*-4-Methoxybenzaldoxime hydrochloride. Atomic coordinates and isotropic thermal parameters with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	$B_{eq/iso}$
C1	0.09432(2)	0.23271(3)	0.52823(2)	1.425[a]
O11	0.15149(6)	0.61025(9)	0.28120(5)	1.67[a]
O10	0.68948(6)	0.04832(9)	0.45917(6)	2.08[a]
N9	0.76924(7)	0.1999(1)	0.45760(6)	1.46[a]
C8	0.02920(9)	0.4923(1)	0.26677(7)	1.72[a]
C4	0.28285(8)	0.5354(1)	0.31711(6)	1.20[a]
C3	0.30734(8)	0.3527(1)	0.34418(6)	1.25[a]
C2	0.44629(8)	0.2891(1)	0.38185(6)	1.22[a]
C1	0.56357(7)	0.4061(1)	0.39255(6)	1.10[a]
C6	0.53680(8)	0.5896(1)	0.36484(6)	1.30[a]
C5	0.39871(8)	0.6538(1)	0.32811(6)	1.39[a]
C7	0.71259(7)	0.3559(1)	0.43002(6)	1.27[a]
H82	0.030(1)	0.437(2)	0.3353(9)	2.1(3)
H81	0.029(1)	0.401(2)	0.2129(9)	2.1(3)
H83	−0.052(1)	0.573(2)	0.244(1)	2.8(3)
H3	0.233(2)	0.278(2)	0.338(1)	2.5(3)
H2	0.459(1)	0.165(2)	0.4014(9)	1.7(2)
H6	0.612(1)	0.666(2)	0.3721(9)	1.6(2)
H5	0.380(1)	0.781(2)	0.310(1)	1.8(3)
H7	0.785(1)	0.445(2)	0.4381(9)	1.6(2)
H9	0.875(2)	0.189(2)	0.483(1)	3.6(3)
H10	0.751(2)	−0.040(2)	0.466(1)	3.0(3)

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j b_{ij}\,\mathbf{a}_i\mathbf{a}_j$

Table 4. Bond lengths (Å) in *Z*-4-methoxybenzaldoxime and in *Z*-4-methoxybenzaldoxime hydrochloride. e.s.d.'s in parentheses.

Bond	*Z*-4-methoxybenzaldoxime		*Z*-4-methoxybenzaldoxime hydrochloride
	Molecule A	Molecule B	
C1–C2	1.405(2)	1.400(2)	1.404(1)
C2–C3	1.395(2)	1.398(2)	1.388(1)
C3–C4	1.391(2)	1.389(2)	1.401(1)
C4–C5	1.398(2)	1.398(2)	1.399(1)
C5–C6	1.382(3)	1.380(3)	1.381(1)
C6–C1	1.408(2)	1.410(2)	1.411(1)
C1–C7	1.464(2)	1.467(2)	1.445(1)
C7–N9	1.287(2)	1.285(2)	1.288(1)
N9–O10	1.390(2)	1.399(2)	1.363(1)
C4–O11	1.361(2)	1.360(2)	1.353(1)
O11–C8	1.434(3)	1.430(3)	1.441(1)

C1B–C7B–N9B–O10B. The methoxy group and the oxime side chain are turned to the same side of the ring plane, torsional angles being: C2–C1–C7–N9, A: ∓7.4°, B: ±13.2° and C3–C4–O11–C8, A: ±11.0°, B: ∓11.4°. The above mentioned small conformational differences between molecules A and B may be ascribed to the packing conditions in the crystal. A short intramolecular distance $O_{oxime}\cdots H_{ortho}$ is noted in both molecules, viz. in A, 2.26(3) and in B, 2.33(3) Å. Chains of hydrogen bonds, $\cdots N_A–O_A–H_A\cdots N_B–O_B–H_B\cdots N'_A$-

Table 5. Bond angles (°) in *Z*-4-methoxybenzaldoxime and in *Z*-4-methoxybenzaldoxime hydrochloride. e.s.d.'s in parentheses.

Angle	*Z*-4-methoxybenzaldoxime		*Z*-4-methoxybenzaldoxime
	Molecule A	Molecule B	hydrochloride
C6–C1–C2	117.6(2)	118.4(2)	118.50(5)
C1–C2–C3	121.1(2)	120.4(2)	120.60(6)
C2–C3–C4	120.1(2)	120.3(2)	120.09(6)
C3–C4–C5	119.7(2)	119.9(2)	119.90(6)
C4–C5–C6	120.0(2)	119.9(2)	119.81(6)
C5–C6–C1	121.6(2)	121.2(2)	121.10(6)
C1–C7–N9	132.4(2)	132.5(2)	129.75(6)
C7–N9–O10	113.7(2)	114.5(2)	122.64(5)
C7–C1–C2	126.1(2)	126.6(2)	125.74(6)
C7–C1–C6	116.4(2)	115.0(2)	115.77(5)
C4–O11–C8	117.0(2)	117.0(2)	117.54(5)
C3–C4–O11	124.9(2)	125.2(2)	124.34(6)
C5–C4–O11	115.4(2)	114.9(2)	115.75(6)

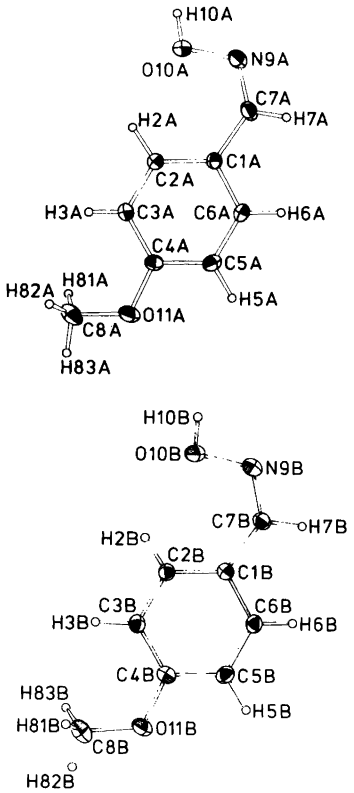


Fig. 1. ORTEP drawings[10] of molecules A and B in *Z*-4-methoxybenzaldoxime showing the numbering of the atoms. The ellipsoids enclose 50 % probability. Hydrogen atoms are represented by spheres of arbitrary radius.

$-O'_A-H'_A\cdots N'_B-O'_B-H'_B\cdots$ link the molecules in the *a* direction; the chain atoms project onto the *bc* plane as an irregular figure eight. The dimensions of the hydrogen-bonding system are given in Table 6, and the packing of the molecules is illustrated in Fig. 3.

Z-4-Methoxybenzaldoxime hydrochloride. Only in the oxime moiety itself do the observed bond lengths and angles deviate significantly from corresponding values found for the parent oxime. C1–C7 and N9–O10 are 0.021(3) and 0.031(3)

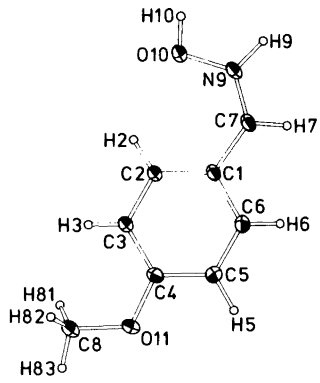


Fig. 2. ORTEP drawing[10] of the *N*-protonated *Z*-4-methoxybenzaldoxime showing the numbering of the atoms. The ellipsoids enclose 50 % probability. Hydrogen atoms are represented by spheres of arbitrary radius.

Table 6. Hydrogen bonding in crystalline *Z*-4-methoxybenzaldoxime and *Z*-4-methoxybenzaldoxime hydrochloride.

Z-4-Methoxybenzaldoxime

Symmetry scheme for the chain association:
···N9A–O10A–H10A···N9B–O10B–H10B···N9A–O10A–H10A···N9B–O10B–H10B···
$(x,y,z-1)$ (x,y,z) $(x-\frac{1}{2},\frac{3}{2}-y,z-1)$ $(x-\frac{1}{2},\frac{3}{2}-y,z)$

OA–HA···NB 176(5)°	OA···NB 2.758(2) Å	HA···NB 1.89(6) Å	OA–HA 0.87(6) Å
OB–HB···NA 176(4)°	OB···NA 2.780(2) Å	HB···NA 1.91(4) Å	OB–HB 0.87(4) Å

Z-4-Methoxybenzaldoxime hydrochloride

Symmetry scheme: N–H···Cl$(x+1,y,z)$ ·····H–O
(x,y,z) | | $(2-x,-y,1-z)$
O–H···Cl$(1-x,-y,1-z)$···H–N

O–H···Cl 174(2)°	O···Cl 2.921(1) Å	H···Cl 2.05(1) Å	O–H 0.88(1) Å
N–H···Cl 166(1)°	N···Cl 3.047(1) Å	H···Cl 2.08(1) Å	N–H 0.99(1) Å
	H···Cl···H 125(3)°		

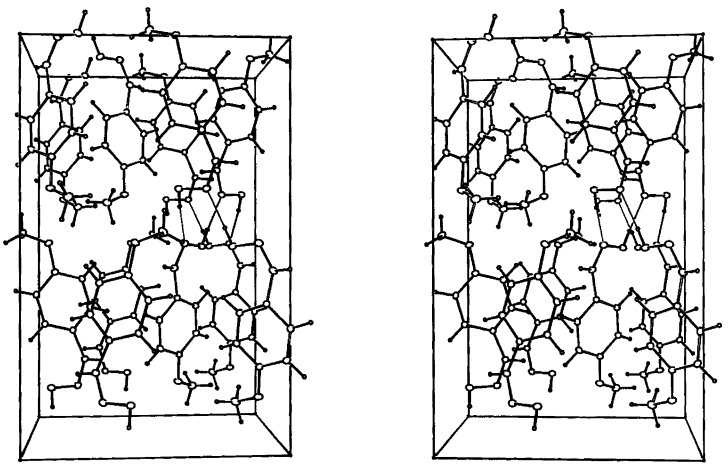


Fig. 3. Stereoview along *a* of the packing and hydrogen bonding in *Z*-4-methoxybenzaldoxime.

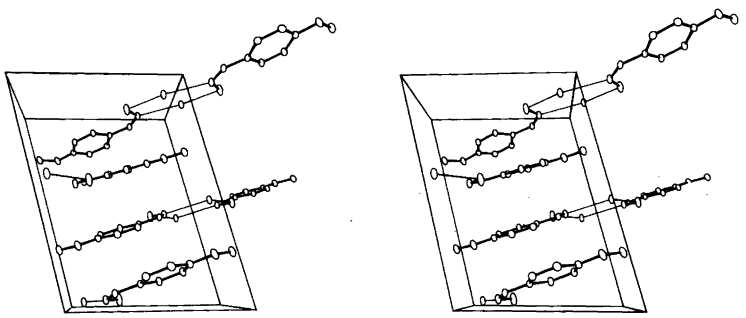


Fig. 4. Stereoview approximately along *b* of the packing and hydrogen bonding in *Z*-4-methoxybenzaldoxime hydrochloride.

Å shorter, respectively, the angle C1−C7=N9 is 2.6(3)° smaller, and the angle C7=N9−O10 is 8.5(3)° larger than the mean of the corresponding values in the parent oxime. The signs of the possibly significant deviations (≥0.008 Å) in bond lengths are in accordance with the expected partial delocalization of the positive charge of the *N*-protonated ion to the O11 atom. No significant lengthening of the C7=N9 bond due to protonation is seen. The torsional angles C2−C1−C7−N9 (±2.3°) and C3−C4−O11−C8 (∓2.1°) are appreciably smaller than in the parent oxime, again in accordance with the delocalization mentioned above. The benzene ring and the attached hydrogen atoms are coplanar and C7 and O11 are only slightly displaced (0.006(1) and −0.012(1) Å, respectively) from the least-squares plane C1−C6. The hydrogen atom H10 is displaced 0.26(1) Å from the benzene plane and 0.20(1) Å from the least-squares plane C1−C7−N9−O10. A short intramolecular distance $O_{oxime}\cdots H_{ortho}$ [2.33(1) Å] is observed, as in the parent oxime. The organic ions are connected pairwise via hydrogen bonds $O-H\cdots Cl^{-}\cdots H-\overset{+}{N}\cdots$ (see Table 6 and Fig. 4). The chloride ions are stacked in zig-zag lines in the *b* direction, Cl···Cl distances in the line being 3.875(1) and 4.335(1) Å. The packing of the ions is shown in Fig. 4.

Discussion

Geometric effects of N-*coordination on a* >*C*=*N*−*O group.* The discussion is based upon data for two related compounds, viz. formamide oxime[11,12] and oxamide oxime,[13] for which crystal data for the protonated forms are also available.

The structure of formamide oxime[11] was determined from neutron diffraction data at 16 K. The experimental results agree well with a much less accurate determination from X-ray data at room temperature,[12] and they are used for comparisons in the following. Protonated formamide oxime was studied as the hydrogen oxalate[14] by X-ray diffraction at 105 K. Oxamide oxime was present in the monoprotonated as well as the diprotonated form in the squarate,[15] and unprotonated oxamide oxime was found together with the bis (oxamide-oximato)Cu(II) complex in a crystal studied.[13] The crystal studies[13,15] were both performed at room temperature. In all the crystal structures mentioned, the amide oxime has the *Z*-configuration, i.e. the oxime oxygen is *cis* to the NH_2 group.

The results show that protonation as well as complex formation take place at the oxime N atom, and that the accompanying changes in the dimensions of the oxime moiety follow a common pattern: The C=N bond becomes slightly longer, the N−O bond clearly shortens, and the angle C=N−O increases by several degrees. For the pair formamide oxime/protonated formamide oxime the changes are C=N: +0.011 and +0.005(2) Å, N−O: −0.0038 and −0.0041(2) Å and C=N−O: +7.1°.

These changes relative to the parent amide oxime dimensions are, as could be expected, very similar to those found on protonation of *Z*-4-methoxybenzaldoxime. Furthermore, a similar pattern for the differences between the dimensions of aromatic *Z*-aldoximes and *N*-alkylated *Z*-oximes has been observed,[2] although the effects of *N*-alkylation are appreciably greater, since an *N*-alkylated oxime has nitrone structure,

$$C=\overset{+}{N}\begin{matrix}/\,O^{-}\\ \backslash\,R\end{matrix}.$$

The results described suggest that the geometry found for *Z*-4-methoxybenzaldoxime hydrochloride may be taken as representative for protonated aromatic *Z*-aldoximes in general.

Chelation O···H−C in aromatic Z-aldoximes and derivatives. In 1970, a short intramolecular distance $O_{oxime}\cdots C_{ortho}$ had been observed in a number of crystal structures of aromatic *Z*-aldoximes.[16] In the same year, Sauvaitre and Deschamps[17] proposed that chelation $O_{oxime}\cdots H-C_{ortho}$ stabilizes the *Z*-isomer; the proposal was based upon thermodynamic data for the $E \rightleftharpoons Z$ isomerization of benzaldoxime and was supported by theoretical calculations (Pariser-Parr-Pople and CNDO) using the published molecular geometries of the 4-chlorobenzaldoximes found in crystal structures. A subsequent analysis of IR and Raman spectra of the two isomers was interpreted as providing confirmation of the proposed chelation.[18] Raman spectra of a number of α-furyl ketoximes had previously led to the same conclusion.[19] The evidence quoted above lends no unambiguous support to the concept of chelation, i.e. short (carbon)H···O dis-

Table 7. Chelation $O_{oxime}\cdots H-C_{ortho}$ in crystal structures of aromatic *Z*-aldoximes and derivatives. Figures in parentheses are based upon calculated hydrogen positions.

	O···C/Å	O···H/Å	C–H/Å	O···H–C/°	Angle ring/ C–C=N plane/°	β–α/° [a]
Z-Aldoximes:						
4-Methoxybenz- A	2.822(2)	2.26(3)	0.99(3)	115(3)	7.4	9.7(2)
B	2.870(2)	2.33(3)	0.96(3)	114(2)	13.2	11.6(2)
4-Chlorobenz-[c]	2.82	2.31	1.00	111	19.5	9
4-Pyridinecarb-[d]	2.81	2.25	0.95	117	7.7	9
4-Pyrimidinecarb-[e]	2.81	2.28	0.93	121	~1	15
2-Furanecarb-[f]	2.86	(2.47)	(0.99)	(103)	6	26
N-Protonated *Z*-aldoxime:						
4-Methoxybenz-	2.913(1)	2.33(1)	0.95(1)	119(1)	2.3	10.0
N-Methylated *Z*-aldoximes:						
4-Nitrobenz-[g]	2.92	2.25			4	10
	2.88	2.26			5	11
4-Chlorobenz-[h]	2.88	2.21	0.98	125	6	13
4-Chloro-2,6-dimethylbenz-[i]	3.01	2.39[b]	1.00	120	55	6
Oxaziridine:						
(*RS*)-*trans*-2-Methyl-3-(4-chloro-2,6-dimethylphenyl)-[j]	2.90	(2.39)[b]	(0.97)	(113)	–	4

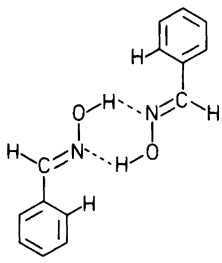
[a]Exocyclic angles $C_{ring}-C_{ring}-C_{oxime}$; β *cis*, α *trans* to C=N. [b]*ortho* methyl hydrogen. [c]Ref. 21. [d]Ref. 22. [e]Ref. 23. [f]Ref. 24. [g]Ref. 25. [h]Ref. 26. [i]Ref. 27. [j]Ref. 28.

tances arising from attraction. However, justification for using the term "chelation" is found in a thorough analysis of short (C)H···O distances observed in crystal structures determined by neutron diffraction.[20] "Short" (C)H···O contacts were considered to be values of 2.4 Å or less. Among the results obtained it can be mentioned that short *inter*molecular contacts appear to be due to electrostatic stabilization, and that the geometry in relation to the positions of the lone pairs of the oxygen atoms supports this idea. *Intra*molecular (C)H···O interactions were also considered, recognizing that the geometry in this case is more likely to be influenced by the environment than in the case of an intermolecular interaction.

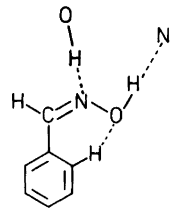
In all crystal structures of aromatic *Z*-aldoximes and *N*-derivatives published so far, chelation C–H···O is observed;[16,21–27] data are given in Table 7. It is noteworthy that even an *ortho* methyl group may take part in chelation.[26–27] It is likewise noteworthy that in the heteroaromatic *Z*-oximes, [22–23] O···H–C chelation is preferred to chelation $O-H_{oxime}\cdots$ ring hetero-atom. The chelation is accompanied by an increase in the exocyclic angle $C-C-C_{oxime}$ *cis* to the oxime moiety relative to the *trans* angle, the difference between the two angles being for the benzene aromatic *Z*-oximes 11 ± 2°. The dihedral angle ring plane/oxime side chain is more variable and may be influenced appreciably by the packing conditions in the crystal, as observed for *Z*-4-methoxybenzaldoxime.

It is concluded that chelation $O_{oxime}\cdots H-C_{ortho}$ is a general structural feature of aromatic *Z*-aldoximes and their *N*-substituted derivatives.

Association of aromatic oximes by hydrogen bonding. The discussion in this section is confined to association of aromatic oximes in which no hydrogen bonds other than those involving the =NOH moiety are likely to be formed. For con-



E-OXIME, ASSOCIATED DIMER



Z-OXIME, ASSOCIATED CHAIN

Scheme 1.

venience, these oximes are termed "simple oximes". Since only few crystal structures of simple aromatic oximes have been published, an unequivocal systematization of the association schemes adopted is not warranted, although some trends can be seen.

Of the four simple aromatic *E*-aldoximes studied, three of them (4-chlorobenzaldoxime,[28] 4-dimethylaminobenzaldoxime[29] and 4-nitrobenzaldoxime[30]) form cyclic dimers, whereas benzaldoxime[2] associates to a cyclic tetramer. Cyclic dimerization has also been reported for an aromatic *E*-ketoxime, *E*-1-(2,4,6-trimethylphenyl)ethanone oxime.[31] In contrast, the three simple aromatic *Z*-aldoximes studied (4-chlorobenzaldoxime,[28] 2-furaneoxime[23] and the present structure) associate in chains.

Cyclic dimerization of simple aromatic *Z*-aldoximes seems at first glance just as likely as for the *E*-forms. However, the chelation, the *E*-forms. However, the chelation, $O_{oxime}\cdots H-C_{ortho}$, found in all known crystal structures of *Z*-aldoximes must have some influence on the geometry of the bonding of the oxygen atom. This may well prevent the formation of the nearly parallel hydrogen bonds which are necessary for cyclic dimerization. Only one other crystal structure of a simple aromatic oxime (beside those discussed so far) has been found in the literature,[32] viz. that of *E*-1-phenyl-2-bromoethanone oxime.[33] In this molecule the oxime group is in a position *cis* to the aromatic ring, as in the aromatic *Z*-oximes. The bulky CH_2Br group necessitates a large angle (54°) between the plane of the benzene ring and the oxime side chain, and thus prevents chelation $O_{oxime}\cdots H-C$. It is therefore not surprising that cyclic association of these molecules is possible, and tetramerization is indeed found.

Ossart, Sauvaitre and Pineau[34] studied association of a number of oximes in tetrachloromethane solutions of concentrations from $3\cdot10^{-4}$ to $50\cdot10^{-4}$ M by quantitative IR spectrometry of the non-associated OH vibration. They concluded that the self-association in this case appears to be limited to the formation of cyclic dimers, but they also noted that this result is in disagreement with the findings of other authors. The compounds examined were acetaldoxime, acetoxime, butanone oxime, cyclohexanone oxime, acetophenone oxime and benzophenone oxime. The stereochemistry of these compounds was not specified. It is interesting that acetoxime[35] and cyclohexanone oxime[36] in the crystalline state form cyclic trimers. Sauvaitre[37] also found cyclic dimerization for both isomers of benzaldoxime. It is, however, difficult to accept that cyclic dimerization is a general phenomenon for oximes in solution, considering the variety of association behaviour observed in the crystalline state. A piece of evidence in favour of open chain association for aromatic *Z*-aldoximes is that Sauvaitre[37] found the *Z*-form of benzaldoxime to be very sparsely soluble in a number of organic solvents relative to the *E*-isomer; an analogous observation was made in the present work during recrystallization experiments with *E*- and *Z*-4-methoxybenzaldoxime.

On the basis of the combined evidence it seems reasonable to conclude that cyclic association, usually into dimers, is the preferred mode of association for simple aromatic *E*-aldoximes, whereas chain association is characteristic for simple aromatic *Z*-aldoximes in which chelation $O_{oxime}\cdots H-C_{ortho}$ occurs.

Chelation and the types of association proposed for simple aromatic *E*- and *Z*-aldoximes are shown in Scheme 1.

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References

1. Meisenheimer, J. and Theilacker, W. In: Freudenberg, K., Ed., *Stereochemie,* Franz Deuticke, Leipzig und Wien 1932, Vol. 3, p. 963.
2. Jerslev, B. *Acta Crystallogr., Sect. C39* (1983) 1447.
3. Brady, O. L. and Dunn, F. P. *J. Chem. Soc.* (1923) 1783.
4. Ciajolo, M. R., Lelj, F., Tancredi, T. and Temussi, P. A. *Acta Crystallogr., Sect. B37* (1981) 1130.
5. Jerslev, B. *Ninth European Crystallographic Meeting, Torino, Italy 2–6 Sept. 1985. Abstracts* (1985) Vol. 1, p. 281.
6. Lindemann, H. and Tschang, K.-T. *Ber. Dtsch. Chem. Ges. 60* (1927) 1725.
7. Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A24* (1968) 321.
8. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
9. Enraf-Nonius, *Structure Determination Package, SDP,* Version 1.1, Delft 1982.
10. Johnson, C. K. *ORTEP:* Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, TN 1976.
11. Jeffrey, G. A., Ruble, I. R., McMullan, R. K., DeFrees, D. J. and Pople, J. A. *Acta Crystallogr., Sect. B37* (1981) 1381.
12. Hall, D. *Acta Crystallogr. 18* (1965) 955.
13. Endres, H., Genc, N. and Nöthe, D. *Acta Crystallogr., Sect. C39* (1983) 701.
14. Larsen, I. K. *Acta Crystallogr., Sect. C41* (1985) 749.
15. Endres, H. and Schendzielorz, M. *Acta Crystallogr., Sect. C40* (1984) 453.
16. Jensen, K. G. *Acta Chem. Scand. 24* (1970) 3293.
17. Sauvaitre, H. and Deschamps, J. *Tetrahedron 26* (1970) 1647.
18. Sauvaitre, H. *Tetrahedron 27* (1971) 1859.
19. Dullien, F. *Can. J. Chem. 35* (1957) 1366.
20. Taylor, R. and Kennard, O. *J. Am. Chem. Soc. 104* (1982) 5063.
21. Martínez-Ripoll, M. and Lorenz, H. P. *Acta Crystallogr., Sect. B32* (1976) 2325.
22. Martínez-Ripoll, M. and Lorenz, H. P. *Acta Crystallogr., Sect. B30* (1974) 793.
23. Jensen, B. and Jerslev, B. *Acta Chem. Scand. 21* (1967) 730.
24. Bachechi, F. and Zambonelli, L. *Acta Crystallogr., Sect. B31* (1975) 2499.
25. Folting, K., Lipscomb, W. N. and Jerslev, B. *Acta Crystallogr. 17* (1964) 1263.
26. Jensen, K. G. and Jerslev, B. *Acta Crystallogr., Sect. B25* (1969) 916.
27. Jerslev, B. *Acta Crystallogr. 23* (1967) 645.
28. Jerslev, B. *Nature (London) 180* (1957) 1410.
29. Bachechi, F. and Zambonelli, L. *Acta Crystallogr., Sect. B28* (1972) 2489.
30. Bachechi, F. and Zambonelli, L. *Acta Crystallogr., Sect. B29* (1973) 2598.
31. Fortier, S., Birnbaum, G. I., Buchanan, G. W. and Dawson, B. A. *Can. J. Chem. 58* (1980) 191.
32. *Cambridge Crystallographic Database,* most recent data Nov. 27 1985.
33. Wetherington, J. B. and Moncrief, J. W. *Acta Crystallogr., Sect. B29* (1973) 1520.
34. Ossart, A., Sauvaitre, H. and Pineau, P. *J. Chim. Phys. 64* (1967) 953.
35. Bierlein, T. K. and Lingafelter, E. C. *Acta Crystallogr. 4* (1951) 450.
36. Okaya, Y., Shimada, A. and Nitta, I. *Bull. Chem. Soc. Jpn. 29* (1956) 210.
37. Sauvaitre, H. *J. Mol. Struct. 11* (1972) 403.

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