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Structure of (E)-Benzaldehyde Oxime, C7H7NO, at 100 K and Systematics of Molecular Structures of Aromatic Aldoximes

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Abstract. $M_r = 121.14$, monoclinic, $C2/c$, $a = 18.50$ (1), $b = 8.272$ (1), $c = 17.224$ (7) Å, $\beta = 101.38$ (5)°, $V = 2584$ (4) Å^3, $Z = 16$, D_m (291 K) = 1.196, D_x (100 K) = 1.245 (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.0792$ mm^{-1}, $F(000) = 1024$. Final $R = 0.045$ for 3477 observed unique reflections. The molecules are linked by hydrogen bonds, O–H···N, into cyclic tetramers. No other short *inter*molecular distances are present. The tetramers are stacked in columns along the **b** direction around the twofold axes. The variability of the oxime moiety in aromatic aldoximes, Ar–CH=N–OH, found in the literature has been systematized and to some extent explained by studying the geometry as a function of oxime type (E versus Z) and of the nature of the aromatic moiety (unsubstituted or substituted benzene and heteroaromatic rings). The influence of (E)- and of (Z)-oxime moieties on the geometry of the aromatic ring has also been studied. The available data for N- and O-alkylated oximes are compared with the results obtained for non-alkylated oximes.

Introduction. The crystal structure of the prototype of aromatic (E)-aldoximes, (E)-benzaldehyde oxime, was determined at low temperature in order to obtain reliable data for comparison with the result of a similar study of an O-alkylated, aromatic (E)-aldoxime (Jerslev, Lerche & Larsen, 1983). The aim of the structure determination was furthermore to obtain direct information on the influence of an (E)-aldoxime moiety on the geometry of the aromatic ring.

Numerous room-temperature crystal-structure determinations of compounds containing the oxime moiety, $>$C=N–OH, have been published, and a comprehensive survey of the dimensions of the oxime moieties and of the hydrogen-bonding schemes has recently been given (Bertolasi, Gilli & Veronese, 1982). Direct comparisons between dimensions of oxime moieties found in oximes of different types are common in the literature, although the dimensions of an oxime moiety are likely to be influenced by the nature of the attached atomic groups. Thus, the geometry of the oxime moiety in esters or amides of hydroximic acid, $-C{\displaystyle {\text{N}-\text{OH} \atop \text{OH}}}$ presumably differs from that in ketoximes, ${R \atop R}{>}$C=N–OH, or aldoximes, ${R \atop H}{>}$C=N–OH; also, the dimensions of the oxime moiety in aldoximes may well be different from those in ketoximes, and even between (E)- and (Z)-isomers systematic variations may occur. Likewise, the geometry of an O-alkylated oxime, $>$C=N–OR, or of an N-alkylated oxime (a nitrone), $>$C=N${<}{\text{O} \atop R}$, certainly deviates from that of the corresponding non-alkylated oxime. So far it has not been systematically explored, whether the differences thus expected are discernible with the present accuracy of crystal-structure determinations; a part of this problem is elucidated in the present study. The structural data for aromatic (E)-aldoximes, ${Ar \atop H}{>}$C=N${\diagdown}$OH, are analysed, and the dimensional features found are compared with the available data for aromatic (Z)-aldoximes and for O- and N-alkylated, aromatic aldoximes.

The influence of a number of different atomic groups on the geometry of an attached aromatic ring has been studied by several authors. Based upon the latest and most comprehensive analysis (Norrestam & Schepper, 1981), an attempt has been made to derive such data for oxime moieties.

Experimental. Compound used for structure determination obtained by distillation at reduced pressure of a commercial product (Fluka, *purum*). Fraction collected at 386 K and 1·9 kPa gave upon solidification needle-shaped, somewhat flattened crystals, some of them very large. Under polarizing microscope crystals showed parallel extinction, and smaller or larger inclusions of liquid observed; crystal fragment of dimensions 0·4 × 0·5 × 0·5 mm with only a very small amount of liquid enclosed used for X-ray data collection, m.p. 303–307 K. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, at *ca* 100 K; temperature kept constant within ± 0·5 K, actual temperature indicated estimated to be correct within ± 5 K. Cell dimensions determined by least-squares calculations from 16 reflections. $hk\pm l$ quadrant of intensity (28, 12, ±26), θ–2θ scan technique, $\theta < 34°$. Intensities of three standard reflections (600, 040, 0,0,18) measured for every 100 reflections showed only random variations (< 1·7%) from their mean intensities. 5382 total reflections, 5253 unique reflections of which 3477 with $I_o > 2\sigma I_o$, i.e. 15·7 reflections/variable parameter, used in structure refinement. Lp corrections, but no absorption correction. Absent reflections hkl for $h + k$ odd, and $h0l$ for l odd combined with Wilson statistics indicated centrosymmetric space group $C2/c$, D_m (flotation at 291 K) consistent with two molecules in asymmetric unit. Anisotropic refinement of non-H parameters, isotropic of H parameters minimizing $\sum w(|F_o|-|F_c|)^2$, $w = 1/\sigma(F_o)^2 = Lp[\sigma(I_o)^2 + (0·01\ I_o)^2]^{-1/2}$. Direct-methods program *MULTAN* (Main *et al.*, 1980) using 250 reflections gave approximate positions of all non-H atoms, least-squares refinements and subsequent calculation of a difference electron density map, ρ_{diff}, revealed all H atoms. Further refinements converged with no parameter shifts at $R = 0·045$, $wR = 0·047$. A final ρ_{diff} had a noise level less than 0·1 e Å^{-3} with a few, small volumes in which densities up to ±0·17 e Å^{-3} were observed. Atomic scattering factors from Cromer & Mann (1968). All computations performed using CAD-4 *SDP* programs (Enraf–Nonius, 1980).

Discussion. The atomic parameters are given in Table 1.* The numbering of the two molecules A and B in the asymmetric unit is given in Fig. 1, bond lengths and angles in Table 2. Equivalent bond lengths and angles of molecules A and B do not deviate significantly except for the two angles C—C=N and C=N—O, both of which differ by 0·52 (13)°.

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* Lists of structure factors, anisotropic thermal parameters, distances from least-squares planes and hydrogen-bond geometries have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38692 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic thermal parameters for molecules A and B with e.s.d.'s in parentheses*

	x	y	z	$B_{eq/iso}$(Å^2)
Molecule *A*				
C(1*A*)	0·63761 (7)	−0·2520 (2)	1·02500 (7)	1·86 (2)*
C(2*A*)	0·66979 (7)	−0·3294 (2)	0·96924 (7)	1·81 (3)*
C(3*A*)	0·65935 (6)	−0·2702 (1)	0·89240 (7)	1·58 (2)*
C(4*A*)	0·61642 (6)	−0·1333 (1)	0·87051 (6)	1·29 (2)*
C(5*A*)	0·58200 (6)	−0·0587 (2)	0·92662 (7)	1·75 (2)*
C(6*A*)	0·59330 (7)	−0·1175 (1)	1·00346 (7)	1·98 (3)*
C(7*A*)	0·60929 (6)	−0·0705 (1)	0·78975 (6)	1·36 (2)*
N(8*A*)	0·58660 (5)	0·0733 (1)	0·77235 (5)	1·30 (2)*
O(9*A*)	0·58684 (5)	0·1103 (1)	0·69304 (4)	1·67 (2)*
H(1*A*)	0·6456 (8)	−0·295 (2)	1·0768 (8)	2·6 (3)
H(2*A*)	0·6995 (8)	−0·422 (2)	0·9817 (9)	2·7 (3)
H(3*A*)	0·6822 (8)	−0·324 (2)	0·8549 (8)	2·0 (3)
H(5*A*)	0·5492 (8)	0·034 (2)	0·9119 (8)	2·4 (3)
H(6*A*)	0·5712 (8)	−0·058 (2)	1·0426 (9)	3·0 (3)
H(7*A*)	0·6237 (8)	−0·141 (2)	0·7493 (8)	1·9 (3)
H(9*A*)	0·5630 (9)	0·205 (2)	0·6847 (9)	3·9 (4)
Molecule *B*				
C(1*B*)	0·76554 (7)	0·2024 (2)	0·85617 (9)	2·33 (3)*
C(2*B*)	0·82083 (7)	0·2512 (2)	0·91820 (8)	2·42 (3)*
C(3*B*)	0·89214 (7)	0·1933 (2)	0·92393 (8)	1·88 (3)*
C(4*B*)	0·90847 (6)	0·0841 (1)	0·86826 (7)	1·40 (2)*
C(5*B*)	0·85241 (6)	0·0364 (2)	0·80520 (7)	1·61 (2)*
C(6*B*)	0·78155 (7)	0·0955 (2)	0·79960 (8)	2·00 (3)*
C(7*B*)	0·98383 (6)	0·0209 (1)	0·87795 (7)	1·47 (2)*
N(8*B*)	0·99647 (5)	−0·1118 (1)''	0·84507 (5)	1·40 (2)*
O(9*B*)	1·07157 (4)	−0·1516 (1)	0·86092 (5)	1·76 (2)*
H(1*B*)	0·7163 (8)	0·245 (2)	0·8525 (9)	2·5 (3)
H(2*B*)	0·8100 (8)	0·328 (2)	0·9588 (9)	3·1 (3)
H(3*B*)	0·9312 (7)	0·227 (2)	0·9680 (8)	2·2 (3)
H(5*B*)	0·8641 (8)	−0·035 (2)	0·7648 (8)	2·3 (3)
H(6*B*)	0·7440 (8)	0·064 (2)	0·7556 (9)	2·3 (3)
H(7*B*)	1·0230 (7)	0·080 (2)	0·9106 (8)	1·9 (3)
H(9*B*)	1·0736 (9)	−0·244 (2)	0·8332 (9)	3·9 (4)

$* B_{eq} = \frac{4}{3}\sum_i\sum_j b_{ij}\mathbf{a}_i.\mathbf{a}_j.$

Table 2. *Bond lengths (Å) and angles (°)*

$\sigma_{bond\ lengths}$: non-H = 0·001₂–0·002₁, 1H: 0·01₃–0·01₇ Å;
σ_{angles}: non-H = 0·08–0·13, 1H: 0·8–1·0°.

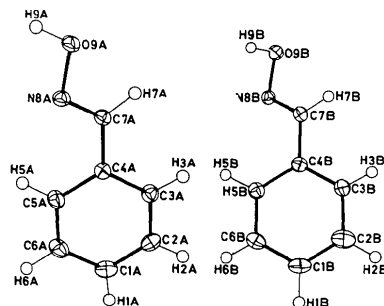|	Mole-cule *A*	Mole-cule *B*		Mole-cule *A*	Mole-cule *B*
C(1)–C(2)	1·383	1·385	C(6)–C(1)	1·388	1·390
C(2)–C(3)	1·388	1·389	C(4)–C(7)	1·466	1·467
C(3)–C(4)	1·392	1·393	C(7)–N(8)	1·277	1·278
C(4)–C(5)	1·401	1·402	N(8)–O(9)	1·400	1·401
C(5)–C(6)	1·386	1·385	C–H$_{mean}$	0·97	0·97
C(1)–C(2)–C(3)	120·04	120·06	C(5)–C(4)–C(7)	122·01	121·92
C(2)–C(3)–C(4)	120·65	120·45	C(4)–C(7)–N(8)	121·10	120·57
C(3)–C(4)–C(5)	118·97	119·19	C(7)–N(8)–O(9)	111·60	112·13
C(4)–C(5)–C(6)	120·02	120·00	N(8)–C(7)–H(7)	120·5	121·0
C(5)–C(6)–C(1)	120·40	120·37	N(8)–O(9)–H(9)	104·5	103·8
C(6)–C(1)–C(2)	119·87	119·91	C–C–H	118–120	118–121
C(3)–C(4)–C(7)	119·01	118·88			

Fig. 1. *ORTEP* drawings (Johnson, 1976) giving the numbering of the atoms in the molecules *A* and *B*. The ellipsoids enclose 50% probability. H atoms are represented by spheres of arbitrary radius.

Calculated best planes, α through the benzene C atoms and β through the atoms of the side chain plus the attached benzene C atom, form dihedral angles αβ of 16·4 (2) (molecule A) and 21·8 (2)° (molecule B). The benzene rings show slight, but statistically significant deviations from planarity; the slight tendency towards a boat shape observed in (E)-4-chloro-2,6-dimethylbenzaldehyde O-methyloxime (Jerslev et al., 1983) with the ipso and the para ring atoms relative to the oxime moiety displaced to the same side of the ring plane as the oxime side chain, and the ortho and meta ring atoms displaced to the opposite side is also found in the present structure, more pronounced in molecule A. Deviations for C(1)–C(6) from the ring plane are for molecule A:−11, 8, 4, −14, 11, 1(1) Å × 10^{-3}, and for molecule B:−4, −1, 7, −8, 3, 3 (1) Å × 10^{-3}. The attached atoms deviate more: the oxime C atom lies 0·075 (1) and 0·050 (1) Å out of the plane for molecules A and B respectively. The deviations from the best planes are systematically larger in molecule A than in molecule B; this may be due to the above-mentioned dihedral angle αβ being smaller in molecule A than in molecule B, thus giving rise to larger intramolecular interactions. The bond lengths and angles in the benzene ring deviate significantly from twofold symmetry around the line C(1)–C(4).

Hydrogen bonds, O–H···N, link two molecules of A, related by a twofold axis, and two molecules of B, related by the same axis, into tetramers. This is the first example of tetramerization of an oxime in the crystalline state. The dimensions of the two independent hydrogen bonds, O–H_A···N_B and O–H_B···N_A are remarkably alike. A small, statistically significant difference was found only between the distances N···O, which are for N(8A)···O(9B) = 2·773 (1) and for N(8B)···O(9A) = 2·784 (1) Å. The angles O(9A)–H(9A)···N(8B) and O(9B)–H(9B)···N(8A) are 172 (2) and 174 (2)° respectively. The 12-membered chelate ring (···N_A–O_A–H_A···N_B–O_B–H_B···)$_2$ has a pseudo $\bar{4}$ symmetry with a structural twofold axis as the rotation axis and an inversion centre at $y = \frac{1}{2}(y_{N_A} + y_{N_B})$; the torsional angles have large e.s.d.'s, but are within the accuracy of the measurements consistent with $\bar{4}$ symmetry in the ring; a stereoview of a tetramer is shown in Fig. 2. There are no other short intermolecular distances in the structure. The packing of the molecules can be described as columns of tetramers stacked in the b direction around the twofold axes and kept together by van der Waals forces.

Structure of the oxime moieties in four classes of aromatic aldoximes: (E)-oximes, (Z)-oximes, O-alkylated (E)-oximes and N-alkylated (Z)-oximes

The bond lengths derived for (E)-benzaldehyde oxime at 100 K are not directly comparable with the results of previous crystal-structure determinations, since these have invariably been calculated from
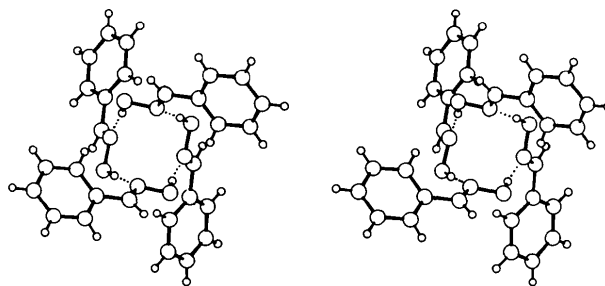

Fig. 2. Stereoview of the hydrogen-bonded tetramer. The twofold axis (not shown) is at a right angle to the paper in the centre of the tetramer.

room-temperature data. Bond angles, however, are only slightly influenced by thermal effects, so comparisons are permissible.

In 13 reasonably accurate structure determinations based on room-temperature data of benzenoid and heteroaromatic (E)-aldoximes (Table 3) the angle C=N–O was found within an interval of 2·2° with a mean value of 111·8°; the angle C–C=N is somewhat more variable and was found within an interval of 6·3° with a mean value of 119·8°. The values obtained for (E)-benzaldehyde oxime at 100 K agree well with those findings. It appears, that a C=N–O angle of 111·8° is within 1° and a C–C=N angle of 120° is within 3–4° characteristic for aromatic (E)-aldoximes. It may be added that crystal-structure determinations have been published for two non-aromatic (E)-aldoximes; the C=N–O angle in the one, glyoxime (ethanedial dioxime) [Calleri, Ferraris & Viterbo, 1966; Jeffrey, Ruble & Pople, 1982 (neutron diffraction at 9 K)], agrees well with the value of 111·8° proposed above, and in the other, (E)-arabinose oxime (Mostad, 1978), this angle was 110·4 (1)°, only slightly outside the proposed interval.

For the other classes of oximes crystal data are sparse, but a similar pattern appears (Table 3). The intervals for the C=N–O angle in the four classes do not overlap, and as would be expected, the magnitude of this angle in N-alkylated oximes differs considerably from those found in the other classes. It is proposed that the most accurate value for the C=N–O angle is within ca 1° characteristic for each class of oxime, and also that the best value for the C–C=N angle is probably within a few degrees characteristic for the class.

The data in Table 3 for the bond lengths C=N and N–O only warrant a few comments. The bond lengths of N-alkylated (Z)-oximes differ significantly from those in the other three classes; the magnitudes of the angles and distances around the oxime N atom have been found as follows: C_{alkyl}–N=C ≃ 120, C_{alkyl}–N→O ≃ 115°, N–C_{alkyl} ≃ 1·48 Å. The bond

lengths C=N and N—O for the (E)-oximes, (Z)-oximes, and O-alkyl-(E)-oximes fall in overlapping intervals. For the (E)-oximes the C=N bond appears to be shorter and the N—O bond longer in benzenoid than in heteroaromatic oximes, which indicates a closer inspection of the (E)-oxime class.

In Fig. 3 the bond lengths C=N for all reasonably accurate structure determinations of (E)-aldoximes are plotted *versus* the bond lengths N—O. A striking linear correlation ($r = -0.987$) between the two bond lengths was found for about one half of the structures studied (represented by filled circles in Fig. 3), whereas the other structures are represented by points, that are placed either far above or substantially below the regression line shown. The structures along the line are distributed roughly with the longest C=N bond attached to the most electron-attracting aromatic moiety — N-substituted pyridinium ions on the left, then heteroaromatic rings followed by benzenoid rings, with 4-(dimethylamino)phenyl- at the right end of the curve.

The only parameter which is varied in the molecules is the nature of the aromatic moiety; however, for a detailed analysis it is also necessary to consider the various hydrogen-bonding schemes in the crystal

structures as well as the dihedral angle between the plane of the aromatic ring and the best plane of the (consistently very nearly planar) oxime side chain. This angle is small — less than ca 20° for all the aromatic oximes, except the compound H^+2, for which this angle is ca 33°. With this one exception the structures are considered comparable with respect to the magnitude of the dihedral angle. As to the hydrogen-bonding schemes, this factor appears to have only a minor influence on the correlation of the C=N and N—O bonds, since crystals with widely differing hydrogen-bonding systems are found close together in Fig. 3 (structures B1, B2, and B5), whereas similar hydrogen-bonding schemes are found in widely scattered points (H^+1–5). The tendency observed by Bertolasi *et al.* (1982) from an analysis of all available structural data for oximes, that the more hydrogen bonds attached to an oxime moiety, the longer the N—O bond, is partly borne out by the aromatic (E)-aldoximes plotted in Fig. 3. Eight molecules with one hydrogen bond attached to the oxime moiety have N—O distances of 1.372–1.404 Å, four molecules with two hydrogen bonds attached to the oxime moiety have N—O distances of 1.405–1.420 Å, but surprisingly the only oxime with

Table 3. Geometry of the oxime moieties in aromatic aldoximes

The table is based upon crystal-structure determinations refined to $R < 0.06$. Figures in parentheses are from less accurate structure determinations. Figures in brackets are from low-temperature studies.

Classification of the oximes	Compounds	Number of molecules	C=N (Å)	N—O (Å)	C=N—O(°)	Ar—C=N(°)	Torisonal/ dihedral angle Ar/oxime (°)
(E)-Oximes, benzenoid	B100K	2	[1.277 (1)]	[1.401 (1)]	[111.9 (2)]	[120.8 (2)]	[16–22]
	B1–3	3	1.261–1.269	1.405–1.408	111.2–112.2	121.6–122.4	1–9
	B4–5	2	(1.264–1.270)	(1.405–1.420)	(112.1–112.9)	(118.9–121.5)	(0–3)
(E)-Oximes, heteroaromatic	H1–2,H^+1–4	6	1.268–1.286	1.372–1.393	110.7–112.5	116.1–121.2	1–9, 33(H^+2)
	H3,H^+5	2	(1.275–1.288)	(1.379–1.390)	(111.1–111.5)	(119.7–121.2)	(5–14)
(Z)-Oximes, benzenoid			(1.28)	(1.395)	(113–115)	(130–132)	
(Z)-Oximes, heteroaromatic	a	1	1.278 (3)	1.375 (3)	114.2 (2)	132.0 (2)	8
(Z)-N-Methyloximes, benzenoid	b	2	1.304 (4)	1.294 (4)	125.3 (3)	126.9 (3)	4–7
			(1.30–1.31)	(1.29–1.30)	(124–125)	(124)	(5,55)
(E)-O-Methyloxime, benzenoid	c	1	[1.280 (2)]	[1.414 (2)]	[109.7 (1)]	[123.3 (1)]	[23]

Compounds: (B100K) Ar = phenyl (present paper). (B1) Ar = 4-chlorophenyl (Arte, Declercq, Germain & Van Meerssche, 1980; supplementary data from Cambridge Database). (B2) Ar = 2-hydroxy-5-methoxyphenyl (Pfluger, Pfluger & Brackett, 1978). (B3) Ar = 4-nitrophenyl (Bachechi & Zambonelli, 1973). (B4) Ar = 4-(dimethylamino)phenyl (Bachechi & Zambonelli, 1972). (B5) Ar = 2-hydroxyphenyl (Pfluger & Harlow, 1973). (H1) Ar = 4-pyrimidyl (Martinez-Ripoll & Lorenz, 1973). (H2) Ar = 5-nitro-2-furyl (oxime + urea) (Mathew & Palenik, 1972). (H3) Ar = 4-pyridyl (Martínez-Ripoll & Lorenz, 1976 a). (H^+1) Ar = 2-(N-benzylpyridinium) (,Br⁻) (Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982 a). (H^+2) Ar = 2-(N-benzylpyridinium) (,CH₃SO₂O⁻) (Van Havere *et al.*, 1982 a). (H^+3) Ar = 2-(N-methylpyridinium) (,Cl⁻) (Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982 c). (H^+4) Ar = 2-{4'-carbamoyl-1,1'-[oxybis(methylene)]dipyridinium} (,2Cl⁻,H₂O) (Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982 d). (H^+5) Ar = 4,4'-{1,1'-[oxybis(methylene)]dipyridinium} (,2Cl⁻) (Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982 b). (a) Ar = 4-pyridyl (Martinez-Ripoll & Lorenz, 1976 b). (b) Ar = 4-nitrophenyl (Bachechi & Zambonelli, 1975). (c) Ar = 4-chloro-2,6-dimethylphenyl (Jerslev et al., 1983).
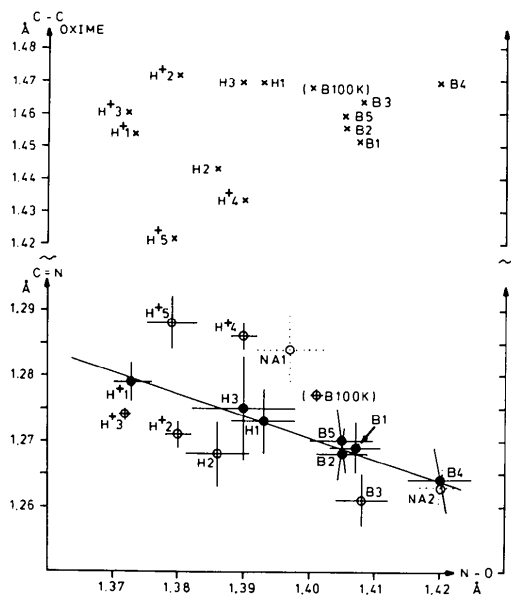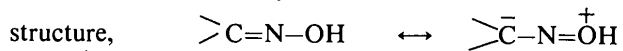
Fig. 3. Relation between bond lengths C=N and N—O in aromatic (E)-aldoximes (room-temperature data). Crosses indicate ± 1 standard deviation. The type of aromatic ring is indicated by H⁺ (pyridinium ion), H (heterocyclic), B (benzene). Non-aromatic structures NA1 = glyoxime, NA2 = arabinose oxime. Compound numbers: see Table 3. The equation of the straight line is calculated from the values represented by filled circles: (C=N) = −0·335(N—O) + 1·740 Å. Bond lengths C—C$_{oxime}$ are plotted in the upper part of the figure.

three hydrogen bonds [connecting the oxime moiety with O=C(NH$_2$)$_2$ molecules] has the rather short N—O distance of 1·386 Å, e.s.d.'s less than 0·005 Å. This study indicated no significant correlation between the lengths of the N—O and C=N bonds. From the above reasoning it is inferred that the scattering of the points in Fig. 3 has to be explained mainly by electronic interactions.

The general trend of electronegativity correlating the points along the regression line has been mentioned. The deviations from that line can be qualitatively explained by considering the possibilities for conjugation between the aromatic moiety and the oxime moiety. An oxime may be written as a resonance structure, $>$C=N—OH ⟷ $>\overset{-}{C}$—N=$\overset{+}{O}$H ⟷ $>\overset{+}{C}$—$\overset{-}{N}$—OH; the first of the two charged forms is enhanced by conjugation with electron-withdrawing substituents in the aromatic ring, the second one is enhanced by conjugation with electron-donating substituents. In both cases conjugation causes a lengthening of the C=N bond and a shortening of the N—O and the C—C$_{oxime}$ bonds. Points placed above the line in Fig. 3 should presumably represent strongly conjugated molecules. This is confirmed for H⁺4–5 by the unusually short bonds C—C$_{oxime}$; furthermore the

non-aromatic oxime, glyoxime (NA1), is known to be strongly conjugated. Points placed below the curve should represent weakly conjugated molecules. H⁺2 represents the same cation as H⁺1, but in a conformation deviating considerably from planarity and thus less conjugated; this is confirmed by the C—C$_{oxime}$ bond being longer than in H⁺1, see Fig. 3. H⁺3 deviates structurally from H⁺1 only in having a methyl substituent at the pyridine N atom, whereas H⁺1 has a benzyl substituent. This is expected to favour conjugation in H⁺1 as compared with H⁺3, and again this is confirmed by the bond lengths C—C$_{oxime}$ in the two compounds. The positions of the nitro oximes H2 and B3 below the line are in keeping with work by Colapietro, Domenicano, Marciante & Portalone (1982); they reported, based upon measurements of ring deformation parameters, that mesomeric interactions between ring and substituent are less pronounced for nitro groups than for dialkylamino groups. The experimental data shown in Fig. 3 are, however, not conclusive. As to nitro-2-furaldehyde oxime H2, no other data for furaldehyde oximes are available for comparison. As to the benzenoid oximes, the scattering of the bond lengths C—C$_{oxime}$ is so small that no significant correlation with conjugation is indicated; however, it is noted, that the C—C$_{oxime}$ bond is slightly longer for nitrobenzaldehyde oxime, B3, than for the other benzenoid oximes with approximately the same N—O bond length.

Based upon the above reasoning it is tentatively proposed that a certain degree of conjugation between the oxime moiety and the substituents in the aromatic ring is present in the molecules that are represented by points along the straight line shown in Fig. 3.

Though the relations between the C=N and N—O bond lengths thus have been given a qualitative explanation, it is surprising that the lengths of the C=N and N—O bonds are strictly linearly correlated in so many of the structures, and also that all the deviations observed are large. This may be associated with the fact that the structures studied do not form a representative sample of the population of aromatic (E)-aldoximes. In all compounds a substituent in the ring is placed in either the 2- or the 4-position relative to the oxime moiety, with (E)-benzaldehyde oxime as the only exception; and as the bond lengths in the present structure are derived from low-temperature data they are, as previously mentioned, not directly comparable to the other bond lengths.

An analysis of the C=N/N—O bond relations for the other three classes of oxime discussed is not warranted, owing to the scarcity of experimental data.

Geometry of the ring in aromatic aldoximes. The present structure determination has provided direct information on the influence exerted by an (E)-aldoxime substituent on the geometry of a six-membered aromatic ring, Fig. 4. Neglecting the slight deviations

from coplanarity of the ring atoms, the deformation of each ring angle is given by the deviation from 120°, and the deformation of each ring bond is the deviation from the mean bond length of the ring. Angular deformation parameters in Table 4 are given as $\Delta1$ for the *ipso* angle (at the C atom to which the oxime moiety is attached) and $\Delta4$ for the *para* angle; $\Delta2$ is the mean value of the deformations of the two *ortho* angles 2_c and 2_t that are placed in *cis* and *trans* positions respectively relative to the oxime moiety, and similarly $\Delta3$ is the mean value for the two *meta* angles. The differences $\Delta2_c-\Delta2_t$ and $\Delta3_c-\Delta3_t$ are also given. Fig. 4 and the Δ values obtained for (E)-benzaldehyde oxime show that the angular influence of the aldoxime substituent on the *cis* angles differs significantly from the influence on the *trans* angles; the *ortho cis* angle is significantly smaller than the *ortho trans* angle, whereas the *meta cis* angle is larger than the *meta trans* angle. Bond-length deformation parameters, dl_i, in Table 4 are given as mean values of the deviations from the mean ring bond length, $\bar{l}$; dl_1 refers to the *ipso–ortho* bonds, dl_2 to the *ortho–meta* bonds and dl_3 to the *meta–para* bonds. For (E)-benzaldehyde oxime the asymmetry of the ring found in the bond angles is only just observable in the bond lengths. The differences $dl_{ic} - dl_{it}$ are 0·009 (2) for $i = 1$, −0·002 (2) for $i = 2$, and 0·005 (2) Å for $i = 3$; only the first of these values deviates significantly from zero.
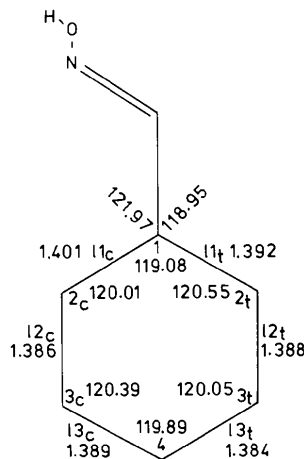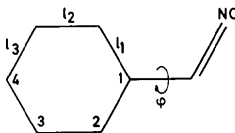
Fig. 4. Geometry of the benzene ring in (E)-benzaldehyde oxime at 100 K. The bond lengths (Å) and angles (°) are mean values for the two independent molecules; largest deviations from the individual measurements are 0·001 Å and 0·11°.

The deformation parameters and the mean ring bond lengths given in Table 4 are, with (E)-benzaldehyde oxime as the only exception, calculated from the results of crystal-structure determinations refined to $R < 0.06$ by subtracting the influence on the ring geometry of all other substituents than the oxime moieties; this was

Table 4. *Influence of aldoxime moieties on the geometry of aromatic rings*

Calculated from accurate structure determinations ($R < 0.06$) and data from Norrestam & Schepper (1981).

Classification	φ	Angular deformations (°)						Bond deformations Å × 10³			
		$\Delta1$	$\Delta2$	$\Delta3$	$\Delta4$	$\Delta2_{cis}-\Delta2_{trans}$	$\Delta3_{cis}-\Delta3_{trans}$	dl_1	dl_2	dl_3	$\bar{l}$ (Å)
(E)-Oximes											
Benzaldehyde oxime (100K) (exptl. values)	16 } 22	−0·92 (7)	0·28 (6)	0·22 (6)	−0·11 (7)	−0·54 (8)	0·34 (8)	7 (1)	−3 (1)	−3 (1)	1·3901 (5)†
4-Chlorobenzaldehyde	9	−1·5 (3)	0·8 (2)	0·0 (2)	0·0 (3)	0·4*(4)	0·0 (4)	8 (4)	−7 (5)	−1 (4)	1·382 (2)
4-Nitrobenzaldehyde	8	−1·6 (3)	0·6 (2)	0·3 (2)	−0·2 (3)	−0·8 (3)	0·2 (3)	10 (4)	−10 (5)	0 (4)	1·384 (2)
4-Pyrimidinecarb-aldehyde	5	−0·8 (3)	0·2 (2)	0·2 (2)	0·0 (3)	0·1 (4)	0·3 (4)	7 (4)	−7 (4)	0 (4)	1·384 (2)
(Z)-Oximes											
4-Pyridinecarbaldehyde	8	−1·2 (2)	0·6 (2)	−0·2 (2)	0·5*(2)	−0·6 (3)	0·6 (3)	6 (4)	1 (4)	−7 (4)	1·385 (2)
N-Alkyl-(Z)-oximes											
4-Nitrobenzaldehyde N-methyl-	4 5	−2·0*(3)	0·6 (2)	0·5 (2)	−0·1 (3)	−0·7 (3)	0·8 (3)	18*(3)	−13*(4)	−5 (3)	1·387 (3)
O-Alkyl-(E)-oximes											
4-Chloro-2,6-dimethyl-benzaldehyde O-methyl- (93K)	23	−1·5*(2)	0·3 (2)	0·4 (2)	0·0 (2)	−0·7 (2)	0·6 (2)	13 (3)	−4 (3)	−9 (3)	1·390 (2)†

* Value differs by more than 2σ from the corresponding value for benzaldehyde oxime.

† Low-temperature l values; not directly comparable to the other l values.

achieved using for each substituent the deformation parameters Δ_{1-4} and dl_{1-3} calculated by Norrestam & Schepper (1981) and also using the influence of each substituent on the mean ring bond length calculated by these authors. The standard deviations of the deformation parameters thus obtained are rather large since they include the e.s.d.'s of the structure determination as well as those of the deformation parameters.

Table 4 shows, that the data for three aromatic (E)-aldoximes, based upon room-temperature crystal-structure determinations, agree reasonably well with the directly measured data for (E)-benzaldehyde oxime at 100 K. For the (Z)-aldoxime the agreement is less convincing, and definite differences are seen between the set of data for the N-alkylated (Z)-aldoxime and that for (E)-benzaldehyde oxime. The deformation parameters for the O-methylated (E)-aldoxime and for (E)-benzaldehyde oxime do not differ significantly, except for the $\Delta1$ values. None of the obtained differences $\Delta2_c-\Delta2_t$ and $\Delta3_c-\Delta3_t$ deviate significantly from zero, except for the O-methylated (E)-aldoxime; however, there is a tendency to negative differences for the ortho angles and positive for the meta angles. As to the bond-length differences, $|dl_{ic}-dl_{it}|$ values up to 0·014 Å were found, but none of them deviated significantly from zero.

Based upon a crystal-structure determination of (E)-2,4,6-trimethylacetophenone oxime, Fortier, Birnbaum, Buchanan & Dawson (1980) calculated the angular ring deformation parameters for the ketoxime substituent and found values deviating significantly from those found for the (E)-aldoxime substituent in (E)-benzaldehyde oxime, and furthermore the planar ring had a twofold symmetry axis through the ipso- and para-C atoms. This result is probably associated with the large dihedral angle, 70·8 (3)°, between the plane of the benzene ring and that of the oxime side chain in the (E)-2,4,6-trimethylacetophenone oxime molecule. The influence of the magnitude of this dihedral angle on the deformation of an aromatic ring is demonstrated by the results of crystal-structure determinations of (E)-N-benzyl-2-[(hydroxyimino)methyl]pyridinium bromide and methanesulphonate (Van Havere et al., 1982a); in the two chemically identical cations the dihedral angle was found to be ca 4 and ca 33° respectively, and considerable differences between the dimensions of the pyridinium rings in the two salts were noted. Thus, the deformation parameters found for (E)-benzaldehyde oxime should not be regarded as generally applicable for predicting the ring geometry of aromatic (E)-aldoximes.

Norrestam & Schepper (1981) presented equations for calculating the angular deformations Δ_{1-4} for a given substituent from the σ and π charge distribution over the ring atoms in a benzene ring with the substituent in question attached. Such data have not been found for benzaldehyde oximes; however, ab-initio-calcula-

ted charge distributions in benzylideneamines, $C_6H_5-CH=NH$, have been published by Hehre, Radom & Pople (1972). From these data the following angular deformation parameters for (E)-benzylideneamine were calculated, using Norrestam & Schepper's equations: $\Delta_1 = -0\cdot7$, $\Delta_2 = 0\cdot3$, $\Delta_3 = 0\cdot1$, and $\Delta_4 = 0\cdot0°$. These calculated deformation parameters are very close to the experimental values for (E)-benzaldehyde oxime (cf. Table 4). The similarly calculated values for (Z)-benzylideneamine ($\Delta_1 = -1\cdot2$, $\Delta_2 = 0\cdot5$, $\Delta_3 = 0\cdot1$, and $\Delta_4 = -0\cdot1°$) are consistent with the deformation parameters for (Z)-benzaldehyde oxime, indirectly derived from the crystal-structure analysis of (Z)-4-pyridinecarbaldehyde oxime (cf. Table 4). These results suggest, that the influence on the ring geometry of an aldoxime substituent, $-CH=NOH$, is predominantly exerted by the $-CH=N-$ part of the oxime moiety.

It is concluded, that the deformation parameters $\Delta_{1\ 4}$ and dl_{1-3} obtained from the structure determination of (E)-benzaldehyde oxime, combined with the deformation parameters given by Norrestam & Schepper (1981), are applicable for predicting the approximate geometry of six-membered rings in aromatic and N-heteroaromatic (E)-aldoximes, on condition that the dihedral angle ring/oxime is smaller than 20–25°. On the same condition the other deformation parameters in Table 4 may be used for predicting the ring geometry – though with less accuracy – of (Z)-aldoximes, N-alkylated (Z)-aldoximes and O-alkylated (E)-aldoximes.

These predictions do not, however, take into account that the asymmetric oxime moieties must be expected to induce asymmetry in the planar ring, as indicated by the significant differences $\Delta2_c-\Delta2_t$ and $\Delta3_c-\Delta3_t$ observed in the experimental data obtained from the low-temperature studies.

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Structure and Superstructure of Dipyridamole, 2,2',2'',2'''-(4,8-Dipiperidinopyrimido[5,4-d]pyrimidine-2,6-diyldinitrilo)tetraethanol, $C_{24}H_{40}N_8O_4$

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Abstract. $M_r = 504.64$, monoclinic, Pa, $a = 20.746 (7)$, $b = 11.280 (6)$, $c = 11.441 (5)$ Å, $\beta = 105.07 (2)°$, $V = 2585.3$ Å^3, $Z = 4$, $D_m = 1.28 (1)$, $D_x = 1.288$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 7.50$ cm^{-1}, $F(000) = 1088$, $T = 298$ K, $R = 4.7\%$ for 4019 observed reflections. The two independent molecules are related approximately by an inversion center at (0,7/8,0). The main deviation from this symmetry is disorder of one ethanol residue which is observed only in one of the two molecules. Although suggested by the chemical formula, neither of the two molecules is centrosymmetric; however, the centric parts of the molecules form a subcell with half the unit-cell length in the **b** direction, space group $P2_1/a$, which was indicated by weak intensities of the $k =$ odd reflections.

Introduction. The title compound is well known for its pharmacological activity. For many years it has been in use (Persantin®) in the attendance of cardiac diseases. Moreover, in combination with aspirine it is used as Asasantin® for prevention of arterial and venous thromboembolism. Because of this pharmacological importance it seemed useful to obtain detailed information of the molecular geometry for a study of the structure–activity relationship of this compound. Therefore, a single-crystal X-ray investigation of dipyridamole was executed and the results are reported here.

Experimental. Yellow prismatic crystals obtained from a solution in ethanol; rotation and Weissenberg photographs with **a** and **b** rotation axes showed Laue