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5-Methoxysalicylaldoxime

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Abstract. $C_8H_9NO_3$, monoclinic, $P2_1/c$, $a = 3{\cdot}914\ (2)$, $b = 9{\cdot}631\ (7)$, $c = 21{\cdot}100\ (15)$ Å, $\beta = 97{\cdot}33\ (6)°$, $t = 22\ °C$, $Z = 4$, $D(\text{exp}) = 1{\cdot}405$, $D(\text{calc}) = 1{\cdot}407$ g cm^{-3}. The structure consists of molecules which are hydrogen-bonded to form infinite chains in the direction of the *b* axis.

Introduction. This structure is one of a series of hydrogen-bonded salicylaldoxime derivatives studied by Pfluger & Harlow (1973, 1977). The unit-cell dimensions given above were determined from the least-squares refinement of observed 2θ values for 22 reflections (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å). Intensity data were collected for 1033 reflections on a Canberra Industries automated GE XRD-6 diffractometer with θ–2θ scans of 1° min^{-1} ($\sin\theta/\lambda < 0{\cdot}54$ Å^{-1}). 30s background counts were taken at each end of the scan range. Two reference reflections were monitored periodically and showed no systematic changes in intensity. The intensities were corrected for Lorentz and polarization effects; correction for absorption was considered unnecessary ($\mu = 1{\cdot}02$ cm^{-1}).

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined with full-matrix least-squares methods (*ORFLS*; Busing, Martin & Levy, 1962) with weights based on experimental counting statistics. The H atoms were located on a difference map calculated after the isotropic refinement of the non-hydrogen atoms ($R = 0{\cdot}133$). The H positions and their thermal parameters were allowed to vary in one cycle of refinement. Those thermal factors of H that became abnormally large were then reset at 5·0 Å^2.

Refinement was continued on the coordinates of all atoms and the anisotropic thermal parameters of the non-hydrogen atoms. The $10\bar{4}$ reflection was omitted from the refinement when it was clear that the observed value was in error because of exceeding the capacity of the counter. The H atoms bonded to unsaturated C atoms as well as those bonded to O atoms refined to unacceptably short distances, and were fixed at 0·92 and 0·86 Å respectively. All angles refined to acceptable values for both H and non-hydrogen atoms. The final refinement cycle led to a conventional *R* of 0·069 for all reflections, 0·053 for the 842 significant reflections, and 0·036 for the weighted *R*. The final positional parameters are given in Table 1. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962), except for H where those of Stewart, Davidson & Simpson (1965) were used.*

Table 1. *Final atomic positional parameters* (×10^4) *and isotropic thermal parameters for the hydrogen atoms, with standard deviations in parentheses*

	x	*y*	*z*	*B* (Å^2)
C(1)	598 (7)	−794 (3)	1325 (1)	
C(2)	1636 (8)	−93 (3)	1895 (2)	
C(3)	1002 (8)	1308 (3)	1941 (1)	
C(4)	−633 (8)	2050 (3)	1425 (2)	
C(5)	−1643 (8)	1370 (3)	860 (2)	
C(6)	−1103 (9)	−42 (3)	813 (1)	
C(7)	1184 (9)	−2272 (3)	1246 (1)	
N(8)	2785 (7)	−2997 (3)	1691 (1)	
O(9)	3075 (6)	−4393 (2)	1512 (1)	
O(10)	3280 (5)	−758 (2)	2426 (1)	
O(11)	−3203 (6)	1994 (2)	307 (1)	
C(12)	−4032 (9)	3412 (3)	341 (2)	
H(3)	1495	1757	2328	5·0
H(4)	−995	2984	1469	4·7
H(6)	−1606	−513	433	5·0
H(7)	349	−2685	862	5·0
H(9)	3867	−4783	1869	5·0
H(10)	3970	−1556	2314	5·0
H(12*A*)	−2088	3957	417	2·0
H(12*B*)	−5059	3621	−87	5·0
H(12*C*)	−5500	3559	643	1·6

Discussion. The intermolecular bond distances and angles for the molecule are given in Fig. 1, which also illustrates the atom-numbering scheme used. Estimated standard deviations for distances involving only non-hydrogen atoms are 0·004 Å, those for angles involving

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33186 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Selected bond distances* (Å) *in this series*

	C=N	N–O	O(9)···O(10′)	N(8)···O(10)
Salicylaldoxime	1·270 (5)	1·405 (4)	2·820 (4)	2·622 (4)
5-Methoxysalicylaldoxime	1·267 (3)	1·404 (3)	2·822 (4)	2·649 (4)
5-Chlorosalicylaldoxime	1·274 (2)	1·404 (2)	2·804 (2)	2·626 (2)
Formaldoxime	1·276	1·408		

non-hydrogen atoms average 0·3°. All bond distances and angles are as expected, agreeing very well with those previously reported for salicylaldoxime (Pfluger & Harlow, 1973) and for 5-chlorosalicylaldoxime (Pfluger & Harlow, 1977). It is especially interesting to note the consistency of the C=N and N–O bond lengths, given in Table 2, of the three salicylaldoximes in this series as well as the excellent agreement with the microwave-determined structure of formaldoxime (Levine, 1963). A compilation of C=N and N–O bond lengths for various oximes has been published (Table 5, Bachechi & Zambonelli, 1972) from which additional comparisons may be made.

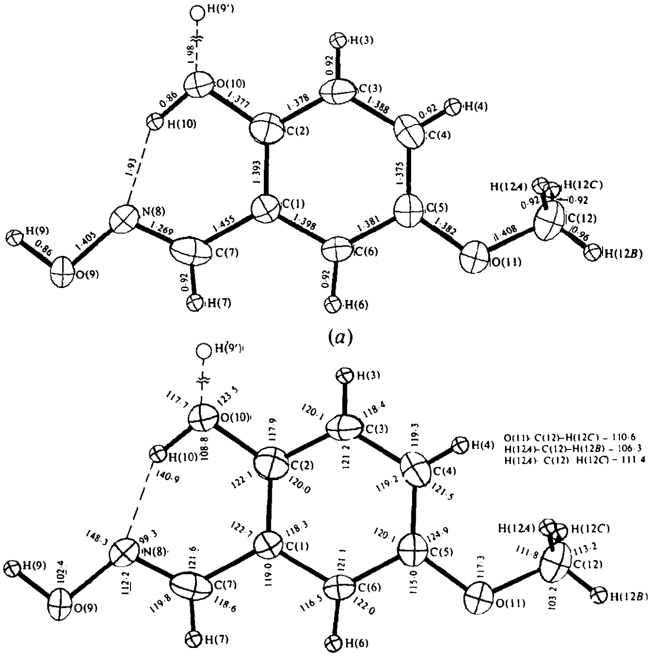

Fig. 1. (*a*) Bond distances (Å), (*b*) bond angles (°) for 5-methoxysalicylaldoxime.

In contrast to the hydrogen-bonded dimer structure found for salicylaldoxime and 5-chlorosalicylaldoxime, the crystal structure of 5-methoxysalicylaldoxime consists of molecules hydrogen bonded between the phenol O and oxime group H atoms in such a manner as to form infinite chains in the direction of the *b* axis. This is illustrated in Fig. 2, which is a stereoscopic drawing of four molecules in this infinite chain. The dihedral angle between the planes of two sequential molecules in the infinite chain is 157°.

Distances between atoms involved in the intermolecular hydrogen bond O(9)···O(10′) and the intramolecular hydrogen bond N(8)···O(10) are summarized for the three members of the series in Table 2. It can be seen that the agreement is rather good. Differences in the intermolecular hydrogen bond are likely the result of electronic effects due to the different substituent groups; however, the increase in the N(8)···O(10) separation observed for 5-methoxysalicylaldoxime is due to the infinite-chain hydrogen-bond geometry of the molecules in this structure in which the H(9′)···O(10) interaction is considerably more perpendicular to the phenol O–ring C vector (see Fig. 2) as opposed to the essentially parallel interaction found in the dimer structure.

The molecule as a whole is quite planar. A calculation of the least-squares plane through the six C atoms of the benzene ring shows the methoxy group orientation to be essentially within this plane with

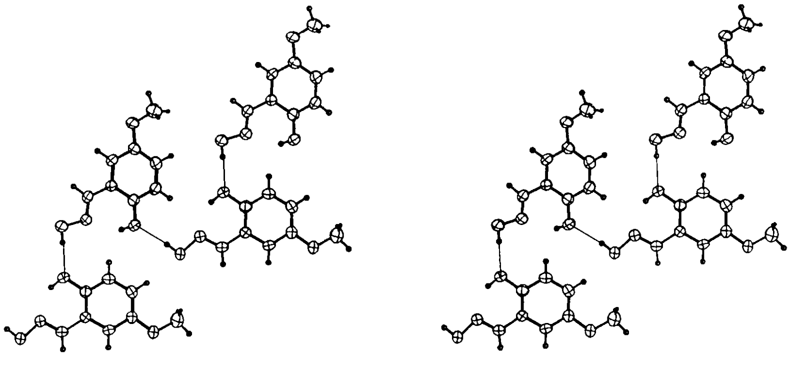

Fig. 2. A stereographic drawing of four molecules of the chain.

displacements of −0·013 (4) [C(12)] and 0·055 (2) Å [O(11)]. Although the oxime group also lies essentially within this plane, a small amount of twist about the C(7)—C(1) bond is evident from the calculated displacements of C(7) [0·015 (3) Å], N(8) [0·064 (3) Å] and O(9) [0·069 (3) Å]. The overall planarity of the molecule is also demonstrated in that the largest deviation of an atom from the mean plane calculated for all 12 non-hydrogen atoms is only 0·042 (2) Å [O(11)].

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1,3-Dioxole-2-spiro-4′-(3′,3′-diethylpyrrolidin-2′-one)

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Abstract. $C_9H_{17}NO_3$, orthorhombic, *Pbca*, $a = 14{\cdot}164$ (4), $b = 15{\cdot}128$ (4), $c = 10{\cdot}012$ (4) Å, $M_r = 187{\cdot}2$, $Z = 8$, $D_x = 1{\cdot}16$ g cm^{-3}. The molecules are linked into centrosymmetric dimers through N—H···O(=C) hydrogen bonds of length 2·91 Å. The pyrrolidine ring is in the envelope conformation with C(4) 0·467 Å above the plane of the other ring atoms.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ diffractometer (Cu K, $\lambda = 1{\cdot}54178$ Å). Intensity measurements were carried out in the θ–2θ mode ($3{\cdot}5 \leq 2\theta \leq 135{\cdot}0°$) with graphite-monochromated Cu $K\alpha$ radiation, at scan speeds varying linearly between 2·93 (150 counts s^{-1} and below) and 29·30° min^{-1} (5000 counts s^{-1} and above). Scan and background times were equal. Lorentz and polarization corrections were made but no absorption corrections [μ(Cu K) = 6·3 cm^{-1}] were applied. After application of the acceptance criterion $F > 3{\cdot}0\sigma(F)$, 1589 unique reflexions were retained for the refinement. The structure was solved by direct methods (*SHELX* 76, G. M. Sheldrick) and refined by full-matrix least squares with anisotropic temperature factors for all the nonhydrogen atoms. The H atom positional parameters were refined with the geometrical constraints d(N—H) = 1·02 ± 0·02, d(C—H) = 1·08 ± 0·02 Å. Group isotropic temperature factors were introduced for the ethyl and 1,3-dioxole ring H atoms. The terminal value of R_G [$= (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$] was 0·057, with R_w ($\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$) 0·056 and R 0·063.‡ The

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33191 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.