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The Crystal and Molecular Structure of *anti*-Furfuraldoxime

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anti-Furfuraldoxime, $OC_4H_3-CH=NOH$, crystallizes as monoclinic needles. The space group is $P2_1/c$, $z = 4$, the b-axis is short. The structure determination is based upon visually estimated intensities of 1007 independent reflections obtained with Cu$K\alpha$-radiation at room temperature. A three-dimensional, sharpened Patterson function gave the clue to the solution of the structure, and least squares, full matrix refinements were carried out. A difference Fourier synthesis revealed 3 of the 5 hydrogen atoms in the molecule.

The bond lengths and valency angles of the molecule are normal. The conformation of the bond system O—C—C=N is $_s$trans. The side chain is turned less away from the plane of the furan ring than expected. This implies a rather short intramolecular distance, 2.86 Å, between the oxime oxygen atom and a ring carbon atom. Hydrogen bonds ···N—O—H···N—O—H··· link the molecules in infinite chains along the screw-axis. This type of molecular association appear to be characteristic for aromatic *anti*-aldoximes.

The main research activity in this laboratory has for some years been concentrated on the structure and chemistry of organic derivatives of hydroxylamine, and the present work is a part of this program. The purpose of studying the crystal structure of *anti*-furfuraldoxime was partly to compare the geometry of the oxime moiety of that molecule with the dimensions found in some benzenoid aldoximes [1,2] and partly to establish whether intramolecular or intermolecular hydrogen bonding is present. *A priori* one would expect a monomeric structure, since the geometry of the *anti*-furfuraldoxime molecule apparently is favourable for the formation of an intramolecular hydrogen bond with the ring oxygen as the acceptor atom. In the *syn*-isomer, however, molecular association by hydrogen bonds would be expected, since intramolecular hydrogen bonding is geometrically prevented. Yuan and Hua [3] tried to obtain experimental support for these ideas by cryoscopic measurements but the results indicated a molecular association which is even more pronounced with the *anti*-form than with the *syn*-form. To explain these results the authors reluctantly suggested that the configurations assigned to the isomers might have to be interchanged. Another explanation of Yuan and Hua's results was given by Jerslev,[4] *i.e.* that the *syn*-isomer is associated to dimers and the *anti*-isomer to infinite chains by hydrogen bonds O—H ··· N

in analogy to the associations found in the crystal structures of *syn*- and *anti*-*p*-chlorobenzaldoximes, respectively. This suggestion was supported by the observation, Jerslev,[4a] that similar hydrogen bonding systems apparently exist in the crystal structures of a number of other benzenoid *syn*- and *anti*-aldoximes as indicated both by IR-spectra and by the fact, that the melting point of the *trans*-form (*syn*-isomer, proposed dimerized) invariably is lower than that of the *cis*-form (*anti*-isomer, proposed infinite molecular chains).

EXPERIMENTAL

anti-Furfuraloxime was prepared by reacting furfural with hydroxylamine [5] and purified by recrystallization from 10 % ethanol. By slow evaporation of a benzene-ligroin solution crystals were obtained (m.p. 90–91°) which under the polarizing microscope were found to be monoclinic needles elongated in the *b*-direction. The faces {100} and {10$\bar{2}$} were observed, but only the former were well developed. The crystals are very easily cleaved parallel to (100). The density, 1.38 g/cm^3, was found by flotation in potassium iodide solution. The crystals are rather volatile.

X-Ray data were collected at room temperature using Cu$K\alpha$-radiation and Weissenberg equi-inclination techniques. Multiple film exposures were made and the intensities were estimated visually by means of intensity scales calibrated to make each spot about 10 % more intense than the previous one. During the exposures the crystals were enclosed in Lindemann capillaries. The reflections *hKl* with $K = 0-4$ were registered from a needle with dimensions 0.8 × 0.2 × 0.35 mm^3. Another crystal was partly dissolved by careful brushing with dioxane to give a needle elongated in the [10$\bar{2}$] direction with the dimensions 0.7 × 0.25 × 0.35 mm^3. This specimen was used for registration of the layers 0–14 obtained by rotating the crystal around the [10$\bar{2}$] axis. No corrections for absorption or extinction were applied, but variations in spotshape were taken into account following Phillips.[6] Corrections for Lorentz-, polarization-, and Cox-Shaw-factor were carried out on the GIER-computer. Correlation of the data was made by hand using reflections common to the two sets of films. Preliminary scale factor and temperature factor were found by Wilsons method [7] using *h*0*l*-reflections only. 1007 independent reflections were observed corresponding to 82 % of the theoretically obtainable. Some two-dimensional computations were carried out on the analogue computer built by Frank.[8] Most calculations were performed on GIER machines or on the IBM 7090 computer at NEUCC. A table of observed and calculated structure factors may be obtained from the authors. Please refer to project number C 1055.

STRUCTURE DETERMINATION

The unit cell dimensions were determined from zero zone Weissenberg photographs taken with only one film in the camera. $a = 9.74$ Å, $b = 4.96$ Å, $c = 14.26$ Å, $\beta = 128.8°$. The systematic absence of reflections *h*0*l* when *l* is odd and of 0*k*0 when *k* is odd indicate the space group $P2_1/c$. There are 4 molecules in the unit cell corresponding to a crystallographic density of 1.37 g/cm^3. The absorption coefficient μCu$K\alpha$ is 9.5 cm^{-1}.

The structure was deduced from the sharpened Patterson function $^sP(xyz)$.[9]

$$^sP(xyz) = \sum_h \sum_k \sum_l \left|\frac{F(hkl)}{\hat{f}}\right|^2 \exp[(2B-B_1)\ \sin^2\theta/\lambda^2]\ \cos\ 2\pi(hx + ky + lz).$$

$B_1 = 1.5$

A fourier program written for GIER by Lauesen was used.[10] From the approximate knowledge of the dimensions of the planar part of the molecule which comprises the furan ring and C-6 (Fig. 1) it is obvious, that many intramolec-

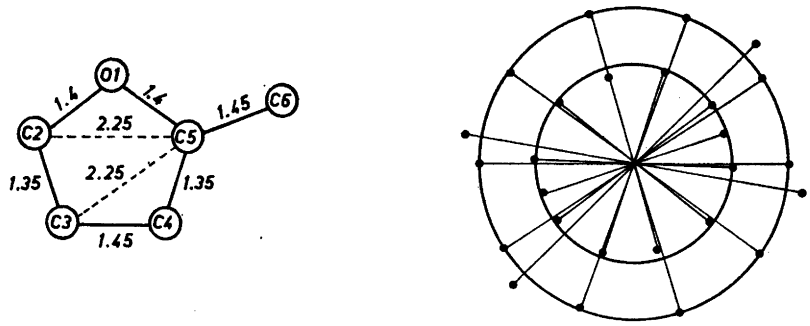

Fig. 1. Approximate dimensions of the planar part of the molecule and the corresponding Patterson vectors of length about 1.4 Å and 2.3 Å.

ular vectors of lengths 1.4 Å and 2.3—2.4 Å must be coplanarily situated around origo. By inspection of the distribution of peaks on the surfaces of two spherical sections of ${}^{s}P(xyz)$ with radii 1.4 and 2.3 Å and centered in origo the corresponding peaks were found, and this gave the orientation of the molecular plane as well as the orientation of the furan ring in that plane. This in combination with a study of the Harker section ${}^{s}P(x\frac{1}{2}z)$ (Fig. 2) and of ${}^{s}P(xz)$ gave a few plausible trial structures for the projection on the *b*-plane. The final projection was found using the *R*-minimisation method of Bhuiya and Stanley.[11] An ALGOL program written by Danielsen was used.[12] The $R(h0l)$ value dropped to 22.5 %.

The *y*-coordinates of the atoms were readily deduced from the Harker line ${}^{s}P(0y\frac{1}{2})$ and the section ${}^{s}P(x\frac{1}{2}z)$.

Fig. 2 shows clearly, that high peaks appear midway between the Harker peaks corresponding to C-3 and C-4, C-3 and O-8, and C-4 and C-8, thus indicating that C-3, C-4, and O-8 are probably situated at approximately the same *y*-level. Similarly the atoms C-2, C-5, and N-7 appear to have a common *y*-

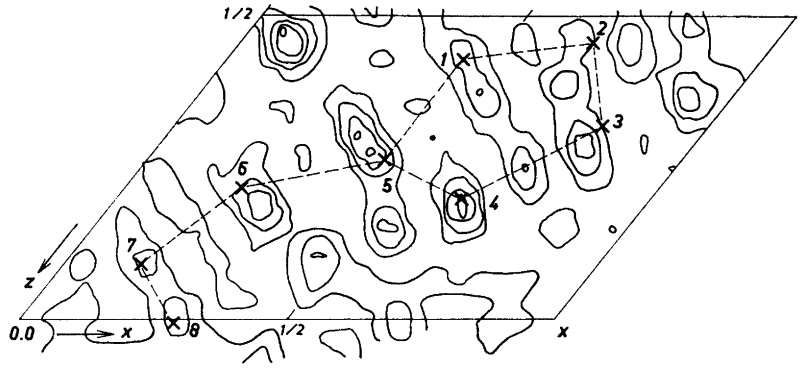

Fig. 2. The Harker section ${}^{s}P(x\frac{1}{2}z)$ and its interpretation.

coordinate as well as the two atoms O-1 and C-6. Trial y-parameters were obtained from these deductions combined with the fact, that the Harker line ${}^{s}P(0y\frac{1}{2})$ showed a peak at $y = 0$, and a greater one at $y \approx \frac{1}{4}$ indicating that one of the above named three groups of atoms is situated approximately in one of the glide planes and the other two lie at y levels separated about $\frac{1}{8}y$ from a glide plane. Subsequent R-minimisation reduced in four cycles the $R(hk0)$ value to 22 %.

Refinement was performed by Busing, Martin and Levy's least squares full matrix program ORFLS [13] first using isotropic temperature factors and with all observed reflections introduced in the calculations. One cycle reduced the overall R-factor from 26 to 22 %, and further refinement did not take place. Then all (189) structure factors with $\sin\theta/\lambda < 0.35$ were removed to avoid influence from the hydrogen atoms, and three cycles of refinement including individual, anisotropic temperature factors for the C, N, and O-atoms reduced the R-factor for the $1007-189 = 818$ structure factors to 12 %; in the final cycle all coordinate shifts were smaller than their standard deviation, but some β_{ij}-shifts were still of the same order of magnitude as their standard deviation.

A three dimensional F_o-F_c synthesis including all observed structure factors did only reveal three of the five hydrogen atoms in the molecule. Attempts to refine hydrogen positions based upon considerations of a model of the molecule were unsuccessfull. Structure factor calculations including the three hydrogen atoms found, all with a common $B = 3.0$, lead to $R = 13.7$ % for all observed reflections.

DISCUSSION OF THE STRUCTURE

The structural parameters found are shown in Tables 1 and 2; Fig. 3 shows the molecular dimensions and Fig. 4 the packing of the molecules in

Table 1. Final atomic coordinates and their standard deviations, in fractions of the corresponding cell edges. (Based upon 818 refl.)

	x	σx	y	σy	z	σz
O1	0.2192	0.0007	0.2226	0.0010	0.0372	0.0005
C2	0.3282	0.0010	0.3559	0.0018	0.0223	0.0007
C3	0.3951	0.0009	0.5815	0.0016	0.0895	0.0007
C4	0.3241	0.0008	0.6001	0.0014	0.1519	0.0006
C5	0.2197	0.0007	0.3786	0.0011	0.1183	0.0005
C6	0.1077	0.0008	0.2672	0.0012	0.1419	0.0005
N	0.0672	0.0007	0.3756	0.0011	0.2051	0.0005
O8	0.1496	0.0007	0.6210	0.0010	0.2548	0.0005
H3	0.4750	0.0147	0.7500	0.0251	0.1000	0.0101
H4	0.3500	0.0149	0.0760	0.0258	0.2050	0.0105
H6	0.0500	0.0149	0.1000	0.0257	0.1000	0.0101
H2						
H8						

Table 2. Anisotropic temperature parameters U_{ij} Å^2 and their standard deviations. (Based upon 818 refl.)

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{13}	σ	U_{23}	σ
O1	0.0584	(28)	0.0408	(25)	0.0501	(26)	−0.0065	(21)	0.0475	(24)	−0.0011	(20)
C2	0.0610	(40)	0.0744	(50)	0.0626	(40)	0.0031	(36)	0.0578	(37)	0.0045	(37)
C3	0.0424	(33)	0.0574	(41)	0.0594	(40)	0.0008	(30)	0.0453	(33)	0.0067	(33)
C4	0.0321	(27)	0.0415	(32)	0.0444	(31)	−0.0019	(26)	0.0316	(26)	0.0014	(28)
C5	0.0339	(26)	0.0269	(27)	0.0307	(25)	0.0031	(22)	0.0282	(23)	0.0003	(22)
C6	0.0412	(30)	0.0258	(27)	0.0363	(28)	−0.0023	(23)	0.0329	(26)	0.0006	(22)
N	0.0435	(26)	0.0289	(25)	0.0413	(26)	0.0008	(21)	0.0376	(24)	0.0034	(21)
O8	0.0564	(27)	0.0405	(25)	0.0607	(28)	−0.0118	(20)	0.0530	(25)	−0.0159	(21)

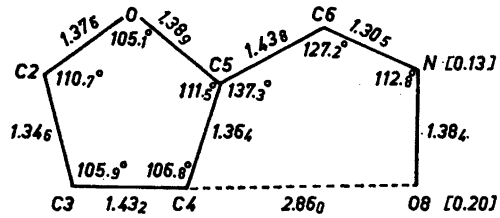

Fig. 3. Intra-molecular distances (Å) and angles (°). Standard deviations on bond lengths are 0.007 Å—0.016 Å and on angles 0.5°—0.9°. The numbers in angular parentheses are the distances in Ångström of the atoms from the plane through C-2, C-4, and C-6.

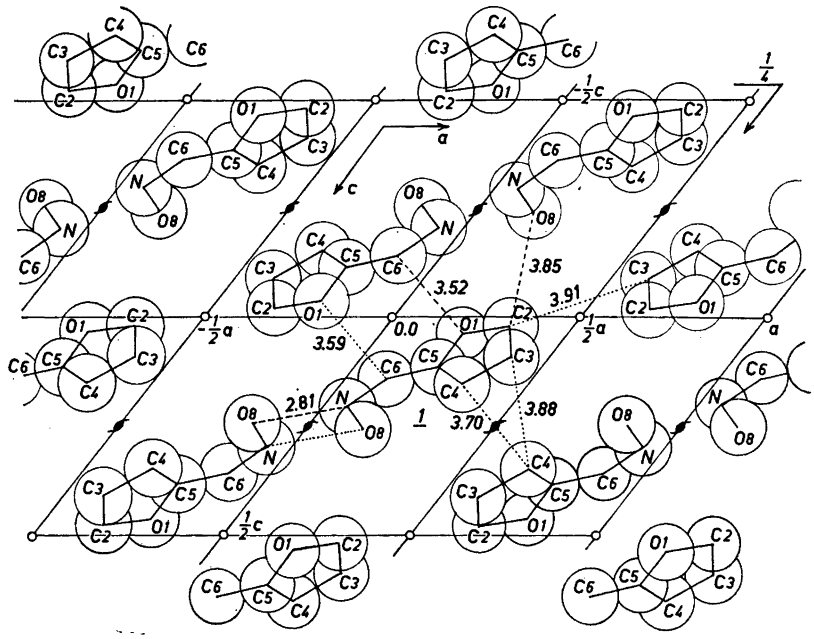

Fig. 4. The structure viewed along the *b*-axis. The O—H···N hydrogen bonds are shown together with a selection of van der Waals' contacts. Referred to molecule 1 dotted lines point upwards and broken lines downwards.

the crystal lattice. The carbon atoms and the ring oxygen are coplanar within 0.01 Å. The bond lengths and valency angles in the ring agree excellently with the values found by Bak, Hansen and Rastrup-Andersen [14] in their microwave study of furan. The dimensions of the oxime moiety do not differ significantly from those found in a number of other oximes. The sidechain is turned only 6° out of the plane of the ring, giving rise to a rather close van der Waals' contact between C-4 and O-8. The three hydrogens, which showed up in the difference synthesis, were situated in the expected positions; C—H distances,

which may be very inaccurate, were found as C-3—H 1.09 Å, C-4—H 1.01 Å and C-6—H 0.97 Å. It may be worth mentioning, that the hydrogen at C-4 as expected is very much displaced from the straight line between C-4 and O-8.

Hydrogen bonds O—H···N link the molecules in infinite chains as proposed by Jerslev.[4] The hydrogen bonds connect the molecules in the *b*-direction, but otherwise only intermolecular distances corresponding to weak van der Waals' contacts are seen. The molecular packing found explains readily the cleavage parallel to the *b*-axis and the rather pronounced volatility of the crystals.

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