The Molecular and Crystal Structure of 3,4-Furandicarboxylic Acid

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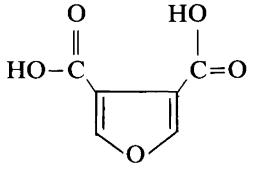
The structure of 3,4-furandicarboxylic acid was studied by Williams and Rundle in 1964. The reported space group was $P2_1/m$, implying C_s symmetry of the molecule. As a consequence, the two hydrogen bonds of lengths 2.56 (intra) and 2.64 Å (inter) would be situated across special positions. For this reason, a renewed inspection of the material at low temperature was initiated. The present investigation showed that the true space group of the material is $P2_1/c$ at low temperature and at room temperature as well. The cell dimensions at 125 K were $a = 6.007(2)$, $b = 14.440(5)$, $c = 7.191(2)$ Å and $\beta = 91.46(2)$, which implies a unit cell doubling along the c axis repeat compared with the previous work. The present structural model gives a chemically consistent picture of the molecules with asymmetric hydrogen bonding in the crystal. The pseudosymmetric arrangement of molecules along hydrogen-bonded chains makes cooperative motions of the acidic protons possible. Thus, pseudo-one-dimensional phase transition to $P2_1/m$ between room temperature and the melting point of the compound (214 °C) may take place.

The compound 3,4-furandicarboxylic acid (FA) has two carboxylic acid groups in neighbouring positions, facilitating the formation of an intramolecular hydrogen bond in the molecule (1). For this reason, the structure of the compound was first investigated in 1964 by Williams and Rundle (W&R hereafter),[1] and they assigned the space group $P2_1/m$ to the material. It was further found that the mirror plane of the space group coincided with a mirror plane in the molecule normal to the plane of the molecule; thus, half the molecule constitutes the asymmetric unit, implying equivalence between pairs of carbonyl and hydroxyl groups.



(1)

In the crystal, the molecules form chains through intermolecular hydrogen bonds of length 2.64 Å. These alternate with intramolecular hydrogen bonds (2.56 Å) and are, in spacegroup $P2_1/m$, situated across centers of inversion. By and large, there are three possibilities for the protons in the hydrogen bonds: they may be truly symmetric, there may be some sort of random or disordered arrangement of the protons in one or both hydrogen bonds, or there may be an asymmetric disposition of the protons and a wrong space group assignment. The authors concluded that their data were insufficient to distinguish between the first two possibilities, but seemed to favour the first since there was no apparent sign of disorder in the pertinent thermal amplitudes of the carboxylic oxygen atoms. Apparently, the third possibility was not considered.

Quite a few structure determinations of 1,2-dicarboxylic acids[2–4] and their acid salts[5,6] are now available. Results from these studies indicate that the first possibility is highly unlikely. A distinction between the last two possibilities may be a matter of temperature alone, since both alternatives could imply a low-temperature and a high-

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Table 1. Cell constants and refinement results from the three analyses of 3,4-furandicarboxylic acid.

Ref.	W&R[1]	This work (I)		This work (II)	
Space group	$P2_1/m$	$P2_1/m$		$P2_1/c$	
a/Å	6.0629(6)	6.002(2)		6.007(2)	
b/Å	14.4126(14)	14.433(5)		14.440(5)	
c/Å	3.6677(4)	3.596(1)		7.191(2)	
β/°	92.60(6)	91.48(2)		91.46(2)	
T	room temp.	116 K		125 K	
$(\sin\theta/\lambda)_{min}$(Å^{-1})	0.00	0.00	0.70	0.00	0.70
$(\sin\theta/\lambda)_{max}$(Å^{-1})	1.15	0.90	0.90	0.99	0.99
no. refl. (obs.), n	768	1684	759	2810	1445
no. param., p	61	64	52	116	100
R^a	0.047	0.036	0.025	0.045	0.039
$R_w{}^b$	–	0.045	0.025	0.058	0.047
S^c	1.19	2.88	1.09	2.73	1.82
average $\sigma_{pos.}$ (Å)	.0023	.0005	.0005	.0007	.0012

$^a R = \Sigma\Delta F/\Sigma F_o$. $^b R_w = (\Sigma w(\Delta F)^2/wF_o^2)^{\frac{1}{2}}$. $^c S = (\Sigma w(\Delta F)^2/n-p)^{\frac{1}{2}}$.

temperature space group with a phase transition in between. The immediate choice of low temperature space group would be $P2_1$, the polar counterpart of $P2_1/m$, yielding a ferroelectric arrangement of the hydrogen-bonded chains of molecules. With this in mind and after the symmetry of the crystal had been checked by film methods, data were collected at 116 K. However, all subsequent refinements in space group $P2_1$ failed, and eventually, we had to resort to refinements in the higher, symmetric space group $P2_1/m$. These converged rapidly with reliable R factors (Table 1). The results, which are considered in some detail below, were similar to those obtained by W&R,[1] and even though the thermal parameters had been reduced, roughly by a fac-

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2), (B_{iso} for H) for 3,4-furandicarboxylic acid in the final refinement of all data; e.s.d.'s in parentheses. $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\,\tilde{a}_i\,\tilde{a}_j$.

Atom	x	y	z	B
O(1)	.62492(10)	.24437(3)	.48431(9)	1.36(1)
C(2)A	.49939(13)	.16985(5)	.43454(12)	1.28(2)
C(2)B	.50605(13)	.32149(5)	.43902(12)	1.23(2)
C(3)A	.30087(13)	.19755(5)	.35696(11)	1.06(2)
C(3)B	.30532(12)	.29809(5)	.35954(11)	1.05(2)
C(4)A	.12546(13)	.13550(5)	.28551(11)	1.14(2)
C(4)B	.14176(13)	.36801(5)	.29501(11)	1.18(2)
O(5)A	−.04425(10)	.16437(4)	.20442(9)	1.40(1)
O(5)B	−.04233(10)	.34042(4)	.20899(9)	1.42(1)
O(6)A	.16339(11)	.04735(4)	.31352(10)	1.77(2)
O(6)B	.17632(11)	.45104(4)	.31905(10)	1.77(2)
H(7)A	.5615(21)	.1115(9)	.4575(20)	1.9(2)
H(7)B	.5758(21)	.3777(10)	.4661(20)	2.0(3)
H(O5B)	−.0479(32)	.2689(12)	.1982(27)	4.4(4)
H(O6A)	.0357(26)	.0110(10)	.2626(19)	4.2(4)

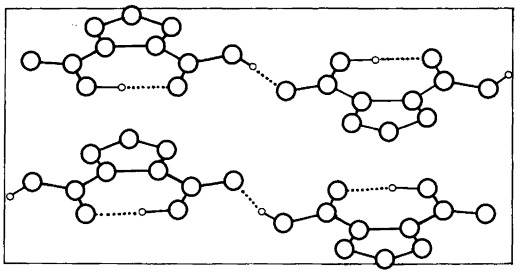

Fig. 1. Schematic drawing of structure on to the (100) plane. The *b* axis is horizontal.

tor of three compared to the previous room temperature study, no conspicuous features in these parameters were detected.

At this stage, the partially deuterated compound was synthesized and film investigations revealed unambiguously that the d_2-furandicarboxylic acid crystallizes in space group $P2_1/c$ with a unit cell doubling along the *c*-repeat compared to the previous work.[1] Renewed inspection of the protonated material by film methods indicated after long exposure time a similar doubling of the *c*-repeat (Table 1), and the space group could irrefutably be assigned as $P2_1/c$ at room temperature. Consequently, new intensities had to be collected. After some trial and error a reasonable structure solution was found, the results of which are communicated below.

Experimental

In the present work, the *b* axis was chosen as the unique axis. The cell of W&R[1] is transformed to ours by the matrix $100/00\bar{1}/020$. Commercially available FA (Fluka) was crystallized from saturated aqueous solutions. The colourless monoclinic needles showed a pronounced cleavage along $(10\bar{2})$, and some difficulties were encountered in finding suitable specimens. In the following, the experimental conditions for collection of the final set of data at 125 K (set II) is described. The conditions during the first data collection at 116 K (set I) were similar, except that reciprocal lattice nets with odd *l*'s were not recorded. The selected specimen of dimensions 0.20×0.20×0.45 mm was mounted on a Syntex P1 diffractometer at the Chemistry Department, University of Oslo. The instrument is equipped with an Enraf-Nonius liquid nitrogen gas flow cooling device, and data were collected in the ω-2θ mode with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The temperature at the position of the crystal was 125(.3) K. The scan rate varied between 1 and 6° min^{-1}, depending on intensity to achieve reasonable counting statistics for the weak reflections with *l* odd. To avoid measurements of intensities for which $I < 3\sigma(I)$ above $\sin\theta/\lambda = 0.595$ Å^{-1}, a threshold value was applied. All data within a quadrant of reciprocal space with $\sin\theta/\lambda \leq 1.0$ were considered. The scan range was from 0.8° below the λ_1 position to 0.9° above that of λ_2. The intensities and their standard deviations derived from counting statistics were L.P.-corrected in the usual manner, and a 2% uncertainty was included in the latter to account for experimental instabilities. The cell parameters were derived from a least-squares fit to the 2θ values of 15 reflections centered in the counter aperture. Crystal data are given in Table 1.

Refinements. As the starting point for the refinements, the transformed coordinates of W&R[1] were used. Random positional shifts in these paremeters up to about 0.05 Å were introduced to avoid matrix singularities. Initially, least-squares refinements failed, and several cycles of Fourier refinements were necessary. Subsequent full matrix least-squares refinements converged rapidly.

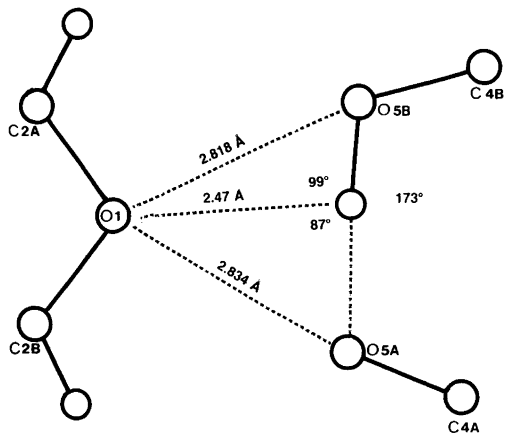

Fig. 2. Details of interaction between the furan ring oxygen atom and the atoms of the intramolecular hydrogen bond of the neighbouring chain in the $(10\bar{2})$ plane.

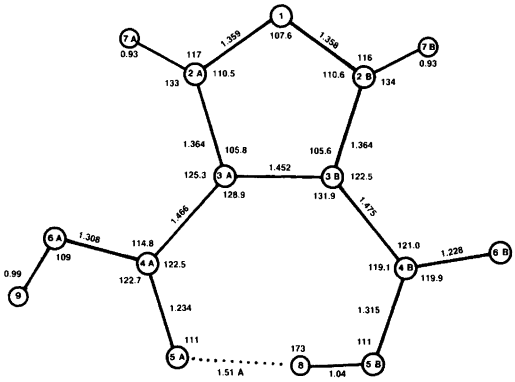

Fig. 3. Bond distances and angles of the molecule with atom numbering scheme as indicated. Standard deviations are less than 10^{-3} Å and 10^{-1} degree for heavy atoms; ×10 when hydrogen atoms are involved.

Hydrogen atoms were located in a difference map, and were included in the refinements with individual isotropic thermal parameters. A refinement of the heavy atom parameters with an inner cut-off limit at $\sin\theta/\lambda = 0.7$ Å^{-1} was also carried out. A summary of the refinements and their results is given in Table 1, while positional parameters and equivalent isotropic thermal parameters from the final refinements with all data are given in Table 2. A list of structure factors, anisotropic parameters, details of rigid-body analysis and results from refinements of the biased data set (set I) is available from the authors on request. The function minimized in the refinements was $\Sigma w\,(F_o\text{-}F_c)^2$ with $w = [\sigma(F_o)]^{-2}$.

Discussion

The unit cell doubling implies a reduction in symmetry, namely every second centre of inversion in the *c* direction and the mirror planes of $P2_1/m$ being lost and replaced with corresponding pseudo-elements of symmetry. The previously reported *c* axis repeat of space group $P2_1/m$ is thus replaced with a pseudo–translation. The approximate nature of this latter element causes the weak reflections with odd *l*. As will be seen, the results of the structure determination at 125 K, in concordance with the above, give a coherent physical and chemical picture. From the film investigations at room temperature, we conclude that a similar disposition of atoms persists up to this temperature.

Packing. The projection of the contents of the unit cell in the *bc* plane is shown in Fig. 1. Except for the asymmetry of the hydrogen bonds in the material (see below), the main features of the packing arrangement were adequately described by W&R.[1] The molecules are approximately situated in the $(10\bar{2})$ planes, thus explaining the large intensity of the $(10\bar{2})$ reflection and the facile cleavage of the material. In this direction there is also a reversal of polarity between adjacent chains. The structure may therefore be considered as being made up of layers in the $(10\bar{2})$ plane, with an antiferroelectric ordering of the protons in the hydrogen bonds. Successive layers are stacked ferroelectrically. The furan ring oxygen atom participates in nonbonded contacts with two neighbouring molecules; these contacts may be of particular significance. There are short contacts between this atom and the atoms participating in the intramolecular hydrogen bond in the adjacent chain in the $(10\bar{2})$ plane (Fig. 2). The interaction is reminiscent of a bifurcated hydrogen bond system. Although not formally satisfying the criteria for such a bond,[7,8] the contact is nevertheless a very important polar interaction between molecules in adjacent chains. The furan ring oxygen atoms also participate in a contact with the proton in the intramolecular hydrogen bond of the molecule in $(1+x,y,z)$ of 2.90 Å. It is proposed that the interactions above may be of particular importance for the ordering scheme

Table 3. Hydrogen bond distances and angles (e.s.d.'s amount to about 1 in the last digit given).

	O-H	O---O	H--O	<C-OH	<O---H---O	<C-O--H
intra	1.04	2.542	1.51	111	173	111
inter	0.99	2.628	1.64	109	179	110

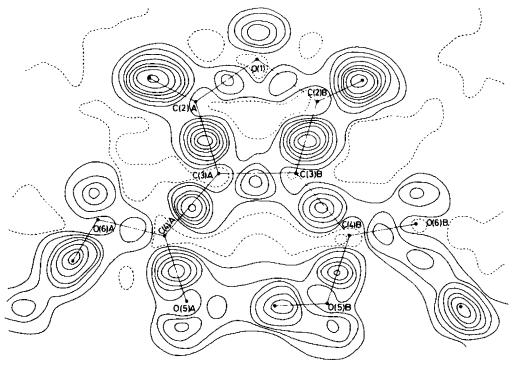

Fig. 4. Difference Fourier map from the final refinements with data set II showing residual electron densities and hydrogen atoms.

adopted by the molecules in the crystal. The distance between neighbouring furan ring systems is 3.2 Å, the furan ring oxygen atom being located above the centre of the furan ring of the foregoing layer.

Hydrogen bonding. As seen from Table 3 and Fig. 3, the two hydrogen bonds in the material are definitely asymmetric and therefore in keeping with the results from the structure determination of maleic acid (MA)[2] and cyclobutene-1,2-dicarboxylic acid (CA).[3] The length of the intramolecular bond, 2.542 Å, is intermediate between that found in CA (2.625 Å) and MA (2.502 Å). Probably the size and rigidity of the backbone of the molecules and the mode of packing are decisive factors in determining the length of this bond. The length of the intermolecular hydrogen bond is normal (2.628 Å) and is very similar in all three compounds. The topologies of the hydrogen-bonded chains in FA and CA correspond closely while that in MA differs slightly: the proton in the intermolecular hydrogen bond is accepted along the opposite lone-pair direction of the carbonyl group.

Bond distances and angles. Bond lengths and angles are given in Fig. 3, which also displays the atom numbering scheme adopted. Table 4 compares distances from the refinements using all data with those obtained using only high-angle data. There are hardly any significant differences, except perhaps for the C(4B)-O(6B) bond length. Rigid-body thermal analyses gave no correction to bond lengths exceeding 0.002 Å. These

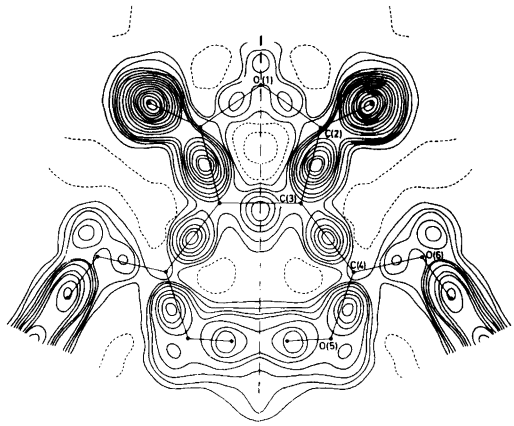

Fig. 5. Difference Fourier map at the end of the refinements with data set I. Note the well-resolved half hydrogen atoms in the hydrogen bonds.

Table 4. Interatomic distances with estimated standard deviations from the refinement including all data and with an inner cut-off at $\sin\theta/\lambda = 0.70$ Å^{-1} for data set II.

	All data		High-angle data	
Bond	A	B	A	B
O(1)-C(2)	1.3568(9)	1.3580(9)	1.3543(16)	1.3549(15)
C(2)-C(3)	1.3636(10)	1.3637(10)	1.3642(15)	1.3672(15)
C(3)-C(3)	1.4521(10)		1.4523(11)	
C(3)-C(4)	1.4662(10)	1.4754(10)	1.4665(15)	1.4747(15)
C(4)-O(5)	1.2340(9)	1.3151(9)	1.2351(14)	1.3119(15)
C(4)-O(6)	1.3078(9)	1.2282(9)	1.3058(14)	1.2325(14)

corrections were not applied. The results of the refinements with all data are considered below.

The agreement for chemically similar but crystallographically different bonds in the furan ring is very good. However, the values of 1·364 Å found here for the ethylenic linkages are somewhat larger than those reported by W&R,[1] and that for the acid potassium salt of FA (KFA),[5] viz. 1.351 Å and 1.328 Å, respectively. We attribute these differences to the lower thermal motion in the present study and consequently, the larger number of high-angle data observable at 125 K.

The C-O bonds are now well resolved, with values within the ranges quoted for other ordered carboxylic groups. As expected, the longer member of each of the carboxyl and hydroxyl bonds participates in the stronger (intramolecular) hydrogen bond.

The two C(sp^2)-C(sp^2) single bonds and the angles within the seven-membered "ring" with the intramolecular hydrogen bond show deviations from standard values in much the same manner as those found in MA.[2] These distortions have been discussed in detail by James and Williams in their structure determination of MA.[2] However, the geometry of alternating single and double bonds in FA is different from that in MA; in FA, the shorter of the C(sp^2)-C(sp^2) single bonds is to the carboxyl group having the CO double bond *trans* to the double bond of the furan ring moiety. Quite the opposite relationship was found in the structure determination of MA. Probably, therefore, nonbonded repulsions between the hydrogen-bonded proton and the heavy atom skeleton are responsible for the differences in the terminal C-C bonds as well.

Planarity of the molecule. The furan ring moiety and the C(3) atoms are coplanar within estimated standard deviations, while the oxygen and hydrogen atoms of the carboxyl groups deviate from this plane by approximately 0.03 Å. The deviations take the form of rotations of about 4.2° about the C(3)-C(4) bonds. The direction of rotation is opposite in the two bonds, thus bringing the two oxygen atoms in the intramolecular hydrogen bond on the same side of the furan ring plane. As pointed out by W&R,[1] the twists of the carboxyl groups are such as to move these atoms closer to the furan ring oxygen atom with the short intermolecular approach discussed above [although hardly significant, it seems that the intramolecularly hydrogen-bonded proton is even further displaced in the direction of O(1)].

Difference Fourier map. The difference Fourier map, including contributions from the hydrogen atoms and residual electron densities, is shown in Fig. 4. The most important feature in the map is the completely ordered arrangement of the acidic hydrogens. The small residuals in the opposite positions of the hydrogen bonds are attributed to the lone-pairs of the oxygen atoms. The latter maxima are less than those found in the other lone-pair position of each of the carbonyl oxygen atoms. Larger residuals due to bonding electrons are clearly shown in the C-C bonds of the furan ring, in the C(sp^2)-C(sp^2) single bonds, and in the C-O of the hydrogen-bonded "ring". The lone-pair of the furan ring oxygen atom also shows clearly. Interestingly, the larger maxima of the furan ring residual electron densities are situated slightly outside the ring system, whereas those of the C(sp^2)-C(sp^2) single bonds are displaced from the intermolecular line so that they are located inside the seven-membered hydrogen-bonded "ring". The disposition of these maxima thus clearly reveals the strains associated with the two ring systems.

Refinements with data set I. Despite the erroneous model, the refinements in $P2_1/m$ with set I converged rapidly with excellent R factors (Table 1). We think some of the results of these refinements merit mention in some detail, since a fairly coherent structural description resulted. Hydrogen atoms were easily located in a difference Fourier map (Fig. 5). Contrary to what was found in the room temperature study of W&R,[1] the two acidic hydrogens were significantly displaced from the special positions, giving a convincing impression of a disordered hydrogen-bonded system. Also, bond lengths in the carboxyl group were intermediate between single and double bond values. Other interatomic distances had acceptable values. Thermal parameters revealed no other conspicuous features. In particular, the components of thermal motions of the heavy atoms in the molecular plane were to a large extent isotropic. Thus, these parameters gave, somewhat surprisingly, no direct evidence of any disorder in the heavy atom skel-

eton, since the magnitude of thermal motions had been reduced roughly by a factor of three compared to the room temperature study.[1]

After a satisfactory structural solution was found, the thermal parameters were again critically analyzed. It now became evident that, whereas the thermal components perpendicular to the molecular plane were generally larger in set II than in set I, those describing in-plane motion were generally smaller. Furthermore, for the thermal parameters of set I, the directions of the main motion in the plane closely corresponded to the displacements from the true symmetric structure to that of the "average" symmetric model. We also found that the rigid-bond test of Hirshfeld[9] provided valuable information. Applied to set I, the calculated differences in thermal motions along interatomic vectors gave particularly large values for the C(4)-O(5) and C(4)-O(6) directions ($5 \cdot 10^{-3}$ Å^2) compared to the other directions ($5 \cdot 10^{-4}$ Å^2). (A similar analysis for set II gave values close to $8 \cdot 10^{-4}$ Å^2, no single value being particularly large). This may be taken as evidence of "disorder" in the C(4) atomic position since the major contributions were those of C(4). Moreover, the results of the Hirshfeld rigid-bond test on data set I is in agreement with the comparison between the two structural models ($P2_1/m$ and $P2_1/c$) since a particularly large displacement was found for C(4). Thus, the only direct evidence for the incorrectness of the symmetric model came from the Hirshfeld rigid-bond analysis; conventional crystallographic indicators failed to convey such information (Table 1).

Collective motion of protons. The pseudo-symmetry of FA crystals is indeed similar to that found in materials known to have antiferro-distortive phase transitions where the acidic hydrogens play an essential role.[10,11] We suggest that a similar phase transition may occur in FA. The following evidence supports this view: From the presence of superlattice reflections at room temperature, we inferred that the asymmetric arrangement persists up to this temperature. However, since their intensities were significantly reduced, the average magnitudes of positional shifts were also reduced. This may indicate a continuous development towards zero displacements (and hence $P2_1/m$ symmetry) at temperatures above room temperature. We also noticed that, at room temperature, the intensities of superlattice reflections increase on deuteration. This may indicate that displacements in the deuterated compound are larger that in FA itself, which is consistent with an isotope effect in the transition temperatures of the two compounds. Such isotope effects are commonly found in hydrogen-bonded materials undergoing phase transitions where structural reversal takes place through a proton transfer. Furthermore, the preliminary film investigations disclosed the presence of diffuse scattering in several regions of reciprocal space. Although its distribution has not yet been studied, we suggest that its presence may be correlated with the intensity variations of superlattice reflections and hence indicative of a collective dynamic mode of motion in the hydrogen-bonding arrangement of the crystal.

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