

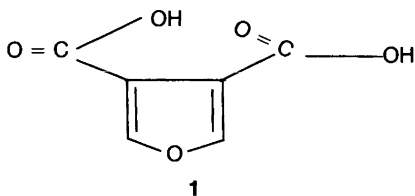
Hydrogen-Bonded Chain Structure in Crystalline Furan Dicarboxylic Acid*

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Samuelsen, E. J., Fjær, E. and Karlsson, A., 1987. Hydrogen-Bonded Chain Structure in Crystalline Furan Dicarboxylic Acid. – *Acta Chem. Scand.*, Ser. A 41: 573–575.



Furan dicarboxylic acid (**1**; $C_6H_4O_5$) is an interesting example of a material made up of infinite linear chains in the crystalline state.¹ The molecules are linked together by asymmetric H-bonds² with $O \cdots O$ distance 2.63 Å. There is also an intramolecular H-bond² with an $O \cdots O$ distance of 2.54 Å.

In the previous X-ray structure determination¹ the space group $P2_1/m$ was proposed, implying non-polar chains. However, recently it was found² that the space group is $P2_1/c$. Thus, each chain is polarized, and in fact alternating \pm polarization is found for chains stacked along the monoclinic c -axis, which is doubled relative to the results of the original work.¹ A projection of the structure is shown in Fig. 1. The monoclinic unit cell has the following parameters at room temperature:¹ $a = 6.063$, $b = 14.413$, c (doubled) $= 7.337$ Å; $\beta = 92.6^\circ$.

*Part of a lecture on "Order-Disorder Phenomena Studied by Raman Spectroscopy and Diffraction" presented at the *XII Nordiska Strukturkemistmötet* in Sänga-Säby, Sweden, June 8–13, 1987.

Diffuse X-ray scattering. Single crystals were obtained by slow evaporation both from water and from ether solutions. The sample crystals for the X-ray and the Raman studies were needle-like, of approximate dimensions $0.5 \times 1 \times 4$ mm, with the c -axis along the longest edge.

The X-ray investigation was performed at room temperature on the climbing two-axis instrument LØFTE, which can be used both as a diffractometer and as a film camera.^{3,4} Upper layer ($l = 1$) Weissenberg pictures with the c -axis as the rotation axis $[(hk1)]$ showed not only Bragg spots due to the c -axis doubling, but also pronounced diffuse scattering centred around $(h + \frac{1}{2}, k, 1)$. Closer examination using the automatic diffractometer mode⁴ revealed diffuse rods along $[10\bar{2}]$ (see Fig. 2).

Only slow intensity variation is seen along the rod direction, indicating the presence of stacks of independent $[10\bar{2}]$ planes. From the widths of the rod, observed along $\sim[302]$ and $[010]$, we deduce a correlation length of about six unit cells along the a - $c/2$ -diagonal direction and about three unit cells along the b -axis direction [this conclusion is deduced from an Ornstein-Zernike type correlation decay,⁵ $\exp(-|r|/\xi)/r$, where r is the distance and ξ is the correlation length, giving rise to Lorentzian line-shapes of widths proportional to ξ^{-1}].

The correlated planes are, in fact, coincident with the molecular planes containing the carboxy groups and the furan moieties; this coincidence is

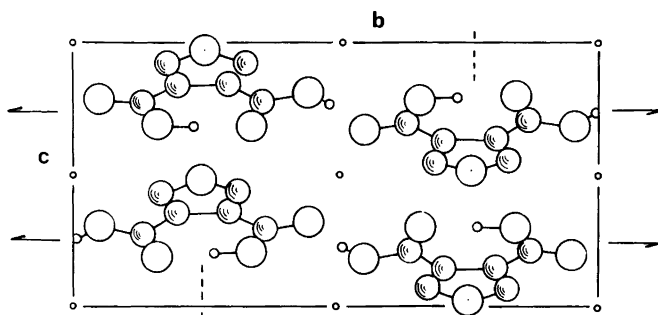


Fig. 1. The 100-projection of the crystal structure of furan dicarboxylic acid, space group $P2_1/c$. The inversion centres and the screw axes are indicated. The glides along c are at $y = \frac{1}{2}$. Large spheres: oxygen atoms (the furan oxygen is marked by a dot); shaded spheres: carbon atoms; small spheres: hydrogen atoms. The molecules are essentially planar, lying in the $[10\bar{2}]$ planes.

probably due to a tendency to ferroelectric coupling between chains along the a - $c/2$ diagonal, mediated by the furan oxygens. A detailed analysis will be given elsewhere.

Low-temperature Raman scattering. Unpolarized Raman spectra in part of the external vibrational region are shown in Fig. 3. The various lines have not yet been assigned, since the full unit cell contains as many as four molecules. It is noteworthy, however, that the background at room temperature is fairly high, and the line at about 92 cm^{-1} is broad and slightly asymmetric. We interpret both these effects as due to the presence of disorder.

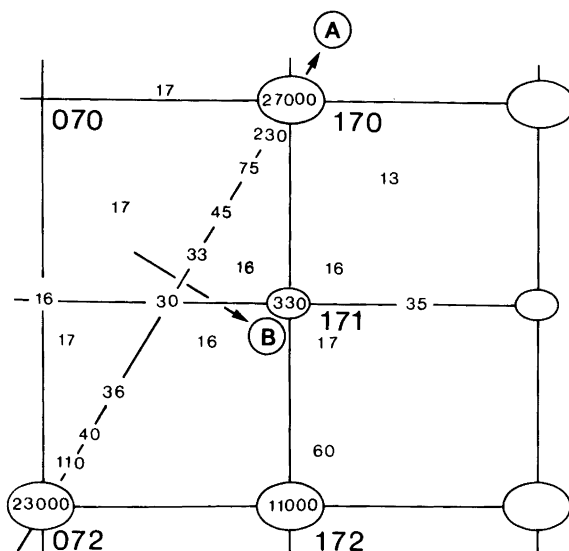
As is seen, pronounced changes take place as the sample is cooled: The background decreases,

the lines narrow and, most importantly, a new line at about 110 cm^{-1} grows in intensity as the temperature is lowered below 200 K. The temperature effects are summarized in Fig. 4.

Conclusions. The observed diffuse X-ray scattering at room temperature may be accounted for by the presence of structural disorder, resulting from short-range ordered $[10\bar{2}]$ planes without interplanar correlation. Within the correlated regions the chains all have the same polarization direction, entailing inversion of polarization of every second chain relative to the average structure. The correlation has a range of about three unit cells along the chains (6 molecular units).

The general picture strongly indicates that competing interaction exists between the neigh-

Fig. 2. Intensity distribution in the $h7l$ region ($h, l = 0, 1, 2$) as observed by the diffractometer. Small-print numbers are intensity readings, and numbers enclosed in ellipses are Bragg peaks, the smaller ellipses corresponding to superlattice reflections due to c -axis doubling. The large-print numbers are indices. Intensity ridges run through the strong Bragg peaks along $[10\bar{2}]$, as verified in detail by scans of type A (along ridge) and type B (across ridge).



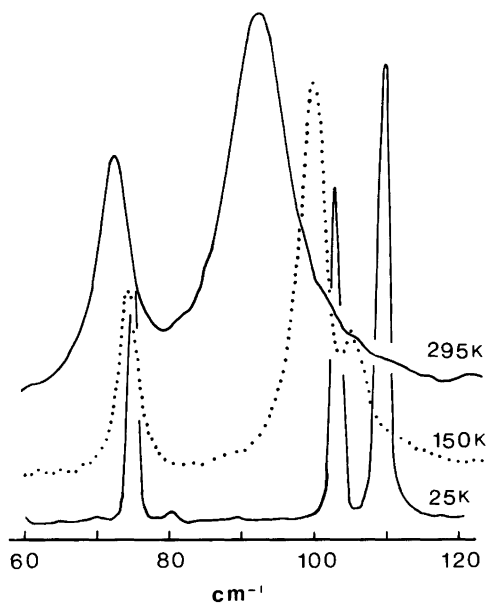


Fig. 3. Unpolarized Raman spectra in the 60–120 cm^{-1} region at three temperatures, showing the background and peak-width decrease on cooling, and the appearance of a new line at low temperatures.

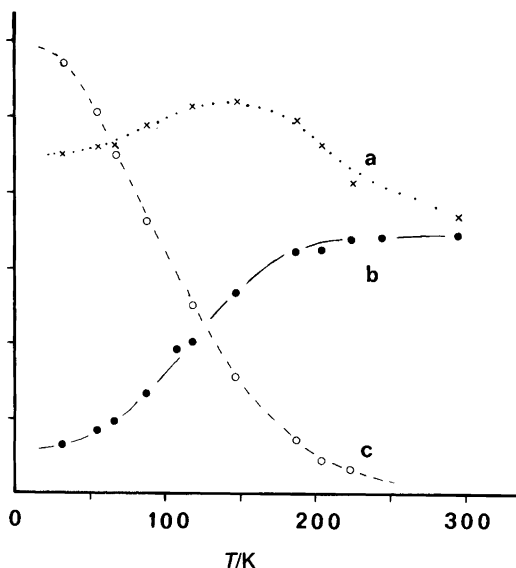


Fig. 4. Temperature dependences of the Raman scattering around 100 cm^{-1} , shown on a common, arbitrary scale: (a) peak intensity of the 92 to 102 cm^{-1} line, (b) background intensity, (c) peak intensity of the 105 to 110 cm^{-1} (new) line.

bouring chains in the c -axis, a -axis and $2a+c$ directions. Whereas the first is antiferroelectric the latter two are ferroelectric. The diagonal interaction may be mediated via the furan oxygen atom and the intramolecular H-bond.

The Raman study strongly indicates that the disorder decreases at lower temperatures, in particular below 200 K. The appearance of a new Raman line below this temperature may be due to the increased order, since disorder may sometimes broaden some peaks considerably. However, a phase transition to a different chain sequence structure below 200 K is also possible. Low-temperature X-ray studies are in progress to settle this point and to explore the system in greater detail.

Acknowledgement. Part of the work was supported through the research fellowship programme of the Norwegian Research Council for Science and Humanities (NAVF).

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Received July 13, 1987.