

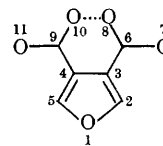
The Crystal Structure of the Monorubidium Salt of Furantetracarboxylic Acid

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EVIDENCE¹ for strong intramolecular hydrogen bonding in furan-3,4-dicarboxylic acid (I) was recently confirmed by the determination of the crystal structure of this acid.² The *X*-ray study revealed an oxygen-oxygen distance of 2.555 Å between atoms O(8) and O(10) across a mirror plane perpendicular to the furan ring

Cocker and his co-workers³ found that furantetracarboxylic acid and its monopotassium salt have infrared spectra indicative of strong hydrogen



(I)

¹ S. Oae, M. Hamada, Y. Otsuji, and N. Furukawa, *Ann. Rept. Radiation Center Osaka Prefect.*, 1961, **2**, 106.

² D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, 1964, **86**, 1660.

³ W. Cocker, W. J. Davis, T. B. H. McMurry, and P. A. Start, *Tetrahedron*, 1959, **1**, 299.

bonding, and they have proposed structures for these compounds involving intramolecular hydrogen bonding of the type found in furan-3,4-dicarboxylic acid. We have prepared a monorubidium salt of furantetracarboxylic acid, which shows considerable isomorphism⁴ with the monopotassium salt, although the rubidium salt contains no water of crystallization. We have

unit cell. A small, well-formed crystal was selected for intensity measurements and 1190 independent reflexions were measured on an automated X-ray diffractometer⁵ with Cu- $K\alpha$ radiation. The analysis followed the usual heavy-atom methods, and after several cycles of least-squares refinement on atomic positions and isotropic temperature factors and later on anisotropic

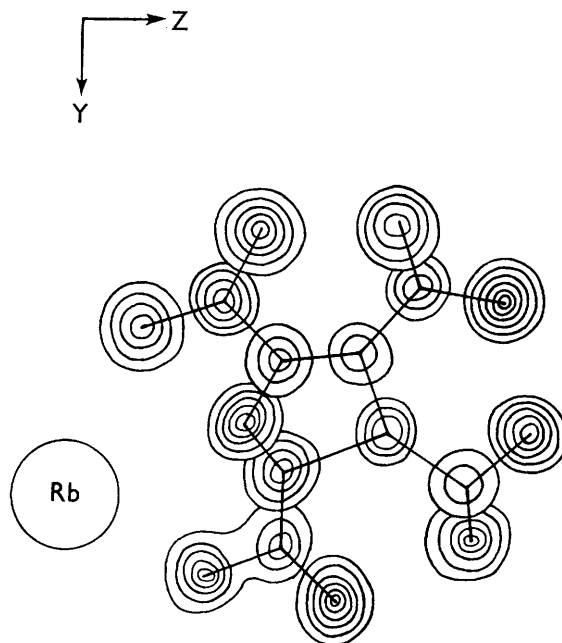


FIGURE 1: Diagram showing superimposed contour sections of the molecule projected down a -axis. Contours are at equal, arbitrary intervals, and the rubidium atom is represented by a circle.

undertaken the X-ray crystal-structure analysis of the rubidium salt to find out whether the intramolecular hydrogen bonding involves all four carboxyl groups, and also to determine the range of O...O distances between the various carboxyl groups.

A preliminary study⁴ of the monorubidium salt of furantetracarboxylic acid showed that it crystallizes as white needles, elongated along the b -direction. The following dimensions were found, $a = 9.70 \text{ \AA}$, $b = 6.38 \text{ \AA}$, $c = 17.70 \text{ \AA}$, and $\beta = 115^\circ 40'$. The space group is $P2_1/c(C_{2h}^5)$ and the measured density, $\rho = 2.20 \text{ gm./c.c.}$, shows that there are four molecules of $[\text{C}_8\text{H}_3\text{O}_9]^- \text{Rb}^+$ in the

temperature factors, the R -factor is 0.10. The estimated standard deviation in the position of the rubidium atom is 0.0013 \AA and of a typical oxygen atom is 0.007 \AA , and of a typical carbon atom is 0.001 \AA . The estimated standard deviation in bond length between two oxygen atoms is therefore of the order of 0.010 \AA . A diagram showing superimposed contour sections of the molecule, viewed down the a -axis, is given in Figure 1. Further refinement is in progress.

The bond distances and angles of the furantetracarboxylic acid moiety are shown in Figures 2 and 3. These bonded distances are close to expected values,⁶ and the furan ring is planar

⁴ I. C. Paul; Ph.D. Thesis (Appendix III), University of Glasgow, 1962.

⁵ I. C. Paul and L. L. Martin; further details of the operation of the diffractometer and the means of data collection in this compound will be published elsewhere.

⁶ International Tables for X-ray Crystallography, Vol. III, Section 4, Kynoch Press, 1962.

within the accuracy of the analysis, as was also the result in the study on furan-3,4-dicarboxylic acid. Overcrowding among the four carboxyl groups is reduced in three main ways. The angles between the carbon atoms of the carboxyl groups and furan ring show considerable deviations from

acid,² α -thiophenic acid,⁷ α -selenophenic acid,⁷ or β -thiophenic acid,⁸ but none of those molecules could be described as overcrowded structures. Deformations of this nature, but not quite to this extent, have been recorded in some other overcrowded substituted aromatic compounds.⁹

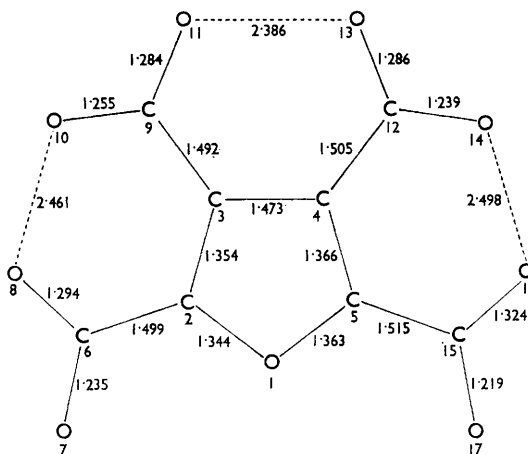


FIGURE 2: Bonded distances in the furantetracarboxylate anion.

120°. This feature is most obviously shown by consideration of the angles involving C(6) C(2) O(1), C(15) C(5) O(1), C(6) C(2) C(3), and C(15) C(5) C(4). The first two angles are close to 112°, while the latter two approach 140°. These large deviations from 120° can be rationalized in that there is no substituent on O(1) to hinder deformation of the carboxyl groups on C(2) and C(5) away from the groups on C(3) and C(4).

A second effect which reduces the overcrowding of carboxyl groups is deviation of the carbon atom of the carboxyl groups from the plane of the furan ring. The distances from the plane are listed in Table I. The atoms, C(6) and C(12), are 0.192 Å above, and 0.175 Å below the plane respectively. These large distortions from planarity with the ring, involving these two non-adjacent substituents, allow the remaining two substituent atoms to approach the plane much more closely. No such "out of plane bending" is observed in furan-3,4-dicarboxylic

In all cases, the three atoms of the carboxyl group and the ring carbon atom to which they are bonded are accurately planar, but there is a definite rotation of each of these planes with respect to the plane of the furan ring. The angles of inclination of the carboxyl groups to the ring are given in Table 1. Once again, the angles of twist involving the carboxyl groups containing C(6) and C(12) are greater than the other two

TABLE I

Carboxyl group	Distance of carbon atom of carboxyl group from plane of furan ring	Angle of Twist of Carboxyl groups from Furan ring
O(7) C(6) O(8)	+0.192 Å	7° 3'
O(10) C(9) O(11)	+0.014 Å	5° 45'
O(13) C(12) O(14)	-0.175 Å	9° 6'
O(16) C(15) O(17)	+0.051 Å	3° 54'

⁷ M. Nardelli, G. Fava, and G. Giraldi, *Acta Cryst.*, 1962, **15**, 737; P. Hudson and J. H. Robertson, *ibid.*, p. 913.

⁸ P. Hudson and J. H. Robertson, *Acta Cryst.*, 1964, **17**, 1497.

⁹ G. Ferguson and G. A. Sim, *Acta Cryst.*, 1962, **15**, 346.

angles of twist. A rotation of 3.8° has been reported between the heterocyclic ring and the carboxyl groups in furan-3,4-dicarboxylic acid,² and a value of 4.5° is found in β -thiophenic acid,⁸ where the rotation is attributed to packing forces.

hydrogen atom in the hydrogen bond, but were unable to draw any conclusions mainly because the hydrogen bond was bisected by a crystallographic mirror plane. In the present case, we have no crystallographic symmetry element in

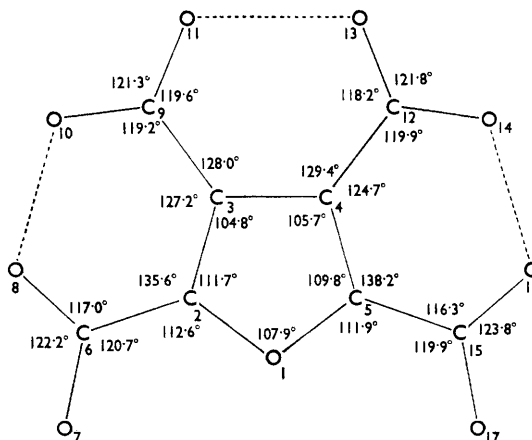


FIGURE 3: Bond angles in the furantetracarboxylate anion.

Despite these various effects which all tend to increase the O---O separations, the distances between O(8) and O(10), O(11) and O(13), and O(14) and O(16) are 2.461 Å, 2.386 Å, and 2.498 Å respectively. These are all shorter than the separation found in furan-3,4-dicarboxylic acid between the oxygen atoms forming the intramolecular hydrogen bond. In the case of furan-3,4-dicarboxylic acid, the authors² speculated on the possible symmetrical location of the

the molecule and attempts are under way to try to locate the three hydrogen atoms of the furantetracarboxylate anion.

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