Vainshtein, 1960). Both hydrogen atoms take part in hydrogen bonds, H(1) in a bond of 3·54 Å from N to the S at $\frac{1}{2}+x,y,\frac{1}{2}-z$ and H(2) in a bond of 3·24 Å from N to the S at $-x,-y,-z$; thus the hydrogen atom in the shorter hydrogen bond has the lower vibration parameter. In the electron diffraction study H(2) was found to be 0·2 Å from the plane of the heavy atoms, the displacement being towards the sulphur atom to which it was bonded. A similar effect is found in this study but the displacement, +0·23 Å, is only possibly significant statistically. For H(1) the displacement from the plane is −0·18 Å, again towards the sulphur atom, but it is not statistically significant.

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The Crystal and Molecular Structure of the Monorubidium Salt of Furantetracarboxylic Acid

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The crystal structure analysis of the rubidium salt of furantetracarboxylic acid has been carried out on three-dimensional counter data collected on an automatic diffractometer. The salt crystallizes in the monoclinic system with $a=9{\cdot}70\pm0{\cdot}01$, $b=6{\cdot}38\pm0{\cdot}01$, $c=17{\cdot}70\pm0{\cdot}02$ Å, and $\beta=115°40'\pm10'$. The space group is $P2_1/c$. Considerable overcrowding exists in the anion, and the resulting strain is accommodated in three principal ways. The bond angles made by the carbon atoms of the carboxyl groups to the ring show large deviations from the expected values. The carbon atoms of the carboxyl groups lie at distances of up to 0·194 Å from the best plane through the five ring atoms and the planes of all of the carboxyl groups are twisted with respect to the plane of the ring. Despite the magnitude of the distortions due to intramolecular overcrowding, there is a very close approach of 2·386 Å between two oxygen atoms on adjacent carboxyl groups. This distance is effectively the same as that found in potassium hydrogen chloromaleate, in which a centered hydrogen bond has been established.

Introduction

There has been speculation (Cocker, Davis, McMurry & Start, 1959) as to the structure of furantetracarboxylic acid [Fig. 1(*a*)] and its monopotassium salt. The infrared spectrum was interpreted in terms of structure (*b*) for the anion (Cocker *et al.*, 1959). Examination of a model of this structure suggests that there will be considerable steric strain among the carboxyl groups in the ion, and some deformation from ideal molecular dimensions must be expected if the oxygen atoms are not to approach each other very closely. After due allowance has been made for the effects of molecular deformation, there remains the possibility of some very short hydrogen bonds in the furantetracarboxylate anion. A recent determination of the crystal structure of 3,4-furandicarboxylic acid [Fig. 1(*d*)] (Williams & Rundle, 1964) revealed a distance of 2·555 Å between the atoms O(5) and O(5′), and the authors speculated as to whether the hydrogen atom was placed symmetrically between the oxygen atoms.

A crystal structure determination of the monorubidium salt of furantetracarboxylic acid was undertaken to investigate the geometry of the anion.

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Experimental

The monorubidium salt was prepared by the method of Cocker *et al.* (1959), who had indicated that this salt crystallized with half a molecule of water of crystallization, but our analytical data could be interpreted in terms of either the hemihydrate or the anhydrous salt. The analytical data for the Rb salt were as follows:

	Found	Calc. for $C_8H_3O_9.Rb$	Calc. for $C_8H_3O_9.Rb.\frac{1}{2}H_2O$
C	29·4%	29·2%	28·5%
H	1·2%	0·92%	1·2%

The crystals grow as small white needles, elongated along the *b* axis and with a cross-section of approximately 0·02 cm × 0·02 cm. Lattice parameters were determined on a Weissenberg camera by oscillation and moving film methods (Cu *Kα* radiation). The film holder was calibrated by superimposing on the photograph powder lines from a finely drawn piece of copper wire. The experimental density was determined by flotation in a mixture of bromoform ($\varrho = 2{\cdot}90$ g.cm^{-3}) and ethyl iodide ($\varrho = 1{\cdot}95$ g.cm^{-3}). The crystallographic data are summarized below:

$a = 9{\cdot}70 \pm 0{\cdot}01$ Å
$b = 6{\cdot}38 \pm 0{\cdot}01$
$c = 17{\cdot}70 \pm 0{\cdot}02$
$\beta = 115°40' \pm 10'$
$V = 990{\cdot}4 \times 10^{-24}$ cm^3
$M = 328{\cdot}5$
$Z = 4$
$\mu(\text{Cu } K\alpha) = 80{\cdot}7$ cm.$^{-1}$

ϱ(meas.) = 2·20 g.cm^{-3}
ϱ(calc.) = 2·20 (anhydrous)
= 2·26 (hemihydrate)
Absent spectra:
$h0l$, when $l = 2n+1$
$0k0$, when $k = 2n+1$
Space group $P2_1/c$
$F(000) = 636$

Data collection

The intensity data were collected on an automatic diffractometer*, operating on the equi-inclination Weissenberg principle (Cu *Kα*, $\lambda = 1{\cdot}5418$ Å). The intensities were measured by a stationary-counter moving-crystal technique. Background readings were taken at the commencement and conclusion of the measurement scan for each reflexion. The reciprocal lattice levels $h0l$ to $h5l$ were recorded by this method. The equivalent reflexions, hkl and $\bar{h}k\bar{l}$, were recorded at crystal settings differing by 180°. This duplication allows an assessment of the accuracy of the readings to be made. Some difficulty was encountered owing to spot lengthening for reflexions in upper levels, as it was found that large portions of the peak could easily be taken for background. This problem was largely overcome by selecting a standard background count for these reflexions, or in certain extreme cases, controlling the instrument manually. The position of the diffractometer with respect to the X-ray tube prevents the measurement of reflexions with $\Upsilon > 120°$. A total of 1165 independent reflexions was obtained, and the average standard deviation is 7·6% between equivalent measurements. No correction for absorption was applied.

Structure determination

The rubidium atom position was obtained from the three-dimensional Patterson function. The standard heavy atom technique was used to locate the positions of the carbon and oxygen atoms. Adjustment of interzonal scaling, atomic positions and isotropic temperature factors for all atoms other than hydrogen gave a trial structure with an R index of 0·28, $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.

Full-matrix least-squares refinement was begun at this point with the program of Gantzel, Sparks & Trueblood (1962). The quantity minimized was $\Sigma\,||F_o| - |F_c||^2$. Initially, a weighting scheme compounded from reliability estimates of the two independent measurements and counting statistics was used, but later, scheme 2 of Rollett (1961), with $F^* = 35{\cdot}0$, was put into effect and proved to be more satisfactory.

Least-squares refinement, allowing the positional parameters and isotropic temperature factors of all the atoms to vary, reduced R to 0·20. Examination of a difference map calculated at this stage failed to reveal the presence of any water of crystallization. Two cycles of refinement which varied the positional and isotropic parameters of the carbon and oxygen atoms, and the positional and anisotropic temperature factors of the rubidium atom, gave an R index of 0·120. Two further cycles of refinement with all eighteen atoms varying anisotropically have produced a final R value of 0·089

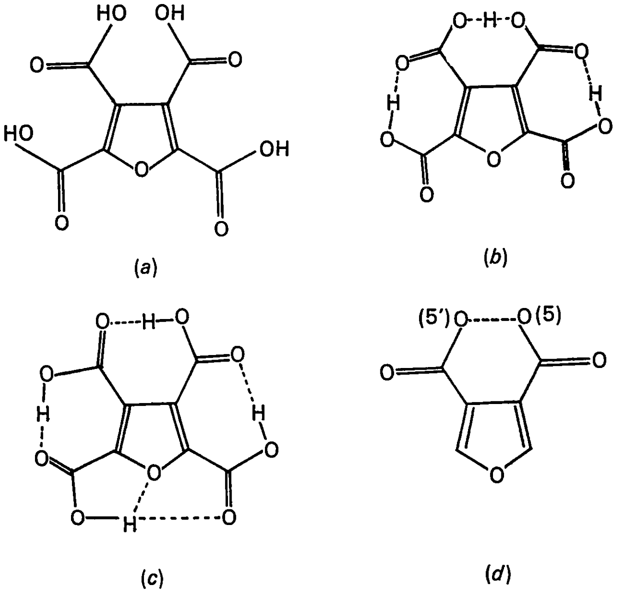

Fig. 1. Structures for (*a*) furantetracarboxylic acid, (*b*) proposed disposition of hydrogen bonds in the furantetracarboxylate anion (Cocker *et al.*, 1959), (*c*) proposed arrangement of hydrogen bonds in the free acid, (*d*) 3,4-furandicarboxylic acid.

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* This instrument was originally developed at the University of Illinois by Drs R. E. Dickerson, J. A. Hamilton, R. S. Palmer, and L. K. Steinrauf, and is supplied jointly by the Datex Corporation, California, and the Philips Electronics Company, Chicago, Illinois.

Table 1. *Final positional parameters in fractions of the unit-cell edges with the estimated standard deviations* ($\times 10^4$) *in parentheses*

The last six columns contain the final anisotropic thermal parameters ($\times 10^4$) as expressed by $\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}$.

	x		y		z		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb	0·1969	[2]	0·1767	[2]	0·0657	[1]	212	305	24	−97	80	−4
O(1)	0·2722	[8]	0·9782	[13]	0·2304	[4]	85	229	14	−6	38	−6
C(2)	0·3341	[10]	0·0852*	[19]	0·3043	[6]	52	174	21	0	13	−31
C(3)	0·3035	[12]	0·9825	[20]	0·3631	[6]	68	187	18	−54	13	2
C(4)	0·2221	[11]	0·7897	[21]	0·3219	[6]	72	252	22	−100	42	−34
C(5)	0·2071	[11]	0·8031	[22]	0·2423	[6]	59	215	20	45	29	13
C(6)	0·4144	[12]	0·2834*	[21]	0·2979	[7]	45	200	29	−54	−1	19
C(7)	0·3359	[12]	0·0682*	[20]	0·4484	[6]	82	151	15	7	−7	−2
C(8)	0·1650	[13]	0·6187	[23]	0·3584	[7]	78	278	28	−49	49	−51
C(9)	0·1287	[12]	0·6768	[21]	0·1637	[7]	64	194	25	18	25	24
O(2)	0·4077	[8]	0·3374*	[14]	0·2303	[4]	145	257	31	−97	68	−9
O(3)	0·4881	[8]	0·3898*	[13]	0·3682	[4]	113	284	21	−105	10	−42
O(4)	0·4090	[9]	0·2334*	[15]	0·4728	[4]	128	334	29	8	48	−33
O(5)	0·2806	[8]	0·9702	[13]	0·4926	[4]	142	299	18	−12	50	−16
O(6)	0·1709	[10]	0·6416	[16]	0·4318	[5]	170	307	23	5	74	−16
O(7)	0·1114	[9]	0·4553	[15]	0·3164	[5]	113	235	27	−94	27	0
O(8)	0·0728	[10]	0·4973	[16]	0·1704	[5]	131	268	32	−115	66	−38
O(9)	0·1152	[10]	0·7457	[16]	0·0956	[5]	155	349	22	99	62	12

* To form an entire molecule, the length of *b* should be added to these coordinates.

Table 2. *Bond lengths with standard deviations* (Å)

O(1)–C(2)	1·363 ± 0·014 Å
O(1)–C(5)	1·344 ± 0·015
C(2)–C(3)	1·366 ± 0·016
C(4)–C(5)	1·354 ± 0·015
C(3)–C(4)	1·473 ± 0·018
C(2)–C(6)	1·515 ± 0·017
C(3)–C(7)	1·505 ± 0·015
C(4)–C(8)	1·492 ± 0·018
C(5)–C(9)	1·499 ± 0·015
C(6)–O(2)	1·219 ± 0·015
C(6)–O(3)	1·324 ± 0·015
C(7)–O(4)	1·239 ± 0·016
C(7)–O(5)	1·286 ± 0·014
C(8)–O(6)	1·284 ± 0·016
C(8)–O(7)	1·255 ± 0·017
C(9)–O(8)	1·294 ± 0·016
C(9)–O(9)	1·234 ± 0·015

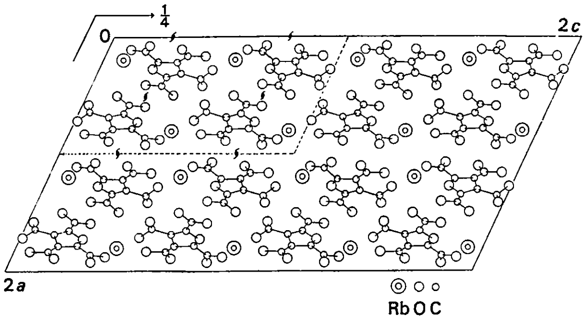

Fig. 3. Intermolecular packing projected onto (010). The drawing shows four unit cells, in only one of which is the crystallographic symmetry indicated.

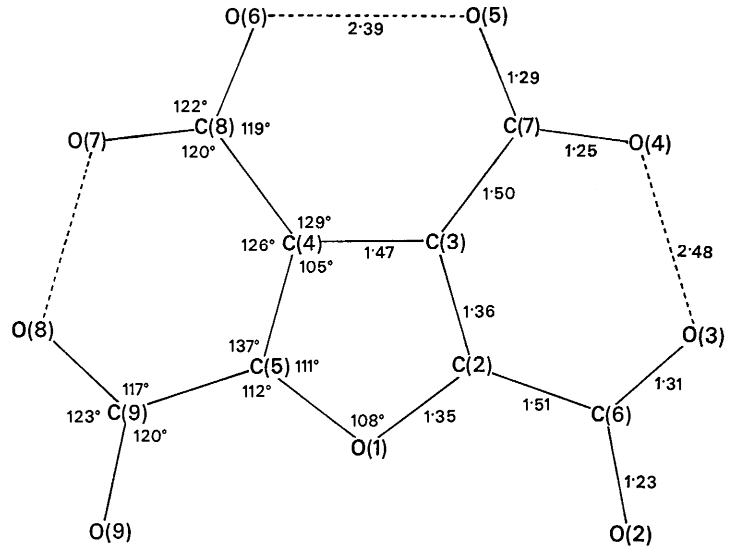

Fig. 2. Bonds lengths and angles in the furantetracarboxylate anion. Distances and angles have been averaged across the apparent mirror plane through O(1) and bisecting the C(3)–C(4) bond. The appropriate standard deviations are given in Tables 2 and 3.

for 1165 observed reflexions. The final shifts in parameters indicated by the least squares were smaller than the estimated standard deviations. The rubidium scattering curve used was that of Watson & Freeman (1961), without correction for the effects of anomalous dispersion, and the carbon and oxygen curves were those of Freeman (1959).

A three-dimensional $F_o - F_c$ map was computed but provided no evidence for the presence of water of crystallization. The regions of the difference map between adjacent carboxyl groups were examined for peaks due to hydrogen atoms. Unfortunately, there were usually two or three peaks in these areas, and in view of this uncertainty it was thought best not to attempt to include hydrogen atoms in further refinements. Despite the reasonably low discrepancy factor and the moderately accurate standard deviations in bond length, the presence of a heavy rubidium atom in this structure makes the precise location of the hydrogen atoms uncertain according to the arguments of Cruickshank (1960).

The final atomic coordinates and anisotropic thermal parameters are listed in Table 1, together with the estimated standard deviations. The calculated bond lengths and angles with standard deviations are given in Tables 2 and 3, respectively. The intramolecular contacts necessary to describe the geometry of the molecule are shown in Table 4, and all intermolecular contacts less than 3·50 Å are listed in Table 5. Diagrams showing intermolecular packing are shown in Figs. 3 and 4, while a list of h, k, l, F_{obs} and F_{calc} is given in Table 6.

Table 3. *Bond angles with standard deviations*

C(2)–O(1)–C(5)	107·9 ± 0·8°	C(2)–C(6)–O(2)	119·9 ± 0·6°
O(1)–C(2)–C(3)	109·8 ± 1·1	C(2)–C(6)–O(3)	116·3 ± 1·1
O(1)–C(2)–C(6)	111·9 ± 0·8	O(2)–C(6)–O(3)	123·8 ± 1·0
C(3)–C(2)–C(6)	138·2 ± 0·7	C(3)–C(7)–O(4)	119·9 ± 0·7
C(2)–C(3)–C(4)	105·7 ± 0·8	C(3)–C(7)–O(5)	118·2 ± 0·8
C(2)–C(3)–C(7)	124·7 ± 0·8	O(4)–C(7)–O(5)	121·8 ± 1·1
C(4)–C(3)–C(7)	129·4 ± 1·1	C(4)–C(8)–O(6)	119·6 ± 0·6
C(3)–C(4)–C(5)	104·8 ± 1·0	C(4)–C(8)–O(7)	119·2 ± 0·6
C(3)–C(4)–C(8)	128·0 ± 1·1	O(6)–C(8)–O(7)	121·3 ± 1·1
C(5)–C(4)–C(8)	127·2 ± 0·9	C(5)–C(9)–O(8)	117·0 ± 1·1
C(4)–C(5)–O(1)	111·7 ± 0·9	C(5)–C(9)–O(9)	120·8 ± 0·9
C(4)–C(5)–C(9)	135·6 ± 1·1	O(8)–C(9)–O(9)	122·2 ± 1·3
O(1)–C(5)–C(9)	112·6 ± 0·6		

Table 4. *Intramolecular distances describing the geometry of the molecule*

O(1)–C(3)	2·234 ± 0·013 Å	C(2)–O(3)	2·413 ± 0·014 Å
O(1)–C(4)	2·233 ± 0·014	C(3)–O(4)	2·380 ± 0·015
C(2)–C(4)	2·264 ± 0·017	C(3)–O(5)	2·398 ± 0·013
C(2)–C(5)	2·189 ± 0·017	C(4)–O(6)	2·401 ± 0·014
C(3)–C(5)	2·241 ± 0·016	C(4)–O(7)	2·371 ± 0·016
O(1)–O(2)	2·642 ± 0·012	C(5)–O(8)	2·384 ± 0·016
O(1)–O(3)	3·578 ± 0·011	C(5)–O(9)	2·380 ± 0·014
O(1)–O(8)	3·536 ± 0·013	O(3)–O(4)	2·498 ± 0·011
O(1)–O(9)	2·658 ± 0·013	O(5)–O(6)	2·386 ± 0·013
C(2)–O(2)	2·371 ± 0·014	O(7)–O(8)	2·461 ± 0·013

Table 5. *Intermolecular distances* (< 3·50 Å)

′	denotes an atom related to the positions given in Table 1 by	$x,\ 1+y,\ z$
″		$-x,\ 1-y,\ -z$
‴		$x,\ 1\frac{1}{2}-y,\ \frac{1}{2}+z$
iv		$-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$
v		$x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$
vi		$1-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$

Rb ---- O(8)	3·316 Å	O(4) --- O(6′)	3·345 Å	C(9) --- O(7$^{\text{iv}}$)	3·069 Å
O(1) --- Rb′	2·965	O(4) --- O(7′)	3·328	O(5) --- O(8$^{\text{iv}}$)	3·396
C(2) --- O(7′)	3·269	O(9) --- Rb′	2·972	O(6) --- O(8$^{\text{iv}}$)	3·211
C(3) --- O(7′)	3·452	Rb ---- O(9″)	3·174	O(8) --- O(7$^{\text{iv}}$)	3·486
C(6) --- O(7′)	3·284	C(7) --- Rb‴	3·348	O(9) --- O(7$^{\text{iv}}$)	3·466
C(6) --- O(8′)	3·384	O(4) --- Rb‴	3·193	O(6) --- Rb$^{\text{v}}$	3·047
C(7) --- O(7′)	3·448	O(5) --- Rb‴	2·885	O(2) --- O(1$^{\text{vi}}$)	3·010
O(2) --- Rb′	2·926	O(5) --- O(9‴)	3·215	O(2) --- C(2$^{\text{vi}}$)	3·237
O(2) --- C(9′)	3·262	O(6) --- O(9‴)	3·252	O(2) --- C(6$^{\text{vi}}$)	3·474
O(2) --- O(8′)	3·120	O(1) --- O(7$^{\text{iv}}$)	3·447		
O(3) --- C(4′)	3·464	C(3) --- O(8$^{\text{iv}}$)	3·437		
O(3) --- C(8′)	3·393	C(4) --- O(7$^{\text{iv}}$)	3·273		
O(3) --- O(7′)	3·385	C(4) --- O(8$^{\text{iv}}$)	3·209		
O(4) --- C(8′)	3·405	C(8) --- O(8$^{\text{iv}}$)	3·224		

Table 6. *Final list of h, k, l,* 10·0 F_{obs} *and* 10·0 F_{calc}

The empty spaces in the F_{obs} list indicate that the peak reading was not above background. A line in the F_{obs} column indicates that it was impracticable to measure this reflexion on account of the geometry of the diffractometer.

H	K	L	F_{obs}	F_{cal}
0	0	16	421	516
0	0	14	452	459
0	0	12	298	289
0	0	10	561	-520
0	0	8	941	-925
0	0	6	510	-491
0	0	4	54	46
0	0	2	177	137
1	0	-18	379	400
1	0	-16		-21
1	0	-14	94	117
1	0	-12	362	-356
1	0	-10	609	-598
1	0	-8	1506	-1539
1	0	-6	237	237
1	0	-4	381	388
1	0	-2	346	404
1	0	-0	242	287
1	0	2	71	-56
1	0	4	1374	-1526
1	0	6	479	-494
1	0	8	25	-61
1	0	10	298	312
1	0	12	992	1043
1	0	14	41	-95
1	0	16	178	199
2	0	-18	94	-114
2	0	-16	358	-381
2	0	-14	669	-673
2	0	-12	451	-456
2	0	-10	69	46
2	0	-8	908	877
2	0	-6	1253	1318
2	0	-4	433	428
2	0	-2	449	447
2	0	0	—	-1573
2	0	2	—	-1511
2	0	4	967	-1040
2	0	6	264	267
2	0	8	352	359
2	0	10	491	530
2	0	12	27	-115
2	0	14	160	-188
2	0	16	351	-358
3	0	-18	313	-321
3	0	-16	598	-608
3	0	-14	78	-127
3	0	-12	53	94
3	0	-10	659	620
3	0	-8	1921	962
3	0	-6	133	40
3	0	-4	163	102
3	0	-2	557	-609
3	0	0	—	-1253
3	0	2	280	-274
3	0	4	903	938
3	0	6	894	974
3	0	8	293	321
3	0	10	239	246
3	0	12	327	-363
3	0	14	322	-334
4	0	-18	294	-305
4	0	-16	71	107
4	0	-14	643	624
4	0	-12	704	682
4	0	-10	210	276
4	0	-8	682	634
4	0	-6	691	-711
4	0	-4	665	-702
4	0	-2	157	-181
4	0	-0	236	-222
4	0	2	361	388
4	0	4	655	664
4	0	6	188	174
4	-0	8		117
4	0	10	267	-236
5	0	-18	102	145
5	0	-16	336	353
5	0	-14	367	418
5	0	-12	163	-162
5	0	-10	542	-535
5	0	-8	874	-845
5	0	-6	667	-708
5	0	-4	252	261
5	0	-2	517	534
5	0	-0	357	346
5	0	2	254	236
5	0	4	358	334
5	0	6	558	-573
5	0	8	293	-299
5	0	10	199	-176
6	0	-18	343	381
6	0	-16	558	588
6	0	-14	40	42
6	0	-12	635	-633
6	0	-10	633	-633
6	0	-8	220	-216
6	0	-6	47	-36
6	0	-4	38	-33
6	0	-2	705	672
6	0	-0	49	56
6	-0	2		21
6	0	4	534	-501
6	0	6	246	-222
6	0	8	83	-92
7	0	-18	88	138
7	0	-16	252	-292
7	0	-14	208	-220
7	0	-12	31	-74
7	0	-10		-64
7	0	-8	522	569
7	0	-6	467	491
7	0	-4	369	377
7	0	-2	154	-155
7	0	-0	104	-97
7	0	2		-29
7	0	4		-23
7	0	6		-15
7	0	8	166	159
8	0	-18	39	-107
8	0	-16	493	-372
8	0	-14	271	-290
8	-0	12		14
8	0	-10	319	348
8	0	-8	210	214
8	0	-6	229	226
8	0	-4	312	-311
8	0	-2	254	-235
8	0	-0	253	-209
9	0	-14	41	-94
9	0	-12	303	314
9	0	-10	275	291
9	0	-8	146	-167
9	0	-6	97	-93
9	0	-4	234	-212
9	0	-2	119	-109
10	0	-14	141	170
10	0	-12		-10
10	0	-10		-13
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8	5	-7	151	132
8	5	-6	132	145
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Discussion

Covalent bonds

The distances within the ring are in reasonably close agreement with equivalent bonds found in furan and other related derivatives (Williams & Rundle, 1964; Bak, Christensen, Dixon, Hansen-Nygaard, Andersen & Schottländer, 1962; Hudson, 1962; Nardelli, Fava & Giraldi, 1962).

The alternation of the C–O lengths in the carboxyl groups is only definitely significant in the groups attached to C(2) and C(5). In 3,4-furandicarboxylic acid (Williams & Rundle, 1964), the difference in the two C–O distances was very slight, whereas in all the other five-membered heterocyclic acids studied, there is a substantial difference.

Hydrogen bonding

It is unfortunate that it did not prove possible to locate the positions of the hydrogen atoms in this structure, as this information would throw considerable light on the nature of hydrogen bond formation. The distances O(1)–O(2), O(3)–O(4), O(5)–O(6), O(7)–O(8), and O(1)–O(9) all lie well within the range of accepted hydrogen bond distances involving oxygen atoms of carboxylic acids (Pimentel & McClellan, 1960). There are, therefore, five possible sites for hydrogen bonding to occur, but only three available hydrogen atoms. The most plausible description of the hydrogen bonding in this structure would be that the pairs of oxygen atoms which are closest to each other, namely O(3) and O(4), O(5) and O(6) and O(7) and O(8), each form hydrogen bridges. In the first and last of these cases the hydrogen atoms are probably attached to O(3) and O(8) respectively, as C(6)–O(3) is longer than C(7)–O(4), and C(9)–O(8) is longer than C(8)–O(7), and the lengths of C(6)–O(2) and C(9)–O(9) closely approach the length of 1·23 Å for a pure carbon–oxygen double bond (Kennard, 1962). This latter finding confirms the theory of the 'exposed' carbonyl groups in the anion put forward by Cocker *et al.* (1959). In the case of the bridge between atoms O(5) and O(6), the separation of 2·386 Å is one of the shortest ever reported between carboxyl groups involved in hydrogen bonding. It is shorter than the value of 2·555 Å found by Williams & Rundle in 3,4-furandicarboxylic acid, or that of 2·457 Å found in potassium hydrogen di-*p*-chlorobenzoate (Mills & Speakman, 1963). A recent neutron diffraction analysis of potassium hydrogen chloromaleate O---O, 2·411 Å) has established that the hydrogen atom can be situated symmetrically in O---H---O hydrogen bonds (Ellison & Levy, 1965). A similar situation probably applies to potassium hydrogen maleate (O---O, 2·44 Å) which has been studied by both neutron (Peterson & Levy, 1958) and X-ray (Darlow, 1961) diffraction, but a definite conclusion cannot be reached in the latter case as the hydrogen bond is bisected by a mirror plane. In the furantetracarboxylate anion, we find that there is a hydrogen bond which is effectively the same length as the bridge found in potassium hydrogen chloromaleate (where there is a centered hydrogen atom) and apparently shorter than the distance found in potassium hydrogen maleate (where there may be a symmetrically located hydrogen atom). Additional credence is given to our theory by considering the C–O distances of the two oxygen atoms forming the hydrogen bond in potassium hydrogen chloromaleate which are 1·284 and 1·288 Å as compared with 1·230 and 1·244 Å for the two C–O bonds not involved in intramolecular hydrogen bridging; the last two values approach the accepted value of 1·23 Å for a pure $C=O$ double bond (Kennard, 1962). In the furantetracarboxylate anion, the two oxygen atoms forming the shortest hydrogen bond have C–O distances of 1·286 and 1·284 Å, whereas the C–O distances of the other two oxygen atoms attached to C(7) and C(8) are 1·239 and 1·255 Å. This division of C–O distances into long and short occurs also in 3,4-furandicarboxylic acid (1·267 and 1·234 Å) and in potassium hydrogen maleate (1·284 and 1·235 Å). A necessary criterion for the existence of a symmetrical hydrogen bond appears to be that the two constituent C–O distances must be of the order of 1·28 Å, a condition which is met in the present structure.

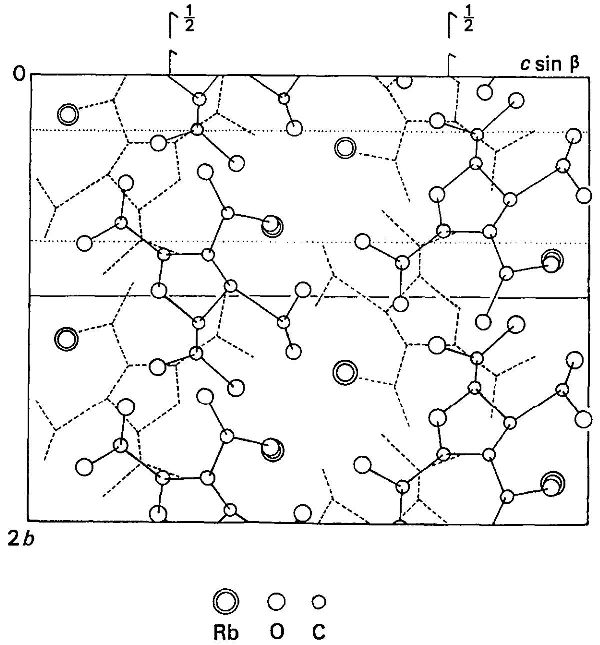

Fig. 4. Intermolecular packing projected onto (100). It shows two unit cells, in only one of which is the crystallographic symmetry indicated. The molecules shown in discontinuous lines are below the molecules drawn as solid lines.

Effects due to overcrowding in the molecule

The deformations from idealized geometry can be classified into three types:

(*a*) Deviations of bond angles from anticipated values.
(*b*) Out of plane bending of the substituents from the plane of the furan ring.

(*c*) Rotation of the plane of the carboxyl groups with respect to the plane of the furan ring.

The bond angles formed by the carbon atoms of the carboxyl groups and the furan ring show wide discrepancies from the values close to 123° found in 3-thiophenic acid (Hudson & Robertson, 1964) and in 2-thiophenic acid (Nardelli *et al.*, 1962). It is significant that the angle deviations are most marked in the groups substituted on C(2) and C(5), as in these cases there is no substituent on the adjacent O(1) to prevent bending of the carboxyl groups away from the substituents on C(3) and C(4). These deformations act in such a way as to increase the separation O(5)–O(6). Bond angles deviations of this type but not to this extent were found in other structures exhibiting intramolecular overcrowding, such as 3,4-furandicarboxylic acid (Williams & Rundle, 1964) and *o*-bromobenzoic acid (Ferguson & Sim, 1962). The details of the best planes through several groups of atoms in the anion and the deviations of other atoms from these planes are given in Table 7. The furan ring is accurately planar within the limits of the analysis, but the carbon atoms of the carboxyl groups deviate significantly from the plane of the five ring atoms. This out of plane bending has been a feature of the analyses of *o*-bromobenzoic acid (Ferguson & Sim, 1962), and potassium hydrogen di-*p*-chlorobenzoate (Mills & Speakman, 1963), where the Cl atom is 0·13 Å from the plane of the benzene ring. The largest deviations that we have found are −0·194 and −0·084 Å involving C(7) and C(9) respectively. It is significant that alternate substituents are most affected, and the effect is almost certainly due to intramolecular forces.

The three atoms of the carboxyl groups and the ring carbon atom on which the group is substituted are accurately planar in all four cases. None of the groups, however, is planar with respect to the furan ring. The angles of twist of the carboxyl groups to the ring are listed in Table 8. Significant values of such angles of twist are common among carboxylic acid groups attached to trigonal hybridized carbon atoms, *e.g.* ammonium oxalate (Robertson, 1965), and are usually attributed to packing forces. In the present instance, however, the effect is probably intramolecular in origin.

Table 8. *Angles of twist formed between the carboxyl group and the plane of the furan ring*

The angle is defined + or − as the rotation is counterclockwise or clockwise looking along the bond outward from the ring.

Group	Angle of twist
C(2)–C(6)–O(2)–O(3)	−5°40′
C(3)–C(7)–O(4)–O(5)	+9 54
C(4)–C(8)–O(6)–O(7)	−8 30
C(5)–C(9)–O(8)–O(9)	+8 23

Despite these deformations from ideal molecular geometry, all of which tend to lengthen the O---O distances, it is significant that a very short O---O separation is found. We feel that, in view of the results of Ellison & Levy (1965), we have considerable evidence to allow us to predict a symmetrical hydrogen bond in the furantetracarboxylate anion, and we are looking into the possibility of examining the sodium or ammonium salt where the possibility of locating the hydrogen atom by X-ray methods would be much greater.

The rubidium atom is surrounded by eight oxygen atoms at distances ranging from 2·89 [involving O(5)] to 3·32 Å. It therefore appears that the negative charge

Table 7. *Deviations of atoms from planes** (Å)

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
O(1)	−0·009	−0·003	0·006				
C(2)	0·013	0·016	0·049	−0·001			
C(3)	−0·019	−0·021	−0·029		−0·008		
C(4)	0·011	0·009	0·015			0·000	
C(5)	−0·004	−0·000	0·052				−0·003
C(6)	0·048	0·053	0·100	0·003			
C(7)	−0·185	−0·194	−0·249		0·014		
C(8)	0·022	0·014	−0·010			0·001	
C(9)	−0·090	−0·084	0·007				0·010
O(2)	−0·050	−0·039		−0·001			
O(3)	0·173	0·176		−0·001			
O(4)	−0·163	−0·171			−0·005		
O(5)	−0·402	−0·415			−0·001		
O(6)	−0·138	−0·151				0·000	
O(7)	0·183	0·177				0·000	
O(8)	0·013	0·017					−0·004
O(9)	−0·288	−0·276					−0·003

* Best planes through:
(*a*) C(2), C(3), C(4), C(5).
(*b*) C(2), C(3), C(4), C(5), O(1).
(*c*) C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), O(1).
(*d*) C(2), C(6), O(2), O(3).
(*e*) C(3), C(7), O(4), O(5).
(*f*) C(4), C(8), O(6), O(7).
(*g*) C(5), C(9), O(8), O(9).

is widely distributed throughout the anion rather than concentrated on any particular oxygen atom.

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The Structure of the Twinned Crystal of D,L-6-Thioctic Acid, $C_8H_{14}O_2S_2$

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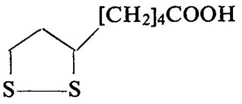
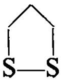
Crystals of 5-[3-(1,2-dithiolanyl)]pentanoic acid (D,L-6-thioctic acid, α-lipoic acid),



occur as twins with the twinning occurring along the *c* axis. The twinned crystals form an orthorhombic supercell with $a = 133·2$, $b = 9·89$, $c = 9·22$ Å. The real cell is monoclinic, space group $P2_1/c$, with $a = 11·75$, $b = 9·89$, $c = 9·22$ Å and $\beta = 109°05'$. The molecules occur as dimers with the acid groups hydrogen-bonded across centers of symmetry. No four atoms in the five-membered ring are coplanar. Phases for the structure determination were obtained by the symbolic addition procedure.

Introduction

The naturally occurring (+) α-lipoic acid (Reed, De Busk, Gunsalus & Hornberger, 1951) is an essential factor for the enzymatic decarboxylation of pyruvate to acetate and is also required in the subsequent introduction of acetate into the citric acid cycle. The synthetic product, called D, L-6-thioctic acid (Bullock, Brockman, Patterson, Pierce, von Saltza, Sanders & Stokstad, 1954), has biological properties similar to those of α-lipoic acid. The initial interest in this material concerned the configuration of the  S—S ring; how-