

Crystal Structures of the Acid Salts of Some Dibasic Acids. Part VIII.¹ An X-Ray Study of the β -Form of Rubidium Hydrogen Acetylenedicarboxylate, and a Comparison with the Isomorphous α -Forms of the Potassium and Rubidium Salts

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Rubidium hydrogen acetylenedicarboxylate, RbH(adc), in its α -form crystallises in the monoclinic system with $a = 7.956$, $b = 12.307$, $c = 6.216$ Å, $\beta = 105.6^\circ$, $Z = 4$ in space group $I2/a$, and is isomorphous with the analogous potassium salt. In its β -form, RbH(adc) is triclinic with $a = 6.344$, $b = 7.18$, $c = 7.92$ Å, $\alpha = 96.9^\circ$, $\beta = 106.1$ Å, $\gamma = 116.4^\circ$, $Z = 2$ in $P\bar{1}$. Thus the crystal symmetries of the α - and β -forms are quite different. The crystal structure of the β -form has been determined and refined from two independent sets of diffractometer data, to R 5.9% (530 terms) and 12.5% (1640 terms), which yield concordant positional parameters. Despite the difference of crystal symmetry the structures found for the hydrogen-anion and for the environment of the cation are very similar to those in the α -form. The hydrogen bond, unsymmetrical in the β -form, which links the anions into infinite chains has $O \cdots O$ 2.464(8) Å.

Cell data are also given for some other acid salts of H_2 (adc).

THE crystal structure of KH(adc) ($H_2adc = HO_2C \cdot C \equiv C \cdot CO_2H$) has been determined at Ljubljana by X-ray analysis.¹ It is an elegant and simple example of Type A_2 :² the H(adc)⁻ anions, themselves symmetrical about a two-fold axis of the crystal, are linked into infinite chains by very short $O \cdots H \cdots O$ bonds which lie across two-fold axes of another set. A sample of RbH(adc) was made in Ljubljana. Though its structure was not determined in detail, it must resemble that of KH(adc) closely because of the isomorphism implied by its belonging to the same (monoclinic) space group, having almost the same cell dimensions (Table 1), and giving very similar X-ray patterns.

About the same time, a specimen of the acid rubidium salt was made in Glasgow, and was shown to be triclinic. X-Ray analysis showed its structure to be quite different crystallographically from that of the RbH(adc) made in Ljubljana. These two polymorphic forms may be called α -RbH(adc) (Ljubljana) and β -RbH(adc) (Glasgow). We report an analysis of the β -form, and compare the details of its molecular geometry with those in α -KH(adc). The extraordinarily close 'chemical' resemblances, in different crystal structures, encourages the assumption that the comparison may also be extended to cover α -RbH(adc), though the structure of the latter has not in fact been determined.

EXPERIMENTAL

Acid salts of acetylenedicarboxylic acid are easily made by dissolving H_2 (adc) (1 mol) and Rb_2CO_3 (0.5 mol), or other equivalent base, in a little warm water. Crystals, which are generally very soluble, appear on cooling or evaporation. The preparation of RbH(adc) at Ljubljana yielded the α -form, and that at Glasgow the β -form, though it was hard to pick out good crystals. In several preparations at Glasgow we recognised alien crystals, but never positively identified them as α -RbH(adc).

Crystal data for β -RbH(adc) are given in Table 1. The lattice was explored by rotation and Weissenberg photographs using $Cu-K_\alpha$ radiation ($\lambda = 1.542$ Å) and $Mo-K_\alpha$

for precession photographs ($\lambda = 0.71069$ Å). The values finally adopted for the lattice parameters were derived from a least-squares treatment of moderately high-order reflexions measured on a four-circle diffractometer, by use of two different crystals. The space group $P\bar{1}$ (No. 2) was adopted and is deemed to have been vindicated by the successful structure analysis. This also rules out the possibility that α - and β -forms differ because the latter is hydrated. It is further excluded by the i.r. spectrum, which is identical with that of α -KH(adc) (see Figure 1 of Part VII),¹ and shows no absorption near 3450 cm^{-1} .

Table 1 includes cell data for α -RbH(adc), and for some other acid salts prepared at Ljubljana.

Structure Analysis.—The structure was first determined (by L. A. S.) in its a axial projection, by the heavy-atom method applied to some 100 intensity data, estimated visually, or by densitometer, from photographic films. Lacking information about the x co-ordinates, we were not successful, at that stage, in guessing the topology of the structure.

Two sets of three-dimensional data were collected on a Hilger and Watts four-circle diffractometer, by use of $Mo-K_\alpha$ radiation. Set (I) was from a rather large crystal ($0.21 \times 0.23 \times 0.77$ mm³) mounted about $[1\bar{1}0]$; the X-rays were 'monochromated' by a Zr filter, and reflexions were covered only out to θ 20°. Only two of the 530 independent reflexions were too weak to be recorded. Set (II) was from a smaller, but less regular, crystal ($0.08 \times 0.15 \times 0.39$ mm³), mounted about a ; a graphite monochromator yielded purer radiation, and this resulted in lower background counts. Some 1640 independent reflexions were covered out to θ 25°; zero, or formally negative, intensities were recorded for 100 of these, but all were included in the later cycles of refinement.

The presence of Rb gave rise to high absorption errors: even for Mo -radiation ($\mu = 87$ cm^{-1}). For the larger of our two crystals μr (where r = effective radius) varied from 1.0 to 3.0 in different orientations, whilst for the smaller it varied from 0.4 to 1.7. As our concern was entirely with co-ordinates, not with vibrational parameters as such, we did not apply any corrections for absorption. Perhaps we may justify this nonchalant attitude, *a posteriori*, by reference to

¹ Part VII, I. Leban, Lj. Golić, and J. C. Speakman, preceding paper.

² M. Currie and J. C. Speakman, *J. Chem. Soc. (A)*, 1970, 1923; see also, 1970, 1919.

the results. Though the two sets of data were from crystals of notably different sizes and shapes, they led to remarkably concordant molecular geometries.

The π co-ordinate of Rb was readily found from a three-dimensional Patterson function based on Set (I) data, and

No great significance necessarily attaches to the vibrational parameters in Table 3. They may, to a considerable extent, be merely a means of covering errors in the data owing to the neglect of absorption. The overall differences between the two sets can be rationalised in this sense.

TABLE 1
Comparison of crystal data for acid salts of acetylenedicarboxylic acid, MH(adC)

M Form Salt	K α KHC ₄ O ₄	NH ₄ α NH ₄ HC ₄ O ₄	Rb α RbHC ₄ O ₄	Rb β RbHC ₄ O ₄	Na NaHC ₄ O ₄ ·2H ₂ O	Cs CsHC ₄ O ₄ ·H ₂ O
<i>M</i>	152.2	131.1	198.8	198.8	154.1	264.0
<i>a</i>	7.954	7.971	7.956(2)	6.344(5)	5.298	12.758
<i>b</i>	11.926	12.057	12.307(2)	7.180(9)	9.262	7.961
<i>c</i>	5.918	6.205	6.216(2)	7.920(9)	3.598	6.790
α				96.9(2)	98.4	
β				106.1(2)	80.4	
γ				116.4(2)	92.8	
<i>U</i> ₀ /Å ³	541.3	578.6	586.2	297.8	172.2	689.1
<i>D</i> _m	1.84	1.52	2.19	2.23	1.56	2.54
<i>Z</i>	4	4	4	2	1	4
<i>D</i> ₀	1.867	1.506	2.166	2.214	1.66	2.544
Space group	<i>I</i> 2/ <i>a</i>	<i>I</i> 2/ <i>a</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> * <i>c</i> *

this led to positions for all the other atoms, except the one hydrogen. Full-matrix least-squares refinement, with Set (I), converged at *R* 6.3%, with anisotropic vibrational parameters for rubidium, and isotropic for carbon and oxygen. *R* fell to 5.9% {with *R'* [= ($\Sigma w\Delta^2$)/($\Sigma w|F_o|^2$)] = 0.6%} when all atoms were allowed to vibrate anisotropically. The weighting-scheme was $w = 1.0$ for $|F_o| \leq 12$, otherwise $w = (12/|F_o|)^2$. Final parameters are listed in Tables 2 and 3. An electron-density difference synthesis showed no features of serious significance.

TABLE 2

Fractional co-ordinates ($\times 10^5$) [upper value obtained from Set (I) data, lower from Set (II)], with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Rb	39994(17) 39888(18)	33039(15) 33077(17)	20810(12) 20653(11)
O(1)	33136(172) 33333(194)	64960(140) 64968(154)	4759(114) 4821(116)
O(2)	17311(137) 17290(162)	86540(121) 86384(139)	-2020(97) -1770(87)
O(3)	25195(143) 25430(163)	84546(123) 84300(165)	69322(105) 69514(96)
O(4)	-16031(179) -16116(179)	69510(161) 69322(211)	52441(116) 52596(115)
C(1)	23747(206) 23914(191)	75636(175) 75617(163)	8086(148) 8252(106)
C(2)	18563(213) 18280(229)	76704(160) 76515(186)	24967(166) 24884(124)
C(3)	12949(209) 13168(228)	77129(172) 77096(198)	37937(182) 38228(130)
C(4)	6030(245) 6137(200)	77072(172) 76753(171)	54330(147) 54422(115)

Refinement was repeated with Set (II) data. In the final, anisotropic, cycles the weighting-scheme was $w = 1 - \exp\{-5.0 [(\sin \theta)/\lambda]^2\} / \{1 + 0.2 |F_o| + 0.0015 |F_o|^3\}$, and convergence was at *R* 12.5% (*R'* 2.8%). Set (II) parameters are also included in Tables 2 and 3. Atomic scattering factors were taken from ref. 3. Both sets of structure factors are listed in Supplementary Publication No. SUP 20655 (7 pp., 1 microfiche)*. Table 4 gives a weighting analysis for each set.

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, Index issue, 1972 (items less than 10 pp. are sent as full size copies).

The positions found for each atom from the two sets of data differ by an average of 0.021 Å, which only a little

TABLE 3

Vibrational parameters (10^{-3} Å²), with standard deviations in parentheses [upper value from data of Set (I), lower from Set (II)]

Rb	27(1) 52(1)	38(1) 73(1)	40(1) 36(1)	19(1) 28(1)	35(1) 37(1)	28(2) 82(1)
O(1)	48(6) 71(5)	33(5) 66(4)	39(5) 38(4)	23(8) 34(7)	49(9) 52(7)	44(10) 92(8)
O(2)	26(4) 62(4)	32(4) 71(4)	33(4) 24(3)	19(8) 36(5)	26(7) 35(5)	24(8) 91(7)
O(3)	22(5) 53(4)	49(5) 84(5)	33(5) 25(3)	14(8) 27(6)	26(9) 29(6)	22(8) 75(8)
O(4)	23(6) 47(4)	72(7) 106(8)	36(5) 31(3)	16(9) 19(8)	29(9) 26(6)	26(10) 66(9)
C(1)	25(7) 52(5)	18(6) 58(5)	38(7) 20(3)	-1(11) 20(6)	32(11) 39(6)	9(11) 69(8)
C(2)	33(8) 62(6)	23(6) 62(5)	35(8) 25(3)	16(10) 15(7)	42(13) 35(7)	20(11) 65(9)
C(3)	20(8) 59(6)	30(7) 70(6)	44(9) 24(4)	10(11) 25(7)	23(13) 29(7)	-5(12) 73(10)
C(4)	30(10) 50(5)	25(6) 56(5)	18(7) 26(3)	4(10) 16(6)	21(15) 32(7)	6(12) 50(8)

TABLE 4

Weighting analyses: $\Sigma w\Delta^2$ averaged for groups of *N* reflexions

(a) Set (I)	0.0—0.2	0.2—0.4	0.4—0.6	All	
(sin θ)/ λ	0.0—0.2	0.2—0.4	0.4—0.6	All	
$\Sigma w\Delta^2$	1.19	0.67	0.71	0.72	
<i>N</i>	41	271	222	534	
$ F_o $	0—3	3—6	6—11	11—23	
$\Sigma w\Delta^2$	1.22	0.89	0.49	0.79	
<i>N</i>	25	40	75	179	
				183	
				32	
(b) Set (II)	0.0—0.2	0.2—0.4	0.4—0.6	0.6—0.8	All
(sin θ)/ λ	0.0—0.2	0.2—0.4	0.4—0.6	0.6—0.8	All
$\Sigma w\Delta^2$	0.20	0.64	0.44	0.59	0.52
<i>N</i>	41	271	765	563	1640
$ F_o $	0—3	3—6	6—11	11—23	23—46
$\Sigma w\Delta^2$	0.58	0.38	0.48	0.65	0.59
<i>N</i>	248	396	434	324	195
					33

³ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

exceeds the combined standard deviation. However respective dimensions within the $\text{H}(\text{adc})^-$ ion agree more closely: bond-lengths differ by 0.010 Å on average, and angles by 0.8°, which is considerably less than the standard deviations led us to expect. Some elucidation can be gained by reference to the 'centroid' of the anion, defined as the mean of each co-ordinate for all eight atoms. The effect of changing from one set of data to the other is then seen to

RESULTS AND DISCUSSION

Figure 1 gives a stereoscopic impression of the crystal structure of $\beta\text{-RbH}(\text{adc})$, and Figure 2 explains the atom-numbering system. Table 5 lists interatomic distances and angles derived from each of the data sets. Not only do these results agree well; they also show a close approach to symmetry about the mid-point of the triple

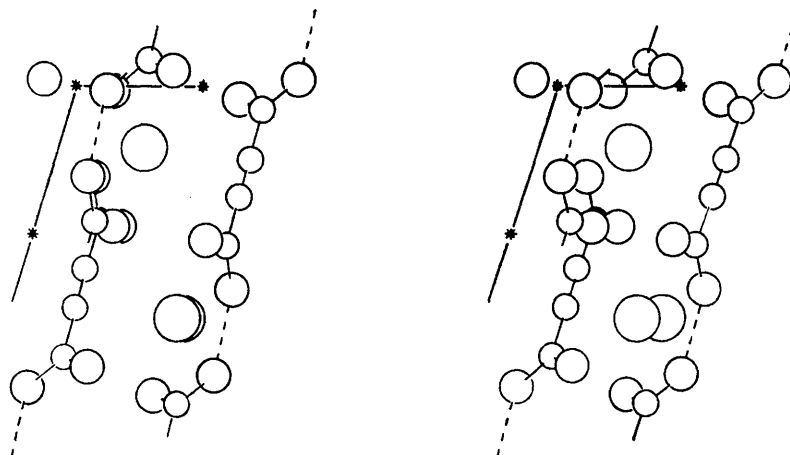


FIGURE 1 Stereoscopic view of the crystal structures of rubidium hydrogen acetylenedicarboxylate, $\beta\text{-RbH}(\text{adc})$

be movements of ca. 0.011 Å of the Rb^+ and the 'centroid' of the anion in opposite directions. With this taken into account, the change in the relative positions of the carbon

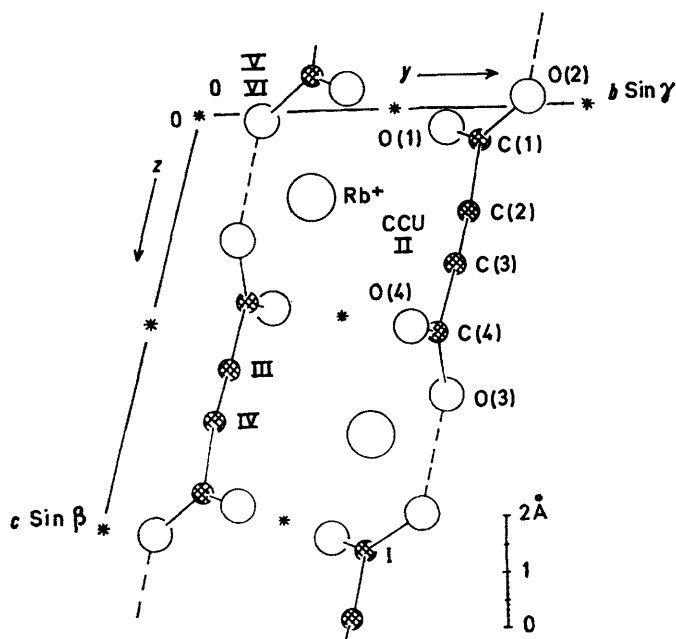


FIGURE 2 Structure of $\beta\text{-RbH}(\text{adc})$ in its α axial projection, with the numbering scheme for the atoms. Hydrogen bonding is marked by broken lines. The larger open circles represent rubidium ions, the hatched circles carbon atoms, and asterisks mark centres of symmetry

and oxygen atoms diminishes to an average of 0.014 Å. The apparent shifts of Rb^+ and $\text{H}(\text{adc})^-$ are presumably due to absorption errors.

bond. This corresponds to the exact, crystallographic symmetry of the anion in the α -form, and justifies our averaging chemically equivalent dimensions in $\beta\text{-RbH}(\text{adc})$ for comparison with the dimensions in $\alpha\text{-KH}(\text{adc})$, as we have done in Table 6.

TABLE 5

$\beta\text{-RbH}(\text{adc})$: dimensions within and between the acid-anions from the two sets of data, (I) and (II), with standard deviations in parentheses

(a) Distances (Å)

	(I)	(II)
C(1)-O(1)	1.206(14)	1.209(14)
C(4)-O(4)	1.210(16)	1.224(14)
C(1)-O(2)	1.294(13)	1.287(13)
C(4)-O(3)	1.281(14)	1.290(13)
C(1)-C(2)	1.464(16)	1.459(12)
C(3)-C(4)	1.481(17)	1.470(13)
C(2)-C(3)	1.178(18)	1.190(14)

(b) Angles (deg.)

O(1)-C(1)-O(2)	126.5(1.0)	126.4(0.8)
O(3)-C(4)-O(4)	127.5(1.0)	127.3(0.9)
C(2)-C(1)-O(1)	114.0(1.0)	113.6(0.9)
C(3)-C(4)-O(4)	112.6(1.0)	112.6(0.9)
C(2)-C(1)-O(2)	119.0(1.0)	120.0(0.9)
C(3)-C(4)-O(3)	119.6(1.0)	120.1(0.9)
C(1)-C(2)-C(3)	176.1(1.2)	178.6(1.3)
C(4)-C(3)-C(2)	178.2(1.1)	177.4(1.3)
O(2) ... O(3)	2.457(10)	2.470(10)
C(4)-O(3) ... O(2)	117.2(1.0)	116.9(0.9)
C(1)-O(2) ... O(3)	115.2(1.0)	114.4(0.9)

The validity of this comparison of the β -form of $\text{RbH}(\text{adc})$ with the α -form of $\text{KH}(\text{adc})$ may be questioned. Comparison between α - and $\beta\text{-RbH}(\text{adc})$ would be more logical, had a structure analysis of the former been available. However, we feel that the remarkable agree-

ment between corresponding dimensions in Table 6 justifies the comparison. Differences would have been harder to take so seriously.

TABLE 6

Some dimensions within and between the acid-anions: Comparison of values for α -KH(adc) with those for β -RbH averaged for the two refinements, and averaged again over chemically equivalent features. Distances in Å, angles in deg. standard deviations in parentheses

	α -Form	β -Form
C-O(H)	1.284(3)	1.288(9)
C=O	1.221(3)	1.213(10)
\equiv C-C	1.466(3)	1.469(10)
C \equiv C	1.191(4)	1.184(11)
O(H) \cdots O	2.445(3)	2.464(8)
O-C-O(H)	126.1(0.2)	127.0(0.7)
C-C-O(H)	114.1(0.2)	113.2(0.7)
C-C=O	119.8(0.2)	119.7(0.6)
C-O(H) \cdots O	116.2(0.2)	{117.1(0.8) 114.8(0.8)}

The chemical resemblances between the α - and β -forms are not restricted to the hydrogen-anions. The environments of the cations are also alike. Figure 4 of Part VII¹ shows the arrangement of three pairs of oxygen atoms round K⁺. The Rb ion in the β -form is in a general position, surrounded by six independent oxygens. Nevertheless the chemical environments are qualitatively identical (Figure 3). Whereas a crystallographic two-fold axis passes through K⁺ (in α), Rb⁺ (β) has only a local pseudo-axis; but the close approach to metrical identity of the cation environments is shown by the angles which are compared in the pseudo-symmetrical array of Table 7.

TABLE 7

Comparison of the cation environments in α -KH(adc) and β -RbH(adc). The resemblance is shown by the close approach to symmetry about the mid-point (marked X) of the array. Cation-oxy distances are in Å; oxygen-cation-oxygen angles in degrees; standard deviations, respectively, 0.010 Å and 0.3°. The oxygen atoms are specified only by their numbers

	I	I ^I	I ^{III}	I ^{IV}	2 ^V	2 ^{VI}	O \cdots K ⁺
		94.8	75.8 104.5	104.5 75.8 179.7	77.3 143.4 71.9 107.9	143.4 77.3 107.9 129.0	1 I ^I I ^{III} I ^{IV} 2 ^V 2 ^{VI}
3.054	3 ^{IV}			X			2.774
2.954	2 ^V	135.6					2.774
2.902	4 ^{III}	69.1	108.7				2.796
2.955	1 ^{VI}	114.2	67.5	176.1			2.796
3.001	4 ^{II}	77.9	140.0	80.3	97.6		2.852
2.870	1	143.0	74.2	102.6	80.7	88.5	2.852
Rb ⁺ \cdots O	3 ^{IV}	2 ^V	4 ^{III}	1 ^{VI}	4 ^{II}	1	

The superscript numbering system for α -KH(adc) is explained in Part VII,¹ footnote to Table 4. For β -RbH(adc) Roman numeral superscripts denote the following equivalent positions relative to the CCU at x, y, z :

I $x, y, 1+z$ II $1+x, y, z$ III $-x, 1-y, 1-z$ IV $1-x, 1-y, 1-z$ V $-x, 1-y, -z$ VI $1-x, 1-y, -z$

Though the hydrogen-anions and the regions round the cations are so alike in the α - and β -forms, they are put together so as to yield different crystal symmetries. The mean planes of the atoms C(2), C(1), O(1), and O(2), and C(3), C(4), O(3), and O(4) are, respectively, represented by the equations:

$$0.907 X' + 0.405 Y' + 0.115 Z' = 2.974 \text{ \AA}$$

$$\text{and } 0.112 X' + 0.989 Y' - 0.096 Z' = 4.914 \text{ \AA}.$$

(None of the atoms deviates significantly from the mean plane of its set.) The dihedral angle between these planes is 61°, which differs significantly from the corresponding dihedral angle in α -KH(adc) (66°), the standard deviations of these angles being *ca.* 1.5 and 0.7° respectively. Rotation about the acetylenic chain is almost

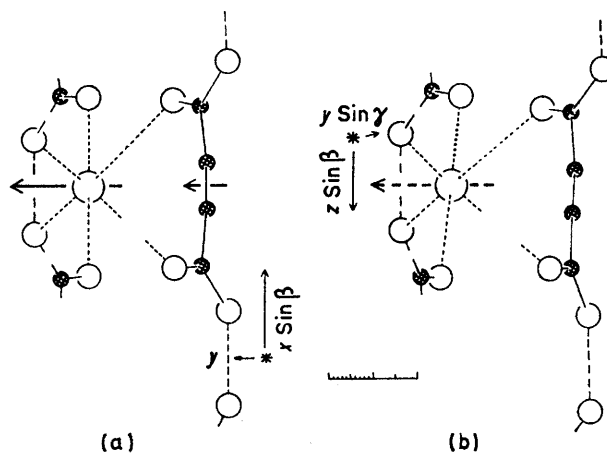


FIGURE 3 Comparison of the environments of the cation in (a) the α - (z up), and (b) the β -form (x down) of RbH(adc). Two-fold axes, at different levels are indicated by arrows in (a); in (b) a pseudo-axis is indicated by an arrow with a broken 'shaft.' Cation-oxygen contacts are shown by dotted lines. Asterisks represent centres of symmetry

free, in the gaseous state, and the difference can be seen as an adjustment due to the different crystal symmetries.

The hydrogen bond which links the H(adc)⁻ units into infinite chains has no crystallographic symmetry in β -RbH(adc). The almost identical geometries of the

carboxy-groups (Table 4) and the favourable C-O \cdots O angles are consistent with the existence of a virtually symmetrical hydrogen bond. However, though this bond is short, an O \cdots O distance of 2.464(8) Å is perhaps rather long for a genuinely symmetrical O \cdots H \cdots O situation.⁴ Symmetry merely due to disorder of the

⁴ See *e.g.*, G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960, p. 259.

proton between sites up to 0.15 Å on either side of the mid-point cannot be ruled out.

Our final difference map showed no important features, apart from a meagre amount of density between O(3) and O(2¹). Accordingly the acidic hydrogen atom was included, for two supplementary least-squares cycles, mid-way between these atoms, and allowed to vibrate isotropically. Apart from these four parameters, and a scale factor, only the eighteen parameters of O(3) and O(2¹) were refined. At convergence the new positions corresponded to the following dimensions: O(3)-H 1.32(14), H-O(2¹) 1.14(15), O(3) ··· O(2¹) 2.461(8) Å, O-H-O = 172(13)°. These are in accord with the assumption that the bond is unsymmetrical and the proton more closely associated with O(2¹). However, the difference between this structure and one with a symmetrical hydrogen bond is hardly significant.

It has been the opinion of one of us (J. C. S.) that the crystallographic, and therefore total environmental, symmetry of the O ··· H ··· O bond in a Type A structure might exert a significant influence in symmetrising and shortening the bond itself and in giving rise to the Type (ii) spectrum.⁵ (Exact symmetry of a double-minimum potential facilitates tunnelling of the proton, for instance.⁶) This opinion has been questioned by Pimental and McClellan,⁷ and some of the evidence against it is conceded. For example, the adduct between pyridine *N*-oxide and trichloroacetic acid⁸ has a Type (ii) spectrum, and the hydrogen bond is very short [O ··· O 2.411(8) Å]. Yet even local chemical symmetry

is impossible in -N-O ··· H ··· O-C-. Again, in the basic salt *L*-leucine hemihydrochloride,⁹ O ··· O is 2.429(7) Å, but a centrosymmetric bond is impossible between disymmetric molecules. Another pseudo-Type A basic salt, though less accurately studied, B₂·HAsF₆ (where B is α -methylquinolone),¹⁰ has a Type (ii) spectrum and a short hydrogen bond [O ··· O 2.439(12) Å].

The two forms of (K/Rb)H(adc) are relevant to this problem. The i.r. spectra of α -KH(adc) and β -RbH(adc) are of Type (ii) and indistinguishable (see Figure 1 of Part VII).¹ The pseudo-Type A₂ symmetry of the β -form is entirely adequate to produce this type of spectrum.

There remains the possibility that a symmetrical environment might tend to shorten an already short hydrogen bond. These α - and β -forms should offer a good test-case, for the structures are chemically identical, but only the α -form has crystallographic symmetry about the bond. In α -KH(adc) O ··· O is 2.445(3), and in β -RbH(adc) it is 2.464(8) Å. The symmetrically sited bond is found to be a little shorter. Unfortunately our precision is such that the difference is no better than of possible significance. Still more disappointing, a preliminary result (by I. L.) for α -NH₄H(adc) gives, in this clearly Type A₂ structure, O ··· O 2.472(3) Å.

We thank the authors of various KDF 9 programs, notably Drs. J. G. Sime and K. W. Muir.

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⁵ See e.g., J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

⁶ M. D. Harmony, *Chem. Soc. Rev.*, 1972, **1**, 211.

⁷ G. C. Pimentel and A. L. McClellan, *Ann. Rev. phys. Chem.*, 1971, **22**, 357.

⁸ Lj. Golić, D. Hadži, and F. Lazarini, *Chem. Comm.*, 1971, 860.

⁹ Lj. Golić and W. C. Hamilton, *Acta Cryst.*, 1972, *B*, **28**, 1265.

¹⁰ M. Calleri and J. C. Speakman, *J. Chem. Soc. (A)*, 1969, 1664.