Crystal Structures of the Acid Salts of Some Monobasic Acids. Part XIV.[1] Neutron-diffraction Studies of Potassium Hydrogen Bis(trifluoroacetate) and Potassium Deuterium Bis(trifluoroacetate): Crystals with Short and Symmetrical Hydrogen Bonds

By **A. L. Macdonald** and **J. C. Speakman,*** Chemistry Department, The University, Glasgow G12 8QQ, Scotland
D. Hadži, Chemistry Department, The University, Ljubljana, Jugoslavia

The crystal structures of potassium hydrogen bis(trifluoroacetate) (I) and its deuterium analogue (II) have been determined by neutron-diffraction analysis. For (I) $a = 8{\cdot}773(5)$, $b = 10{\cdot}169(6)$, $c = 9{\cdot}255(6)$ Å, $\beta = 98{\cdot}85(7)°$, $Z = 4$, space group $I2/a$, final R 5·2% for 849 non-zero data; for (II), $a = 8{\cdot}784(4)$, $b = 10{\cdot}177(5)$, $c = 9{\cdot}264(8)$ Å, $\beta = 98{\cdot}83(10)°$, $Z = 4$, space group $I2/a$, final R 5·0% for 1048 data. The hydrogen bond, lying across a centre of inversion, has $O \cdots H \cdots O$ 2·437(4) in (I), and $O \cdots D \cdots O$ 2·437(3) Å in (II). The absence of significant isotope effect suggests that this may be a genuinely symmetrical hydrogen bond, with the hydrogen nucleus vibrating (anharmonically) in a single potential-energy well. This is strongly supported by spectroscopic measurements, as well as by analysis of the vibrational motions of the proton or deuteron, within its $O \cdots O$ environment. Some of the problems of studying hydrogen bonds in crystallographically symmetrical sites by diffraction methods are discussed.

An X-ray study[2] of potassium hydrogen bis(trifluoroacetate) [$KH(tfa)_2$, where Htfa = $CF_3{\cdot}CO_2H$] showed it to be an acid salt of Type A,[3] with a very short hydrogen bond [$O \cdots O$ 2·435(7) Å] lying across a centre of inversion of the crystal. This material is of special interest because the absence of any hydrogen, apart from the acidic atom, simplifies the interpretation of relevant spectra.

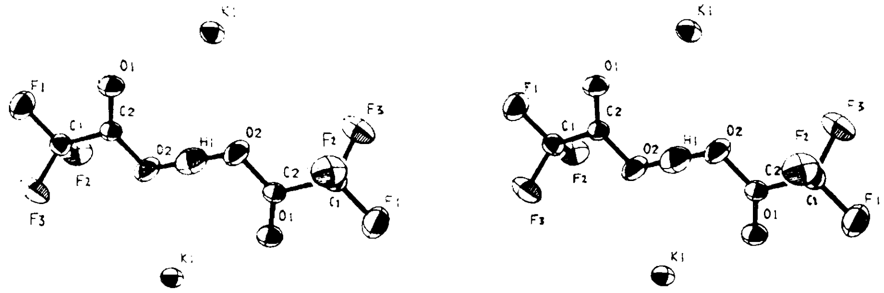

FIGURE 1 Stereoscopic view of the structure, approximately in the b axial direction

Suitably large crystals of both $KH(tfa)_2$ and $KD(tfa)_2$ were grown in Ljubljana, where they were studied spectroscopically. They were also used in Britain for full neutron-diffraction analyses, which confirmed the results of the earlier X-ray work, with a better precision. We hoped that these measurements, in combination, might throw light on the hydrogen bonding between the trifluoroacetate residues.

RESULTS

Results of the Crystal-structure Analysis.—A simplified view of the structure is shown in Figure 1, which should be

---

[1] Part XIII, D. R. McGregor and J. C. Speakman, *J. Chem. Soc.* (*A*), 1968, 2106.

[2] Part X, Lj. Golič and J. C. Speakman, *J. Chem. Soc.*, 1965, 2530.

[3] H. N. Shrivastava and J. C. Speakman, *J. Chem. Soc.*, 1961, 1151.

TABLE 1

Fractional co-ordinates (x, y, $z \times 10^5$), and orthogonal co-ordinates (X', Y, and Z', in 10^{-4} Å,* with standard deviations in parentheses). The neutron results for KH(tfa)$_2$ are in the first row, those for KD(tfa)$_2$ in the second, and the X-ray results (from ref. 2) for KH(tfa)$_2$ in the third

	x	y	z	X'	Y	Z'
K+	50,000	28,118	25,000	43,218	28,593(36)	15,634
		28,091			28,588(30)	
		28,124				
F(1)	6212	32,487	59,654	5369(22)	33,036(28)	54,277(27)
	6245	32,498	59,670	5405(18)	33,073(22)	54,342(21)
	6204	32,461	59,619			
F(2)	23,693	38,706	77,438	20,479(28)	39,360(26)	68,113(20)
	23,649	38,717	77,436	20,468(22)	39,402(21)	68,190(15)
	23,590	38,638	77,440			
F(3)	10,601	53,006	63,732	9163(27)	53,902(26)	57,393(28)
	10,583	53,013	63,722	9160(21)	53,951(21)	57,445(22)
	10,544	53,053	63,729			
O(1)	27,750	33,843	43,060	23,986(18)	34,415(18)	35,687(17)
	27,748	33,876	43,040	24,016(15)	34,476(14)	35,711(13)
	27,638	33,947	43,080			
O(2)	39,973	49,559	57,613	34,551(22)	50,397(23)	47,322(21)
	40,013	49,542	57,639	34,631(16)	50,419(19)	47,396(16)
	39,977	49,506	57,579			
C(1)	17,267	41,248	63,791	14,925(14)	41,945(15)	56,447(14)
	17,291	41,245	63,762	14,965(12)	41,975(12)	56,476(10)
	17,507	41,230	63,804			
C(2)	29,365	41,250	53,497	25,382(13)	41,947(13)	45,104(13)
	29,351	41,245	53,502	25,403(10)	41,975(11)	45,163(10)
	29,307	41,198	53,617			
H(D)	50,000	50,000	50,000	43,218	50,845	38,771

* Where $X' = ax \sin \beta$ and $Z' = cz + ax \cos \beta$.

TABLE 2

Vibrational parameters: neutron-diffraction results for KH(tfa)$_2$ and KD(tfa)$_2$ in the first two rows, and X-ray results (from ref. 2) for KH(tfa)$_2$ in the third row. (U_{ij} are the tensor components for mean-square amplitude, as 10^{-4} Å^2, with standard deviations in parentheses)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
K+	347(16)	240(14)	312(15)	0	250(25)	0
	358(12)	348(12)	380(12)	0	279(20)	0
	377	316	379		302	
F(1)	381(10)	550(13)	560(13)	−113(21)	271(18)	−307(18)
	400(8)	644(10)	592(9)	−84(16)	280(14)	−257(14)
	443	644	598	−102	186	−392
F(2)	612(13)	506(12)	288(9)	19(15)	151(16)	−35(19)
	639(10)	604(10)	333(7)	56(12)	202(13)	−4(16)
	659	585	343	100	154	16
F(3)	522(12)	446(12)	581(13)	−150(19)	263(20)	409(19)
	551(9)	549(10)	604(10)	−138(15)	299(15)	409(15)
	564	528	641	−170	266	420
O(1)	384(8)	328(7)	305(7)	−227(12)	150(12)	−64(13)
	416(6)	416(6)	367(6)	−220(9)	197(9)	−79(10)
	389	373	397	−152	114	−46
O(2)	407(9)	487(11)	405(9)	−372(16)	227(13)	−381(16)
	422(7)	584(9)	466(7)	−364(13)	284(11)	−350(13)
	422	519	478	−308	254	−324
C(1)	304(6)	328(7)	299(6)	−59(11)	148(9)	42(10)
	354(5)	411(6)	353(5)	−35(8)	181(7)	60(8)
	382	395	317	−106	24	118
C(2)	284(6)	264(6)	242(5)	−88(9)	71(8)	−27(9)
	309(5)	347(5)	293(4)	−92(7)	97(6)	−1(7)
	316	305	376	32	72	−16
H	571(28)	543(27)	582(28)	−437(47)	102(44)	−252(44)
	588(18)	609(18)	588(17)	−421(24)	84(22)	−272(23)

(Isotropic, 410.)

supplemented by Figures 1 and 4 of Part X.[2] This stereoscopic picture also carries the numbering scheme for atoms of the crystal-chemical unit (CCU), and gives a clearer impression of the hydrogen bond. Fractional and orthogonal co-ordinates for the atoms of the CCU are listed in Table 1 for both KH(tfa)$_2$ and KD(tfa)$_2$, as well as those for the former, obtained in the X-ray study * for comparison. Other symmetry-related units needed in the description of the structures are denoted as follows (CCU at x, y, z):

I $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
II $x, 1 - y, -\frac{1}{2} + z$
III $\frac{1}{2} + x, -\frac{1}{2} + y, -\frac{1}{2} + z$
IV $1 - x, 1 - y, 1 - z$
V $\frac{1}{2} + x, \frac{1}{2} - y, z$
VI $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$
VII $1 - x, y, \frac{1}{2} - z$
VIII $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$

Table 2 compares the vibrational parameters similarly.

---

* Two typographical errors in Part X should be declared: a for the rubidium salt in Table 1 should be 8·813 Å; y for K in Table 4 should be 28,124 ($\times 10^{-5}$).

The more important interatomic distances (in Å, 1 Å = 100 pm) and angles in the double trifluoroacetate ion are listed in Table 3. Table 4 describes the environment of the potassium ion. As it lies on a two-fold axis of the crystal, and makes contact with three pairs of oxygen and one pair of fluorine atoms, there are four independent $K^+ \cdots O/F$ distances and sixteen independent angles at K^+. So far as the results in Tables 3 and 4 are concerned, the two neutron analyses agree impressively; the *X*-ray results agree satisfactorily, having regard to their lower precision. The vibrational parameters in Table 2 are also in fair agreement. The U_{ii} values from the *X*-ray analysis are larger than those from neutron diffraction, as is usual.[4] That the neutron values of U_{ii} differ [those for $KD(tfa)_2$ being consistently higher] we attribute to some under-correction for the large extinction effects with $KH(tfa)_2$ (see p. 831).

TABLE 3

Bond-lengths (Å) and angles (deg.) in, and between, the trifluoroacetate residues with standard deviations in parentheses

	By *X*-rays *	By neutrons		
	$KH(tfa)_2$	$KH(tfa)_2$	$KD(tfa)_2$	$KH(tfa)_2$ †
C(1)–F(1)	1·341(6)	1·324(3)	1·324(2)	1·334
C(1)–F(2)	1·310(6)	1·318(3)	1·320(2)	1·327
C(1)–F(3)	1·348(6)	1·331(3)	1·335(2)	1·340
C(1)–C(2)	1·515(7)	1·543(2)	1·539(2)	1·549
C(2)–O(1)	1·212(6)	1·214(2)	1·215(2)	1·223
C(2)–O(2)	1·268(6)	1·266(3)	1·271(2)	1·277
$O(2) \cdots O(2^{IV})$	2·435(7)	2·437(4)	2·437(3)	2·430
$C(2)–O(2) \cdots O(2^{IV})$	115·6(4)	114·63(15)	114·64(12)	114·1
F(1)–C(1)–C(2)	111·7(4)	111·64(16)	111·79(13)	111·58
F(2)–C(1)–C(2)	113·0(4)	111·42(15)	111·70(13)	111·21
F(3)–C(1)–C(2)	110·9(4)	110·22(16)	110·39(13)	110·15
F(1)–C(1)–F(2)	107·7(4)	108·50(19)	108·25(15)	108·66
F(2)–C(1)–F(3)	107·1(4)	107·21(19)	106·98(15)	107·35
F(3)–C(1)–F(1)	106·3(4)	107·68(19)	107·52(15)	107·74
O(1)–C(2)–O(2)	128·4(4)	129·28(17)	129·06(13)	129·47
O(1)–C(2)–C(1)	120·1(4)	119·49(14)	119·64(11)	119·33
O(2)–C(2)–C(1)	111·6(4)	111·23(14)	111·30(11)	111·20

* From ref. 2. † Corrected for libration.

TABLE 4

Interatomic distances (Å) and angles (deg.) round the potassium ion

	By *X*-rays *	By neutrons		
	$KH(tfa)_2$	$KH(fta)_2$	$KD(tfa)_2$	$KH(tfa)_2$ †
$K^+ \cdots O(2^{II})/O(2^{IV})$	2·840(4)	2·834(4)	2·838(3)	2·824
$K^+ \cdots O(1)/(O(1^{VII})$	2·850(4)	2·839(2)	2·842(2)	2·836
$K^+ \cdots O(1^V)/O(1^{VI})$	2·966(4)	2·968(2)	2·971(2)	2·960
$K^+ \cdots F(3^{III})/F(3^{VIII})$	2·962(4)	2·967(4)	2·967(2)	2·956

	$KH(tfa)_2$	Neutrons: σ ± 0·10°		
	$O(2^{II})$	O(1)	$O(1^V)$	$F(3^{III})$
$O(2^{II})$				
$O(2^{IV})$	73·55			
O(1)	89·55			
$O(1^{VII})$	71·30	156·33		
$O(1^V)$	142·47	109·44		
$O(1^{VI})$	82·15	80·52	131·61	
$F(3^{III})$	125·12	132·21	64·47	
$F(3^{VIII})$	143·45	71·41	74·07	61·24

	$KD(tfa)_2$	Neutrons: σ ± 0·10°		
	$O(2^{II})$	O(1)	$O(1^V)$	$F(3^{III})$
$O(2^{II})$				
$O(2^{IV})$	73·36			
O(1)	89·43			
$O(1^{VII})$	71·20	156·09		
$O(1^V)$	142·38	109·56		
$O(1^{VI})$	82·27	80·51	131·60	
$F(3^{III})$	125·13	132·35	64·48	
$F(3^{VIII})$	143·55	71·50	74·07	61·30

* From ref. 2. † Corrected for libration.

Spectroscopic Results.—The i.r. spectra of $KH(tfa)_2$ and $KD(tfa)_2$ (Figure 2) are characteristic of Type *A* acid salts.[4,5] A more detailed analysis of the spectra will be published separately (by D. H.). Here we concentrate on points relevant to a discussion of the symmetry of the hydrogen bond.

The most important feature is the strong, broad absorption centred at *ca.* 800 cm^{-1} (Figure 2a), and appearing at about *ca.* 600 cm^{-1} after deuteriation (Figure 2b). Neither peak is well defined because of its breadth, and the superposed sharp bands and transparency regions. This feature is assigned to the asymmetric stretching vibrations of OHO and ODO respectively. The assignment results from an extended study of the i.r. spectra of acid salts, and is confirmed by the direction found for the transition dipole moment from transmission and attenuated-total-reflection spectra of single crystals.[6] The (ν_{OH}/ν_{OD}) ratio in $KH(tfa)_2$ and in some other Type *A* acid salts (*e.g.* sodium hydrogen

---

[4] *E.g.*, M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923.

[5] D. Hadži and A. Novak, *Nuovo Cimento*, 1955, Suppl. 2, 715; D. Hadži, *Pure and Appl. Chem.*, 1965, **11**, 435.

[6] B. Orel and D. Hadži, to be published.

diacetate) is close to 4/3, which is compatible with a symmetrical, single-minimum potential for the hydrogen bond.

In agreement with the truly symmetrical structure in $KH(tfa)_2$ we may also cite the difference between the frequencies of the Raman-active (1720 cm^{-1}) and i.r.-active (1735 cm^{-1}) carbonyl stretching modes. The symmetrical OHO-stretching mode is not allowed under the C^{6}_{2h} factor group, and it has not been found in the i.r., but the band at 130 cm^{-1} in the Raman spectrum is believed to correspond to it.

The deuteron quadrupole coupling constant (DQCC) also supports the symmetry of the hydrogen bonding in $KD(tfa)_2$. With the crystal used for neutron diffraction, we obtained a value of 55·6 kHz.[7] This is the lowest value known, and it corresponds to the low value in potassium deuterium maleate. Bearing in mind the sensitivity of DQCC to the electric-field gradient,[8,9] this result is important.

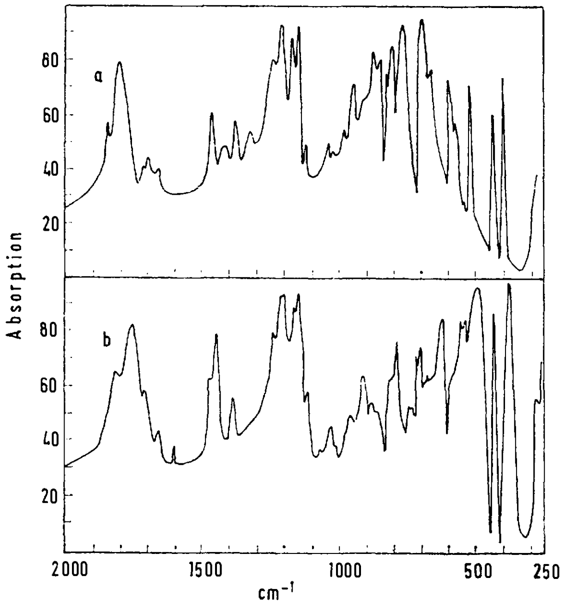

FIGURE 2 I.r. spectra at −180 °C in Nujol mull: a $KH(tfa)_2$ and b $KD(tfa)_2$

Deuterium Content.—During the least-squares refinement of $KD(tfa)_2$, the occupancy-factor of the deuteron site was allowed to vary, and it refined to 0·85(2). Owing to the opposite signs of the neutron-scattering lengths of H and D, this is a sensitive test of the completeness of deuteriation. To be sure, there is some uncertainty about the correct scattering length for D.[10] Taken to be 6·50 fermi, (1 fermi = 10^{-15} m) as it was in our analysis, the occupancy-factor implies 90·5% deuteriation; or 92·3% if it be as low as 6·30 fermi. We conclude that our crystal was not less than 90% deuteriated at the end of the experimental work, and Figure 2b supports this.

DISCUSSION

Symmetry of the O · · · H · · · O *Bond.*—We now consider the crystallographic evidence concerning the hydrogen bond in $KH(tfa)_2$.

The F · · · H · · · F bond in the bifluoride ion has, for many years, been generally regarded as symmetrical. Its crystal structure has been studied by McGaw and Ibers,[11] who made accurate *X*-ray measurements on $NaHF_2$, and neutron measurements on both $NaHF_2$ and $NaDF_2$. These isomorphs have Type *A* structures: they have three molecules in a cell belonging to the twelfth-order space group $R\bar{3}m$; and the F · · · F distance was found, by neutrons, to be 2·264(3) in HF_2^- and 2·265(7) Å in DF_2^-.

Refinement was conducted on the basis of two models in particular: (*a*) the hydrogen nucleus vibrating about a single potential-well at the centre of the F · · · H · · · F bond; and (*b*) a disordered situation, with statistical half-protons (or half-deuterons) vibrating, with smaller amplitudes, about two close minima of a double potential-well. It was impossible to decide between these alternatives on the sole basis of the neutron-diffraction intensities, since a judicious choice of parameters enabled either model to account for the observations.

However neutron-diffraction analysis may lead to reliable nuclear vibrational parameters. The mean-square amplitude found for any atom is additive over the various types of vibrations in which that atom may be supposed to be involved. The differences between the mean-square amplitudes of H and F were taken to measure the anisotropic vibration of the proton within the F · · · H · · · F unit. The amplitude was significantly greater along the bond than athwart it. With certain other assumptions, and using the spectroscopically determined frequencies, McGaw and Ibers [10] were able to account for the amplitudes of the proton on the basis of model (*a*), which therefore was validated for HF_2^-. Against this background, we consider the crystallographic results for $KH(tfa)_2$ and its deuteriate.

Rundle [12] has considered the effects of deuteriation on very short, symmetrical O · · · H · · · O bonds. In a double-minimum potential, with the central energy-barrier only a little higher than the (split) zero-point level, O · · · D · · · O should be markedly longer than O · · · H · · · O; if it is not, then a single-minimum potential is indicated. Subsequently Singh and Wood [13] have done more detailed calculations, leading to a similar conclusion. Our results for the acid trifluoroacetates are O · · · H · · · O 2·437(4) and O · · · D · · · O 2·437(3) Å. At the level of our analyses, there is a zero isotope effect. We conclude in accord with the spectroscopic evidence, that these bonds have a symmetrical, single-well potential like those in the bifluorides.

Table 5 gives the overall vibrational parameters of

---

[7] R. Blinc, D. Hadži, and J. Stepišnik, to be published.

[8] P. L. Olympia and B. M. Fung, *J. Chem. Phys.*, 1969, **51**, 2976.

[9] M. Žaucer, E. Zakrajšck, J. Koller, D. Hadži, and A. Ažman, *Mol. Phys.*, 1971, **21**, 461.

[10] P. Coppens and T. M. Sabine, *Acta Cryst.*, 1969, *B***25**, 2442.

[11] B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.

[12] R. E. Rundle, *J. Physique*, 1964, **25**, 487.

[13] T. R. Singh and J. L. Wood, *J. Chem. Phys.*, 1969, **50**, 3572.

O(2) and H, or D, after transformation to orthogonal axes, X' parallel to x, Y parallel to y, and Z' perpendicular to x and y. The O(2) $\cdots$ O(2^{IV}) direction lies close to the xz-plane and almost bisects the angle between $-X'$ and Z', its direction cosines being l_1 0·71, l_2 0·04, and l_3 $-$0·70. A simple calculation then yields the values (Table 5) for the mean-square amplitudes parallel to the bond, and in two mutually perpendicular directions transverse to it. Adopting the assumption made for the bifluoride, we take the differences to represent the amplitudes of the hydrogen nucleus within O $\cdots$ H/D $\cdots$ O. They correspond to root-mean-square amplitudes, for H, of 0·17 Å along, and *ca.* 0·08 Å across, the bond; and, for D, 0·16 and 0·06 Å. Such marked anisotropy, which can be seen by inspection of Figure 1, is typical of very short hydrogen bonds. Following discussions by Ellison and Levy [14] and by Hamilton and co-workers,[15] we notice that the amplitude along the bond is, in each case, so large that it would carry the hydrogen nucleus from one well to the other if, indeed, there were a double-well potential with its minima separated by the largest distance reasonably acceptable in so short a hydrogen bond. (This argument is equally valid for the rather smaller longitudinal amplitude of the proton, remaining after subtraction of a mean-square amplitude of 0·01 Å^2 to allow for disorder due to minima 0·1 Å on either side of a central barrier.) Thus a distinction between models (*a*) and (*b*) would have been unrealistic, in any case.

TABLE 5

Mean-square amplitudes (Å^2) of atoms O(2) and H (or D) with respect to orthogonal axes, defined in Table 1. Derived mean-square amplitudes of these atoms parallel to, and in two mutually perpendicular directions normal to, the hydrogen bond

KH(tfa)$_2$						
	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(2)	0·0407(9)	0·0487(11)	0·0389(9)	$-$0·0311(16)	0·0089(13)	$-$0·0381(16)
H	0·0571(28)	0·0543(27)	0·0599(28)	$-$0·0400(47)	$-$0·0096(44)	$-$0·0252(44)
	$U_{\parallel}$	$U_{\perp}$	$U_{\perp}'$			
O(2)	0·0344	0·0487	0·0094			
H	0·0634	0·0543	0·0189			
Δ	0·0290	0·0056	0·0095			
KD(tfa)$_2$						
	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(2)	0·0422(7)	0·0584(9)	0·0443(7)	$-$0·0309(13)	$-$0·0142(11)	$-$0·0350(13)
D	0·0588(18)	0·0609(18)	0·0599(17)	$-$0·0260(24)	$-$0·0070(22)	$-$0·0272(23)
	$U_{\parallel}$	$U_{\perp}$	$U_{\perp}$			
O(2)	0·0358	0·0584	0·0105			
D	0·0626	0·0609	0·0164			
Δ	0·0268	0·0025	0·0059			

Figure 3 sketches some types of potential-energy function for the proton moving, in a hydrogen bond, between two oxygen atoms. The crystal symmetry in KH(tfa)$_2$ reduce the possibilities to (b), (c), (d), or (e). Gross disorder, needed to accommodate (a), can be ruled out. As the O $\cdots$ O distance is very short, (b) can also be rejected. Theoretical calculations for a simple model (*e.g.* ref. 16) support the intuitive notion that there should be a sequence of the kind suggested by (c), (d), and (e), as the O $\cdots$ O distance diminishes: a flattened single minimum (d) may obtain before the parabolic curve (e) is reached. The effective potential function in KH(tfa)$_2$ and KD(tfa)$_2$ is probably of the form (d), with the proton, or deuteron, vibrating anharmonically along the bond. Such a model is in accord with the vibrational properties described above. Also relevant is a precise neutron-diffraction study [17] of a very short

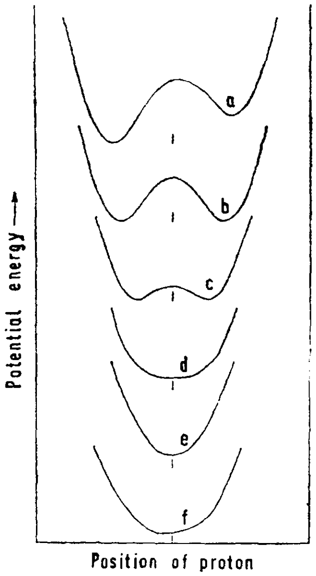

FIGURE 3 Schematic representations of the potential-energy function for a hydrogen nucleus moving along the line between two oxygen atoms, and its possible variation as the O $\cdots$ O distance and the environment change

---

[14] R. D. Ellison and H. A. Levy, *Acta Cryst.*, 1965, **19**, 260.

[15] A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Struct.*, 1967—1968, **1**, 283.

[16] P. Schuster, *Theoret. Chim. Acta*, 1970, **19**, 212; see also P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, 1970, **92**, 6101

[17] E. O. Schlemper, W. C. Hamilton, and S. J. La Placa, *J. Chem. Phys.*, 1971, **54**, 3991.

intramolecular hydrogen bond in a non-symmetrical site. With O···H distances of 1·187(3) and 1·242(5) Å, the proton is very significantly off-centre. A small dissymmetry of environment has had a large effect in shifting the potential minimum to yield a curve of the type sketched in Figure 3(f). This would not be unexpected if the unperturbed curve had a flattened minimum like that in (d). This bond has O···O 2·420(3) Å. *A fortiori*, a flattened potential minimum is even more likely when O···O 2·437 Å in KH(tfa)$_2$.

Using an harmonic approximation, Coppens and Sabine [10] have plotted a relationship (Figure 3 of ref. 10) between frequency and root-mean-square amplitude for a proton, or a deuteron, moving in a potential field between two oxygen atoms. The frequencies of 800 and 600 cm^{-1}, given earlier in this paper, and the root-mean-square amplitude above fit the Coppens–Sabine graph rather well.

The Kroon–Kanters–McAdam Effect.—This adjective (KKM) may be applied to an effect discovered at Utrecht during an *X*-ray study of potassium hydrogen *meso*-tartrate,[18] and independently at Glasgow by McAdam in a study of potassium hydrogen succinate.[19] This effect is often (but not always) observed when a ' difference ' electron-density synthesis is computed in the region of the short and symmetrical O···H···O bond of a Type *A* (or A_2) crystal; the coefficients in the Fourier series are ($F_o - F_c'$), where F_c' is the structure factor calculated for all atoms except the acidic hydrogen. The bonding situation being presumably of the kind described, the elementary expectation would be for the neglected hydrogen atom to appear as a peak centred at the midpoint of the O···H···O bond, though perhaps elongated by the anisotropic vibration. When the KKM effect is operative, we find a pair of electron-density peaks, necessarily related by the two-fold symmetry of the bond, and so situated as to imply, if taken at their face value, that the hydrogen atom is disordered between two sites 0·2—0·35 Å on either side of the bond-centre. In other words, we seem to have a wide double-minimum potential [as in Figure 3(b)], with the minima as widely separated as are those in ice. This conclusion is unacceptable in hydrogen bonds with O···O <2·5 Å.

This effect may be found in well refined structures. It is not due to gross errors in the *X*-ray analysis.

As the structure of KH(tfa)$_2$ has been studied both by *X*-rays and by neutrons, and as we believe there is good evidence for symmetry of the O···H···O bond, it may be appropriate to examine our results in relation to the KKM effect. Figure 4(a) reproduces a ' difference ' map based on the *X*-ray data and parameters.[2] Though elongated in the bond-direction, the peak is not split.

Figures 4(b) and (c) are versions of the ($F_X - F_N$), synthesis of Coppens:[20] F_X are the observed *X*-ray structure factors, whilst F_N are the *X*-ray factors calculated from the neutron parameters in Tables 1 and 2, the hydrogen atom being excluded in (b), but included in (c). Elongation of the peak is enhanced in (b) compared with (a); it is widely split in (c). This last diagram indeed corresponds to the classical ' difference ' pattern indicating vibrational anisotropy. But it cannot be due to anisotropy here because anisotropic vibration has been adequately included in the neutron-refinement. We suggest that Figure 4(c) is a version of the KKM effect.

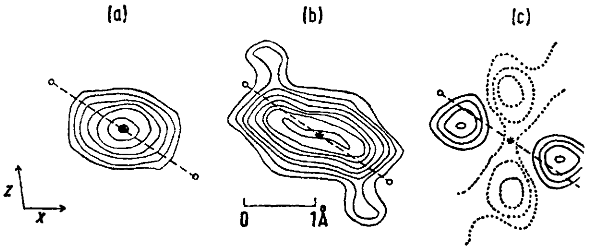

FIGURE 4 Electron-density ' difference ' syntheses in a plane including the H···O···H bond. [Contours are drawn at intervals of 0·05 eÅ^{-3}, with negative lines broken. The small ' knobs ' lying in directions NW and SE from the centre of (b) are little above ' noise ' level and not regarded as significant]

A straightforward ' difference ' synthesis, based on the observed neutron-diffraction structure factors less those calculated for all nuclei except that of the hydrogen atom, gave maps very different from those in Figure 4. Figure 5 shows sections through the centre of the O···D···O bond in KD(tfa)$_2$: the peak is only slightly elongated in the bond direction in the *xz* plane, and almost circular in a perpendicular plane. A similarly shaped peak was found in KH(tfa)$_2$.

We have already published a preliminary discussion of the KKM effect,[4] and suggested, in agreement with ref. 21, that the double peaks do not necessarily indicate meaningful positions for a disordered hydrogen atom. In seeking an alternative explanation, the following considerations are relevant: (i) neutron diffraction

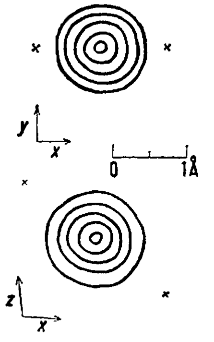

FIGURE 5 Neutron-scattering density ' difference ' synthesis in two planes including the centre of the O···D···O bond

---

[18] J. Kroon, J. A. Kanters, and A. F. Peerdeman, *Nature* (*Physical Science*), 1971, **229**, 120.

[19] A. McAdam, M. Currie, and J. C. Speakman, *J. Chem. Soc.* (*A*), 1971, 1994.

[20] *E.g.*, P. Coppens, T. M. Sabine, R. G. Delaplane, and J. A. Ibers, *Acta Cryst.*, 1969, **B25**, 2451.

[21] J. Kroon, J. A. Kanters, A. F. Peerdeman, and A. Vos, *Nature* (*Physical Science*), 1971, **232**, 107.

establishes, in the Type *A* crystals to which it has been applied, that the proton vibrates anharmonically about a single energy-well at the centre of the very short O · · · H · · · O bond; (ii) there must always be a local electron-density maximum at, or very close to, the position of the proton; (iii) however, when the hydrogen atom is covalently bonded to an electronegative neighbour, such an electron-density condensation will be far from symmetrical; (iv) hence the spherical model for the atoms, used in refining the results of *X*-ray analyses, is liable to produce misleading artefacts, especially when it is applied at the low level of density near a hydrogen atom (this is why O–H, N–H, and even C–H distances, measured by *X*-rays, usually turn out too small); (v) the magnitudes and shapes of electron-density peaks at positions of special crystallographic symmetry are particularly sensitive to small errors in the scaling of the intensity data.

Other Details of the Structure.—These do not differ considerably from those reported in the *X*-ray study [2] of KH(tfa)$_2$, and need only brief discussion. We shall restrict ourselves to the undeuteriated salt. Results for KD(tfa)$_2$ are virtually identical.

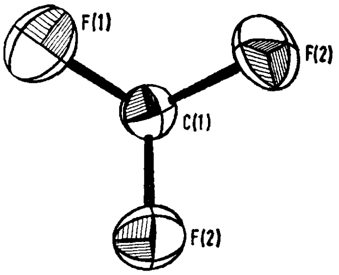

FIGURE 6 Vibrational ellipsoids (drawn to 50% probability limits) of the fluorine atoms viewed along the C–C direction

The atoms O(1), O(2), C(1), C(2), and F(1) are coplanar with C(1)–F(1) *trans* to C(2)–OH. Their mean plane is represented by the equation: $0{\cdot}5289\,X' - 0{\cdot}6981\,Y + 0{\cdot}4826\,Z' = 0{\cdot}5905$ Å, only C(1) diverging by as much as 0·006 Å. The proton of the O · · · H · · · O bond is also near the same plane, which implies that all the atoms of the double H(tfa)$_2^-$ anion, except the pairs of F(2) and F(3), are almost coplanar.

The C–C bond is significantly longer than those in unsubstituted acetate residues, *e.g.* 1·505 Å in ammonium acetate.[22] This effect of perfluorination has already been observed in ammonium trifluoroacetate.[23]

The thermal motions of the atoms of the trifluoroacetate unit were analysed in the usual way. The best fit between observed atomic vibrational parameters and those calculated for rigid-body vibration of the unit was achieved when libration was about C(2), rather than about the centre of mass. (This suggests that the hydrogen bonding does exercise some restraint on the libration.[10] We hope to discuss this in a later paper on potassium hydrogen glutarate.) The torsional oscillation of the tfa-unit can be described as having a root-mean-square amplitude of 7° about the C–C bond, and smaller amplitudes (<4°) about the other principal axes. The thermal ellipsoids shown in Figure 6 make the libration about the C–C bond evident. Corrections to bond-lengths, to allow for this libration, are small. Corrected values for KH(tfa)$_2$ are included in Table 3.

The fluorine atom which is in contact with the potassium ion is F(3). The distance C(1)–F(3) is significantly longer than the other two C–F distances.

EXPERIMENTAL

Crystal Data.—The cell dimensions for KD(tfa)$_2$ were determined, using a small crystal-fragment, by *X*-rays (Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; film calibrated with lines due to Al-wire, taking *a* as 4·04907 Å at room temperature). They are compared in Table 6 with the *X*-ray values for KH(tfa)$_2$ from Part X. The close agreement between the two sets indicates strict isomorphism.

Collection of Neutron Data.—Intensities were measured with the Hilger and Watts four-circle diffractometers installed in the PLUTO and DIDO reactors of the A.E.R.E., Harwell. The general methods have been described.[24] The copper-monochromated neutron beams had wavelengths of 1·142 and 1·170 Å.

TABLE 6

Comparison of crystal data

	KH(tfa)$_2$	KD(tfa)$_2$
Formula	$KHC_4O_4F_6$	$KDC_4O_4F_6$
M	266·1	267·1
a	8·773(5) Å	8·784(4) Å
b	10·169(6)	10·177(5)
c	9·255(6)	9·264(8)
β	98·85(7)°	98·83(10)°
U	815·9 Å^3	818·4 Å^3
D_m	2·085	
Z	4	4
D_c	2·166	2·168

Space group *I*2/*a* (No. 15).*

* The choice of axis implied by *I*2/*a* gives the equivalent positions: 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $\pm(x, y, z;\ x, -y, \frac{1}{2} + z)$.

To prevent absorption of moisture and loss of deuterium, the crystals were sealed in soda-glass tubes. That of KH(tfa)$_2$ had dimensions 1·3 × 0·6 × 0·2 cm. A complete quadrant of reflexions was recorded to $\theta = 55°$, and of the 1168 measured 849 were statistically above background. The KD(tfa)$_2$ crystal had dimensions 1·0 × 0·8 × 0·4 cm; 1281 intensities were recorded, 1048 being significant. Both sets of data were corrected for absorption, the linear coefficients being 0·47 and 0·37 cm^{-1}, respectively. Extinction, which was particularly severe with KH(tfa)$_2$, was allowed for by introducing, and refining, an appropriate parameter [25] during the later stages of the least-squares analysis.[26]

Structure Refinement.—The *X*-ray parameters [2] were the

---

[22] I. Nahringbauer, *Acta Cryst.*, 1967, **23**, 1653; see also *Acta Chem. Scand.*, 1969, **23**, 1053.

[23] D. W. J. Cruickshank, D. W. Jones, and G. Walker, *J. Chem. Soc.*, 1964, 1303.

[24] M. Currie, J. C. Speakman, and N. A. Curry, *J. Chem. Soc.* (*A*), 1967, 1862.

[25] W. H. Zachariasen, *Acta Cryst.*, 1968, **A24**, 212.

[26] A. L. Macdonald, Ph.D. Thesis, University of Glasgow, 1971.

starting point for full-matrix, least-squares refinement based on the neutron data, the KDF 9 programs being those developed by Cruickshank, Smith, and Sime. The weighting scheme used in the later stages was $w = [1 - \exp\{-p_1((\sin\theta)/\lambda)^2\}]/(1 + p_2|F_o|)$; for KH(tfa)$_2$, $p_1 = 3{\cdot}0$ and $p_2 = 0{\cdot}1$, whilst for KD(tfa)$_2$ corresponding values were 6·0 and 0·5. The final values of the extinction parameter r^*, were 2·45(8) and 0·44(3), respectively; after application of this correction, the U_{ii}-values for KH(tfa)$_2$ increased by *ca.* 10%. The neutron scattering lengths were (K) 3·5, (F) 5·5, (C) 6·61, (O) 5·77, (H) −3·78, and (D) 6·50 fermi. Refinement converged after about a dozen cycles in each case. The final R values were 7·9% (all data) and 5·19% (non-zero terms only) for KH(tfa)$_2$; 7·4% (all data), and 5·04% (non-zero terms) for KD(tfa)$_2$: for the non-zero terms, R' (= $\Sigma w\Delta^2/\Sigma w|F_o|^2$) was 0·0037 and 0·0046, respectively.

TABLE 7

KH(tfa)$_2$: analysis of agreement between $|F_o|$ and $|F_c|$ at the end of the refinement

(*a*) As a function of $|F_o|$

$\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N *	R	$\Sigma\|\Delta\|/N$
0—1·0	23·09	22·22	3·83	26	0·1670	0·148
1·0—2·0	393·64	378·17	36·94	263	0·0938	0·140
2·0—5·0	1373·65	1361·77	57·55	431	0·0419	0·133
5·0—7·0	450·15	456·31	15·18	77	0·0337	0·197
4·0—15·0	441·80	463·85	25·67	52	0·0581	0·494

(*b*) As a function of $(\sin\theta)/\lambda$

$\sin\theta/\lambda$						
0·0—0·1	12·97	14·10	1·13	3	0·0875	0·378
0·1—0·2	123·75	135·21	15·44	25	0·1248	0·618
0·2—0·3	226·95	230·32	14·59	55	0·0643	0·265
0·3—0·4	433·66	428·76	19·47	108	0·0449	0·180
0·4—0·5	693·91	686·96	27·48	183	0·0396	0·150
0·5—0·6	622·05	616·95	27·04	218	0·0435	0·124
0·6—0·7	569·05	570·04	34·01	257	0·0598	0·132
All	2682·34	2682·34	139·16	849	0·0519	0·164

* N is no. of reflections.

TABLE 8

KD(tfa)$_2$: analysis of agreement between $|F_o|$ and $|F_c|$ at the end of the refinement

(*a*) As a function of $|F_o|$

F_o range	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N *	R	$\Sigma\|\Delta\|/N$
0—1·5	425·03	407·97	42·88	442	0·1009	0·097
1·5—3·0	654·61	654·17	29·87	303	0·0456	0·099
3·0—4·5	594·67	594·67	23·05	165	0·0387	0·140
4·5—6·0	342·92	343·30	12·13	67	0·0354	0·181
6·0—9·0	395·53	407·03	15·28	57	0·0386	0·268
9·0—30·0	154·85	160·64	6·27	14	0·0405	0·448

(*b*) As a function of $(\sin\theta)/\lambda$

$\sin\theta/\lambda$						
0·0—0·1	14·56	14·43	0·97	3	0·0668	0·324
0·1—0·2	138·55	138·67	6·52	26	0·0471	0·251
0·2—0·3	244·83	243·14	15·17	63	0·0620	0·241
0·3—0·4	401·46	400·08	21·97	122	0·0547	0·180
0·4—0·5	618·17	621·92	24·13	197	0·0390	0·123
0·5—0·6	590·04	588·81	27·73	273	0·0470	0·102
0·6—0·7	525·60	524·07	30·23	334	0·0575	0·091
0·7—0·8	346·78	366·70	27·52	30	0·0794	0·092
All	2567·89	2567·78	129·48	1048	0·0504	0·124

* N is no. of reflexions.

Observed structure amplitudes and calculated structure factors for the two salts are listed in Supplementary Publication No. SUP 20343 (5 pp., 1 microfiche),* whilst Tables 7 and 8 analyse the agreement over various sub-sets of data.

We thank Professors A. F. Peerdeman and A. Vos, and Drs. W. C. Hamilton, J. Kroon, and J. A. Kanters for valuable discussions (with J. C. S.) during preparation of the manuscript, the Boris Kidrič Fund (D. H.) and the S.R.C. (A. L. M.) for financial support, Mrs. Iva Levstek for skilful work in growing large single crystals. We also thank A.E.R.E., Harwell (and S.R.C.), for providing neutron facilities, and Dr. J. B. Forsyth, and R. S. Dunlop and Dr. A. McAdam, who participated in data collection.

[1/2042 *Received, 2nd November,* 1971]

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.