Deuteriation of an Asymmetric Short Hydrogen Bond. *X*-Ray Crystal Structure of $KF\cdot(CH_2CO_2D)_2$ †

By **John Emsley,* Deborah J. Jones,** and **Reiko Kuroda,** Department of Chemistry, King's College, Strand, London WC2R 2LS

Deuteriation of the strong hydrogen bonds of $KF\cdot(CH_2CO_2H)_2$ shows no isotope effect on the bond lengths. The only significant change is in the bond angle at the fluoride ion which widens to 128.5 from 116°. The i.r. spectrum shows very little change. Since the $O-H\cdots F^-$ hydrogen bonds are highly asymmetric, these observations challenge previous predictions about the effects of deuteriation on such bonds.

THE number of reports of very short/strong hydrogen bonds in crystals continues to grow.[1,2] Most such bonds are homonuclear with OHO being predominant. There are relatively few heteronuclear examples such as the OHF type reported in this paper. The location of the proton in these short bonds is at the centre or nearly so, but not in every case, and in tris(thiourea)copper hydrogenphthalate the OHO bond is very asymmetric.[3] In the OHF hydrogen bonds of $KF\cdot(CH_2CO_2H)_2$ the proton is located much nearer to the oxygen than it is to the fluorine.[4]

TABLE 1

The effect of deuteriation on the bond length of very short/strong hydrogen bonds

Hydrogen bond type	Example	r_{AHB}/Å	r_{ADB}/Å	Δ	Ref.
FHF	$NaHF_2$	2.264(3)	2.265(7)	+0.001	*a*
OHO	$H_5O_2^+$ [b]	2.442(2)	2.454(2)	+0.012	*c*
OHO	$H_5O_2^+$ [d]	2.434(2) 2.421(2)	2.442(3) 2.435(3)	+0.008 +0.014	*e*
OHO	qna	2.398(3)	2.393(2)	−0.005	8
OHO	$KH\cdot(CF_3CO_2)_2$	2.437(4)	2.437(3)	0	*f*
OHO	$[Ni(bambo)_2]Cl\cdot H_2O$	2.420(3)	2.439(8)	+0.019	6
OHO	$[C_3H_5N_2]^+[C_4H_3O_4]^-$	2.393(3)	2.399(4)	+0.006	7
OHO	$HCoO_2$	2.50(2)	2.57(2)	+0.07	*g*
OHF	$KF\cdot(CH_2CO_2H)_2$	2.441(3)	2.445(3)	+0.004	4, this work
NHN	$H_3[Co(CN)_6]$	2.582(19)	2.596(19)	+0.014	*h*

[a] B. L. McGraw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677. [b] In yttrium oxalate trihydrate, $YH(C_2O_4)_2\cdot 3H_2O$. [c] G. D. Brunton and C. K. Johnson, *J. Chem. Phys.*, 1975, **62**, 3797. [d] In 5-sulphosalicylic acid hydrate, $C_6H_3(CO_2H)(OH)SO_3H\cdot 2H_2O$. [e] R. Attig and J. M. Williams, *J. Chem. Phys.*, 1977, **66**, 1389. [f] A. L. Macdonald and J. C. Speakman, *J. Chem. Soc., Perkin Trans. 2*, 1972, 825. [g] R. G. Delaplane, J. A. Ibers, J. R. Ferraro, and J. J. Rush, *J. Chem. Phys.*, 1969, **50**, 1920. [h] H form: R. Haser, B. Bonnet, and J. Roziere, *J. Mol. Struct.*, 1977, **40**, 177; D form: H. U. Güdel, A. Ludi, P. Fischer, and W. Hälg, *J. Chem. Phys.*, 1970, **53**, 1917.

In theory the deuteriated form of a very strong hydrogen bond should be shorter than the protonated bond.[5] However if the single minimum potential well, which characterises this kind of bond, is very asymmetric then it is predicted that the overall bond length will increase on deuteriation, *i.e.* there will be a positive isotope effect.[5] Very short bonds which have been measured in both H and D forms are listed in Table 1. In practice the deuteriated analogues of such bonds are generally indistinguishable within experimental error whether the hydrogen bond is asymmetric or not.

If crystal forces are operating to prevent the expected negative isotope effect of symmetric hydrogen bonds then these would be at a minimum in compounds with internal hydrogen bonds such as are found in bis(3-amino-3-methylbutan-2-one oximato)nickel(II) chloride hydrate, $[Ni(bambo)_2]Cl\cdot H_2O$,[6a,b] in imidazolium hydrogenmaleate, $[C_3H_5N_2]^+[C_4H_3O_4]^-$,[7] and in pyridine-2,3-dicarboxylic acid as its zwitterion (qna).[8a,b] As Table 1 shows, only the last compound shows any shortening but this is insignificant and may be purely technical.

The asymmetric hydrogen bonds in Table 1 do not show any significant lengthening on deuteriation. Even the most asymmetric system, $KF\cdot(CH_2CO_2H)_2$, reported here shows a smaller isotope effect than most of the symmetric bonds.

EXPERIMENTAL

The deuteriated compound $KF\cdot(CH_2CO_2D)_2$, was obtained by the same method as for $KF\cdot(CH_2CO_2H)_2$, *i.e.* by slow evaporation of an aqueous (D_2O) solution of KF and $[^2H_2]$succinic acid (prepared by repeated exchange with D_2O until the i.r. spectrum showed no OH bands) in a 1 : 1 mol ratio. Colourless crystals of $KF\cdot(CH_2CO_2D)_2$ were produced, m.p. 171 °C (decomp.).

Crystal Data.—$C_4H_4D_2FKO_4$, $M = 178.19$, Orthorhombic, space group *Pnam*, $a = 7.0709$ (5), $b = 5.5752$ (5), $c = 16.871$ (3) Å, $U = 665.06$ Å^3, $Z = 4$, $D_c = 1.779$ g cm^{-3}, $F(000) = 360$, μ(Mo-K_α) = 6.98 cm^{-1}. Intensity data were collected, employing θ—2θ scan mode, to a maximum θ of 30° with Mo-K_α radiation ($\lambda = 0.7107$ Å) using an Enraf-

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† Potassium fluoride–$[^2H_2]$succinic acid (1/1).

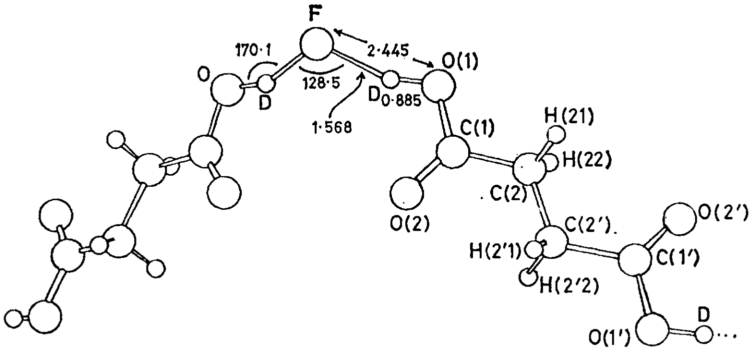

FIGURE 1 The short hydrogen bonds to the fluoride ion in $KF{\cdot}(CH_2CO_2D)_2$

Nonius CAD4 diffractometer; 1 775 symmetry related reflections were averaged, of which 993 were unique. No correction was made for absorption. The structure was solved using the program SHELX-76 (written by Professor G. Sheldrick) with the initial co-ordinates of the atoms in $KF{\cdot}(CH_2CO_2H)_2$.[4] The structure is isomorphous with $KF{\cdot}(CH_2CO_2H)_2$; F^- lies on a crystallographic mirror plane. The structure converged to an R factor of 0.0286 employing 924 reflections with $|F_o| \geqslant 2\sigma(F_o)$. Atomic co-ordinates are given in Table 2. Relevant bond lengths and angles around the fluoride ion are shown in Figure 1, and the environment of the potassium ion is shown in Figure 2. Bond lengths and bond angles are listed in Table 3. Observed and calculated structure amplitudes and thermal parameters are listed in Supplementary Publication No. SUP 23122 (7 pp.).*

TABLE 2

Fractional atomic co-ordinates (× 10^4)

Atom	x	y	z
K	2 229(1)	4 099(1)	2 500
F	5 802(2)	5 727(3)	2 500
O(1)	7 837(2)	1 620(2)	−1 201(1)
O(2)	5 768(2)	−1 347(2)	−1 378(1)
C(1)	6 444(2)	222(3)	−967(1)
C(2)	5 812(2)	776(3)	−133(1)
D(1)	8 291(37)	1 134(46)	−1 663(16)
H(21)	5 433(27)	2 493(38)	−113(11)
H(22)	6 847(27)	483(35)	236(11)

DISCUSSION

The compound $KF{\cdot}(CH_2CO_2D)_2$ has a structure consisting of infinite chains of succinic acid molecules held together by short hydrogen bonds to F^- ions (Figure 3). The only significant difference between the crystal structures of $KF{\cdot}(CH_2CO_2H)_2$ and $KF{\cdot}(CH_2CO_2D)_2$ is the angle which the two hydrogen bonds to the fluoride ion make with each other. This angle increases from 116 to 128.5° on deuteriation. The hydrogen-bond lengths F $\cdots$ O are only marginally longer, 2.445(3) compared to 2.441(3) Å. This slight positive isotope effect of $\Delta = +0.004$ is not statistically significant but the observation is noteworthy because this is the first example of a heteronuclear short hydrogen bond to be studied as its deuteriated derivative. The predicted bond lengthening[5] compared to that of a symmetric bond has not been observed.

Within the hydrogen bonds there are slight changes in the location of the hydrogen atom (O–H 0.849, O–D 0.885 Å and H $\cdots$ F 1.598 and D $\cdots$ F 1.568 Å) but these changes are not meaningful in view of the uncertainty in the hydrogen-atom positions. In $[Ni(bambo)_2]Cl{\cdot}H_2O$ the isotope effect is +0.019 [6a,b] and the hydrogen bond becomes noticeably less symmetric. In the protonated form the O–H bond lengths are 1.187 and 1.242 Å showing an almost centred bond, but in the deuteriated form the O–D bond lengths are 1.058 and 1.391 Å, clearly asymmetric.

TABLE 3

Bond distances (Å), bond angles, and torsion angles (°) in $KF{\cdot}(CH_2CO_2D)_2$

(*a*) Distances

F–D(1)	1.568(30)	C(1)–C(2)	1.509(2)
F–O(1)	2.445(3)	C(2)–H(21)	0.995(21)
D(1)–O(1)	0.885(26)	C(2)–H(22)	0.975(19)
C(1)–O(1)	1.316(2)	C(2)–C(2′)	1.506(3)
C(1)–O(2)	1.214(2)		

(*b*) Angles

D(1)–O(1)–C(1)	110.7(17)	H(22)–C(2)–C(1)	109.9(11)
C(2)–C(1)–O(1)	112.4(1)	H(21)–C(2)–H(22)	109.9(16)
C(2)–C(1)–O(2)	124.3(1)	D(1)–F–D(1′)	128.5(15)
O(1)–C(1)–O(2)	123.4(1)	O(1)–D(1)–F	170.1(28)
H(21)–C(2)–C(1)	108.0(11)		

K–F 2.685(3), 2.874(3)
K–O(2) 2.818(3), 2.818(3), 2.852(3), 2.852(3)

(*c*) Torsion angles

D(1′)–F–D(1)–O(1)	126.7(26)
F–D(1)–O(1)–C(1)	119.4(25)
D(1)–O(1)–C(1)–O(2)	54.5(15)
D(1)–O(1)–C(1)–C(2)	172.4(27)
O(1)–C(1)–C(2)–C(2′)	178.7(2)
O(1)–C(1)–C(2)–H(21)	69.0(16)
O(1)–C(1)–C(2)–H(22)	74.3(16)
C(1)–C(2)–C(2′)–C(1′)	180.0(1)
O(2)–C(1)–C(2)–C(2′)	57.1(1)
C(1)–C(2)–C(2′)–H(2′1)	72.0(14)
C(1)–C(2)–C(2′)–H(2′2)	70.1(15)
O(1′)–C(1′)–C(2′)–H(2′1)	69.0(14)
O(1′)–C(1′)–C(2′)–H(2′2)	74.3(16)
D(1′)–O(1′)–C(1′)–C(2)	172.4(27)
D(1′)–O(1′)–C(1′)–O(2′)	54.5(15)
O(1′)–C(1′)–C(2′)–C(2)	178.7(2)
O(2′)–C(1′)–C(2′)–C(2)	57.1(1)

Atoms D(1)–O(1)–C(1)–C(2)–C(2′)–C(1′)–O(1′)–D(1′) are essentially planar

The atom environment around the potassium ion is

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* For details see Notices to Authors, No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

shown in Figure 2. Each K^+ has a fluoride ion as its nearest neighbour at 2.685 Å (K–F = 2.664 Å in potassium fluoride), two carbonyl oxygens at 2.818 Å, two more at 2.852 Å, and a second fluoride ion at 2.874 Å. The arrangement is somewhat irregular. Essentially the same environment is observed for K^+ in $KF{\cdot}(CH_2CO_2H)_2$, although not reported in detail in the previous publication.[4]

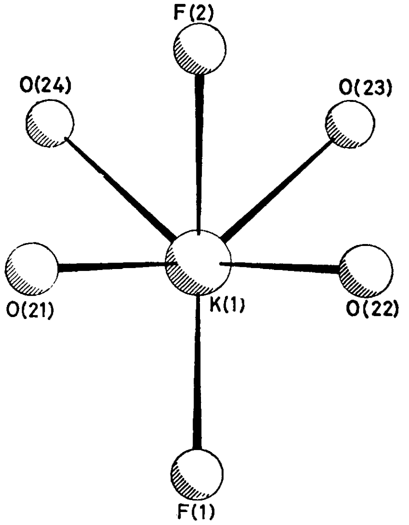

FIGURE 2 The environment of the potassium ion; the O(2) atoms belong to different neighbouring succinic acid molecules

The i.r. spectrum of $KF{\cdot}(CH_2CO_2D)_2$ is almost identical to that of the protonated compound.[9] The eight vibrational modes that can be assigned to the $O\text{–}D \cdots \overline{F} \cdots D\text{–}O$ centre are observed at 330s, 1 050s, 1 078s, 1 365s, 1 460s, 1 900s, 2 200m, and 2 420m cm^{-1}. These are all broad peaks and some are very broad, especially the two centred at 1 365 and *ca.*1 900 cm^{-1}. The only signal among the eight to be noticeably shifted is the one at 1 460 cm^{-1}, which in the spectrum of $KF{\cdot}(CH_2CO_2H)_2$ falls at 1 545 cm^{-1}.[9] This shift can be explained by the nature of the vibration assigned to this band, namely the symmetric stretching mode of the $H \cdots \overline{F} \cdots H$ part of the hydrogen-bond system. In $KF{\cdot}(CH_2CO_2D)_2$ the bond angle at the fluoride ion has widened by 12.5° which should affect the three vibrational modes of the HFH moiety. Thus, its asymmetric stretching mode at *ca.* 1 900 cm^{-1} has broadened considerably, almost obliterating the two carbonyl stretching bands at 1 665 and 1 725 cm^{-1} and its symmetric bending mode in the deuteriated compound has also broadened and shows a slight high-frequency shift from that in the protonated species (1 350 to 1 365 cm^{-1}). For very strong hydrogen bonds an isotope ratio ν_H/ν_D of unity is commonly observed,[10] and this is true of most of the broad hydrogen-bond vibrational modes in the spectra of $KF{\cdot}(CH_2CO_2H)_2$ and $KF{\cdot}(CH_2CO_2D)_2$.

TABLE 4

Bond angles at potassium (°)

F(1)–K–F(2)	130.3(1)	O(21)–K–O(22)	84.4(1)
F(1)–K–O(21)	73.2(1)	O(21)–K–O(23)	140.5(1)
F(1)–K–O(23)	136.8(1)	O(21)–K–O(24)	83.1(1)
F(2)–K–O(21)	70.5(1)	O(23)–K–O(24)	83.2(1)
F(2)–K–O(23)	70.0(1)		

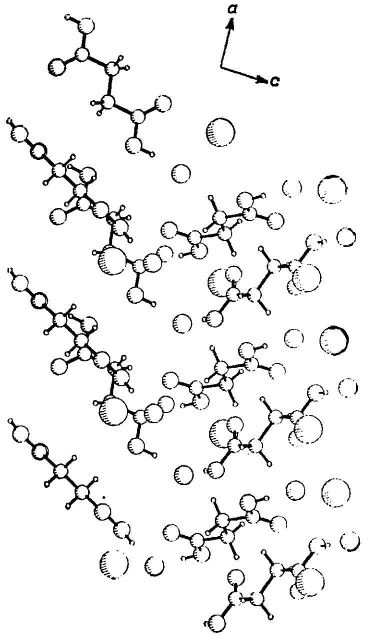

FIGURE 3 Projection down *b* of the crystal structure of $KF{\cdot}(CH_2\text{-}CO_2D)_2$; large non-bonded spheres are K atoms, small non-bonded spheres are F

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