of quencher to the cuvette with a microliter syringe (Et_3SiH, cyclopentene) or by employing stock solutions (PMe_3, ^tBuNC). In the latter case, a measured quantity of gas was condensed into a measured volume of cyclohexane on a high-vacuum line. The absorbances of the solutions for flash photolysis experiments were in the range 0.5–1.0 at 308 nm. Variable-temperature measurements were made by replacing the standard sample holder by an insulated holder mounted on a block through which thermostated water was circulated.

Steady-State Photolysis. Steady-state photolysis experiments were usually performed in NMR tubes in situ. NMR spectra were recorded on a Bruker MSL 300-MHz spectrometer. ^1H spectra were referenced to solvent peaks as follows: C_6D_5H δ 7.13, cyclohexane-d_{11} δ 1.38, methylcyclohexane-d_{13} δ 1.36. ^{31}P spectra were referenced relative to 85% H_3PO_4 at $\delta = 0$.

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Trifluoroacetic Acid Tetrahydrate: A Unique Change from an Ionic to a Molecular Crystal Structure on Deuteration[1-3]

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Abstract: Trifluoroacetic acid has been found from DTA, DSC, and temperature-dependent X–ray powder diffraction to form, besides other stable and metastable hydrates, both an undeuterated (reinvestigation) and perdeuterated stable tetrahydrate. For the undeuterated phase (mp −12 °C) an ionic structure, $(H_5O_2)[(CF_3COO)_2H]\cdot 6H_2O$, has been confirmed by X-ray analysis. In contrast, the perdeuterated tetrahydrate (mp −15 °C) has been found to be molecular, i.e. with $CF_3COOD\cdot 4D_2O$ not only as the empirical but also as the pertinent structural formula. This unprecedented effect of a deuteration is distinct and unmistakable, since there are specific and consistent differences of position not only for certain H and D atoms but also for crucial heavier atoms. In other ways the two structures are strikingly similar, with three of the four water molecules hydrogen-bonded in characteristic layers of identical topologies.

Trifluoroacetic acid, due to the profound (−*I*) effect of the three fluorine atoms on the α-carbon atom, is a carboxylic acid of outstanding strength. The dissociation constant, according to the most recent determination by Raman spectroscopy, is $K = 0.66 \pm 0.25$ mol/L.[4] It is therefore surprising that, by crystal structure analysis of the two hydrates of the acid, only the tetrahydrate, as $(H_5O_2)[(CF_3COO)_2H]\cdot 6H_2O$, was found to be ionic, while the monohydrate, as $CF_3COOH\cdot H_2O$, was found to be molecular.[5] This exceptional 2-fold behavior of an acid as a lower and a higher crystalline hydrate raised the question as to its possible susceptibility to hydrogen/deuterium substitution. Hence it was decided to perform a combined phase and structural analysis on the perdeuterated system of the acid and water as well and, in order to achieve an optimal comparison with the undeuterated one, to reexamine most results for the latter.[5]

Results

Phase Relations. The melting diagram of the undeuterated and perdeuterated (quasi)binary acid–water system, as obtained by DTA and DSC as well as temperature-dependent X-ray powder diffraction, is depicted in Figure 1. The diagrams show the existence of both an undeuterated and perdeuterated mono- and tetrahydrate, each of which melts congruently at reduced temperatures. The perdeuterated tetrahydrate forms a low- and a high-temperature phase. The pertinent transition temperature and all melting points are compiled in Table I, along with additional, metastable phases detected and indications of structural isotype correspondence.

Table I. Undeuterated and Perdeuterated Stable and Metastable Phases of Crystalline Hydrates of Trifluoroacetic Acid

monohydrate mp −39 °C	isotypic	monohydrate metastable	isotypic
monohydrate-d_3 mp −36 °C		monohydrate-d_3 metastable	
tetrahydrate[a] mp −12 °C	isotypic	tetrahydrate metastable	isotypic
tetrahydrate-d_9 low-temp form stable up to −43 °C		tetrahydrate-d_9 metastable, no. 1	
tetrahydrate-d_9 high-temp form[a] mp −15 °C		tetrahydrate-d_9 metastable, no. 2	

[a] The crystal structures of these two phases are dealt with in this paper.

Most of the metastable phases were observed as primary products of crystallization from a glassy state, formed by quenching liquid samples down to the temperature of liquid nitrogen. The second metastable phase of the perdeuterated tetrahydrate was obtained directly from the melt; the undeuterated metastable tetrahydrate was obtained in both ways.

As for the stable phases and in view of the two crystal structures to be dealt with in detail in the following, particular attention is drawn to the fact that the undeuterated tetrahydrate is isotypic with the low-temperature perdeuterated one, while the high-temperature counterpart of the latter has a unique structure.

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(1) Dedicated to Professor Alois Haas on the occasion of his 60th birthday.

(2) This is paper 30 of our series Fluorides and Fluoro Acids and paper 34 of our series Crystal Structures of Acid Hydrates and Oxonium Salts. For papers 29 and 33 see: Mootz, D.; Bartmann, K. *Z. Naturforsch.* **1991**, *46B*, 1659–1663. Mootz, D.; Bartmann, K. *Z. Anorg. Allg. Chem.* **1991**, *592*, 171–178.

(3) Schilling, M. Dissertation in progress Universität Düsseldorf.

(4) Strehlow, H.; Hildebrandt, P. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 173–179.

(5) Mootz, D.; Boenigk, D. *Z. Naturforsch.* **1984**, *39B*, 298–304.

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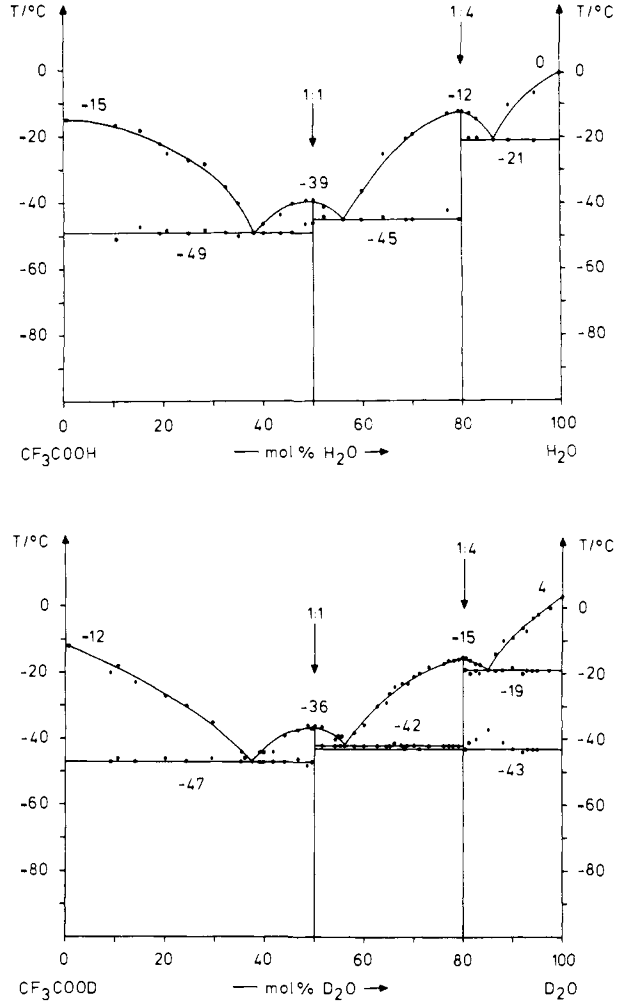

Figure 1. Melting diagrams of the undeuterated (above) and perdeuterated (below) trifluoroacetic acid-water systems.

Table II. Crystallographic Data and Some Numbers Related to the Structure Determinations of Undeuterated (Stable Form) and Perdeuterated (High-Temperature Form) Trifluoroacetic Acid Tetrahydrate

	tetrahydrate	
	undeut	perdeut
mp, °C	-12	-15
measuring temp, °C	-90	-150[a]
cryst system	triclinic	triclinic
space group; Z	$P\bar{1}$; 2	$P\bar{1}$; 2
lattice consts		
a, Å	6.342 (4)	6.316 (5)
b, Å	6.876 (4)	6.928 (5)
c, Å	9.629 (5)	9.480 (7)
α, deg	79.38 (4)	85.94 (6)
β, deg	74.12 (4)	77.30 (6)
γ, deg	71.13 (4)	71.60 (6)
V, Å^3	380.0 (4)	384.0 (5)
calc density, g/cm^3	1.626	1.687
range of 2θ, deg	3-70	3-70
no. of unique data: obsd;[b] all	2817; 3332	2852; 3368
no. of variables in last cycle	152	164
weighting g[c]	0.0004	0.0004
R;[d] R_w[d]	0.043; 0.058	0.034; 0.044
$\Delta\rho$, e/Å^3: min; max	-0.49; 0.45	-0.30; 0.58

[a] Undercooled. [b] $|F_o| \geq 3.92\sigma_F$. [c] g in $w = 1/(\sigma_F^2 + g|F_o|^2)$. [d] Observed reflections only.

Table III. Atomic Parameters with Standard Deviations in Parentheses

atom	x	y	z	U[a]
		Tetrahydrate, Undeuterated		
F1	0.8086 (1)	0.4293 (1)	0.80775 (8)	4.57 (3)
F2	1.1173 (1)	0.2371 (1)	0.68910 (8)	4.60 (3)
F3	0.8308 (2)	0.1177 (1)	0.79013 (9)	5.47 (4)
O1	0.5911 (1)	0.4555 (1)	0.60280 (9)	3.73 (3)
O2	0.9309 (1)	0.2960 (1)	0.46346 (7)	2.59 (2)
O3	0.3741 (1)	0.0320 (1)	0.41656 (8)	2.85 (2)
O4	0.5725 (1)	0.1139 (1)	0.14875 (7)	2.46 (2)
O5	0.8413 (1)	0.3447 (1)	0.16975 (7)	2.64 (2)
O6	1.2637 (1)	0.2579 (1)	−0.02282 (7)	2.58 (2)
C1	0.8900 (2)	0.2830 (1)	0.71844 (9)	2.53 (2)
C2	0.7996 (1)	0.3507 (1)	0.57849 (9)	2.16 (2)
H1[b]	0.538 (6)	0.478 (6)	0.533 (4)	6.1 (8)
H3[b]	0.450 (6)	0.023 (5)	0.466 (4)	5.2 (8)
H31	0.239 (3)	0.111 (2)	0.442 (2)	3.9 (4)
H32	0.443 (3)	0.057 (3)	0.327 (2)	4.5 (4)
H41[b]	0.652 (6)	0.015 (5)	0.116 (4)	2.5 (7)
H42	0.478 (3)	0.179 (3)	0.096 (2)	5.8 (5)
H43[b]	0.659 (4)	0.200 (4)	0.139 (3)	4.8 (6)
H51[b]	0.745 (7)	0.286 (7)	0.179 (5)	3.9 (9)
H52	0.846 (3)	0.335 (3)	0.255 (2)	5.2 (4)
H53[b]	0.969 (5)	0.294 (4)	0.119 (3)	6.1 (7)
H61[b]	1.126 (6)	0.284 (5)	0.036 (4)	1.6 (6)
H62	1.256 (3)	0.368 (3)	−0.078 (2)	5.6 (5)
H63[b]	1.306 (4)	0.161 (4)	−0.070 (2)	4.0 (5)
		Tetrahydrate, Perdeuterated		
F1[b]	0.6945 (1)	0.3866 (1)	0.82793 (8)	2.46 (2)
F2[b]	1.0318 (5)	0.3227 (3)	0.6946 (3)	3.40 (5)
F3[b]	0.8983 (7)	0.0752 (6)	0.7797 (6)	3.98 (9)
F11[b]	0.7234 (5)	0.3921 (3)	0.8150 (2)	5.05 (7)
F21[b]	1.0599 (9)	0.2466 (8)	0.6968 (6)	6.2 (2)
F31[b]	0.847 (1)	0.074 (1)	0.7884 (9)	3.9 (1)
O1	0.54339 (9)	0.2665 (1)	0.61553 (6)	2.52 (2)
O2	0.87880 (9)	0.26367 (9)	0.46809 (6)	2.15 (2)
O3	0.35018 (9)	0.2724 (1)	0.40981 (6)	2.52 (2)
O4	0.56663 (9)	0.12967 (8)	0.14440 (6)	1.87 (1)
O5	0.83891 (9)	0.36028 (8)	0.16247 (6)	1.91 (1)
O6	1.25553 (9)	0.25718 (8)	−0.03006 (6)	1.90 (1)
C1	0.8451 (1)	0.2588 (1)	0.72490 (7)	2.17 (2)
C2	0.7539 (1)	0.2654 (1)	0.58561 (7)	1.70 (2)
D1	0.483 (3)	0.266 (2)	0.537 (2)	5.0 (4)
D31	0.216 (2)	0.258 (2)	0.432 (2)	3.7 (3)
D32	0.416 (2)	0.218 (2)	0.329 (2)	3.2 (3)
D41	0.629 (2)	0.004 (2)	0.118 (1)	2.7 (3)
D42	0.483 (2)	0.171 (2)	0.087 (1)	2.9 (3)
D51	0.758 (2)	0.291 (2)	0.152 (1)	2.8 (3)
D52	0.842 (2)	0.350 (2)	0.249 (2)	3.8 (3)
D61	1.128 (2)	0.288 (2)	0.028 (2)	3.4 (3)
D62	1.247 (2)	0.363 (2)	−0.081 (2)	3.0 (3)

[a] The isotropic displacement parameters U are listed as multiples of 0.01 Å^2 and for the F, O, and C atoms were derived from the anisotropic U_{ij} values by using the expression $U = (1/3)(U_{11}a^2a^{*2} + U_{23}bcb^*c^* \cos \alpha + \ldots)$. [b] Due to disorder, the occupancy factors of these positions are less than unity, viz. 0.5 for H1 and H3, 0.33 for H41–H61, and 0.67 for H43–H63 in the undeuterated structure as well as 0.636 (2) for F1–F3 and 0.364 (2) for F11–F31 in the perdeuterated structure.

The respective phase transition is first order. It is also found in tetrahydrate samples which are not quite fully deuterated. This and the dependency of the transition temperature on the degree of deuteration are shown in the melting diagram of the undeuterated–perdeuterated tetrahydrate system in Figure 2. As one can see, the minimum deuteration for the high-temperature form to be stable corresponds to ca. 77 atom % D. At this composition, the transition temperature is as high as −16 °C and coincides with the temperature of melting. H/D fractionation in the binary system does not appear to be significant for either of these processes.

Crystal Structures. The crystallographic data, as determined by single-crystal X-ray diffractometry, of the undeuterated and the high-temperature perdeuterated tetrahydrate of trifluoroacetic acid are listed in Table II. On the basis of these data alone, also these two phases (cf. the cases in point in Table I) could pass as more or less isotypic, although the difference in one of the unit-cell angles of more than 6° is conspicuous. Both structures have been

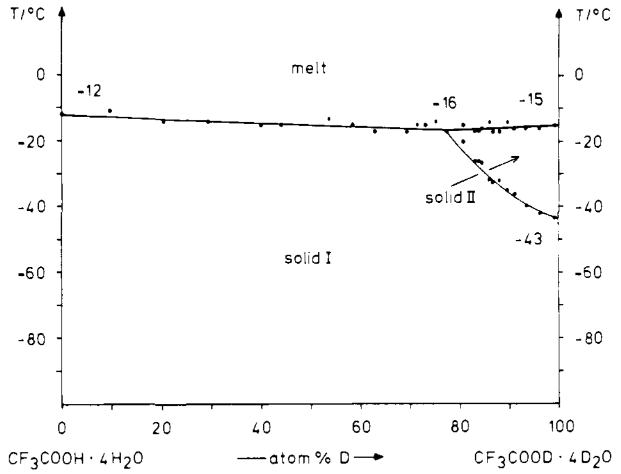

Figure 2. Melting diagram of the undeuterated–perdeuterated trifluoroacetic acid tetrahydrate system. Solids I and II (at 0 and 100 atom % D, respectively) refer to the ionic (I) and molecular (II) structures dealt with in this paper.

determined completely. The atomic parameters obtained are listed in Table III.[6] Single crystals could not be grown for any of the other tetrahydrate phases shown in Table I.

Of the two tetrahydrate structures investigated, the undeuterated one, in confirmation of the previous study,[5] turned out to be ionic, the perdeuterated one, however, to be molecular, with $(H_5O_2)[(CF_3COO)_2H] \cdot 6H_2O$ and $CF_3COOD \cdot 4D_2O$ as the respective structural formulas. The difference between the two structures and the above assignment are obvious from consistent and specific positional differences not only for certain H and D atoms but for decisive heavier atoms as well. In other ways, the structures are strikingly similar, since the resemblance between the unit cells is reflected in the positions and interactions of a number of the remaining atoms.

The structures are drawn in detail in Figure 3. With matching topologies for both, the three water molecules of atoms O4–O6 are hydrogen-bonded in buckled layers parallel to (001) and centered at $z = 0$. The layers comprise two sets of condensed six- and four-membered rings of O atoms and differ only in the arrangement of some of the H and D atoms within the hydrogen bonds. In the undeuterated structure, the four-membered rings can be classified[7] as homodromic; of the six-membered rings, one is homodromic and the other is heterodromic. The assignment is based only on those H atom positions occupied fully or predominantly (the same ones as included in Figure 3). In the perdeuterated structure, with all D atoms ordered, the four-membered rings are heterodromic and both six-membered rings are homodromic. For the six-membered ring which is also homodromic in the undeuterated structure, the polarity of the constituent hydrogen bonds is reversed.

The essential difference between the structures is present in the cell region around $z = {}^1/_2$, which is enclosed by consecutive water layers. As is typical for such ions, the $H_5O_2^+$ cations and $(CF_3COO)_2H^-$ anions are each formed by a strong hydrogen bond, both of which represent, in fact, the shortest ones of the crystal structure. They extend across inversion centers of the space group, with the pertinent proton in each case in an off-centered and therefore statistically only half-occupied position. The cations and anions are linked by another hydrogen bond into unlimited chains along $[2\bar{1}0]$. Adjacent chains are equivalent by translation. In the perdeuterated structure, on the other hand, the two short hydrogen bonds in special positions are elongated to nonbonding O···O distances of 3.738 and 4.093 Å. At the same time, a distinctly weaker new hydrogen bond in a general position is formed by contraction of an O···O distance which at 4.411 Å is nonbonding in the undeuterated structure. The new hydrogen bond is donated from the now neutral CF_3COOD to the analogous D_2O molecule. The CF_3COOD molecule displays the typical difference between the C=O double and the C—OD single bond. Likewise the D_2O molecule is well distinguished from an ionic species by a rather large average O···O distance of the three hydrogen bonds in which it is involved. Endless chains of the two alternating molecules extend along [100], and adjacent chains are equivalent by inversion.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg)

	tetrahydrate	
	undeut	perdeut
C1–F1	1.326 (1)	1.351 (1)
C1–F2	1.331 (1)	1.353 (3)
C1–F3	1.324 (1)	1.309 (4)
C1–C2	1.543 (1)	1.545 (1)
C2–O1	1.265 (1)	1.295 (1)
C2–O2	1.228 (1)	1.214 (1)
O1–H1/D1	0.80 (4)	0.91 (2)
C1–C2–O1	112.2 (1)	111.1 (1)
C1–C2–O2	118.4 (1)	120.1 (1)
O1–C2–O2	129.4 (1)	128.8 (1)
O3–H3	0.75 (4)	
O3–H31/D31	0.85 (2)	0.86 (2)
O3–H32/D32	0.87 (2)	0.84 (1)
O4–H42/D42	0.85 (2)	0.81 (1)
O4–H43/D41	0.91 (3)	0.86 (1)
O5–H52/D52	0.82 (2)	0.82 (2)
O5–H53/D51	0.82 (2)	0.83 (2)
O6–H62/D62	0.84 (2)	0.84 (1)
O6–H63/D61	0.81 (3)	0.84 (1)
H3–O3–H31	114 (3)	
H3–O3–H32	110 (3)	
H31/D31–O3–H32/D32	115 (1)	108 (2)
H42/D42–O4–H43/D41	103 (2)	101 (1)
H52/D52–O5–H53/D51	111 (3)	105 (2)
H62/D62–O6–H63/D61	110 (2)	103 (1)

In each structure, two further hydrogen bonds, involving comparable atoms, connect the chains with the enclosing water layers. These hydrogen bonds are *not* shown in Figure 3.

Stereoscopic drawings of the structures are given in Figure 4. Table IV contains selected bond lengths and bond angles, and Table V lists data on the geometry of the hydrogen bonds. In the listings, atoms with occupancy factors less than ${}^1/_2$ are generally not included.

Discussion

The definite change from an ionic to a molecular structure for an acid hydrate on deuteration is so far unprecedented in the literature and adds to the peculiarity of trifluoroacetic acid hydrates mentioned in the introduction. Since the same change also takes place in the perdeuterated hydrate *alone*, during its phase transition, the concurrent striking retention of many other structural features strongly suggests that the mechanism of the transition is topotactic.

Another interesting aspect of the structures investigated is the layers of condensed small and medium-sized rings of hydrogen-bonded water molecules, which clearly constitute two-dimensional analogues of the three-dimensional host structures of the polyhedral clathrate hydrates. Similar layers are present in some other structures, in part already referred to in the previous work.[5]

In that study, the ionic tetrahydrate structure had been determined with fewer reflections and at a higher temperature, which especially affected the H atom positions and made them appear far less satisfactory than in the present work. The molecular monohydrate structure, on the other hand, had come out so convincingly that here a redetermination, or structural work on the isotypic perdeuterated phase, was *not* considered necessary. Single crystals of the metastable monohydrate, undeuterated or perdeuterated, could not be grown.

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[6] Another analysis, of a crystal deuterated partially (75% D), yielded a unit cell and atomic parameters so similar to those for the undeuterated structure that publishing these data as well was not considered necessary. Listings of pertinent data for this compound are given in the supplementary material.

[7] Saenger, W. *Nature (London)* **1979**, *279*, 343–344.

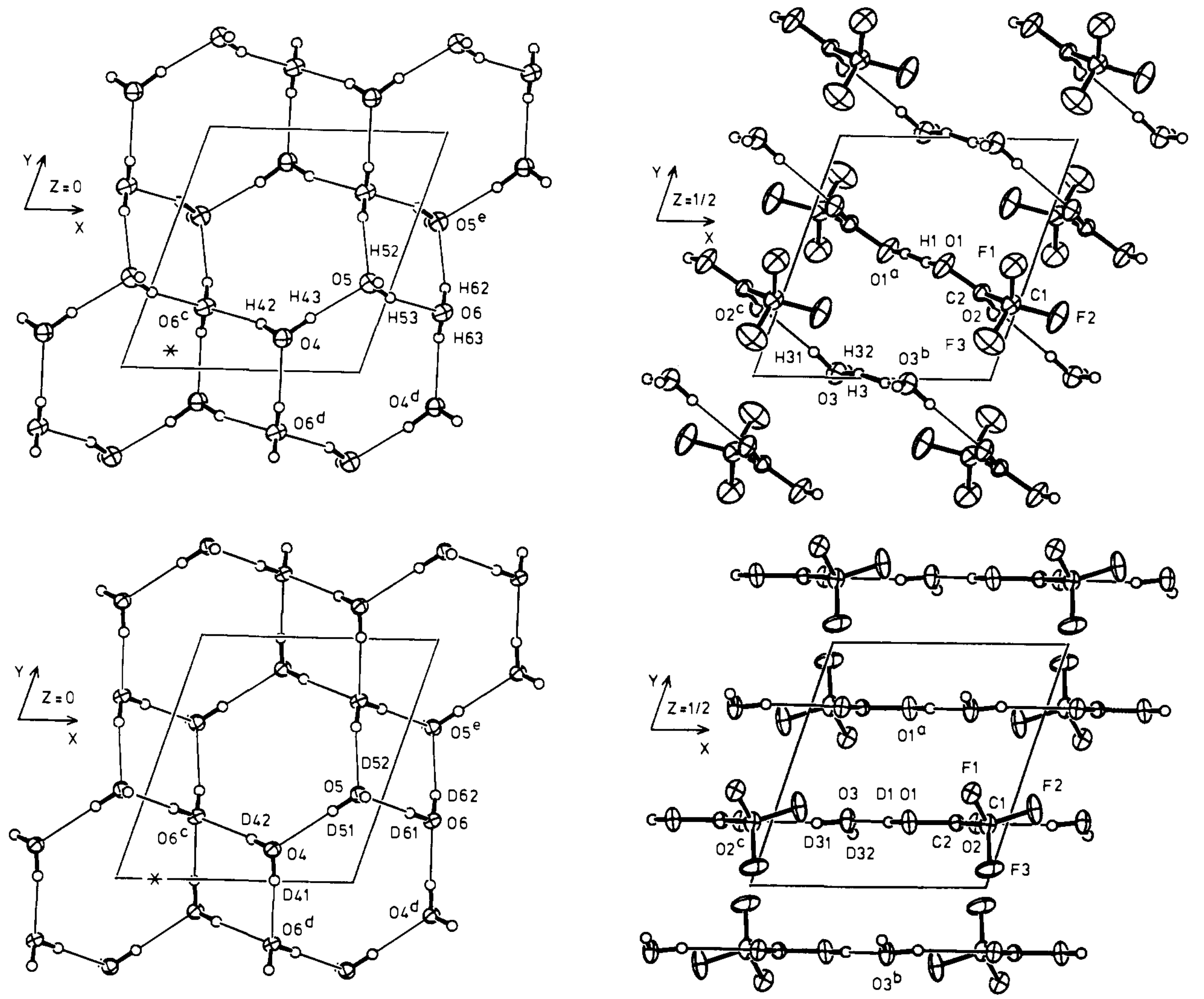

Figure 3. Crystal structures of undeuterated (above) and perdeuterated (below) trifluoroacetic acid tetrahydrate. For clarity, the structures are disassembled to their layers of hydrogen-bonded water molecules (left) and enclosed chains (right) of $H_5O_2^+$ and $(CF_3COO)_2H^-$ ions and D_2O and CF_3COOD molecules, respectively. The ellipsoids are drawn at the 50% probability level. The H atoms within the cations and anions are shown with both their half-occupied positions; the F and H atoms with occupancy factors less than 0.5 are not shown. The asterisk marks the projection of the origin of x and y at $z = {}^1/_2$ down the c^* axis on $z = 0$. The letter codes for symmetry-transformed positions are explained in Table V.

Table V. Geometry of the Hydrogen Bonds

atoms forming H bond	O···O, Å		H/D···O, Å		O–H/D···O, deg	
	undeut	perdeut	undeut	perdeut	undeut	perdeut
O1–H1/H1^a–O1^a	2.445 (2)	no bond^f	1.65 (4)		174 (4)	
O1–D1···O3	no bond^f	2.509 (1)		1.60 (2)		174 (1)
O3–H3/H3^b–O3^b	2.453 (2)	no bond^f	1.71 (4)		172 (4)	
O3–H31/D31···O2^c	2.776 (1)	2.926 (1)	1.94 (2)	2.07 (2)	169 (2)	171 (1)
O3–H32/D32···O4	2.588 (1)	2.677 (1)	1.72 (2)	1.84 (1)	178 (1)	173 (1)
O4–D41/H63^d–O6^d	2.797 (1)	2.756 (1)	2.00 (2)	1.90 (1)	168 (2)	170 (1)
O4–H42/D42···O6^c	2.731 (1)	2.739 (1)	1.90 (2)	1.93 (1)	166 (2)	173 (1)
O4–H43/D51–O5	2.742 (1)	2.728 (1)	1.86 (3)	1.90 (2)	165 (3)	175 (1)
O5–H52/D52···O2	2.973 (1)	2.974 (1)	2.17 (2)	2.17 (2)	169 (2)	170 (1)
O5–H53/D61–O6	2.761 (1)	2.766 (1)	1.96 (3)	1.92 (1)	164 (3)	179 (2)
O6–H62/D62···O5^e	2.798 (1)	2.796 (1)	1.98 (2)	1.97 (1)	164 (2)	166 (1)

[a] $1 - x, 1 - y, 1 - z$. [b] $1 - x, -y, 1 - z$. [c] $-1 + x, y, z$. [d] $2 - x, -y, -z$. [e] $2 - x, 1 - y, -z$. [f] This entry indicates that the O···O distance in the respective structure does not include an H or D atom and accordingly is much too large for a hydrogen bond (see text).

The repeated phase analysis of the undeuterated acid–water melting diagram was again worthwhile, since the tetrahydrate solid now recognized to be metastable (Table I) had previously been taken to be a low-temperature form. In addition, the melting points of the stable phases were found to be 4–5 °C higher than those found in the previous study and in earlier work by Cady and Cady.[8]

Experimental Section

Sample Preparation and Phase Analysis. CF_3COOH (assay 99%, Riedel-de Haën), CF_3COOD (99 atom % D, Janssen Chimica), and D_2O (99.8 atom % D, Aldrich) were used as commercially available. Separate series of storage solutions for setting up the three melting diagrams were prepared by mixing the respective components in varied proportions. The compositions were controlled by titration of the acid, and the degree of deuteration was controlled by ^1H-NMR spectroscopy.

Samples taken from these solutions were subjected to low-temperature DTA and DSC runs on a homemade apparatus and a Mettler DSC30

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[8] Cady, H. H.; Cady, G. H. *J. Am. Chem. Soc.* **1954**, *76*, 915–916.

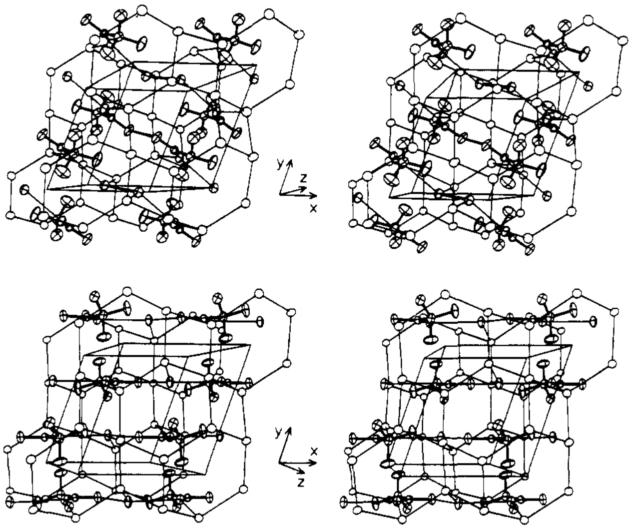

Figure 4. Stereoscopic drawings of the undeuterated (above) and perdeuterated (below) tetrahydrate structures with 50% probability ellipsoids. The chains of $H_5O_2^+$ and $(CF_3COO)_2H^-$ ions and D_2O and CF_3COOD molecules, respectively, near $z = {}^1/_2$ (ellipsoids with equator lines) are shown as enclosed by the two neighboring water layers near $z = 0$ and 1 (ellipsoids without equator lines). All H and D atoms are omitted for clarity.

instrument, respectively. For crucial compositions, the melting diagrams were further clarified on the basis of temperature-dependent X-ray powder diffraction patterns (Enraf-Nonius Guinier-Simon camera). This method also allowed the recognition of structural isotypes in the undeuterated and perdeuterated systems and, along with the thermal analysis and appropriate criteria, the identification of metastable solids besides the stable ones.

Crystal Growth and Structure Analysis. Single crystals for the structure determinations were grown in thin-walled glass capillaries of 0.3 mm diameter. A miniature zone-melting technique[9] using focused heat radiation was applied on a Syntex $P2_1$ diffractometer equipped with a low-temperature device. The X-ray measurements were done in the usual way with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å, ω scan for intensities). Those for the undeuterated crystal, because of a malfunction of the equipment, had to be done at a somewhat higher temperature than previously applied to the perdeuterated sample. Absorption errors were considered negligible, and corrections were not applied. Some numbers related to the structure determinations are given in Table II.

For the undeuterated tetrahydrate, the starting point for the calculations was the structure as determined previously.[5] Only the H atoms were independently located in a difference Fourier map. Five of them were found to be 2-fold disordered, in two symmetric and three asymmetric hydrogen bonds. Best results in the final refinement of all atoms were achieved with fixed occupancy factors of ${}^2/_3$ and ${}^1/_3$ for the latter.

The perdeuterated tetrahydrate structure was solved by direct methods. An orientational disorder of the CF_3 group was treated by introducing and refining a second set of three independent F atoms with the minimum constraint of a common occupancy factor supplementing an analogous factor for the first set of F atoms to unity. This yielded a ratio close to ${}^2/_3$:${}^1/_3$ for the two sets and an average angle for their mutual torsion around the C1–C2 bond of 14.9°. The D atoms were found exclusively ordered and were refined accordingly. The program system SHELXTL[10] was used on an Eclipse S/140 (Data General) minicomputer for the calculations, and a PC version of the program ORTEP II[11] was used to draw the structures.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and further interatomic distances and angles for the undeuterated and perdeuterated compounds and tables of crystallographic data and data related to structure determination, atomic parameters, selected bond lengths and angles, H-bonding parameters, and anisotropic thermal parameters for the 75% deuterated compound (7 pages); listings of structure factors for all three compounds (30 pages). Ordering information is given on any current masthead page.

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