

255. *The Crystal Structure of Ammonium Trifluoroacetate.*

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The crystal structure of ammonium trifluoroacetate has been determined at room temperature from three-dimensional *X*-ray data. Four $\text{CF}_3\cdot\text{CO}\cdot\text{O}\cdot\text{NH}_4$ units crystallise in a monoclinic unit cell of space group $P2_1/a$ and dimensions $a = 12.6$, $b = 8.20$, $c = 4.83$ Å; $\beta = 100.6^\circ$. Refinement by the method of least squares, with allowance for anisotropic thermal motion, and with corrections for rotational oscillations, gave a final disagreement index, R , of 0.113 over 827 planes. The dimensions of the trifluoroacetate ion are: bond lengths $\text{C}(1)\text{--}\text{C}(2) = 1.542 \pm 0.009$ Å; mean $\text{C}(2)\text{--}\text{F} = 1.346 \pm 0.005$ Å, from three independent values; mean $\text{C}(1)\text{--}\text{O} = 1.269 \pm 0.005$ Å (the individual C--O lengths are the same within experimental error); and bond angles $\text{O}(1)\text{--}\text{C}(1)\text{--}\text{O}(2) = 128^\circ 16' \pm 40'$; mean $\text{C}(2)\text{--}\text{C}(1)\text{--}\text{O} = 115^\circ 50' \pm 20'$; mean $\text{F}\text{--}\text{C}(2)\text{--}\text{F} = 107^\circ 24' \pm 20'$; and mean $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{F} = 111^\circ 28' \pm 20'$. All four hydrogen atoms of the ammonium ion are distinguished; they engage in approximately tetrahedral and, at least very nearly, linear $\text{N--H}\cdots\text{O}$ bonds of length 2.87—2.92 Å. These link the structure into a three-dimensional hydrogen-bonded network in which each oxygen atom accepts two hydrogen bonds. The dominant van der Waals contacts are of about 2.6 Å between F and H rather than those between F and F, of which the shortest is 3.1 Å.

AMMONIUM TRIFLUOROACETATE was first obtained by Swarts,¹ following his isolation of the parent acid. Although trifluoroacetic acid has been studied by nuclear magnetic resonance,² infrared spectroscopy,³ electron diffraction,⁴ and other techniques, no *X*-ray structure analysis has been reported for either the acid or its salts in the solid state.

¹ Swarts, *Bull. Classe Sci., Acad. roy. Belg.*, 1922, [5] 8, 343.

² Dunell, Reeves, and Strømme, *Trans. Faraday Soc.*, 1961, 57, 381.

³ Barceló and Otero, *Spectrochim. Acta*, 1962, 18, 1231.

⁴ Karle and Brockway, *J. Amer. Chem. Soc.*, 1944, 66, 574.

The present analysis was originally undertaken as part of a study of the effect on the C-C and C=O bond lengths of replacing CH₃ by CF₃ in unsaturated compounds involving the CH₃·C=O group and which might be expected to display hyperconjugation. Fluorine, with its high electronegativity and a van der Waals radius only slightly larger than that of hydrogen, behaves very differently from other halogens when it replaces hydrogen and there may be a change in bond hybridisation. Instead of causing a small shortening, as predicted by the original hyperconjugation theory, replacement of CH₃ by CF₃ can lengthen the adjacent C-C bond. For trifluoroacetaldehyde, Bowen⁵ suggested an increase to 1.55–1.60 Å; Brockway and Schwendeman⁶ are reported to have obtained 1.54 ± 0.02 Å from electron diffraction measurements in the gas phase, compared with 1.50 ± 0.01 Å (electron diffraction and microwave spectroscopy)⁷ for acetaldehyde itself. Apart from changes in the C-C length with fluorination, there may be a reduction in the C-F bond lengths at this carbon atom, although some of the data quoted as evidence for this⁸ involve estimated standard deviations (e.s.d.'s) comparable with the differences in bond lengths at issue. Determinations both of the C-C bond length and of the dimensions of the CF₃ group itself should be relevant to any discussion of hyperconjugation in these compounds.⁹

EXPERIMENTAL

Crystal Data.—Ammonium trifluoroacetate, C₂H₄F₃NO₂, $M = 131.06$, m. p. 156°. Monoclinic, $a = 12.65$, $b = 8.20$, $c = 4.83$ Å, $\beta = 100.6^\circ$, $U = 492$ Å³, $D_m = 1.78$ (by flotation), $Z = 4$, $D_c = 1.77$, $F(000) = 264$. Space group, $P2_1/a$ (C_{2h}^5 , No. 14). Absorption coefficient for X-rays ($\lambda = 1.542$ Å), $\mu = 20.3$ cm.⁻¹.

Preliminary Crystallographic Measurements.—Colourless tablets and needles of ammonium trifluoroacetate were obtained by recrystallisation from water after treatment of trifluoroacetic acid with an equimolecular quantity of ammonium hydroxide. Most crystals were elongated along the [101] axis and exhibited maximum and minimum refractive indices of 1.49 and 1.39 in the tabular plane. The crystals were slightly deliquescent and so were enclosed in gelatin capsules or thin-walled Lindemann glass tubes for the X-ray intensity photographs; this slightly reduced the accuracy of the visual intensity estimations made by comparison with calibrated strips. Crystal specimens were cut to a radius of 0.4 mm. or less and crystal absorption was neglected. Batches of films interleaved with aluminium foil were exposed with copper K_α radiation as follows: fixed-film rotation and oscillation photographs about [101] on a Unicam S25 camera; equatorial and equi-inclination photographs about the b - (four higher layers) and c -axes (two higher layers) on Unicam and Leeds-Weissenberg goniometers. After correction factors had been applied, correlations between intensities on individual layer lines were made through common reflexions by scale factors dependent on $\sin \theta$. The 841 independent reflections were provisionally scaled by the Wilson method, which gave a value of 3.8 for the Debye factor, $2B$.

Structure Determination.—Since the centrosymmetric space group $P2_1/a$ contains four general positions and there are four CF₃·CO·O·NH₄ units in the cell, eight sets of positional parameters must be found, apart from hydrogen atoms. From a model, it can be seen that the trifluoroacetate ion is likely to give recognisable projections in only very few orientations. Patterson projections were first computed on the Beevers-Lipson strips for the principal zones. In the (xz) projection, Patterson density was low in the band close to $z = \frac{1}{2}$, and attention was concentrated on trial structures in which the C-C bond was close to the b -direction. Structure-factor agreement in the (xz) zone was poor for such structures and did not improve with C-C nearly parallel to the z -direction.

Since ammonium trifluoroacetate is homogeneous with regard to atomic number, an attempt was next made to utilise the large unitary structure factors of $\bar{8}01$, $\bar{8}02$, 604 , 203 , $\bar{1}\bar{2}01$, 1200 , $\bar{4}03$, 401 , and $\bar{1}\bar{2}03$ in applying some Harker-Kasper inequalities,¹⁰ particularly $(U_H \pm U_{H'})^2 \leq (1 \pm U_{H+H'})(1 \pm U_{H-H'})$. Of the ten sign relationships so derived, only one subsequently

⁵ Bowen, *Trans. Faraday Soc.*, 1954, **50**, 452.

⁶ Brockway and Schwendeman, communication reported by Sutton.⁶

⁷ Kilb, Chun Chia Lin, and Wilson, *J. Chem. Phys.*, 1957, **26**, 1695.

⁸ Peters, *J. Chem. Phys.*, 1963, **38**, 561.

⁹ Sutton, *Tetrahedron*, 1959, **5**, 118.

¹⁰ Harker and Kasper, *Acta Cryst.*, 1948, **1**, 70.

TABLE I.

Observed and calculated structure factors ($\times 10$).

	$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c
	0,0,l			1,3,l			2,5,l			3,10,l			5,4,l	
1	469	-486	1	371	-427	0	15	8	0	35	36	1	218	173
2	53	58	2	26	25	1	58	50				2	35	32
3	140	122	3	205	-220	2	98	-87				3	25	-26
4	19	20	4	52	54	3	128	131		4,0,l		4	23	-22
5	58	-61	5	17	-20				0	294	-351			
6	23	23							1	576	-706			
									2	78	63		5,5,l	
	0,1,l			1,4,l			2,6,l					0	33	-25
1	203	-206	0	33	-28	0	126	-141				0	19	-12
2	72	70	1	69	-64	1	171	174						
3	99	-91	2	96	90	2	79	71						
4	27	26	3	127	129	3	21	22						
5	112	121	4	31	-27				0	86	-88		5,6,l	
6	13	8	5	13	-18	0	90	-101	1	185	-147	0	49	-46
						1	27	29	2	150	-128	1	22	12
	0,2,l			1,5,l		2	60	54	3	129	100			
0	265	-324	0	206	244	3	47	-88	5	39	-25	0	48	-48
1	51	-44	1	105	-110							1	56	31
2	221	-232	2	87	82				0	181	-195	2	67	-62
3	70	54	3	77	76	0	48	-49	1	70	53			
4	83	80	4	27	-20	1	98	95	2	242	215		5,8,l	
5	35	-40				2	81	-75	3	43	-40	0	26	-26
						3	29	-35	4	41	-40	1	28	-27
	0,3,l			1,6,l					5	27	-31	2	21	-23
1	352	403	0	140	149									
2	164	-187	1	150	-156	0	20	-18				0	5,9,l	
3	27	-30	2	124	123	1	25	-20	0	70	74	0	20	-19
4	68	76	3	72	-66				1	84	-67	1	47	46
5	11	-3	4	11	2				2	123	-119			
						0	14	13	3	99	101		6,0,l	
	0,4,l			1,7,l		1	10	-11	4	34	-47	0	73	57
0	134	-151	0	45	-53							1	84	-75
1	50	-42	1	29	23				0	67	-60	2	122	104
2	201	-204	2	72	65	0	216	260	1	183	169	3	85	-58
3	212	205	3	32	20	1	230	-235	2	133	127	4	185	-190
4	102	-106	4	15	-16	3	48	-40	3	82	-77		6,1,l	
						4	90	83	4	20	22	0	138	126
	0,5,l			1,8,l					5	15	20	1	150	-113
1	58	56	1	35	41							2	100	95
2	51	51	2	56	-60	0	160	-183	3	101	-89	3	101	-89
3	38	-36	3	26	-25	1	255	-256	4	56	49	4	56	49
4	25	-25				2	292	279	0	175	197			
5	30	-33				3	134	-115	2	25	14		6,2,l	
						4	76	-73				1	83	-68
	0,6,l			1,9,l		5	33	-29				3	58	51
0	186	213	0	46	-45				1	160	-158	4	64	55
1	33	32	1	58	-59				2	56	-46			
2	94	89	2	23	-27				3	81	79	0	66	68
3	24	-23				0	207	235	4	79	-90	1	99	-86
4	45	-38	1	11	-11	1	221	229	5	22	-37	2	26	-35
5	26	22				2	166	-144	0	56	-56	3	125	141
						3	81	79	1	102	-96	4	32	-48
	0,7,l			2,0,l		4	79	-90	2	86	85	5	21	-31
1	25	-21	0	118	-136									
2	64	-62	1	364	418				0	68	-69		6,4,l	
3	18	15	2	217	-203	0	126	-131	1	66	64	0	137	144
4	41	37	3	378	382	1	182	183	2	27	38	1	126	-114
						2	84	-75	0	68	-69	2	13	10
	0,8,l			2,1,l		3	28	26	1	66	64	3	87	-95
0	31	30	0	340	409	4	42	44	2	27	38	4	32	-48
1	69	-68	1	360	-372	5	42	44	0	11	-9	5	21	-31
						0	76	78	0	11	-9			
	0,9,l			3,5,l		1	190	-184	1	24	22		6,5,l	
2	15	-8	3	225	-221	2	91	-73	2	53	-24	0	87	-95
3	27	33	4	30	26	3	124	146				1	21	21
						4	33	-31						
	0,10,l			3,6,l					0	127	127		6,6,l	
0	8	13	0	108	-116				1	167	166	0	119	136
1	24	-24	1	40	27				2	324	-326	1	23	20
2	9	-24	2	87	-63	0	55	56	3	75	-57	2	128	-121
						1	10	11						
						3	13	12						
	1,1,l			2,3,l					0	171	-182	0	94	106
0	177	-207	0	77	76	0	45	43	1	38	26	1	39	-38
1	305	322	1	113	101	1	134	-123	2	79	51			
2	328	356	2	118	-111	2	41	30	3	152	-129		6,8,l	
3	21	8	3	100	-97	3	32	38	4	53	47	1	48	-46
4	116	-105	4	88	104				5	17	20	2	19	18
5	76	86												
	1,2,l			2,4,l					0	93	-104	1	63	51
1	58	-51	0	97	101	1	9	-8	1	205	202		6,9,l	
2	118	-115	1	104	95	2	22	-20	2	183	147		7,1,l	
3	82	68	2	73	-57				3	29	36	0	51	44
4	134	-127	3	169	-169	0	78	80	4	115	138	1	33	-21
5	44	44	4	53	50	1	27	24	5	40	-49	2	26	31
						2	23	-6						

TABLE I. (Continued.)

$ F_o $	F_c	$ F_o $	F_c	$ F_o $	F_c	$ F_o $	F_c	$ F_o $	F_c	$ F_o $	F_c	
0	92	0	87	1	41	45	4	70	-75	1	85	80
1	135	1	215	1	41	45	5	14	15	3	31	33
3	112	3	33	0	36	-33	1	332	-334	1	15	-15
				0	36	-36	2	312	317	2	22	19
				0	42	41	3	15	12	3	106	80
				0	42	41	4	70	-72	4	60	-45
				0	42	41	5	26	30	5	106	80
				0	42	41	1	81	-75	1	195	111
				0	42	41	2	80	-64	2	98	94
				0	42	41	3	101	-106	3	178	-183
				0	42	41	4	30	-34	4	74	-70
				0	42	41	5	30	30	5	33	-25
				0	42	41	1	512	-642	1	391	481
				0	42	41	2	364	403	2	206	-210
				0	42	41	3	45	35	3	76	-66
				0	42	41	4	154	155	4	96	93
				0	42	41	5	154	155	5	25	-22
				0	42	41	1	138	-125	1	23	24
				0	42	41	2	29	13	2	96	94
				0	42	41	3	30	-37	3	100	-105
				0	42	41	4	30	-37	4	20	25
				0	42	41	5	30	-37	5	13	10
				0	42	41	1	13	10	1	31	-24
				0	42	41	2	31	-24	2	24	29
				0	42	41	3	24	29	3	9	8
				0	42	41	4	24	29	4	31	-28
				0	42	41	5	24	29	5	66	57
				0	42	41	1	15	-10	1	17	16
				0	42	41	2	15	-10	2	9	8
				0	42	41	3	15	-10	3	31	-28
				0	42	41	4	15	-10	4	66	57
				0	42	41	5	15	-10	5	17	16
				0	42	41	1	491	-590	1	20	-18
				0	42	41	2	74	-64	2	57	50
				0	42	41	3	190	182	3	9	-4
				0	42	41	4	87	-79	4	73	74
				0	42	41	5	59	-40	5	19	16
				0	42	41	1	321	372	1	70	-70
				0	42	41	2	17	-11	2	21	19
				0	42	41	3	40	23	3	21	19
				0	42	41	4	49	43	4	21	16
				0	42	41	5	63	-61	5	23	16
				0	42	41	1	313	340	1	39	-42
				0	42	41	2	106	-99	2	39	-36
				0	42	41	3	13	14	3	23	16
				0	42	41	4	64	70	4	23	16
				0	42	41	5	25	-31	5	24	-23
				0	42	41	1	202	-199	1	23	-26
				0	42	41	2	224	-237	2	24	-23
				0	42	41	3	83	65	3	20	-25
				0	42	41	4	23	25	4	24	-9
				0	42	41	5	9	-4	5	13	17
				0	42	41	1	62	-54	1	11	26
				0	42	41	2	83	-78	2	384	-307
				0	42	41	3	67	56	3	134	133
				0	42	41	4	44	-43	4	24	-9
				0	42	41	5	36	45	5	13	17
				0	42	41	1	234	260	1	22	-10
				0	42	41	2	142	117	2	109	-107
				0	42	41	3	105	-90	3	149	-159
				0	42	41	4	87	85	4	211	-233
				0	42	41	5	49	48	5	21	18
				0	42	41	1	234	260	1	22	-10
				0	42	41	2	142	117	2	109	-107
				0	42	41	3	105	-90	3	149	-159
				0	42	41	4	87	85	4	21	18
				0	42	41	5	49	48	5	22	-10
				0	42	41	1	212	217	1	47	-44
				0	42	41	2	76	-75	2	15	-18
				0	42	41	3	72	64	3	101	101
				0	42	41	4	23	27	4	66	-67

TABLE 1. (Continued.)

	$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c		$ F_o $	F_c	
	-6,8,l			-7,6,l			-8,4,l			-9,6,l			-10,6,l			-12,4,l		
1	11	9	1	72	-65	4	74	-73	1	39	33	1	108	101	1	37	33	
2	35	-35	2	45	43	5	15	15	2	13	-11	2	29	-11	2	29	25	
3	17	16	3	31	-23				3	11	13				3	46	47	
			4	33	36							1	30	25	4	21	-22	
	-6,9,l			-7,7,l			-8,5,l			-9,7,l			-10,7,l			-12,5,l		
1	41	21	1	49	45	1	92	-88	1	27	30	1	28	28				
2	11	-20	2	12	8	2	22	-16	2	33	23				1	53	54	
			3	21	12	3	17	-14				1	31	32				
			4	21	12	4	17	-16				2	23	-39				
	-7,1,l			-7,8,l			-8,6,l			-9,8,l			-10,8,l			-12,6,l		
1	158	142	1	23	-25	1	68	-73	1	49	45				1	31	-31	
2	127	-127	2	8	-12	2	22	-16				1	64	-59	2	29	-29	
3	41	34	3	56	16	4	29	35				2	72	59				
4	27	34							1	72	69	4	33	-42	1	54	-58	
5	39	63							2	51	-39				2	19	28	
	-7,2,l			-7,9,l			-8,7,l		1	21	18				1	11,2,l		
1	97	75	2	27	-24	2	45	46	4	142	-128				1	94	82	
2	80	-73													1	81	79	
3	25	18													2	19	28	
5	69	43													3	9	22	
	-7,3,l			-8,0,l			-9,1,l			-10,1,l			-11,1,l			-13,3,l		
1	120	113	1	528	-438	1	80	63	1	78	67				1	19	28	
2	67	55	2	381	338	4	45	45	2	108	96	1	44	46	3	9	22	
3	124	-122	3	35	25	5	19	-15	3	61	-63	3	49	58				
4	32	33	4	67	57				4	35	42				2	19	-23	
5	79	-97							5	9	12				3	60	58	
	-7,4,l			-8,1,l			-9,2,l			-10,2,l			-11,2,l			-13,4,l		
1	125	109	1	64	-69	1	52	-44	1	46	42	1	61	-49	2	19	-23	
2	47	38	2	62	69	2	267	297	3	47	-60	3	34	28	3	60	58	
3	66	-51	3	132	123	3	105	-116	4	53	58	4	21	-25	1	49	-54	
4	35	-26	5	26	26	4	68	76	5	47	-60				1	54	-40	
5	16	15				5	20	-20				1	60	-57	2	21	11	
	-7,5,l			-8,2,l			-9,3,l			-10,3,l			-11,3,l			-14,0,l		
1	56	-42	1	13	11	1	22	26	1	62	49	1	27	-27	1	54	-40	
2	77	64	2	62	52	2	164	-165	2	112	-108	2	47	43	2	21	11	
3	53	-48	3	76	-24	4	33	-21	3	48	51	3	12,0,l		3	11	-14	
4	11	11	4	60	-68				4	18	17	4	229	-203				
5	40	21										1	138	-94				
	-7,6,l			-8,3,l			-9,4,l			-10,4,l			-11,4,l			-15,3,l		
1	56	-42	1	56	49	1	33	23	1	102	-97	1	25	-19	2	35	-46	
2	77	64	2	117	-110	2	102	-110	2	77	74	2	41	42	1	17	-25	
3	53	-48	3	66	64	3	11	4	3	54	-56							
4	11	11							4	32	36							
5	40	21																
	-7,7,l			-8,4,l			-9,5,l			-10,5,l			-11,5,l			-15,4,l		
1	56	-42	1	62	55	1	74	-69	1	103	-97	1	113	102	1	17	-25	
2	77	64	2	138	-131	2	20	12	2	53	36	2	53	-73				
3	53	-48	3	39	40	3	56	65										

proved to be invalid. However, the resolution of a series of (xz) Fourier maps computed from sets of about twenty terms, with various sign combinations consistent with the inequalities, was inadequate for identification of the trifluoroacetate group; one difficulty was that, apart from systematic halving, most of the strong $h0l$ reflexions have h a multiple of four. The sign combination which in retrospect came nearest to the correct set included the wrong sign for 400 relative to those of $\bar{1}\bar{2}01$ and $\bar{8}01$. Evidently the sign relationship $[\bar{1}\bar{2}01] = [400][\bar{8}01]$ deduced from the inequality $(U_{400} \pm U_{\bar{8}01})^2 \leq (1 \pm U_{401})(1 \pm U_{\bar{1}\bar{2}01})$ was unjustified, possibly owing to an overestimate for the intensity of $\bar{8}01$. Subsequently, Professor G. A. Jeffrey made some trials with these data on the Pepinsky X-RAC machine, but again without success.

Some years later, the three-dimensional Patterson function was computed, and unsuccessful attempts were made to solve this by minimum-function methods. When, later, the structure had been solved, it became evident that these methods had failed because all inversion peaks lay within other larger peaks and, further, the *effective* scattering powers of the F, O, N, and C atoms, *i.e.*, allowing for thermal motion (see Table 3), were roughly equal.

Ultimately, the Patterson synthesis was solved directly from the $y = 5/30$ section, which exhibited two parallel sets of three collinear peaks, the end peaks each being about 2.9 Å from the central one. Similar triplets were observed in the $y = 0, 10/30$, and $15/30$ sections, and these were interpreted in terms of four atoms, later assigned as O(1), O(2), N, and F(1), all with y co-ordinates near $5/30$. Thus a triplet existed in the direct cell, consisting of a nitrogen atom 2.9 Å from both an O(1) and an F(1) atom in different ions. Since O(2) was only 2.3 Å from O(1), these two atoms were evidently part of one carboxyl group and a search revealed the corresponding carbon C(1) in the section at $y = 7/30$. A space group symmetry transformation of the co-ordinates of the above F(1) yielded another F(1) only 2.3 Å from C(1). With four atoms C(1), O(1), O(2), and F(1) in the trifluoroacetate group now fixed, the assumption of likely geometry for the ion was enough for the positions of the remaining three atoms C(2), F(2), and F(3) to be predicted, and appropriate peaks were found in the Patterson function.

Least-squares Refinement.—The atomic co-ordinates deduced from the Patterson function were refined by 20 cycles of structure factor and least-squares calculations performed on the Leeds University Pegasus Computer with programmes due to Cruickshank, Pilling, *et al.*¹¹ Berghuis atomic scattering factors¹² were used, modified by anisotropic thermal parameters for the heavier atoms (and also isotropic ones for the hydrogen atoms when these were included later); thermal parameters and the scale factor were also refined in the least-squares process. With $|F_o|$ on the scale of Table 1, in which the final F_c and $|F_o|$ are compared, the weighting scheme had the form $w = 1.35 \pm |F_o| + |F_o|^2/23.6$. Only reflexions of measurable intensity were included in the least-squares minimisations. Hydrogen atoms were included when the disagreement index, R , had dropped to 0.13. Since the positional co-ordinates and isotropic vibration parameters of all four hydrogen atoms refined without divergence, the existence of the NH_4 group was confirmed directly.

In the later cycles some weak reflexions were removed because of uncertain sign, and some strong ones because of suspected extinction. In the last cycle, which led to a final R of 0.113 over 827 planes and to the atomic co-ordinates given in Table 2, the biggest change in a co-ordinate was 0.014 Å for z of H(1), *i.e.*, one quarter of its estimated standard deviation, and the average co-ordinate change was one-tenth of an e.s.d.; the average change, Δ/σ , in the anisotropic temperature factors was less than this. The final vibrational parameters are given with

TABLE 2.

Uncorrected monoclinic atomic co-ordinates (x , y , and z) and their nominal estimated standard deviations, σ , in Å.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
F(1)	-3.0785	0.0037	2.8626	0.0043	-2.2040	0.0039
F(2)	-1.0146	0.0040	3.3827	0.0040	-1.3148	0.0037
F(3)	-1.9757	0.0046	-4.0236	0.0033	1.5605	0.0042
O(1)	-0.1180	0.0036	1.6077	0.0040	1.8952	0.0036
O(2)	-2.2457	0.0040	1.3948	0.0036	0.6740	0.0042
C(1)	-1.3628	0.0047	1.9068	0.0044	1.5798	0.0046
C(2)	-1.8502	0.0051	3.0893	0.0051	2.3441	0.0051
N	-1.4787	0.0040	-1.3291	0.0041	0.1996	0.0040
H(1)	-1.814	0.061	-0.651	0.051	0.253	0.056
H(2)	-0.873	0.069	-1.377	0.062	-0.493	0.064
H(3)	-0.859	0.087	-1.565	0.083	1.117	0.087
H(4)	-2.285	0.082	-1.781	0.076	0.028	0.080

TABLE 3.

Vibration tensor components and corresponding estimated standard deviations with respect to crystal axes (in units of 10^{-4} Å²).

Atom	U_{11}	σ	U_{22}	σ	U_{33}	σ	$2U_{12}$	σ	$2U_{13}$	σ	$2U_{23}$	σ
F(1)	340	16	866	26	576	21	-19	36	-256	39	360	32
F(2)	543	22	708	24	402	18	-69	34	363	31	-183	33
F(3)	817	28	356	16	671	23	235	34	172	30	142	41
O(1)	301	17	579	21	359	17	211	31	-9	31	7	31
O(2)	406	20	428	19	498	21	113	31	-188	32	-147	34
C(1)	288	23	358	20	305	21	-15	35	106	34	-28	36
C(2)	294	22	453	24	383	24	-35	38	19	40	60	39
N	288	20	438	20	328	19	51	33	-12	33	35	33

their e.s.d.'s in Table 3. No significance is attached to the wide spread in the isotropic motions assigned to the four hydrogen atoms (Table 7).

Analysis of Molecular Vibrations.—Table 3 shows that the fluorine and oxygen atoms undergo more motion than the carbon atoms, and that the fluorine vibrations have appreciable anisotropy; consequently, the whole trifluoroacetate ion must be undergoing angular oscillations. The establishment of the form of these motions, assumed to be those of a rigid body, is of intrinsic interest and also enables corrections to be made for apparent shortening of bond

¹¹ Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter, in Pepinsky, Robertson, and Speakman, "Computing Methods and the Phase Problem in X-Ray Analysis," Pergamon, London, 1960, p. 32.

¹² Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

lengths.¹³ In the co-ordinate system $X = x + z \cos \beta$; $Y = y$; $Z = z \sin \beta$, the mass centre is at $(-2.078, 2.709, 2.038)$, which is 1.03 \AA from C(1) towards C(2). With this mass centre, the axis of minimum moment of inertia ($I_1 = 213 \times 10^{-40} \text{ g. cm.}^2$) is roughly along the C-C bond; the axis roughly normal to the carboxyl group has $I_3 = 395 \times 10^{-40} \text{ g. cm.}^2$; and the other axis has $I_2 = 325 \times 10^{-40} \text{ g. cm.}^2$. The corresponding moments of inertia about C(1) are 213, 593, and $523 \times 10^{-40} \text{ g. cm.}^2$. The inertial axes, X' , Y' , Z' , about O(1), have direction cosines $(0.416, -0.769, -0.485)$, $(0.827, 0.099, 0.553)$, and $(-0.377, -0.631, 0.678)$ with respect to the crystallographic axes, X, Y, Z .

Vibrational analyses, carried out on the assumption that the angular oscillation was centred, in turn, at the mass centre (M), the carboxyl carbon atom [C(1)], and the mid-point (P) of O(1) ··· O(2) [which is 0.55 \AA from C(1)], showed that the effective oscillation centre is close to C(1). Evidently, the oxygen atoms are being anchored by hydrogen bonds. For the case of C(1) as centre, the components of the symmetric tensors, \mathbf{T} and ω , representing translational and angular motion, respectively, are given in Table 4. Table 5 gives the mean-square ampli-

TABLE 4.

Components, A_{ij} of rigid-body vibration tensors and their estimated standard deviations, \mathbf{T} for translation and ω for rotation (T_{ij} values in 10^{-4} \AA^2 ; ω_{ij} in deg.^2), with respect to inertial axes for anion with C(1) as centre of angular oscillation. (Axis 1 is almost parallel to C(1)-C(2), axis 2 is almost in the plane of the carboxyl group, and axis 3 is almost normal to the carboxyl group.)

	A_{11}	A_{22}	A_{33}	A_{12}	A_{13}	A_{23}
\mathbf{T}	429 ± 21	259 ± 27	267 ± 32	-7 ± 20	6 ± 20	-32 ± 26
ω	72.0 ± 7.8	23.6 ± 2.9	9.5 ± 3.0	-1.1 ± 2.3	-4.4 ± 2.4	1.9 ± 2.5

TABLE 5.

Magnitudes (in \AA^2), and direction cosines ($l, m,$ and n) with respect to inertial axes, of principal axes of translational and oscillational ellipsoids for rigid-body anion having C(1) as centre of angular oscillation.

\AA^2	Translational			Rotational			
	l	m	n	deg.^2	l	m	n
0.023	0.01	0.75	0.66	9.0	0.07	-0.13	0.99
0.043	1.00	-0.05	0.05	72.4	1.00	-0.03	-0.07
0.030	0.07	0.66	-0.75	23.8	0.04	0.99	0.12

tudes and directions of principal axes of the corresponding translation and librational ellipsoids; in each, the directions of greatest amplitude are close to the axis of minimum inertia. In Table 6, individual vibration tensor components, U_{ij} , calculated from the rigid body tensors,

TABLE 6.

Observed and calculated vibration tensor components with respect to inertial axes (in units of 10^{-4} \AA^2).

Atom	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
F(1) ...	565	510	450	480	731	759	-77	-59	247	150	121	88
F(2) ...	508	475	385	391	828	867	122	54	78	63	-131	-116
F(3) ...	534	533	763	763	573	574	-10	-9	-220	-164	-135	-149
O(1) ...	436	466	295	269	529	572	-81	-26	87	29	-84	-30
O(2) ...	401	466	323	267	668	566	23	10	-85	20	-60	-28
C(1) ...	417	429	249	259	310	267	-3	-7	-21	6	-36	-32
C(2) ...	447	429	291	328	404	436	-18	-7	24	6	13	-45

\mathbf{T} and ω (Table 4), are compared with the observed values derived in the least-squares refinement (as in Table 3, but transformed to the axes of inertia). The root-mean-square (r.m.s.) discrepancy of 0.0043 \AA^2 between the two sets of final U_{ij} is about twice the nominal e.s.d. of the U_{ij} ; this suggests that some internal vibrations remain unaccounted for by the rigid-body

¹³ Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

hypothesis. [At an earlier state of refinement the r.m.s. discrepancy was 0.0046 \AA^2 for C(1) as centre, and 0.0077 and 0.0053 \AA^2 for M and P as centre, respectively, showing that the optimum oscillation centre was close to C(1).] Some part of the predominant angular oscillation (Table 5) of 72.4 deg.^2 , or 8.5° r.m.s., about the C-C axis will correspond to an out-of-phase twisting of the trifluoromethyl group relative to the carboxyl group rather than to a rigid-body rotation. However, external and internal vibrations cannot be distinguished by the X-ray results, and the rotational corrections to the atomic co-ordinates will be little affected. There are smaller r.m.s. angular oscillations of 4.9° about the axis perpendicular to C(1)-C(2) in the plane of the carboxyl group, and 3.0° about the axis perpendicular to the carboxyl plane; the largest translational vibration is 0.043 \AA^2 (or 0.21 \AA r.m.s.) in the C(1)-C(2) direction.

The largest rotational correction to an atomic position was 0.017 \AA to F(3); corrections to other atoms were smaller but not negligible [except to C(1)]. Corrected atomic co-ordinates are given in Table 7; the effect on the bond lengths may be gauged from Table 8. No corrections were made for torsional motion of the cation. E.s.d.'s in Tables 8 and 9 have been increased by 25% over the nominal values from the least-squares calculations, in order to allow for neglected off-diagonal terms in the matrix and inaccuracy in the rotational corrections.

TABLE 7.

Final corrected monoclinic co-ordinates (x , y , and z), and the corresponding orthogonal co-ordinates (referred to X parallel to a , Y parallel to b , Z perpendicular to X and Y), all in \AA ; together with isotropic thermal vibration parameters, U , and their e.s.d.'s (in 10^{-4} \AA^2) for hydrogen atoms.

Atom	x	y	z	X	Y	Z	U
F(1)	-3.0915	2.8621	2.6308	-3.5755	2.8621	2.5858	—
F(2)	-1.0079	3.3880	3.5268	-1.6568	3.3880	3.4666	—
F(3)	-1.9771	4.1918	1.5534	-2.2629	4.1918	1.5268	—
O(1)	-0.1058	1.6072	1.9002	-0.4554	1.6072	1.8678	—
O(2)	-2.2563	1.3916	0.6665	-2.3789	1.3916	0.6551	—
C(1)	-1.3628	1.9068	1.5798	-1.6535	1.9068	1.5528	—
C(2)	-1.8523	3.0954	2.3469	-2.2842	3.0954	2.3068	—
N				-1.5154	-1.3291	0.1962	—
H(1)		as in Table 2		1.860	-0.651	0.249	81 ± 126
H(2)			-0.782	-1.377	-0.484	221 ± 155	
H(3)			-1.065	-1.565	1.098	422 ± 220	
H(4)			-2.290	-1.781	0.027	341 ± 197	

TABLE 8.

Dimensions of trifluoroacetate ion, without and with rotational corrections, and their e.s.d.'s (increased by 25% over nominal values as mentioned in text). Lengths in \AA .

Bond	Uncorrected	Corrected	Angle	Uncorrected	Corrected
C(1)-C(2)	1.535	1.542 ± 0.009	O(1)-C(1)-O(2)	$127^\circ 59'$	$128^\circ 16' \pm 40'$
C(2)-F(1)	1.329	1.342 ± 0.008	O(1)-C(1)-C(2)	$116^\circ 32'$	$116^\circ 24' \pm 40'$
C(2)-F(2)	1.340	1.351 ± 0.008	O(2)-C(1)-C(2)	$115^\circ 24'$	$115^\circ 15'$
C(2)-F(3)	1.332	1.346 ± 0.008	Mean O-C(1)-C(2)	$115^\circ 58'$	$115^\circ 50' \pm 20'$
Mean C(2)-F...	1.334	1.346 ± 0.005	C(1)-C(2)-F(1)	$111^\circ 23'$	$111^\circ 10' \pm 30'$
C(1)-O(1)	1.263	1.274 ± 0.008	C(1)-C(2)-F(2)	$113^\circ 34'$	$113^\circ 23'$
C(1)-O(2)	1.252	1.264 ± 0.008	C(1)-C(2)-F(3)	$109^\circ 52'$	$109^\circ 46'$
Mean C(1)-O...	1.258	1.269 ± 0.005	Mean C(1)-C(2)-F	$111^\circ 36'$	$111^\circ 28' \pm 20'$
			F(1)-C(2)-F(2)	$107^\circ 42'$	$107^\circ 49' \pm 30'$
			F(2)-C(2)-F(3)	$108^\circ 9'$	$108^\circ 17'$
			F(1)-C(2)-F(3)	$105^\circ 51'$	$106^\circ 6'$
			Mean F-C(2)-F	$107^\circ 14'$	$107^\circ 24' \pm 20'$

Description of the Structure.—The four crystallographically independent hydrogen atoms of the ammonium ion have a mean apparent N-H distance of $0.92 \pm 0.05 \text{ \AA}$ and are directed roughly tetrahedrally; the smallest H-N-H angle, of 94° , between H(1) and H(4) is not significantly different from the tetrahedral value. Hydrogen bonds of closely similar lengths (see Table 9) link the ammonium ions to the carboxyl oxygens by a three-dimensional system in which each oxygen atom accepts two N-H...O bonds. There are no N-H...F hydrogen bonds. From Fig. 1, the hydrogen bonds N-H(2)...O(1) = 2.87 \AA , N-H(3)...O(1) = 2.91 \AA , and N-H(4)...O(2) = 2.92 \AA can be seen to link ions in sheets roughly parallel to (010), while Fig. 2 shows that the N-H(1)...O(2) = 2.89 \AA bonds connect these sheets in the

TABLE 9.

Intra-cation distances, with their e.s.d.'s (in Å) and angles, and hydrogen-bond lengths (in Å) and angles.

N-H(1) ... 0.76 ± 0.08	N...O(2) ... 2.89 ± 0.006	H(1)···O(2) 2.15 ± 0.08	H(1)-N-O(2) 11°
N-H(2) ... 1.00 ± 0.08	N...O(1) ... 2.87 ± 0.006	H(2)···O(1) 1.87 ± 0.08	H(2)-N-O(1) 4°
N-H(3) ... 1.04 ± 0.11	N...O(1) ... 2.91 ± 0.006	H(3)···O(1) 1.89 ± 0.11	H(3)-N-O(1) 9°
N-H(4) ... 0.91 ± 0.10	N...O(2) ... 2.92 ± 0.006	H(4)···O(2) 2.02 ± 0.10	H(4)-N-O(2) 6°
Mean N-H 0.92 ± 0.05	Mean N...O 2.90 ± 0.003	Mean H···O 1.98 ± 0.05	Mean H-N-O 8°

H-N-H angles

H(1)-N-H(2) 115°	H(1)-N-H(3) 110°	H(1)-N-H(4) 94°
H(2)-N-H(3) 105°	H(2)-N-H(4) 118°	H(3)-N-H(4) 115°
Mean ² H-N-H 109°		

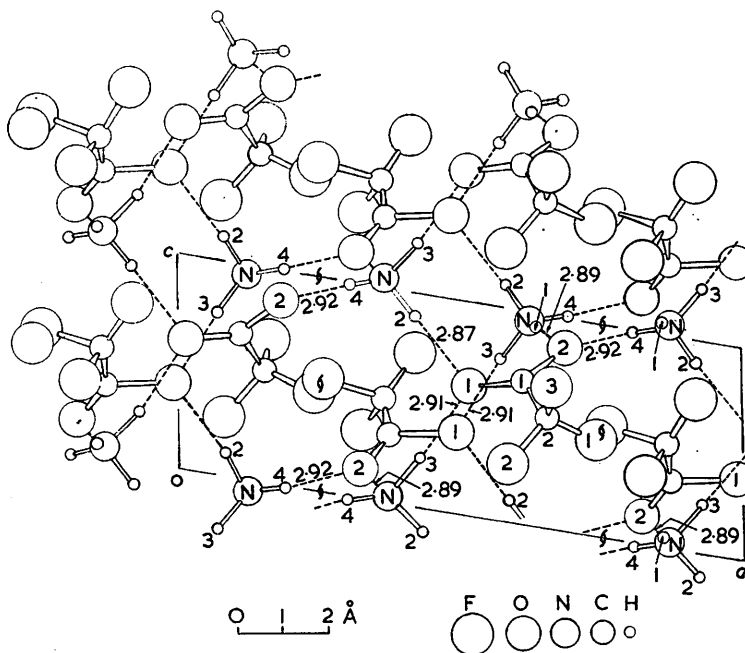


FIG. 1. Projection of structure on (010).

b-direction, each cation being held between two anions. Since the average e.s.d. of a hydrogen atom is 0.09 Å, our results do not determine whether the hydrogen atoms lie exactly on or just off the N...O lines; the O-N-O angles range from 93 to 122°.

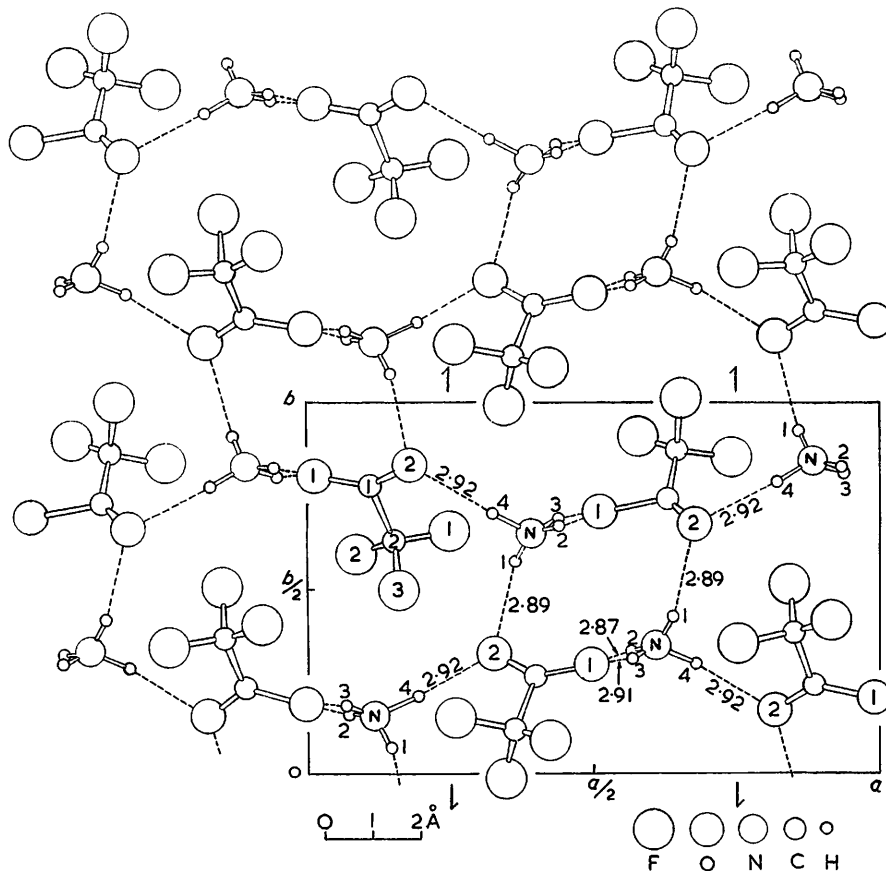
Table 10 shows how closely the fluorines approach the nearest ammonium tetrahedra. Although probably less important than the shorter intra-ionic F...O distances, the several F...H approaches of 2.6–2.8 Å are comparable with the sum of van der Waals radii, 2.65 Å,

TABLE 10.

Shortest interatomic approaches (in Å) between fluorines and ammonium tetrahedra.

Atoms	N	H(1)	H(2)	H(3)	H(4)	Description of F approach
F(1)	3.0	3.0	2.8	—	2.6	On H(1)-H(2)-H(4) base, nearest H(4)
F(2)	3.3	—	3.1	2.6	—	Near H(3) corner [or H(2)-H(3) edge]
F(3)	3.1	—	(3.6)	2.7	2.8	On H(3)-H(4) edge [or H(2)-H(3)-H(4) base]
F(1') ...	2.9	2.7	—	2.8	2.6	On H(1)-H(3)-H(4) base
F(3') ...	3.4	2.9	—	—	2.9	Near H(1)-H(4) edge

whereas the shortest F...O and F...F distances (3.05 and 3.10 Å, respectively) are distinctly greater than the sums of van der Waals radii. (We have taken the radius of hydrogen as 1.3 Å, which is suggested by recently determined hydrocarbon structures.)

FIG. 2. Projection of structure down c -axis.

DISCUSSION

The three crystallographically independent C-F bonds (Table 8) of the trifluoroacetate ion (Fig. 3) are equal, within experimental error; similarly, the differences between the two C=O bonds and between the two O-C(1)-C(2) angles are not significant, but the deviation from 120° of the angles at C(1) is significant. Individual C(1)-C(2)-F and F-C(2)-F angles differ slightly more than would be expected merely from experimental error. All the F-C-F angles are less than the C-C-F angles, an effect in the opposite sense from fluorine-fluorine repulsion. The approximate planarity of the carboxyl group is indicated by the Z' co-ordinates with respect to the inertial axes: C(2) = 0.00; C(1) = 0.00; O(2) = -0.01; O(1) = -0.05 Å; the sum of the angles at C(1) is $359^\circ 45'$. Intra-ionic repulsions do not result in the completely symmetrical distribution of the trifluoromethyl group with respect to the carboxyl group (Table 11) suggested by Fonteyne¹⁴ from the Raman spectrum of the sodium salt; there is probably a six-fold barrier to rotation about C(1)-C(2).

It has been proposed recently that a carbon-carbon single bond between sp^3 and sp^2

TABLE 11.

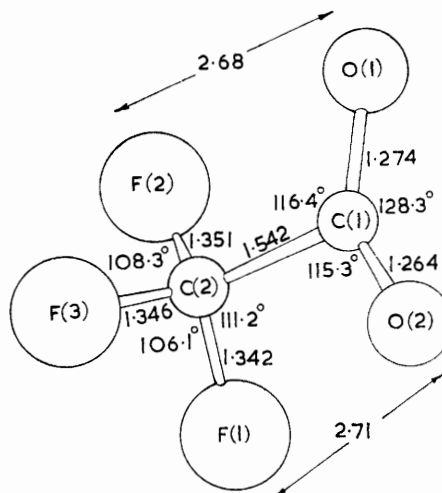
Intra-ionic fluorine-oxygen distances in Å (e.s.d. 0.01 Å).

Atoms	F(1)	F(2)	F(3)
O(1)	3.44	2.68	3.17
O(2)	2.71	3.52	2.94

¹⁴ Fonteyne, *Nederl. Tijds. Natuurk.*, 1942, **24**, 161.

carbon atoms would be expected¹⁵ to have a length of about 1.505 Å compared with 1.544 Å between Csp^3 and Csp^2 ; greater *s* character in the bond tends to reduce the length.¹⁶ Compared with 1.485 ± 0.013 Å for the carboxyl C-C bond of β-succinic acid,¹⁷ however, the C-C lengths of 1.542 ± 0.009 Å in ammonium trifluoroacetate, the 1.55 ± 0.02 Å in the recently refined¹⁸ acetic acid structure,¹⁹ and to a lesser extent the 1.533 ± 0.006 Å in monofluoroacetamide,²⁰ must be regarded as examples of long Csp^3 - Csp^2 bonds, more in accord with an sp_2 -single bond radius of 0.76 Å.²¹ Whilst replacement of one methyl group in ethane by a trifluoromethyl group²² reduces the C-C bond to 1.492 Å, the trifluoromethyl group evidently does not have a shortening effect in the present compound.

FIG. 3. Dimensions of trifluoroacetate ion.



Nor, by comparison with acetic acid, does it have the lengthening effect suggested earlier for acetaldehyde.⁵

The tendency for C-F bond lengths to decrease with increasing numbers of fluorine atoms attached to the carbon atom has been ascribed by Peters⁸ to charge-transfer from carbon to fluorine, and regarded as part of a general shortening of bonds attached to the carbon atom. The C-F length of 1.346 ± 0.004 Å in ammonium trifluoroacetate is considerably shorter than the 1.406 ± 0.005 Å in monofluoroacetamide²⁰ (both compounds have, in the context, long C-C bonds) and significantly shorter than the 1.374 ± 0.006 Å of the difluoro-groups in 1,2-diphenyltetrafluoroethane.²³ It is close to the values listed in Table 12.

TABLE 12.
Bond lengths of C-F, and their e.s.d.'s (in Å) in related structures.

C-F	σ	Compound	Reference
1.350	0.003	CHF ₂ Cl	24
1.348	—	CF ₃ CH ₃	22
1.332	0.008	CHF ₃	25
1.325	0.005	CF ₃ ·NO ₂	26

¹⁵ Brown, *Trans. Faraday Soc.*, 1959, **55**, 694.

¹⁶ Bent, *J. Chem. Phys.*, 1960, **33**, 1259.

¹⁷ Broadley, Cruickshank, Morrison, Robertson, and Shearer, *Proc. Roy. Soc.*, 1959, *A*, **251**, 441.

¹⁸ Cruickshank and Smith, unpublished results.

¹⁹ Jones and Templeton, *Acta Cryst.*, 1958, **11**, 484.

²⁰ Hughes and Small, *Acta Cryst.*, 1962, **15**, 933.

²¹ Sunderaligam and Jeffrey, *Acta Cryst.*, 1962, **15**, 1035.

²² Thomas, Heeks, and Sheridan, *Z. Elektrochem.*, 1957, **61**, 935.

²³ Cruickshank, Jeffrey, and Nyburg, *Z. Krist.*, 1959, **112**, 385.

²⁴ McLay and Mann, *Canad. J. Phys.*, 1962, **40**, 61.

²⁵ Ghosh, Trambarulo, and Gordy, *J. Chem. Phys.*, 1952, **20**, 605.

²⁶ Karle and Karle, *J. Chem. Phys.*, 1962, **36**, 1969.

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The apparent mean N-H distance of 0.92 ± 0.05 Å (uncorrected for torsional motion) shows no sign of a lengthening with hydrogen bonding and is, indeed, somewhat shorter than the value of 1.03 ± 0.02 Å accepted²⁷ for the internuclear distance of a hydrogen-bonded ammonium ion.

We should like to thank Professor G. A. Jeffrey for suggesting the problem, the staff of the Leeds University Computing Laboratory and Dr. Mary R. Truter for help with the calculations, and the D.S.I.R. and the British Rayon Research Association for financial support.

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²⁷ Ondik and Smith in MacGillavry and Rieck, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, p. 270.
