833. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part VII.*[1] *Ammonium Hydrogen Dicinnamate.*

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Ammonium hydrogen dicinnamate, $(Ph{\cdot}CH{:}CH{\cdot}CO_2)_2HNH_4$, is isomorphous with the acid potassium salt and crystallises in the monoclinic system with $a = 37{\cdot}87$, $b = 5{\cdot}84$, $c = 7{\cdot}62$ Å, $\beta = 95{\cdot}5°$, and with four stoicheiometric molecules in the unit cell belonging to the space group $I2/a$. The crystal structure has been determined and refined by partial three-dimensional analysis. High accuracy was not achieved (possibly because of some disorder), but the structure proves to be of the "symmetrical" type: the two (*trans*-)cinnamate residues are crystallographically equivalent and joined by a short hydrogen bond with $O \cdots O = 2{\cdot}51 \pm 0{\cdot}03$ Å, lying across a centre of inversion.

Crystalline acid salts of *trans*-cinnamic acid have been known since 1877.[2] The infrared spectra of the potassium and the ammonium compound indicate that they are acid salts of type *A*.[3] The crystal structure of the former, determined by *X*-rays, confirmed this; refinement was confined to the latter, which is isomorphous and has the advantage of a lower absorption coefficient for *X*-rays.

Experimental

Preparation and Crystal Data.—These acid salts are easily prepared by dissolving an equivalent of cinnamic acid and half an equivalent of either potassium hydroxide or of concentrated aqueous ammonia in warm alcohol and setting the solution aside; suitable crystals can be produced by recrystallisation from 95% alcohol. The face (100) is most prominently

[1] Part VI, Speakman and Mills, *J.*, 1961, 1164.
[2] Perkin (W. H., jun.), *J.*, 1877, **31**, 391; Carrick, *J. prakt. Chem.*, 1892, [ii], **45**, 514; Erlenmeyer, *Ber.*, 1904, **42**, 513.
[3] Part V, Shrivastava and Speakman, *J.*, 1961, 1151.

TABLE 1.

Ammonium hydrogen dicinnamate: calculated structure factors (F_o) and observed structure amplitudes (F_c). (Certain unobserved terms, mentioned in the text, are appended.)

h	k	l	F_o	F_c
0	0	2	36	-34
		4	19	14
		6	25	-22
		8	5	-1
0	1	1	116	-125
		3	35	42
		7	11	8
0	2	0	76	55
		2	21	-16
		4	7	-10
		6	6	-6
0	3	1	34	-34
0	4	0	2	-2
		4	6	5
1	1	0	94	80
		2	44	-61
		4	19	-19
		6	6	5
		-2	92	94
		-4	13	15
		-6	4	-4
		-8	5	-5
1	2	1	36	-38
		3	18	18
		-1	16	-18
		-3	16	-17
		-5	25	23
1	3	0	1	-5
		2	22	23
		4	12	-12
		-2	26	29
		-4	12	-10
1	4	1	14	15
		-1	10	-11
1	5	0	11	-12
		2	7	-11
		-2	6	-7
2	0	0	51	47
		2	63	57
		4	25	21
		6	3	-8
		8	3	-6
		-2	93	89
		-4	24	27
		-6	12	15
		-8	3	2
2	1	1	112	119
		3	25	27
		-3	32	-36
		-5	19	-20
2	2	0	7	12
		2	11	-10
		-2	15	-14
		-4	12	-14
		-6	11	-7
2	3	1	16	17
		3	25	-27
		-1	15	15
		-3	12	-10
2	4	0	7	10
		2	12	-14
		4	7	5
		-2	6	-8
		-4	6	-3
3	1	0	15	15
		2	53	55
		4	32	-30
		8	9	-10
		-2	171	194
		-4	57	-62
		-6	4	3
		-8	5	-3
3	2	1	9	15
		3	49	-51
		5	10	-10
		-1	25	-26
		-3	63	66
		-5	33	-32
3	3	0	17	12
		4	15	-14
		-4	8	13
3	4	3	8	-8
		-3	9	9
3	5	0	13	-10
		2	9	8
		-2	6	-10
3	6	3	16	-12
4	0	0	21	-22
		2	105	-93
		4	24	-22
		6	18	-19
		8	3	-5
		-2	312	294
		-4	64	55
		-8	4	-5
4	1	1	34	42
		3	16	16
		5	5	7
		-1	46	-45
		-3	72	79
		-5	9	-9
		-9	4	-4
4	2	0	6	13
		2	43	-47
		4	20	16
		-2	15	-14
		-4	34	33
		-6	17	-13
4	3	1	34	-36
		-1	20	-17
4	4	2	5	-4
		-2	9	-9
		-4	7	7
5	1	0	51	-56
		2	9	6
5	1	4	7	· 7
		6	5	3
		-4	38	44
		-6	13	9
		-8	5	-0
5	2	1	11	-13
		3	18	-23
		-1	8	-1
		-3	34	-34
5	3	0	2	-1
		-2	5	6
5	4	-1	27	29
5	5	0	23	-18
		2	6	2
6	0	0	104	93
		2	50	-43
		4	6	-10
		6	32	-32
		8	3	1
		-2	51	-50
		-4	75	90
		-6	9	-14
		-8	17	15
6	1	1	29	28
		5	14	-14
		9	4	-6
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		-5	10	12
		-7	16	-14
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		2	19	-19
		4	11	11
		-2	4	2
		-4	18	16
		-6	20	-17
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		-3	7	-7
6	4	2	9	-7
		4	11	13
		-2	5	-2
6	5	1	17	-14
		-1	14	11
6	6	0	3	-3
7	1	0	66	-68
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		4	27	-27
		6	10	-16
		-2	56	59
		-4	54	58
		-8	5	-4
7	2	1	24	-27
		3	28	-30
		5	6	-8
		-1	39	-37
		-3	6	-6
		-5	32	28
		-7	17	-14
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		2	8	-13
		4	12	-8
		-2	19	22
		-4	5	-2
7	4	-1	20	-20
		-3	16	13
7	5	0	15	13
		2	6	2
8	0	0	73	-80
		2	105	-92
		4	36	-37
		6	3	-5
		8	11	13
		-2	71	-75
		-4	69	68
		-6	31	28
		-8	3	2
8	1	1	17	-16
		-1	30	27
		-3	3	0
		-5	27	29
		-9	4	1
8	2	0	7	-7
		2	21	24
		4	11	10
		-2	11	-9
		-4	9	-10
		-6	21	21
8	3	1	8	-12
		3	16	-15
		-1	29	-30
		-3	6	-2
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		2	11	-10
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8	6	0	2	2
9	1	0	17	-16
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		4	19	-21
		6	15	14
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		-1	30	-32
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		-3	35	31
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		2	58	-63
		4	54	-51
		8	5	-8
		-2	69	-79
		-4	4	10
		-6	21	19
		-8	3	-3
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		3	48	-42
		5	8	-6
		7	10	-10
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		-3	15	-15
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13	1	0	46	-46
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		6	10	-14
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		-4	21	-17
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		5	20	-19
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14	2	0	32	-26
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14	3	-1	12	-11
		-3	12	-11
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		-4	18	18
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		2	12	-12
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		4	17	-16
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		4	36	31
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		-8	4	-6
18	1	1	12	-15
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		5	12	13
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		-3	11	-11
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		6	13	-13
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		-4	15	11
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18	3	3	36	38
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19	3	0	4	3
		2	23	23
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19	3	-4	7	-5
19	5	0	3	-7
20	0	0	63	72
		2	4	-4
		4	5	3
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		-6	12	18
		-8	4	-8
20	1	1	10	-11
		3	20	19
		-1	26	23
		-3	28	-27
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		2	13	-16
		4	12	-15
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		2	7	9
21	1	0	29	-27
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		4	7	-9
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		3	13	11
21	3	0	6	-11
		2	27	28
		-2	5	2
		-4	11	-9
21	4	1	30	32
		-1	13	-14
21	5	0	6	7
		-2	10	-6
22	0	0	36	36
		2	10	6
		4	3	3
		-2	6	11
		-4	17	16
		-6	6	-9
		-8	3	2
22	1	1	24	20
		3	23	23
		-3	18	-17
		-7	7	-5
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		·4	9	-10
		-2	14	-17
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22	3	1	28	30
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		-1	11	7
22	4	0	28	23
23	1	0	3	-7
		2	12	-17
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		-8	3	7
23	2	1	14	14
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		6	3	-6
		-2	10	15
		-4	3	1
		-6	3	-6
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24	1	1	27	27
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		-3	13	16
		-5	4	-8
		-7	7	-8
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		4	17	17
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24	4	0	10	8
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		-2	16	17
		-4	16	19
		-6	4	4
26	1	1	29	30
		5	5	6
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26	2	0	7	6
		2	9	-9
26	3	3	11	-9
		-1	13	12
27	1	0	34	-34
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27	2	1	14	16
		3	11	-11
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		-2	9	10
27	4	1	10	12
		-3	10	11
28	0	0	16	19
		2	16	-11
		6	3	-7
		-2	17	-19
		-4	10	10
		-6	3	-3
28	1	1	10	-6
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		-5	12	10
28	2	2	16	14
		4	9	7
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29	1	0	7	9
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		4	6	-7
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29	4	-3	12	14
30	0	0	2	0
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		6	7	-0
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		-4	11	11
		-6	13	5
30	1	-1	27	21
		-5	10	8
30	2	0	6	7
31	1	0	7	9
		2	20	19
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31	2	-3	9	9
31	3	0	1	6
32	0	0	15	-16
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		4	4	-4
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		-6	3	1
32	1	-1	20	-18
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		-5	4	4
33	1	0	6	-11
		2	13	13
		-2	8	9
		-4	10	-9
		-6	9	5
33	2	1	16	11
		-1	15	-15
33	3	0	1	0
		4	5	-6
		-2	7	-5
34	0	0	15	18
		2	4	3
		4	3	6
		-2	13	-14
		-4	14	-16
34	2	0	19	14
35	1	0	17	14
		-2	7	8
35	2	1	6	-8
36	0	0	2	3
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		-2	11	-14
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36	1	-3	14	-17
		-5	12	10
36	2	0	2	6
37	1	0	3	4
		-2	7	7
		-6	4	0
37	2	-1	6	3
38	0	0	4	7
		2	3	5
		-2	16	16
		-4	3	-5
38	1	-1	2	-8
		-5	3	3
38	2	0	1	0
39	1	0	2	-2
		-2	7	7
40	0	0	4	10
		2	3	2
		-2	3	-2
40	1	-5	5	-7
41	1	0	1	2
42	0	0	4	7
		-2	3	5
		-4	3	8
42	1	-5	2	-0
42	2	0	4	-3
44	0	-2	3	4
45	1	0	2	-3

h	k	l	F_o	F_c
0	6	0	2	-6
1	2	7	3	-4
2	6	2	4	-7
5	1	-2	2	-6
5	2	-5	3	-5
5	4	3	5	-6
6	6	2	4	6
7	1	8	3	8
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9	4	1	6	-8
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11	1	-8	3	6
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12	3	-1	5	-9
13	2	-5	3	-7
13	4	1	6	-9
14	2	6	3	12
16	1	-7	3	-4
16	2	4	4	-4
16	4	-2	4	8
17	1	-4	4	6
17	3	-4	4	8
18	5	3	5	7
20	2	-6	3	6
20	5	-1	6	-10
22	0	6	2	-8
22	2	-6	3	-4
23	2	5	3	-7
23	4	3	5	7
24	1	3	5	9
24	2	-6	3	-7
24	3	-3	5	-8
24	5	-1	6	8
26	2	-6	3	-6
26	4	-2	4	10
27	5	0	2	-6
28	3	3	5	-7
28	3	-3	5	9
30	1	5	3	-6
31	2	3	5	-10
32	3	-1	6	-10
34	0	-6	2	6
35	1	-4	3	6
36	0	-6	2	-12
37	1	2	4	8
38	2	-2	4	8.

developed, and there is usually elongation in the *c*-direction. The following parameters were derived from photographs taken with copper K_α-radiation.

Potassium hydrogen dicinnamate, $KH(C_9H_7O_2)_2$; $M = 334{\cdot}4$; monoclinic prismatic, $a = 37{\cdot}7$, $b = 5{\cdot}74$, $c = 7{\cdot}65$ Å, $\beta = 93{\cdot}5°$ $U = 1652$ Å^3, $D_m = 1{\cdot}34$, $Z = 4$, $D_c = 1{\cdot}34$; space group as below.

Ammonium hydrogen dicinnamate, $NH_4H(C_9H_7O_2)_2$; $M = 313{\cdot}3$; monoclinic prismatic, $a = 37{\cdot}87 \pm 0{\cdot}12$, $b = 5{\cdot}84 \pm 0{\cdot}02$, $c = 7{\cdot}62 \pm 0{\cdot}03$ Å, $\beta = 95{\cdot}5°$ ($\pm 3'$), $U = 1677$ Å^3, $D_m = 1{\cdot}25$, $Z = 4$, $D_c = 1{\cdot}240$, absorption coefficient for (Cu) *X*-rays = 8·4 cm.$^{-1}$. Absent reflexions, (*hkl*) when $h + k + l$ is odd, (*h*0*l*) when either *h* or *l* is odd, and (0*k*0) when *k* is odd: space group, either *Ia* (No. 9) or *I*2/*a* (No. 15); the latter was indicated by statistical tests and seems to be confirmed by the success of the analysis. This choice of axes gives as equivalent positions, $(000 \pm \frac{1}{2}\frac{1}{2}\frac{1}{2}) \pm (xyz;\ x, -y, \frac{1}{2} + z)$, and implies that the ammonium ions and the acidic hydrogen atoms effectively occupy special positions, either on digonal axes or at centres of inversion.

Structure Analysis.—Intensity data were derived visually from multiple-film exposures. The structure of the potassium salt was determined from the Patterson projections along the *b*- and *c*-axes. For refinement effort was concentrated on the ammonium isomorph, initially by two-dimensional methods (R. F. B.) and subsequently by three-dimensional (H. H. M.), 687 independent reflexions being measured—about half of those theoretically accessible. There was a rapid fall-off of intensity with sin θ and this was the principal reason for the meagre coverage of reciprocal space. Absorption was small and no correction was made for it.

From a value of 28·4%, based on parameters from the two-dimensional work, three-dimensional refinement ultimately reduced *R* to 13·4% for all observed terms. However, convergence was slow, there being need for several cycles of F_o- and F_c-synthesis with back-shifts, for an $(F_c - F_o)$-synthesis, and for some dozen cycles of least-squares analysis with anisotropic vibrational parameters. In the later cycles hydrogen atoms were included, though not refined; their positions corresponded to appropriate peaks in the $(F_o - F_c)$-synthesis, and were chosen so as to lie 1·04 Å from their respective carbon atoms. In the final stages those unobserved reflexions whose $|F_c|$-values suggested that they should have been observable were included with amplitudes equal to half the minimum locally observable. Computations were made with the DEUCE crystallographic programmes [4] developed by Rollett and by Sime, the detailed least-squares procedure being as described in Part VI.[1] The atomic scattering curve for NH_4^+ was constructed so as to have the value 10 at $\sin^2\theta = 0$ and to converge on to a normal [5] curve for nitrogen at $\sin^2\theta = 0{\cdot}25$. Observed structure amplitudes and calculated structure factors are given in Table 1.

Description of the Structure and Discussion

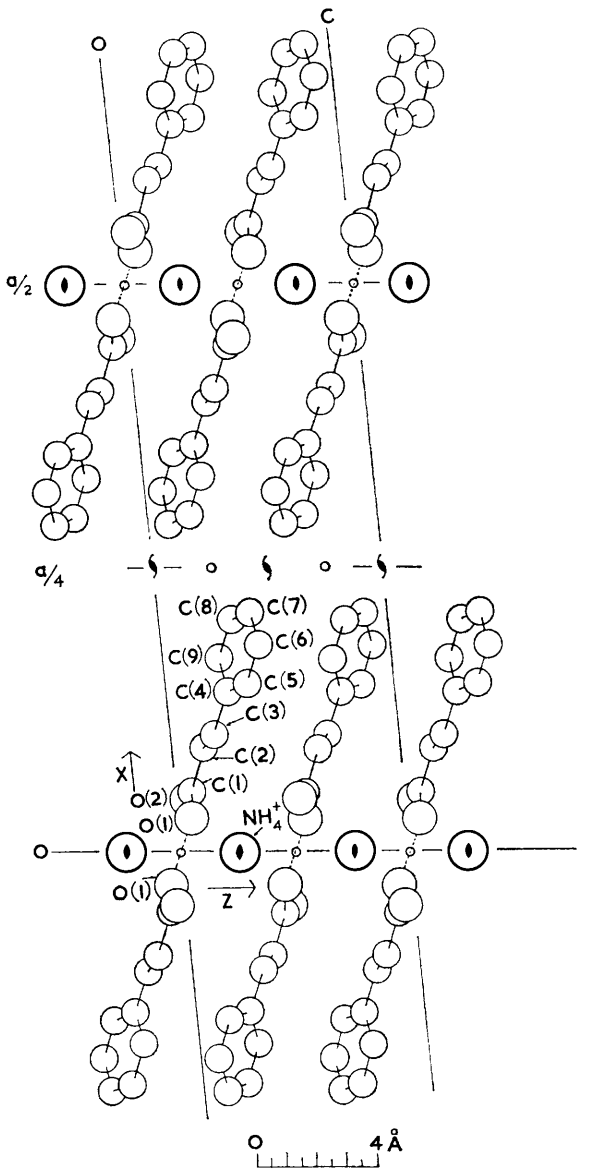
The Figure gives a general view of the structure, as well as the numbering of the atoms. Hydrogen atoms are numbered by reference to their carbon atoms. Co-ordinates appear in Table 2, and thermal parameters in Table 3 as tensor components for the mean-square amplitudes of vibration. For the reason implied above the positional parameters for hydrogen lack special significance; their thermal parameters correspond to isotropic $B = 8{\cdot}0$ Å^2.

The slowness of the refinement, the high values of many vibrational parameters, the notable anisotropy of some vibrational ellipsoids, and the fact that certain molecular dimensions are anomalous despite a reasonably satisfactory *R*-value suggest that some subtle disorder may affect atoms C(1), C(2), C(3), and O(1) in particular. (The effect may resemble that obtaining in butyric acid described by Strieter and Templeton.[6]) Therefore the standard deviations (σ) derived from the least-squares residuals were probably optimistic and have been doubled. For all bond-lengths σ is then about 0·025 Å (except for the hydrogen bond which lies in a special situation), and for angles σ is about 1·5°.

[4] " Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961.

[5] *E.g.*, " International Tables for *X*-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962.

[6] Strieter and Templeton, *Acta Cryst.*, 1962, **15**, 1240.



The crystal structure of ammonium hydrogen dicinnamate seen in its *b*-axial projection.

The carbon atoms of the benzenoid ring do not deviate significantly from the plane,

$$0{\cdot}2376X' + 0{\cdot}4684Y - 0{\cdot}8510Z' = 0{\cdot}0987,$$

where X', Y, and Z' are in Å as in Table 2. The four atoms of the ethylenic group are also coplanar, but in a plane inclined at some 17° to that of the ring, *viz.*:

$$0{\cdot}3241X' + 0{\cdot}1902Y - 0{\cdot}9267Z' = 0{\cdot}0651,$$

whilst the three atoms of the carboxyl group define

$$0{\cdot}3202X' + 0{\cdot}1303Y - 0{\cdot}9383Z' = 0{\cdot}0579,$$

TABLE 2.

Ammonium hydrogen dicinnamate: fractional (x, y, z, $\times 10^4$) and orthogonal (X', Y, Z', in Å, $\times 10^3$) co-ordinates. (X' and Y are, respectively, parallel to x and y, and Z' is perpendicular to both; the numbering of atoms is shown in the Figure.)

Atom	x	y	z	X'	Y	Z'
NH_4^+	0000	4747	2500	−0183	2772	1896
O(1)	0302	0772	0509	1105	0451	0386
O(2)	0466	−2849	0405	1736	−1664	0307
C(1)	0531	−0837	0683	1960	−0489	0518
C(2)	0921	−0404	1407	3386	−0236	1067
C(3)	1034	1552	1895	3776	0906	1438
C(4)	1414	2039	2616	5165	1191	1984
C(5)	1480	4055	3540	5348	2368	2685
C(6)	1821	4644	4233	6585	2712	3211
C(7)	2099	3140	3995	7657	1834	3030
C(8)	2033	1155	3098	7474	0675	2350
C(9)	1694	0581	2380	6242	0339	1805
H[C(5)]	1270	5170	3690			
H[C(6)]	1870	6170	4920			
H[C(7)]	2360	3550	4540			
H[C(8)]	2240	0040	2930			
H[C(9)]	1650	−0980	1700			
H[C(2)]	1090	−1750	1460			
H[C(3)]	0870	2820	1820			

TABLE 3.

Ammonium hydrogen dicinnamate: vibrational parameters (Å², $\times 10^4$; see text).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
NH_4^+ ...	649	658	658	—	—	31	C(5)	669	749	599	−9	25	50
O(1)	798	777	1282	−60	−157	88	C(6)	828	719	536	−43	0	14
O(2)	604	1027	875	−19	−23	32	C(7)	664	890	542	−79	−1	13
C(1)	554	1049	670	−90	−46	29	C(8)	609	755	580	9	9	39
C(2)	983	1112	671	−131	−12	91	C(9)	629	781	444	−74	−8	34
C(3)	798	1181	517	−202	24	86	All H ...	1008	1010	1012	—	—	48
C(4)	644	868	444	−69	45	18							

TABLE 4.

Ammonium hydrogen dicinnamate: bond-lengths (Å) and angles (for estimated standard deviations see the text).

C(1)–O(1)	1·28	C(5)–C(6)	1·39	O(1)–C(1)–O(2)	125°	C(5)–C(6)–C(7)	119°
C(1)–O(2)	$1{\cdot}21_5$	C(6)–C(7)	1·40	O(1)–C(1)–C(2)	122	C(6)–C(7)–C(8)	120
C(1)–C(2)	1·55	C(7)–C(8)	1·36	O(2)–C(1)–C(2)	113	C(7)–C(8)–C(9)	122
C(2)–C(3)	1·26	C(8)–C(9)	1·39	C(1)–C(2)–C(3)	122½	C(8)–C(9)–C(4)	119
C(3)–C(4)	1·52	C(9)–C(4)	$1{\cdot}38_5$	C(2)–C(3)–C(4)	124	C(9)–C(4)–C(5)	119
C(4)–C(5)	1·38	O(1) ··· O(1^I)	2·51	C(3)–C(4)–C(5)	118	C(9)–C(4)–C(3)	123
				C(4)–C(5)–C(6)	121	C(1)–O(1) ··· O(1^I)	110

a plane turned through a further 2°. The difference between the latter two planes is probably not significant; but significance certainly attaches to the twisting of the atoms O(1)–C(3), themselves roughly coplanar, out of the plane of the benzene ring.

Bond-lengths and angles are listed in Table 4. The bonds C(1)–C(2) and C(3)–C(4) are longer than would be expected for single bonds between sp^2-hybridised atoms, whilst C(2)–C(3) is short for a double bond; these discrepancies are unlikely to be significant. The C–O distances in the carboxyl group resemble those found in other acid salts, where the group represents a hybrid between neutral carboxyl and carboxylate ion; but the angles C(2)–C(1)–O(1) and C(2)–C(1)–O(2) are anomalous. As is implied by the space group, the two cinnamate residues of the formula are crystallographically equivalent, being related by a centre of symmetry. This confirms the spectral indication that this is an acid salt of type *A*. The acidic hydrogen atom links these residues by a short hydrogen bond that is formally symmetrical, with O ··· O = 2·51 ± 0·03 Å.

Each ammonium ion lies on a two-fold axis and makes contacts with six oxygen atoms belonging to different acid residues. These atoms lie at the corners of a very distorted

octahedron: two are O(2) atoms at 2·86 Å and are above the ammonium ion (*i.e.*, at a greater value of y); two are O(2) atoms at 2·91 Å and rather below the ion; two are O(1) atoms at 3·05 Å and further below the ion. The four hydrogen atoms of the ion were not located, but they are presumed to occupy randomly a larger number of positions. There are no abnormal intermolecular contacts.

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