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Crystal Structure of DL-Tryptophan Formate

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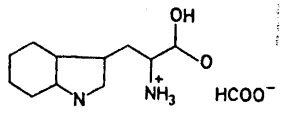
The crystal structure of DL-tryptophan formate has been determined by X-ray methods using 2346 reflections recorded by counter methods. The crystals are monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 11.23_7$ Å; $b = 6.72_8$ Å; $c = 16.01_3$ Å; $\beta = 96.2_9°$. The structure was refined to a conventional R-factor of 0.051; estimated standard deviations are 0.002 – 0.003 Å in interatomic distances and 0.15° in angles.

The 3-indolylmethyl part of the molecule is planar and the alanine moiety exists in the extended form with the acid group *anti* relative to the aromatic part. The crystals are built up by layers of molecules; within each layer there is an extensive network of hydrogen bonds whereas the layers are held together by van der Waals forces.

The crystal structure of tryptophan formate has been determined as part of the series of structure determinations of tyrosine and tryptophan derivatives being carried out in this laboratory. Preliminary results have previously been published.[1] In the present paper a more detailed account of the structure is given.



EXPERIMENTAL

Plate formed single crystals were formed by diffusion of diethyl ether into a solution of DL-tryptophan in formic acid.

Oscillation, Weissenberg and precession photographs indicated monoclinic symmetry. Systematically absent reflections were $h0l$ for l odd and $0k0$ for k odd; the space group is thus $P2_1/c$.

Unit cell dimensions were determined from diffractometer measurements on twelve general reflections and their Laue-symmetric equivalents. A manual Picker four-circle diffractometer was used with Cu$K\beta$ radiation ($\lambda = 1.3922$ Å). The computer program applied for the least-squares calculations as well as the computer programs used for the structure investigation are described in Ref. 2.

Three-dimensional intensity data were recorded on an automatic Picker four-circle diffractometer using graphite crystal monochromated Mo$K\alpha$ radiation. The crystal had dimensions $0.50 \times 0.25 \times 0.06$ mm^3 and was mounted with the [302] direction along the diffractometer ϕ-axis. The $\omega - 2\theta$ scanning mode with a 2θ scan speed of 1° min^{-1} was applied through the scan range of 0.5° below $2\theta(\alpha_1)$ to 0.5° above $2\theta(\alpha_2)$. Background counts were taken for 20 sec at each of the scan range limits. The take-off angle was 4° and the temperature was kept constant at 18°C. The intensities of three standard reflections were measured for every 100 reflections of the data set. They showed slow variation and also a small net decrease, and the data was accordingly adjusted. The standard deviations in the intensities were taken as the square root of the total counts with a 2 % addition.

The measurements included 2757 unique reflections with $\sin\theta/\lambda$ less than 0.7; 2346 had net intensity larger than $2\sigma(I)$ and were regarded as observed whereas the remaining reflections were excluded from the further calculations.

The intensity data were corrected for Lorentz and polarization effects.

Atomic form factors used were those of Hanson *et al.*[3] for oxygen, nitrogen, and carbon, and of Stewart *et al.*[4] for hydrogen.

CRYSTAL DATA

DL-Tryptophan formate (DL-α-ammonium-β-indolepropionic acid formate), $C_{11}H_{13}N_2O_2.CHO_2$, monoclinic. $a = 11.237(0.003)$ Å; $b = 6.728(0.002)$ Å; $c = 16.013(0.003)$ Å; $\beta = 96.29(0.01)°$. $V = 1203.4$ Å^3, $M = 250.26$, $F(000) = 528$, $Z = 4$. $D_{obs} = 1.37$ g cm^{-3}, $D_{calc} = 1.381$ g cm^{-3}. Absent reflections: $h0l$ when l is odd, $0k0$ when k is odd, space group $P2_1/c$.

STRUCTURE DETERMINATION

Preliminary scale and isotropic thermal vibration factors were calculated using Wilson's statistical method and unitary structure factors were computed. Three origin defining reflections were given positive sign and three additional reflections were assigned symbolic signs. The symbolic addition procedure[5,6] yielded signs or symbols for nine additional structure factors (acceptance probability 97 %). The fifteen unitary structure factors were now used for sign determination by the application of Sayre's equation[7] for each of the eight sign combinations of the three symbols. Signs for 165 structure factors were evaluated in each case followed by a Fourier synthesis.

In one of the Fourier maps the position of the indole part and the carbon atom directly bonded to it could readily be found and one Fourier refinement based on these atoms yielded information of the coordinates of all non-hydrogen atoms. Further Fourier refinements followed by several cycles of least squares refinement with anisotropic thermal parameters gave a conventional R-factor of 0.08. Most of hydrogen atoms were assigned coordinates from stereochemical considerations, the hydrogen atoms of the hydroxyl and ammonium groups were localized from difference Fourier maps. Final least squares refinement calculations with individual isotropic thermal parameters for hydrogen atoms yielded an R-factor of 0.051 ($R_w = 0.047$). A total difference Fourier map showed no electron density exceeding 0.3 e Å^{-3}.

A comparison of the observed and calculated structure factors is given in Table 1; the parameters for non-hydrogen atoms are listed in Table 2 and for hydrogen atoms in Table 3. The anisotropic temperature factor is given by

Table 1. Observed and calculated structure factors. The columns are h, k, l, $10|F_o|$ and $10\,F_c$

h	k	l	$10\|F_o\|$	$10\,F_c$
-15	0	8	92	-81
-15	0	2	86	-81
-14	0	4	52	45
-14	0	6	95	-83
-13	0	14	21	-17
-13	0	12	41	39
-13	0	10	22	25
-13	0	6	62	-57
-13	0	4	27	-27
-13	0	2	35	36
-12	0	2	58	-59
-12	0	4	53	-46
-12	0	6	54	-49
-12	0	10	36	-34
-12	0	12	59	56
-12	0	14	61	-64
-12	0	16	37	33
-11	0	16	40	30
-11	0	10	29	-31
-11	0	8	71	-68
-11	0	6	110	105
-11	0	4	189	-180
-11	0	2	91	-89
-10	0	2	77	75
-10	0	4	74	76
-10	0	6	68	-65
-10	0	10	21	21
-10	0	14	65	66
-10	0	16	21	16
-10	0	18	32	-26
-9	0	12	174	177
-9	0	10	40	41
-9	0	8	77	76
-9	0	6	16	12
-9	0	4	257	247
-9	0	2	19	24
-8	0	2	264	261
-8	0	6	38	-37
-8	0	8	268	264
-8	0	10	22	-14
-8	0	12	17	18
-8	0	14	36	32
-8	0	16	32	-32
-8	0	18	104	96
-8	0	20	27	-39
-7	0	20	29	28
-7	0	18	28	23
-7	0	16	56	-55
-7	0	14	59	58
-7	0	12	224	-228
-7	0	10	116	116
-7	0	8	43	50
-7	0	6	165	-164
-7	0	4	54	-52
-7	0	2	75	79
-6	0	2	387	394
-6	0	4	289	-280
-6	0	6	224	-209
-6	0	8	189	188
-6	0	10	156	-162
-6	0	12	145	-149
-6	0	14	45	44
-6	0	16	189	187
-6	0	18	118	-118
-6	0	20	24	24
-5	0	20	34	32
-5	0	18	103	109
-5	0	16	55	58
-5	0	14	70	78
-5	0	12	19	-21
-5	0	10	184	179
-5	0	8	422	415
-5	0	6	294	-299
-5	0	4	45	48
-5	0	2	409	397
-4	0	2	250	236
-4	0	4	560	552
-4	0	8	100	98
-4	0	10	419	441
-4	0	14	257	265
-4	0	16	115	119
-4	0	20	83	83
-4	0	22	31	27
-3	0	22	23	-22
-3	0	20	78	75
-3	0	18	19	-15
-3	0	16	98	99
-3	0	14	40	43
-3	0	12	26	18
-3	0	10	275	293
-3	0	8	90	90
-3	0	6	183	186
-3	0	4	870	857
-3	0	2	1061	-1078
-2	0	2	674	687
-2	0	4	165	-180
-2	0	6	391	415
-2	0	8	188	-185
-2	0	10	15	5
-2	0	12	157	162
-2	0	14	180	188
-2	0	16	168	-178
-2	0	18	90	-94
-2	0	20	45	49
-1	0	20	61	63
-1	0	18	77	-82
-1	0	12	211	224
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-1	0	8	204	211
-1	0	6	765	821
-1	0	4	246	241
-1	0	2	288	302
0	0	2	509	-515
0	0	4	326	-331
0	0	6	578	564
0	0	8	423	429
0	0	10	227	229
0	0	14	18	-9
0	0	16	109	114
0	0	18	58	-55
0	0	20	34	28
0	0	22	67	62
1	0	20	49	-42
1	0	18	31	38
1	0	16	131	129
1	0	14	66	64
1	0	12	258	-262
1	0	10	92	86
1	0	8	61	-51
1	0	6	835	827
1	0	4	334	-339
1	0	2	394	370
1	0	0	518	535
2	0	0	302	-309
2	0	2	42	-50
2	0	4	438	-433
2	0	6	138	-135
2	0	8	173	156
2	0	10	254	-250
2	0	12	63	-62
2	0	14	41	45
2	0	20	49	-49
3	0	18	88	78
3	0	14	201	-215
3	0	12	382	394
3	0	10	72	-70
3	0	8	400	-395
3	0	6	63	-67
3	0	4	307	302
3	0	2	389	376
3	0	0	445	-458
4	0	0	338	330
4	0	2	46	37
4	0	4	69	67
4	0	6	433	416
4	0	8	108	-109
4	0	10	95	100
4	0	12	404	422
4	0	14	88	-94
4	0	16	113	-119
4	0	18	123	114
5	0	18	104	91
5	0	16	59	-63
5	0	12	20	11
5	0	10	173	179
5	0	8	32	-27
5	0	6	226	233
5	0	4	322	315
5	0	2	87	-88
5	0	0	188	190
6	0	0	59	-58
6	0	2	99	-100
6	0	4	118	-127
6	0	6	149	148
6	0	8	69	68
6	0	10	193	-202
6	0	12	48	53
6	0	16	83	-87
6	0	18	77	-59
7	0	16	53	-55
7	0	12	66	-66
7	0	10	249	-262
7	0	8	60	64
7	0	6	40	-39
7	0	4	137	-134
7	0	2	112	113
7	0	0	176	-173
8	0	0	64	69
8	0	2	65	73
8	0	4	51	-48
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8	0	8	64	63
8	0	10	21	-14
8	0	12	53	-60
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8	0	16	36	-29
9	0	16	67	55
9	0	12	71	-75
9	0	10	33	26
9	0	8	34	-35
9	0	6	168	-168
9	0	4	212	220
9	0	0	31	-32
10	0	0	232	-237
10	0	4	111	-110
10	0	6	28	-29
10	0	8	78	-76
10	0	10	59	56
10	0	12	81	-77
11	0	8	54	-56
11	0	6	236	-238
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11	0	2	31	31
11	0	0	211	-208
12	0	0	65	67
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13	0	6	25	12
13	0	4	69	-77
13	0	2	105	99
14	0	0	36	-41
14	0	2	46	-48
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11	1	5	23	-25
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11	1	8	63	-64
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4	1	14	119	128
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4	1	11	26	-24
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4	1	8	122	124
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-1	1	6	65	-63
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-1	1	13	88	88
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-2	1	14	57	58
-2	1	12	143	140
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-2	1	6	118	112
-2	1	5	522	-506
-2	1	4	180	-175
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-3	1	14	73	71
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-3	1	22	88	80
-4	1	21	50	47
-4	1	19	33	-34

Table 1. Continued.

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-4	1	13	226	228	-11	1	6	96	- 98	-7	2	9	24	- 8	-1	2	10	148	- 148	5	2	10	102	109
-4	1	12	131	- 130	-11	1	9	63	61	-7	2	8	34	42	-1	2	9	263	262	5	2	9	46	- 50
-4	1	11	171	- 167	-11	1	10	132	24	-7	2	7	44	38	-1	2	8	299	- 370	5	2	8	221	- 222
-4	1	10	86	- 83	-11	1	11	56	- 58	-7	2	6	101	- 104	-1	2	7	320	- 306	5	2	7	22	12
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-4	1	4	87	82	-12	1	13	53	- 52	-6	2	1	278	274	0	2	2	787	- 774	5	2	1	309	304
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6	4	16	42	-	34	6	5	0	176		175	-2	5	10	111	-	112	-10	6	1	44	-	39	1	6	8	27	-	20
6	4	17	50	-	48	5	5	0	108		104	-2	5	9	31		31	-10	6	2	54		55	1	6	7	102		100
7	4	11	31	-	34	5	5	1	147		153	-2	5	8	154		163	-10	6	3	38	-	43	1	6	6	94		95
7	4	9	37	-	35	5	5	2	71		73	-2	5	7	148		155	-10	6	5	51	-	48	1	6	5	31		29
7	4	8	126	-	134	5	5	3	62	-	71	-2	5	6	24	-	34	-9	6	5	33	-	26	1	6	4	168	-	168
7	4	7	33	-	30	5	5	5	209		212	-2	5	5	150	-	146	-9	6	8	51		43	1	6	3	136	-	136
7	4	6	32		21	5	5	6	93		100	-2	5	4	55		49	-9	6	7	62	-	56	1	6	2	44		52
7	4	5	87	-	87	5	5	7	31	-	33	-2	5	1	19	-	16	-9	6	2	42		36	1	6	1	281		282
7	4	2	186	-	187	5	5	8	82		79	-3	5	1	97		99	-9	6	1	110	-	111	1	6	0	159		161
7	4	1	122	-	122	5	5	10	43	-	45	-3	5	2	120	-	124	-8	6	1	33	-	36	2	6	0	46		47
8	4	0	73		73	5	5	11	75		71	-3	5	3	103		105	-8	6	4	52		45	2	6	1	76		80
8	4	1	101	-	97	5	5	12	55		52	-3	5	4	64		67	-8	6	5	56		51	2	6	2	56	-	55
8	4	2	230	-	239	5	5	13	71		62	-3	5	5	29	-	37	-8	6	6	30	-	13	2	6	4	90	-	116
8	4	3	62	-	61	5	5	14	32	-	31	-3	5	6	49		46	-8	6	7	36	-	37	2	6	5	76	-	71
8	4	4	58		59	4	5	14	82		80	-3	5	8	153		159	-8	6	8	45		40	2	6	6	77		76
8	4	6	128		123	4	5	12	62		53	-3	5	9	98		98	-8	6	9	40	-	37	2	6	7	197		204
8	4	7	57	-	56	4	5	11	56		57	-3	5	10	68	-	73	-8	6	10	59	-	49	2	6	8	119	-	120
8	4	8	80	-	85	4	5	9	26	-	3	-3	5	11	38		43	-7	6	11	44		33	2	6	9	65		64
8	4	11	38	-	28	4	5	8	116	-	111	-3	5	12	41	-	44	-7	6	12	59	-	60	2	6	10	47		50
8	4	13	26		26	4	5	7	80		74	-3	5	13	63		59	-7	6	13	39	-	31	2	6	11	111	-	100
9	4	13	27		15	4	5	6	186		190	-3	5	14	107		107	-7	6	14	50		46	2	6	12	41		37
9	4	11	52	-	45	4	5	5	145		144	-3	5	15	50		44	-7	6	7	53	-	49	2	6	14	66	-	56
9	4	9	25	-	35	4	5	4	154		156	-3	5	16	59	-	56	-7	6	5	26		28	2	6	15	50		46
9	4	7	56		51	4	5	3	147	-	147	-3	5	17	30	-	26	-7	6	4	25	-	39	2	6	16	69		61
9	4	6	38	-	34	4	5	1	22	-	28	-4	5	17	60		55	-7	6	3	79		84	3	6	15	87		76
9	4	5	36	-	30	4	5	0	167		167	-4	5	15	80		75	-7	6	1	51	-	59	3	6	12	35		36
9	4	4	33		24	3	5	1	126	-	130	-4	5	14	34		26	-6	6	1	89	-	99	3	6	11	107	-	99
9	4	3	110	-	104	3	5	2	306	-	304	-4	5	13	65		59	-6	6	2	57	-	50	3	6	9	60		65
9	4	2	31		25	3	5	3	23	-	27	-4	5	12	77		83	-6	6	3	55	-	55	3	6	7	61		60
9	4	1	61	-	52	3	5	4	87		91	-4	5	11	47	-	50	-6	6	4	55	-	51	3	6	6	49	-	50

Table 1. Continued.

3	6	5	113	- 111	11	6	0	43	- 42	1	7	0	85	90	-4	7	1	35	29	0	8	8	39	- 28
3	6	3	68	67	10	7	1	31	30	1	7	1	53	- 55	-5	7	1	36	35	0	8	9	44	41
3	6	2	119	- 120	9	7	0	49	38	1	7	2	56	47	-5	7	3	35	- 43	1	8	11	28	- 25
3	6	1	50	- 44	9	7	1	40	42	1	7	3	38	- 36	-5	7	7	49	- 45	1	8	10	29	- 8
4	6	0	76	- 74	9	7	3	82	- 77	1	7	4	29	24	-5	7	6	32	- 27	1	8	6	43	45
4	6	1	41	37	9	7	4	36	26	1	7	5	52	51	-5	7	9	44	- 42	1	8	5	27	- 22
4	6	2	74	- 69	9	7	5	34	37	1	7	6	34	- 40	-5	7	10	44	- 40	1	8	4	43	- 44
4	6	3	104	103	8	7	6	37	39	1	7	7	67	- 69	-6	7	11	57	53	1	8	1	25	- 26
4	6	4	53	50	8	7	4	28	- 27	1	7	10	54	55	-6	7	10	43	40	2	8	0	37	- 32
4	6	5	22	- 10	8	7	2	48	42	1	7	11	36	- 42	-6	7	9	46	- 46	2	8	1	27	17
4	6	6	44	- 37	8	7	0	28	27	1	7	14	102	- 92	-6	7	4	48	40	2	8	2	58	58
4	6	7	38	- 43	7	7	1	27	- 24	0	7	14	36	- 29	-6	7	2	28	- 15	2	8	4	31	- 26
4	6	8	31	35	7	7	2	33	35	0	7	11	41	- 38	-6	7	1	27	18	2	8	6	45	41
4	6	11	35	34	7	7	3	82	83	0	7	10	39	33	-7	7	2	53	45	2	8	8	27	- 15
4	6	10	36	40	7	7	5	51	45	0	7	9	28	23	-8	7	5	54	60	2	8	9	34	- 24
4	6	13	46	36	7	7	7	33	- 31	0	7	7	112	- 109	-8	7	3	34	- 28	2	8	10	31	16
4	6	14	41	35	6	7	10	57	46	0	7	6	34	- 23	-8	7	1	38	36	3	8	5	36	31
5	6	12	68	58	6	7	8	58	45	0	7	5	77	- 79	-9	7	0	43	- 35	3	8	3	68	- 64
5	6	12	116	106	6	7	7	30	- 36	0	7	2	83	88	-10	7	4	36	- 31	3	8	1	52	45
5	6	11	78	62	6	7	5	48	47	-1	7	1	65	- 61	-10	7	3	37	46	3	8	0	86	75
5	6	9	49	43	6	7	3	35	36	-1	7	2	59	57	-10	7	2	42	- 43	4	8	1	74	69
5	6	8	116	114	6	7	2	32	- 29	-1	7	3	95	100	-7	8	2	58	- 60	4	8	2	66	- 66
5	6	7	137	132	6	7	1	98	- 90	-1	7	5	134	- 132	-6	8	1	79	91	4	8	5	29	- 14
5	6	1	30	23	5	7	1	83	- 76	-1	7	6	44	- 43	-6	8	4	57	46	4	8	6	44	- 36
5	6	0	65	- 63	5	7	2	65	- 61	-1	7	7	73	74	-5	8	6	75	79	5	8	5	29	- 20
6	6	0	32	- 23	5	7	3	57	- 50	-1	7	8	63	47	-5	8	8	66	- 63	5	8	3	42	- 39
6	6	1	88	- 70	5	7	4	46	- 43	-1	7	9	72	- 62	-5	8	3	42	39	5	8	2	52	- 50
6	6	2	102	102	5	7	5	69	59	-1	7	14	54	48	-5	8	2	124	115	5	8	1	44	- 40
6	6	4	39	43	5	7	7	65	- 66	-2	7	13	63	54	-5	8	1	40	19	5	8	0	47	- 40
6	6	5	79	73	4	7	13	45	36	-2	7	12	36	- 26	-4	8	1	27	- 39	6	8	0	69	- 64
6	6	6	144	144	4	7	11	36	- 32	-2	7	11	88	- 80	-4	8	3	52	47	6	8	1	39	- 32
6	6	7	31	- 20	4	7	10	62	- 59	-2	7	7	131	127	-4	8	5	46	- 41	6	8	6	32	23
6	6	8	42	- 39	4	7	8	70	- 67	-2	7	5	100	- 107	-4	8	6	71	- 66	7	8	2	33	31
6	6	9	72	63	4	7	6	27	23	-2	7	4	44	- 33	-4	8	8	35	32	7	8	1	29	- 7
6	6	10	32	26	4	7	4	32	- 38	-2	7	2	87	- 89	-4	8	10	28	25	7	8	0	28	- 28
6	6	11	88	81	4	7	3	138	- 131	-2	7	1	129	138	-3	8	11	35	- 31	4	9	0	42	- 40
6	6	12	54	55	4	7	2	61	- 58	-3	7	1	41	45	-3	8	10	63	59	3	9	1	34	31
7	6	5	99	97	4	7	0	27	20	-3	7	2	103	- 107	-3	8	8	49	- 47	3	9	2	30	29
7	6	4	69	69	3	7	1	41	- 44	-3	7	3	87	- 84	-3	8	7	49	- 41	2	9	4	29	- 27
7	6	2	31	29	3	7	2	27	- 20	-3	7	5	74	- 77	-3	8	6	51	43	2	9	2	38	30
7	6	1	36	- 31	3	7	3	31	- 31	-3	7	7	94	87	-3	8	4	51	- 43	1	9	1	29	19
8	6	4	82	80	3	7	6	29	- 21	-3	7	8	26	- 22	-3	8	2	41	- 32	0	9	0	41	39
8	6	6	99	- 94	3	7	9	36	- 29	-3	7	9	29	31	-3	8	1	33	- 28	0	9	4	29	- 23
8	6	7	27	23	3	7	10	54	- 55	-3	7	10	27	- 27	-2	8	1	28	- 25	0	9	3	43	- 46
9	6	5	29	9	3	7	13	30	36	-3	7	11	84	- 80	-2	8	10	53	- 45	-1	9	1	32	- 21
9	6	5	31	- 15	2	7	13	36	29	-3	7	14	39	31	-1	8	10	64	- 61	-1	9	2	27	27
9	6	4	49	- 40	2	7	12	35	- 31	-4	7	12	32	23	-1	8	2	82	- 78	-1	9	4	52	- 40
9	6	3	44	33	2	7	9	25	- 26	-4	7	11	39	- 36	-1	8	1	27	- 29	-2	9	5	40	- 40
9	6	2	26	30	2	7	7	39	45	-4	7	10	80	- 73	0	8	6	72	76	-2	9	3	31	- 21
10	6	0	54	- 51	2	7	5	50	- 53	-4	7	8	34	- 32	0	8	2	59	- 64	-2	9	2	41	38
10	6	3	33	- 34	2	7	4	53	53	-4	7	5	78	- 71	0	8	4	45	- 54	-3	9	1	42	39
10	6	4	32	27	2	7	3	70	64	-4	7	4	46	- 40	0	8	5	23	31	-4	9	2	62	- 59
10	6	5	87	81	2	7	2	27	- 22	-4	7	3	82	- 84	0	8	6	24	36	-4	9	1	58	55
10	6	6	29	- 32	2	7	1	144	- 146	-4	7	2	42	39	0	8	7	26	- 19					

$$\exp -(B11h^2+B22k^2+B33l^2+B12hk+B13hl+B23kl).$$

Magnitudes and directions of the principal axes of the ellipsoids of vibration are given in Table 4. The analysis of the thermal parameters showed that the methylindole part of the molecule to a good approximation can be regarded as a rigid body. The positional parameters of the atoms of this group were corrected for librational effects. No corrections were performed for the rest of the molecule.

Standard deviations in bond lengths and angles were calculated using the correlation matrix from the last least-squares refinement cycle but ignoring the standard deviations in cell parameters. For distances and angles the standard deviations were found to be 0.002 – 0.003 Å and 0.15°, respectively, except for the bond lengths involving hydrogen where the standard deviation is 0.02 Å.

DISCUSSION

Interatomic distances and bond angles are listed in Table 5; bond lengths and angles are shown in Fig. 1 in which the numbering of the atoms is also indicated. The molecular arrangement and hydrogen bonding system are illustrated in Figs. 2 and 3.

Table 2. Fractional atomic coordinates and thermal parameters with standard deviations ($\times 10^5$) for non-hydrogen atoms.

Atom	x	y	z	$B11$	$B22$	$B33$	$B12$	$B13$	$B23$
N1	24678	50370	27235	842	1459	437	−6	216	−438
	12	20	9	13	35	7	36	15	25
C2	20728	42927	19447	671	1431	391	−198	88	71
	13	24	10	14	40	7	41	16	29
C3	26182	25425	18144	511	1356	298	−396	106	−88
	12	23	9	11	27	6	36	13	26
C4	41920	6009	28133	646	2393	380	486	97	−261
	14	27	10	14	49	8	36	16	34
C5	48286	6908	36010	757	3765	470	1170	−57	−16
	16	34	12	16	69	9	60	19	43
C6	47011	22972	41392	819	4776	338	213	−157	−427
	15	37	10	17	82	8	64	18	44
C7	39342	38305	39079	833	3248	347	−520	154	−833
	15	31	10	16	62	7	55	17	37
C8	32855	37392	31182	751	1815	334	−397	183	−430
	13	25	9	13	42	7	40	15	30
C9	34028	21394	25630	490	1550	300	−251	162	−245
	12	23	9	12	39	6	37	13	27
C10	24047	12857	10433	702	1686	275	−546	90	−79
	13	25	9	14	42	6	42	15	28
C11	16571	−5641	11741	644	1465	221	−290	−2	−2
	13	24	8	13	38	6	39	13	25
C12	13522	−17159	3597	767	1368	235	−453	60	1
	12	23	8	14	39	6	41	14	25
O13	22810	−21321	−197	747	3169	393	−620	209	−1016
	9	19	6	10	40	5	35	12	25
O14	3278	−21431	197	749	2667	312	−882	63	−545
	8	19	6	11	36	5	33	11	22
N15	5117	−321	15104	710	1491	227	−476	71	−80
	10	18	7	11	33	5	33	12	20
C16	12109	3533	36877	717	1641	216	64	101	−87
	13	24	8	14	41	5	41	14	25
O17	6435	13985	31516	732	1533	239	284	87	52
	8	15	5	9	26	4	27	95	18
O18	15775	−13832	35874	1023	1532	286	765	250	127
	10	16	6	11	27	4	30	11	19

Table 3. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters (Å^2) with standard deviations for hydrogen atoms.

Atom	x	y	z	B
H1	2214	6206	2930	4.9
	15	28	11	.4
H2	1500	4998	1508	3.9
	13	24	10	.4
H4	4264	−516	2430	3.3
	13	23	9	.4
H5	5398	−388	3810	5.7
	15	29	12	.5
H6	5099	2371	4721	5.2
	15	29	11	.4
H7	3836	4914	4272	4.7
	14	26	11	.4
H101	3165	791	864	3.7
	13	24	10	.4
H102	1933	2079	556	3.8
	13	25	10	.4
H11	2134	−1452	1592	2.8
	12	22	9	.3
H13	1983	2773	−603	7.4
	17	31	13	.6
H151	672	542	2047	3.6
	13	23	10	.4
H152	17	−1195	1556	4.7
	14	26	10	.5
H153	108	905	1146	3.8
	13	24	10	.4
H16	1389	963	4250	4.0
	13	24	10	.4

The crystal structure is built up by molecular double layers parallel to (100). The layers are connected through van der Waals forces whereas the ions within the layers are bonded together by an extensive hydrogen bond system. Similar arrangements are reported for the tryptophan halides.[8] Dimers of tryptophan ions are formed about centers of symmetry through hydrogen bonds between carboxyl and amino groups (O14 – N15 3.026 Å). These are the only direct hydrogen bonds between two tryptophan molecules. The formate anions link the dimers together with hydrogen bonds to form the layers. All hetero atoms

Table 4. R.m.s. amplitudes of vibration and B-values (Å^2) along the principal axes of vibration given by the components of a unit vector **e** in fractional coordinates ($\times 10^4$).

Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
	0.249	4.90	343	531	558
N1	0.228	4.09	825	310	141
	0.168	2.22	−54	1353	251
	0.226	4.02	−136	236	599
C2	0.208	3.43	839	430	185
	0.177	2.47	280	1403	−44
	0.202	3.22	521	823	412
C3	0.191	2.89	−404	580	470
	0.155	1.90	606	1093	61
	0.252	5.00	303	1217	−267
C4	0.215	3.64	422	415	555
	0.187	2.77	−729	746	126
	0.312	7.70	381	1322	−75
C5	0.250	4.94	−124	367	589
	0.190	2.86	801	−571	204
	0.335	8.88	96	1448	−116
C6	0.245	4.72	−715	302	299
	0.187	2.77	530	145	540
	0.297	6.96	227	−1286	288
C7	0.226	4.02	850	204	110
	0.180	2.55	164	716	548
	0.238	4.46	343	−1000	421
C8	0.184	2.68	−690	215	335
	0.171	2.31	456	1074	324
	0.213	3.59	347	914	456
C9	0.176	2.43	−318	874	429
	0.167	2.21	762	781	53
	0.229	4.13	712	901	53
C10	0.189	2.81	138	307	593
	0.174	2.40	525	1141	201
	0.212	3.54	−770	646	108
C11	0.177	2.48	270	1271	−243
	0.165	2.15	369	420	569
	0.229	4.14	−820	566	16
C12	0.174	2.39	89	−135	626
	0.167	2.19	348	1367	55
	0.305	7.36	230	−1212	342
O13	0.211	3.52	843	136	−137
	0.178	2.50	194	850	509

Table 4. Continued.

	0.274	5.94	428	−1237	208
O14	0.214	3.62	620	241	−391
	0.167	2.21	483	787	446
	0.224	3.96	778	−733	32
N15	0.176	2.45	275	904	−436
	0.165	2.15	348	925	451
	0.213	3.60	882	249	38
C16	0.195	3.00	156	−1425	152
	0.164	2.13	8	339	609
	0.220	3.83	830	554	37
O17	0.183	2.64	−293	1277	223
	0.174	2.38	164	−522	586
	0.267	5.62	822	560	142
O18	0.187	2.75	112	42	−611
	0.171	2.30	338	−1376	39

Table 5. Bond lengths (Å) and bond angles (°) in DL-tryptophan formate.

	Bond length	Corrected	Bond angle	
N1 – C2	1.372	1.376	N1 – C2 – C3	110.53
N1 – C8	1.371	1.377	N1 – C8 – C9	107.43
C2 – C3	1.354	1.360	C2 – N1 – C8	108.68
C3 – C9	1.434	1.440	C2 – C3 – C9	106.43
C3 – C10	1.494	1.498	C3 – C9 – C8	106.92
C4 – C9	1.393	1.400	C3 – C9 – C4	134.01
C4 – C5	1.382	1.386	C9 – C4 – C5	118.67
C5 – C6	1.399	1.404	C4 – C5 – O6	121.22
C6 – C7	1.369	1.375	C5 – C6 – C7	121.29
C7 – C8	1.390	1.395	C6 – C7 – C8	117.68
C8 – C9	1.412	1.418	C7 – C8 – C9	122.07
C10 – C11	1.529		C8 – C9 – C4	119.07
C11 – C12	1.523		C7 – C8 – N1	130.50
C11 – N15	1.492		C2 – C3 – C10	125.81
C12 – O13	1.295		C9 – C3 – C10	127.74
C12 – O14	1.214		C3 – C10 – C11	112.85
C16 – O17	1.232		C10 – C11 – C12	111.85
C16 – O18	1.255		C10 – C11 – N15	111.27
N1 – H1	0.91		C12 – C11 – N15	108.00
C2 – H2	0.95		C11 – C12 – O13	113.24
C4 – H4	0.98		C11 – C12 – O14	121.88
C5 – H5	1.00		O13 – C12 – O14	124.86
C6 – H6	0.99		O17 – C16 – O18	126.46
C7 – H7	0.95			
C10 – H101	0.99		Hydrogen bond lengths	
C10 – H102	1.04		N1 – O18 (x, $1+y$, z)	3.003
C11 – H11	1.01		O13 – O18 (x, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$)	2.492
O13 – H13	1.05		N15 – O14 ($-x$, $-y$, $-z$)	3.026
N15 – H151	0.94		N15 – O17 (x, y, z)	2.787
N15 – H152	0.97		N15 – O17 ($-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.811
N15 – H153	0.94			
C16 – H16	0.99			

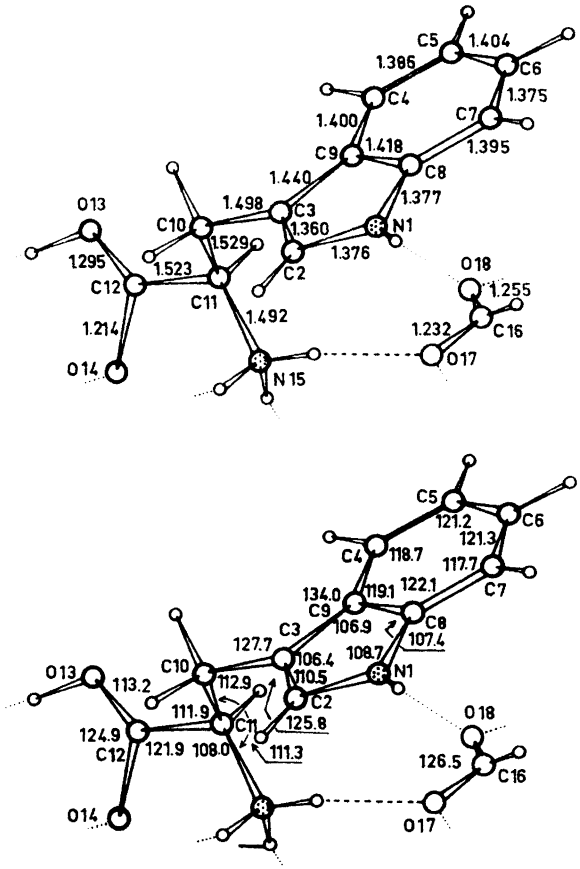

Fig. 1. Bond lengths (Å) and angles (°) in DL-tryptophan formate. Bond lengths in the 3-indolylmethyl-part are corrected for thermal effects.

of the tryptophan molecules are engaged in the hydrogen bond network; each tryptophan molecule is thus donor in five such bonds and acceptor in one. Each formate ion is hydrogen acceptor in four hydrogen bonds involving different tryptophan molecules (N1 – O18 3.003 Å, N15′ – O17 2.787 Å, O13″ – O18 2.492 Å, and N15″ – O17 2.811 Å). The short distance of 2.492 Å between O13″ and O18 indicates a rather strong competition for the proton situated between the carboxy oxygen atoms. The O13 – H bond is found to be relatively long (*cf.* Table 5). The angles O13″ – H···O18 and C16 – O18···H were found to be 179° and 110°, respectively.

The two C – O bond lengths in the formate ion, C16 – C17 1.232 Å and C16 – O18 1.255 Å, are consistent with the ionized state of the molecule. The difference between the two is highly significant, however, and the greater

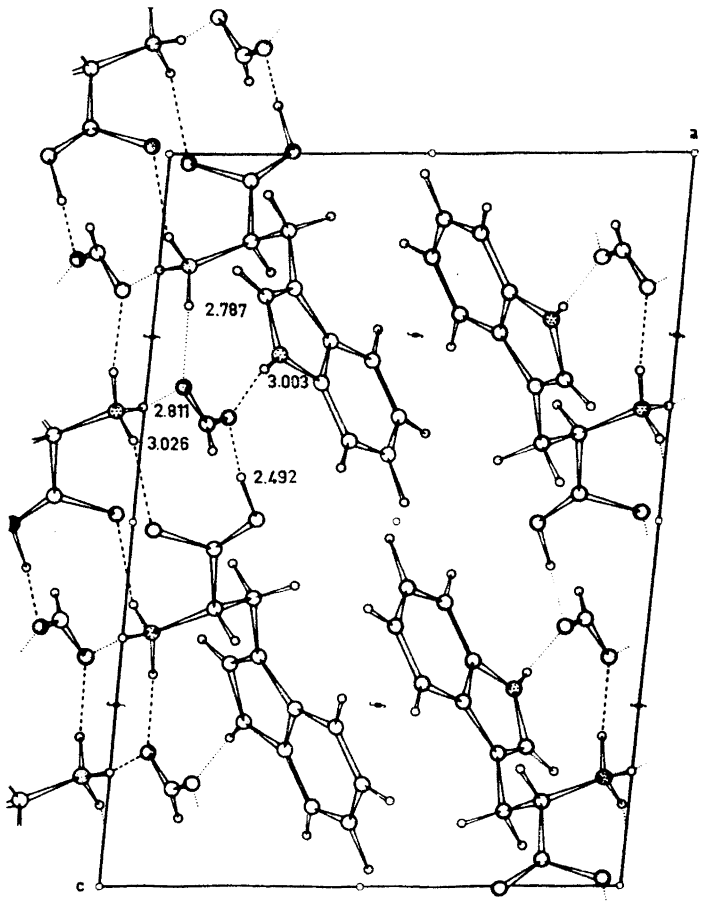

Fig. 2. Molecular arrangement and hydrogen bonds (Å) in the DL-tryptophan formate crystals as seen along the *b*-axis.

length of C16 – C18 is believed to be due to the very strong O18 – O13 hydrogen bond.

In the alanine part of the molecule the two C – O distances agree well with the expected values for a protonized carboxyl group. The slight shortening of the C – OH bond (1.291 Å) relative to the weighted average of such bonds (1.306 Å [9]) is also believed to be a result of the strong hydrogen bond O18 – O13. All other bond lengths and angles in the alanine moiety are in agreement with those reported for other α-amino acids. The dihedral angle N15 – C11 – C12 – O14 is only $-4.3°$ and the N15 atom is thus close to the plane of the carboxyl group.

The atoms of the indole moiety are co-planar, the C10 atom also included. The largest deviation from a least-squares plane through these atoms is 0.008

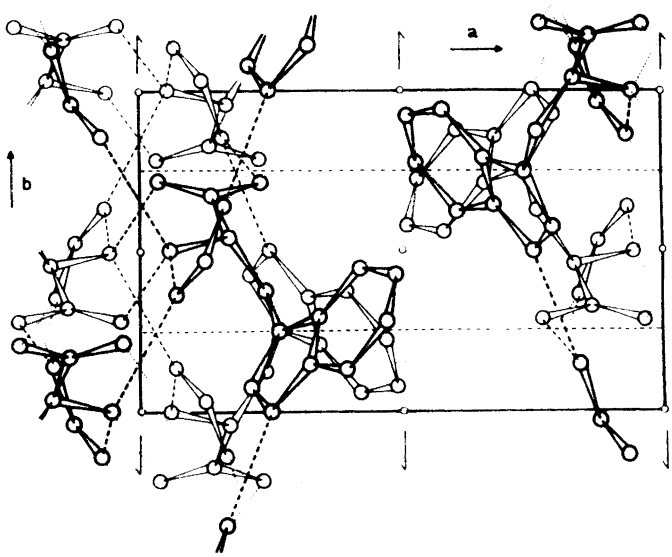

Fig. 3. The crystal structure as seen along the *c*-axis.

Å (C3) The bond lengths and angles in the indole nucleus as given in Table 5 and Fig. 1 are in good agreement with what is found in similar systems, *e.g.* serotonine picrate[10] and 5-methoxy-*N*,*N*-dimethyl tryptamine,[11] and they seem to be typical for such molecules.

The conformation of the tryptophan cation may be described by the torsion angles about the C–C and C–N bonds in the side chain. The dihedral angle C2–C3–C10–C11 is 105.1° and C3–C10–C11–C12 is −174.6°. The C3 atom and the carbon atoms in the alanine part lie thus approximately in a plane which is close to be normal to the indole plane; the carboxyl group is in the *anti* position relative to the indole group. The conformation about the C11–N15 bond is staggered.

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