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The Crystal and Molecular Structure of 3,4-Dihydro-7-chloro-6-diethylamino-2*H*,8*H*-pyrimido[2,1-*b*][1,3]thiazin-8-one

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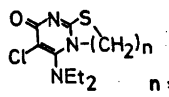
The crystal structure of 3,4-dihydro-7-chloro-6-diethylamino-2*H*,8*H*-pyrimido[2,1-*b*][1,3]thiazin-8-one, $C_{11}H_{16}ON_3SCl$, has been determined from three-dimensional X-ray diffraction data and refined by least squares methods.

The space group is $P2_1$, $a = 10.261$ Å, $b = 7.494$ Å, $c = 8.341$ Å, $\beta = 91.51°$. The geometry seems to favour a possible CH···O hydrogen bond (2.93 Å), and one intramolecular non-bonding contact is rather short (N_{am}···C4 2.712 Å).

The amino nitrogen atom has a pyramidal hybridisation, and the dihedral angles (about the Et_2N-C bond) are 81 and 48°. The thiazine ring moiety has an envelope-like conformation, and the C10 – S bond length (1.750 Å) indicates some double bond character in this bond.

Potential analgesics, with the following general formula

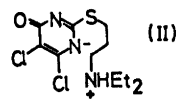


(I)

n = 2,3

have been synthesized by Berg-Nielsen.[1] The compounds were prepared from 2-bromoalkylthiopyrimidin-6-ones by cyclization of the bromoalkylthio side chain. The thiazoles ($n = 2$) formed more readily than the thiazines ($n = 3$). Studies by Reistad and Undheim [2,3] have shown that similar pyridine[2,1-*b*][1,3]thiazines rearrange to their thiazole analogs. These investigations indicate that the [1,3]thiazines are less stable than their thiazole analogs.

In order to examine the conformation of, and the strained conditions obviously present in these thiazine rings, and to shed some light on conformational changes promoted by ring closure, a crystal structure determination of I, $n = 3$ and a 2-propylthiopyrimidin-6-one derivative was initiated. The crystal and molecular structure of 2-(3-diethylaminopropylthio)4,5-dichloropyrimidin-6-one (II) has been published,[4] while the structure of I, $n = 3$ is now reported.



(II)

EXPERIMENTAL

Colourless needle-shaped crystals were obtained by slow evaporation of an acetone solution. The systematic absences were consistent with the space groups $P2_1$ and $P2_1/m$, the former being the actual one as $Z = 2$. Unit cell parameters were determined from diffractometer measurements. Three-dimensional intensity data were collected on a punched card controlled four circle Picker diffractometer with $\omega - 2\theta$ scan technique. The crystal used was approximately $0.40 \times 0.12 \times 0.08$ mm³, and was mounted with b along the ϕ-axis. The Mo$K\alpha$ radiation was monochromated with a highly oriented graphite crystal. The 2θ scan speed was 1° min^{-1}. Three test reflections were measured for every 100 reflections and the intensities accordingly adjusted. Estimated standard deviations in the intensities were taken as the square root of the total number of counts adding 1 % to allow for the uncertainty in the adjustments. 1825 unique reflections with 2θ less than 60° were measured. Only 811 of these had an intensity larger than $2\sigma(I)$, and were regarded as observed. The intensity data were corrected for Lorentz, polarization and absorption effects. Atomic form factors used were those of Doyle and Turner [5] for chlorine, sulfur oxygen, nitrogen, and carbon, and of Stewart *et al.*[6] for hydrogen. All programs but the ORTEP program [7] applied during the structure investigation are described in Ref. 8.

Table 1. Observed and calculated structure factors. The columns are: h, 10 F_{obs}, 10 F_{calc}.

L= 0,K= 0		= 3 175	160	4 234	233	L= 6,K= 3		= 1 169	168	L= 3,K= 6		L= 6,K= 1		3 41	23
1 454	495	= 4 84	72	3 222	219	4 127	132	0 50	70	2 39	51	7 60	31	4 45	22
2 287	279	L= 7,K= 1		2 257	260	2 48	58	1 119	112	1 52	55	= 8 54	42	8 47	36
3 370	351	= 4 120	122	1 284	294	1 61	39	2 90	97	0 78	74	=11 43	30	L= 6,K= 3	
4 47	56	= 3 116	115	L= 0,K= 2		= 1 68	78	4 64	80	= 3 89	79	L= 6,K= 1		10 54	49
5 76	62	= 2 64	55	0 1201	1234	= 2 43	37	5 58	78	L= 4,K= 6		= 8 115	105	5 93	100
6 80	82	0 71	65	1 623	586	= 3 84	106	L= 3,K= 4		0 88	84	L= 4,K= 1		= 7 38	49
7 150	150	2 117	121	2 153	167	= 4 99	114	6 45	39	L= 1,K= 7		12 41	38	=10 48	24
8 34	28	L= 6,K= 1		3 103	114	L= 5,K= 3		2 84	102	0 39	29	= 9 66	60	=11 42	33
9 40	44	5 107	103	4 196	199	= 5 75	60	1 103	108	L= 0,K= 7		=10 42	18	L= 5,K= 3	
L= 1,K= 0		4 249	251	7 127	122	= 4 72	61	0 151	152	1 45	23	L= 3,K= 1		= 8 73	74
9 63	56	2 83	84	9 63	56	= 3 49	64	= 1 101	100	L= 0,K= 0		=13 40	21	= 7 73	79
8 123	130	1 104	93	L= 1,K= 2		= 1 47	52	= 2 56	61	10 61	48	=11 41	32	L= 4,K= 3	
7 121	116	0 47	49	9 43	46	0 49	41	= 3 160	163	11 54	37	= 9 47	40	11 47	16
6 71	75	= 1 126	117	8 89	94	1 156	154	= 4 83	92	L= 1,K= 0		9 45	70	= 8 54	49
5 130	115	= 2 81	97	7 54	61	3 172	162	= 5 95	100	12 61	40	11 57	47	= 9 49	56
4 184	185	= 3 187	169	6 125	131	4 138	151	L= 4,K= 4		10 130	105	L= 2,K= 1		L= 3,K= 3	
3 610	588	= 4 69	71	5 64	79	5 191	189	= 5 54	51	=11 68	64	11 36	24	= 9 46	32
= 3 84	72	= 6 57	54	2 31	43	L= 4,K= 3		= 4 90	80	L= 2,K= 0		=10 47	35	L= 2,K= 3	
= 4 153	153	L= 5,K= 1		1 329	322	5 107	99	= 3 93	104	=11 40	34	=14 42	3	=10 36	34
= 5 39	26	= 7 75	85	0 632	622	4 50	59	= 2 130	125	=10 51	63	L= 1,K= 1		L= 1,K= 3	
= 7 120	135	= 6 106	97	= 1 576	519	3 136	142	= 1 33	54	10 91	49	12 46	52	=10 38	36
= 6 243	225	= 4 93	94	= 2 302	282	2 51	73	0 185	184	L= 3,K= 0		L= 0,K= 1		L= 0,K= 4	
= 9 53	39	= 3 38	66	= 4 100	95	1 43	58	1 79	78	11 41	18	12 67	54	11 55	29
L= 2,K= 0		= 2 78	83	= 7 136	133	0 85	96	5 115	131	10 36	26	10 58	46	L= 1,K= 4	
= 9 42	25	= 1 64	79	= 8 167	174	= 3 38	42	6 64	49	9 70	33	L= 0,K= 2		10 49	42
= 8 156	160	1 187	186	= 9 45	32	= 4 126	125	L= 6,K= 4		=10 79	62	10 64	48	8 61	58
= 6 90	96	2 49	71	L= 2,K= 2		= 5 102	126	2 48	64	=11 37	24	11 57	41	= 8 117	120
= 4 81	72	3 202	205	= 9 38	33	= 6 87	72	= 1 99	97	L= 4,K= 0		13 45	12	=11 51	43
= 3 810	813	4 146	144	= 8 139	149	= 7 147	148	= 2 102	98	=11 53	47	L= 1,K= 2		L= 2,K= 4	
= 2 268	272	5 230	244	= 6 44	68	L= 3,K= 3		0 106	99	9 90	89	12 55	39	=10 39	33
= 1 381	376	6 39	47	= 4 83	72	= 7 73	78	= 3 104	113	11 39	20	10 80	69	= 8 112	102
0 461	430	L= 4,K= 1		= 3 301	315	= 4 71	81	L= 6,K= 4		L= 5,K= 0		=11 66	54	8 74	59
1 121	140	7 86	105	= 2 140	151	= 3 78	96	= 3 177	178	10 91	38	L= 2,K= 2		L= 3,K= 4	
2 406	414	6 41	51	= 1 102	125	= 1 89	65	= 2 66	73	8 86	66	=11 37	19	8 87	81
3 62	72	5 141	137	0 39	70	0 63	76	= 1 42	48	= 8 64	60	=10 53	59	7 43	45
4 35	31	4 127	139	1 173	179	1 205	209	1 43	36	=11 59	45	10 40	38	=10 50	44
5 74	86	3 212	219	2 152	157	2 156	156	L= 5,K= 5		=12 41	14	11 40	21	L= 4,K= 4	
6 40	58	2 187	201	3 30	65	3 57	47	= 1 42	56	=13 50	22	L= 3,K= 2		7 64	56
8 46	61	1 75	88	4 90	85	4 185	183	1 75	75	L= 6,K= 0		10 38	17	L= 5,K= 4	
L= 3,K= 0		0 80	95	6 46	54	6 50	64	L= 4,K= 5		= 8 47	55	=10 65	56	8 47	58
8 88	83	= 3 119	122	8 95	87	7 38	56	3 115	101	= 7 77	61	L= 4,K= 2		5 99	100
7 138	134	= 4 48	70	L= 3,K= 2		L= 2,K= 3		2 52	41	7 57	47	9 71	64	= 7 71	72
6 120	123	= 5 135	128	8 78	76	9 48	37	1 93	86	6 56	26	10 51	41	L= 6,K= 4	
4 56	26	= 6 51	40	L= 2,K= 2		8 118	113	= 3 64	74	9 78	53	12 39	11	= 8 41	41
3 37	46	= 7 135	150	7 40	63	7 147	160	= 4 55	25	L= 7,K= 0		L= 5,K= 2		= 7 39	50
2 195	206	= 8 79	74	L= 3,K= 2		4 255	259	L= 3,K= 5		9 70	65	10 45	29	= 6 45	28
1 167	174	L= 3,K= 1		7 82	95	3 90	91	= 5 42	71	7 65	63	8 73	73	= 5 51	32
0 152	164	= 8 38	31	6 66	71	2 65	81	= 4 71	61	= 5 54	39	= 8 56	58	= 4 39	38
= 1 471	444	= 7 122	110	2 147	135	1 147	144	= 3 47	70	= 7 44	26	=11 53	53	9 57	48
= 2 102	106	= 6 77	85	1 60	42	0 62	51	= 2 34	37	=10 58	35	L= 6,K= 2		10 46	23
= 3 391	395	= 5 87	123	0 282	280	= 2 109	102	= 1 43	66	L= 8,K= 0		= 8 60	39	L= 7,K= 4	
= 4 73	65	= 4 162	158	= 1 266	284	= 3 231	241	0 45	42	= 4 91	53	= 7 73	71	7 54	37
= 5 72	63	= 3 152	158	= 3 316	314	= 6 171	165	1 37	56	= 3 41	35	7 40	33	6 37	29
= 8 64	67	= 2 129	129	= 4 90	100	= 8 72	54	1 92	104	0 36	83	8 88	25	4 47	65
L= 4,K= 0		= 1 106	111	= 5 76	89	L= 1,K= 3		2 40	34	1 78	69	9 52	50	1 54	48
= 8 47	28	0 145	137	= 6 40	41	= 8 132	135	L= 2,K= 5		3 52	55	L= 7,K= 2		0 41	17
= 6 87	89	1 319	337	= 7 34	26	= 7 80	89	6 44	66	4 64	67	9 58	54	= 3 95	92
= 5 73	56	2 210	209	= 8 73	64	= 6 139	148	5 97	93	5 76	29	7 70	55	= 4 39	25
= 4 122	124	3 102	94	L= 4,K= 2		= 4 202	193	4 144	142	L= 9,K= 0		6 52	30	= 9 40	9
= 3 88	80	4 188	195	= 6 43	49	= 3 121	112	3 112	109	5 57	63	4 80	60	L= 8,K= 4	
= 2 154	157	5 44	84	= 5 82	95	= 2 146	141	1 107	121	= 2 46	35	= 4 60	50	= 4 50	43
= 1 66	78	6 72	69	= 4 124	125	= 1 210	217	= 2 46	54	= 3 48	22	= 5 44	32	1 48	58
0 485	472	7 47	40	= 3 132	133	1 56	70	= 3 85	70	= 4 63	59	= 7 40	21	4 46	31
1 247	241	L= 2,K= 1		= 2 161	169	2 50	40	= 5 48	32	= 6 39	24	=10 41	38	L= 9,K= 4	
2 89	94	8 35	57	= 1 31	21	3 138	140	= 6 49	59	= 8 52	33	L= 8,K= 2		5 41	29
3 37	7	9 177	133	0 379	373	4 220	226	L= 1,K= 5		= 9 48	30	= 4 56	53	= 1 45	25
4 67	79	8 214	216	1 203	205	5 286	286	= 6 95	75	L= 10,K= 0		= 3 37	24	= 4 39	36
5 145	146	4 419	416	2 37	59	6 32	18	= 5 50	37	= 3 51	47	0 38	53	= 7 42	8
6 106	98	3 123	124	4 42	55	7 55	48	= 4 131	122	3 43	30	1 66	65	L= 10,K= 4	
7 127	134	2 76	121	5 155	149	L= 0,K= 3		= 3 46	29	6 51	43	4 53	58	3 46	20
L= 6,K= 0		1 293	319	6 78	89	8 66	81	= 2 71	92	L= 11,K= 0		5 46	33	L= 8,K= 5	
6 33	44	0 123	97	7 120	112	7 145	143	= 1 80	67	1 42	2	L= 9,K= 2		2 40	52
5 145	150	= 1 179	174	L= 5,K= 2		6 72	71	0 59	94	L= 11,K= 1		5 53	52	= 5 42	33
2 40	27	= 2 137	150	5 150	142	5 176	182	1 65	69	0 42	14	4 56	48	L= 7,K= 5	
1 36	26	= 3 332	323	2 76	65	4 104	113	3 55	44	2 50	40	= 2 47	35	= 4 48	49
0 155	158	= 4 101	106	1 33	30	3 121	132	4 135	132	L= 10,K= 1		= 4 51	49	= 2 51	36
= 1 284	289	= 6 172	178	0 127	141	1 42	51	5 140	137	6 44	33	= 7 42	11	= 1 37	25
= 2 141	143	L= 1,K= 1		= 1 200	207	L= 0,K= 4		6 36	7	4 61	63	= 8 45	36	2 85	77
= 3 155	147	= 8 184	183	= 2 107	105	0 592	561	L= 0,K= 5		L= 9,K= 1		L= 10,K= 2		L= 6,K= 5	
= 4 144	150	= 7 125	140	= 3 133	137	1 193	202	6 77	68	= 9 42	6	3 52	30	5 48	60
= 5 37	21	= 6 218	207	= 4 63	62	2 114	116	5 85	100	= 6 66	39	6 51	35	4 70	56
= 6 70	80	= 5 327	339	= 5 57	54	3 64	81	4 61	63	= 5 66	63	L= 11,K= 2		3 40	43
= 7 89	98	= 3 102	127	= 6 48	53	4 120	122	1 67	66	1 86	85	= 2 47	31	2 53	55
L= 6,K= 0		= 2 285	295	= 7 85	103	5 51	46	L= 0,K= 6		L= 8,K= 1		L= 10,K= 3		1 41	24
= 5 63	62	= 1 250	247	L= 6,K= 2		7 49	69	0 259	246	8 119	127	= 1 50	32	= 3 58	68
= 4 62	67	0 310	270	= 5 52	62	L= 1,K= 4		1 68	63	1 114	108	L= 9,K= 3		= 4 42	40
= 3 253	261	1 34	41	= 4 42	45	7 36	40	2 78	70	0 65	60	1 64	74	= 6 49	28
= 2 162	162	2 114	116	= 3 278	270	6 42	61	3 61	53	= 1 39	32	L= 8,K= 3		L= 5,K= 5	
= 1 58	53	3 149	144	= 1 76	78	5 57	51	4 78	67	= 2 43	26	2 87	91	= 8 73	73
0 113	112	4 335	325	0 84	87	3 59	49	L= 1,K= 6		= 4 43	35	1 89	89	= 7 80	81
1 93	91	5 454	447	1 76	76	0 334	324	0 139	150	= 5 52	46	0 57	63	3 63	67
2 59	42	6 31	50	2 34	41	= 1 234	256	= 1 94	72	= 6 43	33	= 2 50	49	4 62	85
3 90	89	7 51	50	3 48	55	= 2 154	148	= 2 74	65	L= 7,K= 1		L= 7,K= 3		5 121	121
5 55	21	8 104	95	L= 7,K= 2		= 3 63	74	L= 2,K= 6		= 9 49	40	= 7 44	34	9 39	23
6 80	72	L= 0,K= 1		1 42	68	= 4 53	52	= 3 63	86	= 7 60	46	= 6 38	37	L= 4,K= 5	
L= 7,K= 0		8 105	104	= 2 83	82	= 7 52	83	= 1 97	92	= 5 47	35	= 4 82	74	7 47	20
4 57	63	7 171	182	= 1 133	139	L= 2,K= 4		1 65	48	5 56	69	= 3 98	99	6 75	73
3 38	30	6 74	95	L= 7,K= 3		= 6 37	54	2 51	39	7 37	11	= 2 47	42	= 5 67	58
1 61	75	5 233	240	0 54	36	= 3 128	139	4 37	64	8 52	45	2 133	119	= 7 62	59

Table 1. Continued.

L=	5,K=	5		4	46	40	L=	0,K=	2	L=	3,K=	1	0	342	324	L=	1,K=	0	- 3	156	158	4	134	132
- 7	75	80		5	51	63	- 9	75	56	1	331	337	L=	0,K=	4		2	522	486	- 2	130	129	L=	5,K=	3
	6	37	34	L=	4,K=	7	- 7	123	122	L=	2,K=	1	0	554	561	L=	2,K=	0		0	147	137	1	155	154
	11	40	38		0	41	40	- 4	193	199	4	421	416	L=	1,K=	3	- 3	519	513	2	212	209	3	175	162
	L=	2,K=	5	L=	3,K=	7	- 3	107	114	1	298	319	5	281	286		0	468	430	4	193	195	4	147	151
	8	41	31	- 9	39	3	- 2	156	167	- 3	346	323	L=	2,K=	3	- 1	387	376	L=	2,K=	1	5	190	189
-10	38	29	- 7	41	38	- 1	617	586	L=	1,K=	1	4	282	259	L=	1,K=	0		6	127	133	L=	3,K=	3
	L=	1,K=	5	- 5	45	13	L=	0,K=	3	- 4	325	339	L=	6,K=	2		3	185	185	5	216	216	1	204	209
- 9	68	67		4	72	52	- 1	44	51	- 2	294	295	- 3	272	270	- 4	156	153	- 1	179	174	2	155	156
- 7	67	68	L=	2,K=	7	- 3	124	132	- 1	238	247	L=	4,K=	2	- 8	250	225	- 2	141	150	4	178	183
	12	49	11		5	53	43	- 4	108	113	0	312	270	0	379	373	L=	2,K=	0	- 6	172	178	L=	2,K=	3
	L=	0,K=	5		4	51	58	- 5	183	182	4	341	325	L=	3,K=	2	- 8	153	160	L=	1,K=	1	1	151	144
	12	50	40		3	37	33	- 6	80	71	5	451	447	- 3	305	314	- 2	274	272	- 8	186	183	- 3	228	241
	8	58	65		2	44	22	- 7	149	143	L=	0,K=	1	- 1	283	284	L=	3,K=	0		3	147	144	- 6	175	165
	7	73	80		1	43	49	- 8	61	81	2	259	260	0	283	280		7	135	134	L=	0,K=	1	L=	1,K=	3
	L=	1,K=	6	- 3	48	45	L=	0,K=	4	1	284	294	L=	2,K=	2		2	195	206	7	178	182	- 8	139	135
- 8	64	67	- 6	47	33	- 7	63	69	L=	0,K=	2	- 3	306	315		1	172	174	5	232	240	- 6	143	148
	L=	2,K=	6	L=	1,K=	7	- 5	58	46	0	1134	1234	L=	1,K=	2		0	156	164	4	233	233	- 4	203	193
- 8	67	61	- 6	49	32	- 4	127	122	L=	1,K=	2	- 2	301	282	L=	4,K=	0		3	221	219	- 2	143	141
- 7	49	43	- 4	43	31	- 3	67	81	1	343	322	- 1	561	519	- 2	159	157	L=	0,K=	2	- 1	212	217
	7	36	12	- 3	37	20	- 2	116	116	0	598	622	0	610	622		1	255	241	2	154	167	3	137	140
	L=	3,K=	6	- 1	49	37	- 1	195	202	- 1	561	519	L=	0,K=	2		5	142	148	4	194	199	L=	0,K=	3
- 4	43	25		5	81	78	L=	0,K=	5	- 2	304	282	0	1186	1234		7	126	134	7	122	122	7	150	143
- 5	59	49	L=	0,K=	7	- 3	34	34	L=	2,K=	2	L=	0,K=	1		L=	5,K=	0	L=	1,K=	2	6	177	182
L=	4,K=	6		5	50	51	- 4	56	63	- 3	294	315	1	284	294		5	147	150	- 7	136	133	L=	0,K=	4
- 4	41	50	L=	0,K=	8	- 5	100	99	L=	3,K=	2	2	260	260		0	164	158	- 8	164	174	1	197	202
- 2	44	45		0	88	70	- 6	73	68	0	284	280	L=	1,K=	1	- 2	143	143	L=	2,K=	2	L=	1,K=	4
	5	72	76	L=	1,K=	8	L=	0,K=	6	- 1	271	284	5	461	447	- 3	156	147	- 8	136	149	- 1	252	256
L=	5,K=	6		0	65	67	- 4	82	67	- 3	315	314	4	337	325	- 4	149	150		2	159	157	- 2	152	148
	5	47	49	- 1	54	52	- 3	54	53	L=	4,K=	2	0	303	270	L=	6,K=	0	L=	4,K=	2	L=	2,K=	4
	0	55	49	- 2	39	37	- 2	83	70	0	386	373	- 1	242	247	- 2	159	162	- 3	130	133	- 3	126	139
- 1	39	50	L=	0,K=	0	- 1	60	63	L=	6,K=	2	- 2	287	295	L=	7,K=	0	- 2	166	169	L=	3,K=	4
- 2	66	72	- 9	51	44	L=	2,K=	0	- 3	270	270	- 4	324	339	- 3	184	160	L=	3,K=	2	0	156	152
- 3	77	69	- 7	152	150	2	416	414	L=	2,K=	3	L=	2,K=	1	L=	6,K=	1	2	146	135	- 3	164	163
- 4	40	19	- 6	86	82	- 1	390	376	4	258	259	- 3	350	323	4	248	251	- 2	131	147	L=	4,K=	4
L=	6,K=	6	- 5	67	62	0	467	430	L=	1,K=	3	1	303	319	- 1	125	117	L=	4,K=	2	- 2	128	125
- 7	47	36	- 4	55	56	- 3	515	513	5	286	286	4	425	416	- 3	165	169	1	199	205	0	188	184
- 3	82	80	- 3	373	351	L=	1,K=	0	L=	0,K=	4	L=	3,K=	1	L=	5,K=	1	5	159	149	L=	6,K=	4
	3	38	7	- 2	293	279	2	524	488	0	536	561	1	332	337		3	206	205	L=	6,K=	2	- 3	177	176
L=	7,K=	6	- 1	463	495	L=	3,K=	0	L=	1,K=	4	L=	6,K=	0		4	148	144	5	147	142	L=	2,K=	5
- 3	44	74	L=	0,K=	1	- 1	479	444	0	348	324	- 3	260	261		5	237	244	0	130	141	4	140	142
L=	8,K=	7	- 1	278	294	- 3	399	395	L=	0,K=	6	L=	5,K=	0	L=	4,K=	1	- 1	198	207	L=	1,K=	5
	1	41	46	- 2	252	260	L=	4,K=	0	0	252	246	- 1	291	289		3	219	219	- 3	133	137	4	136	132
L=	7,K=	7	- 3	218	219	0	506	472	L=	2,K=	0	L=	4,K=	0		2	193	201	L=	6,K=	2	5	136	137
- 3	40	46	- 4	239	233	L=	5,K=	0	2	416	414	0	498	472	- 5	141	128	- 2	120	124	L=	1,K=	6
L=	6,K=	7	- 5	233	240	- 1	290	289	L=	0,K=	6	L=	3,K=	0	- 7	136	150	L=	7,K=	2	0	152	150
7	41	24	- 6	71	95	L=	6,K=	0	0	241	246	- 3	393	395	L=	3,K=	1	- 3	137	139	L=	0,K=	3
L=	5,K=	7	- 7	185	182	- 3	256	261	L=	1,K=	4	- 1	476	444	- 4	160	156	L=	6,K=	3	6	177	182
1	43	22	- 8	104	104																		

CRYSTAL DATA

3,4-Dihydro-7-chloro-6-diethylamino-2*H*,8*H*-pyrimido[2,1-*b*][1,3]thiazin-8-one, $C_{11}H_{16}ON_3SCl$, monoclinic, space group $P2_1$ $a=10.261(7)$ Å, $b=7.494(5)$ Å, $c=8.341(5)$ Å, $\beta=91.51(2)°$, $V=641$ Å^3, $M=272.81$, $F(000)=288$, $\mu=0.44$ mm^{-1}, D_{obs}(flotation) $=1.40$ gcm^{-3}, $D_{calc}=1.41$ gcm^{-3}.

STRUCTURE DETERMINATION

Coordinates of the sulfur and chlorine atoms were found from a sharpened Patterson function. A corresponding Fourier map revealed a molecule with an apparent mirror plane through all non-hydrogen atoms but the C3 atom and the ethyl carbon atoms. However, subsequent Fourier and full matrix least squares refinement showed that no disorder was present, and that the space group was truly $P2_1$. In the final refinements calculated positional parameters and estimated thermal parameters (6–8 Å^2) for hydrogen atoms were included but not refined. The refinements converged with a conventional R factor of 0.082 and a weighted

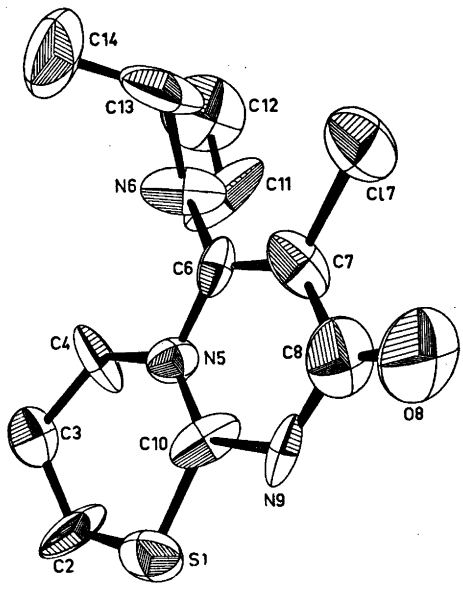


Fig. 1. The 50 % probability ellipsoids.

Table 2. Fractional atomic coordinates for non hydrogen atoms, anisotropic thermal vibration parameters and their estimated standard deviations (multiplied by 10^4). The temperature factors are expressed as:

$$\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)$$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl7	8314	2503	6571	161	386	198	−2	−117	−55
	3	18	4	5	14	6	41	9	48
S1	2706	2459	3898	100	294	217	86	71	20
	4	0	4	4	12	7	34	9	43
O8	5876	2054	8209	268	681	73	−122	14	−26
	9	29	10	16	68	13	76	24	77
N5	5325	2460	3439	81	213	114	−63	2	−36
	8	36	13	11	29	16	92	23	96
N6	7618	2497	2946	98	298	191	−90	35	−472
	9	35	13	11	34	19	71	26	75
N9	4439	2249	6034	183	209	109	−25	53	201
	11	38	12	17	47	18	78	28	83
C2	2631	2496	3898	152	706	105	−411	−6	399
	12	48	12	19	77	20	112	32	122
C3	3858	3228	1131	139	302	77	3	−102	30
	13	22	13	18	63	19	48	31	53
C4	5163	2578	1661	133	441	37	423	−30	51
	10	41	11	16	57	16	85	26	91
C6	6617	2562	4083	141	91	122	−27	18	77
	12	43	13	16	34	21	87	30	103
C7	6814	2346	5685	125	301	104	111	−77	−150
	10	43	13	16	53	19	92	28	101
C8	5708	2296	6733	194	364	142	147	109	−31
	14	53	16	22	65	26	124	43	137
C10	4354	2487	4494	141	135	147	−200	95	−201
	11	40	15	17	35	24	86	38	102
C11	7875	667	2203	293	99	383	−132	250	−227
	21	32	28	32	38	43	63	64	70
C14	8798	5406	2166	245	474	385	37	232	532
	22	33	27	32	93	49	81	65	106
C13	8741	3630	3081	73	675	227	−91	−108	−52
	16	34	20	19	90	31	61	37	84
C12	9101	633	1221	249	791	237	17	139	−151
	19	36	19	30	112	37	99	56	106

R_w factor ($R_w=(\sum w\Delta^2/\sum wF^2)^{\frac{1}{2}}$) of 0.062. Observed and calculated structure factors are given in Table 1, and final parameters for non-hydrogen atoms in Table 2. Magnitudes and directions of the vibrational ellipsoids, and numbering of atoms are given in Fig. 1. Bond lengths and angles with estimated standard deviations are presented in Table 3. The estimated standard deviations were calculated from the correlation matrix. Short intermolecular contacts are given in Table 3 and deviations from a least squares plane through the ring atoms in the pyrimidine moiety are given in Table 4. The r.m.s. discrepancy between the atomic vibration components obtained in the structure determination and those calculated from a rigid-body analysis were 0.022 when excluding the C3 atom and the ethyl carbon atoms. The coordinates were accordingly not adjusted for libration.

DISCUSSION

Figs 2 and 3 show that the spatial packing of the molecules conforms to the concept of molecular close pacing. The geometry seems to favour a possible O···HC3 hydrogen bond. The C3···O distance is 2.931 Å or 0.4 Å shorter than

Table 3. Bond lengths (Å) and angles (°) with their estimated standard deviations in parenthesis.

S1–C10	1.750(9)	C6–N6	1.417(11)
S1–C2	1.787(10)	C7–C17	1.694(9)
C2–C3	1.481(17)	C8–O8	1.252(14)
C3–C4	1.481(17)		
C4–N5	1.490(11)	N6–C11	1.530(26)
N5–C10	1.347(10)	N6–C13	1.433(26)
C10–N9	1.297(12)	C11–C12	1.519(20)
N9–C8	1.413(14)	C13–C14	1.536(28)
C8–C7	1.451(13)		
C7–C6	1.356(12)		
C6–N5	1.420(11)		
C10–S1–C2	107.4(6)	N5–C6–N6	115.6(9)
S1–C2–C3	110.0(10)	N6–C6–C7	125.8(12)
C2–C3–C4	122.9(15)	C6–C7–C17	122.1(9)
C3–C4–N5	113.1(11)	C17–C7–C8	117.1(8)
C4–N5–C6	116.9(9)	C7–C8–O8	120.4(14)
N5–C6–C7	118.6(10)	O8–C8–N9	120.3(14)
C6–C7–C8	119.9(12)		
C7–C8–N9	118.6(10)	C6–N6–C11	115.9(19)
C8–N9–C10	116.3(12)	C6–N6–C13	121.5(14)
N9–C10–S1	108.6(7)	C11–N6–C13	114.6(16)
N9–C10–N5	127.8(10)	N6–C11–C12	112.8(16)
N5–C10–S1	122.7(7)	N6–C13–C14	121.0(18)
C10–N5–C4	125.7(10)		
C10–N5–C6	116.9(8)		
N5C10–S1C2	2.1(37)	N5C6–N6C11	81.1(30)
C10S1–C2C3	29.9(23)	C7C6–N6C13	48.3(25)
S1C2–C3C4	−56.1(31)		
C2C3–C4N5	49.7(31)		
C3C4–N5C10	−9.3(41)		
Possible hydrogen bond			
O8–C3 (a)	2.931	(a): $1-x, y-\frac{1}{2}, 1-z$	
Other intermolecular contacts			
O8···C4 (b)	3.015	(b): $x, y, 1+z$	
O8···C4 (c)	3.522	(c): $1-x, \frac{1}{2}+y, 1-z$	
N9···N5 (a)	3.623		
S1···C7 (a)	3.710		

Table 4. Deviation of atoms from a least-squares plane through the atoms N5, C6, C7, C8, N9, and C10, (Å).

N5	−0.047	C4	−0.064
C6	0.042	N6	−0.036
C7	−0.027	Cl7	0.113
C8	0.021	O8	−0.074
N9	−0.031		
C10	0.055	S1	0.032
		C2	−0.069
		C3	0.416

a normal van der Waals contact. The H···O distance (the position of the hydrogen atom is calculated assuming tetrahedral angles at the C3 atom and a C3–H bond length of 1.086 Å [9]) is 2.101 Å and the CHO angle is 164°. Similar possible bonds have been found in the crystal structure of caffein [10,11] and some other structures.[11] As the C···O distances in these last structures are in the range 3.00–3.20 Å, the corresponding distance in the present structure seems to be short.

The C4···O distance (3.015 Å) is also short, but this is probably not a possible hydrogen

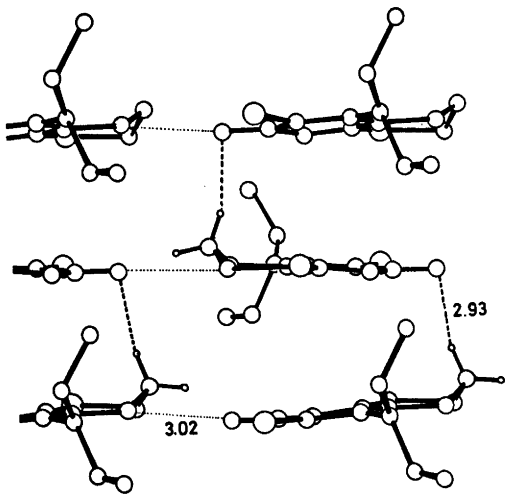


Fig. 2. Packing of molecules viewed down the *a* axis. The possible C3H···O hydrogen bond is indicated by broken line, while a short C4···O contact is indicated by a dotted line.

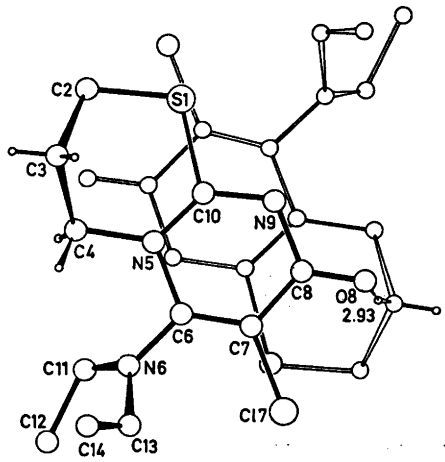


Fig. 3. Packing of molecules, viewed down the *b* axis. The possible C3···O hydrogen bond is indicated by broken line.

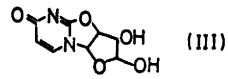
bond as the O···H distance is 2.605 Å. The remaining intermolecular contacts are normal van der Waals contacts.

The pyrimidine ring is planar within the precision of the experiment, and the S1, C2, C4, N6, and O8 atoms deviate approximately as much from the plane as the ring atoms do themselves. The C3 atom, however, deviates significantly and the C17 atom possibly significantly from the plane.

The thiazine ring moiety has an envelope-like conformation, with an angle of 45° between the ring-plane and the plane through the C3, C4, and C2 atoms.

Comparing corresponding bond distances in I with those found in II it is interesting to notice that apart from the N5 – C6 bond no significant differences are found in the pyrimidine ring moiety. The differences are in the range 0.03 – 0.01 Å. However, the N5 – C6 bond length is 0.09 Å longer than the corresponding N3 – C4 bond length in II.

The bond lengths in the present compound agree well with those found in the pyrimidine ring moiety of 2,2′-anhydro-1-(β-D-arabino-furanosyl)-uracil (III) except for the N5 – C6 bond which is 0.05 Å longer than the corresponding bond length in III. Intramolecular



(III)

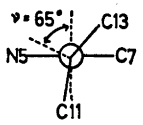
repulsion between the N6 and the C4 atom probably has substantial influence on the N5 – C6 bond length. The contact between the two atoms (2.712 Å) is 0.2 Å shorter than a normal van der Waals contact.

As to the bond angles in the pyrimidine ring moiety, the only important difference between I and II is the N5 – C6 – C7 angle in I being 8° smaller than the corresponding N3 – C4 – C5 angle in II, and the C6 – C7 – C8 angle in I being 5° wider than the corresponding C4 – C5 – C6 angle in II. Comparing I and III no significant differences are found.

In the thiazine ring moiety the S1 – C2, C2 – C3 and C3 – C4 bond lengths are slightly but probably not significantly shorter than the corresponding bond lengths in II. The S1 – C10 bond length (1.750 Å) is of the same order as the corresponding S2 – C2 bond length (1.764 Å) in II, and has a considerable amount of double bond character.[4] This is probably the reason why the thiazine ring moiety gets the observed conformation, and not an expected half chair conformation with a smaller C – S – C angle.

The C2 – C3 – C4 bond angle is significantly wider (11°) and the C10 – S1 – C2 angle probably significantly wider (2.3°) than the corresponding angles in II. The opening of these angles may indicate that the thiazine ring has conformational strain.

The N6 atom deviates 0.24 Å from the plane through the C11, C13, and C6 atoms; thus this amino nitrogen atom has a hybridisation which is neither pure sp^2 (with N in the plane) nor pure sp^3 (with N approximately 0.5 Å from the plane). The following figure shows the conformation about the C6 – N6 bond:



The N6 – C11 and N6 – C13 bond lengths deviate slightly though not significantly from a pure CN single bond distance of 1.475 Å,[13] whereas the N6 – C6 bond length (1.417 Å) is very similar to the $Me_2N - C_{ar}$ bond length in *N,N*-dimethyl-2,6-dichloro-*p*-nitroanaline [14] [1.41(1) Å]. These last bonds also have similar $n_N N - C_{ar}$-dihedral angles (ν) (65° in I and 60° in the aniline derivative).

The C7 – Cl bond length seems quite normal.[15]

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