Acta Cryst. (1973). B**29**, 2089

The Crystal Structure of a Compound with an Uncommon Aza-purine Ring System: 5,7-Bis(dimethylamino)-2-(methylthio)-*s*-triazolo-[1,5-*a*]-*s*-triazine

BY RICHARD D. GILARDI

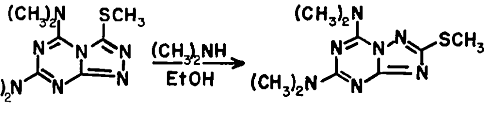
Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375, *U.S.A.*

(*Received* 27 *April* 1973; *accepted* 12 *May* 1973)

The crystal structure of 5,7-bis(dimethylamino)-2-(methylthio)-*s*-triazolo-[1,5-*a*]-*s*-triazine, $C_9H_{15}N_7S$, has been determined by X-ray diffraction. 1358 reflections were measured on an automatic diffractometer with Mo $K\alpha$ radiation. The space group of the crystal is *Cc*, with $a=9{\cdot}370$ (0·0024), $b=17{\cdot}989$ (0·0040), $c=7{\cdot}842$ (0·0014) Å, $\beta=109{\cdot}84$ (2)°, and 4 molecules per unit cell. The ring system of the molecule, which has not been previously characterized by diffraction methods, is planar to within 0·01 Å and resembles the purine ring system in its bond lengths and angles. The dimethylamino and methylthio ring substituents are twisted out of the plane by less than 10°. Bond lengths indicate that the dimethylamino nitrogen atoms are conjugated to the semi-aromatic ring system. The almost planar molecules assemble in approximately coplanar sheets which are separated by only 3·36 Å. The structure was solved by the symbolic addition procedure and refined to an *R* of 0·041 (calculated with all data).

Introduction

Many highly active insect chemosterilants are dimethylamino-substituted derivatives of *s*-triazine or similar heterocyclic ring systems (for references, see DeMilo, Oliver & Gilardi, 1973). Recently, during synthetic work aimed at producing additional chemosterilants, an unexpected rearrangement of the *s*-triazolo-[4,3-*a*]-*s*-triazine ring system was encountered (DeMilo, Oliver & Gilardi, 1973). A synthetic intermediate (I) containing this ring system was treated with excess anhydrous dimethylamine in absolute ethanol. The expected dimethylamino replacement at the thiomethyl site did not occur; analysis of the product indicated, rather, that an isomerization had occurred. The most probable explanation for this isomerization seemed to be a rearrangement in the ring system, yielding a derivative of *s*-triazolo-[1,5-*a*]-*s*-triazine (II).



(I) (II)

The proposed structure (II) of the product, 5,7-bis-(dimethylamino)-*s*-(methylthio)-*s*-triazolo-[1,5-*a*]-*s*- triazine, is corroborated by the X-ray diffraction analysis reported in this article. The ring system is very similar to that of the purine bases, and this compound could, in fact, be named as a 5-azapurine derivative, with the conventional purine numbering scheme. However, in this paper, the compound is named and numbered as a triazolo-triazine so as to conform with existing references in *Chemical Abstracts*. Structural parameters for the heterocyclic ring system in this molecule have not been previously reported.

Experimental

Crystalline samples of (II) were supplied by Dr A. B. DeMilo of the USDA Agricultural Research Center (Beltsville, Md.). The compound was recrystallized by evaporation from an acetone–cyclohexane mixture. Intensities were collected from a single crystal at room temperature with Mo $K\alpha$ radiation (0·71069 Å) on a fully automated computer-controlled 4-circle diffractometer with a θ–2θ scan and a $1{\cdot}4°+2\theta(\alpha_2)-2\theta(\alpha_1)$ scan over 2θ. The crystallographic constants are reported in Table 1.

Table 1. *Physical data*

Molecular formula	$C_9H_{15}N_7S$
M.W.	253·33
Habit	Colorless, monoclinic prisms
Size	0·065 × 0·30 × 0·50 mm
Space group	*Cc*
a	9·370 (0·0024) Å
b	17·989 (0·0040)
c	7·842 (0·0014)
β	109·84 (0·02)°
Volume	1243 Å^3
Density (calc.)	1·353 g cm^{-3}
Density (obs.)	1·35
Molecules per unit cell	4
Radiation	Mo $K\alpha$ ($\lambda=0{\cdot}71069$ Å)
Number of independent reflections measured	1358
Maximum sin θ/λ	0·639
Linear absorption coefficient	2·48 cm^{-1}

The intensities were corrected for Lorentz and polarization factors and placed on an absolute scale by means of a *K*-curve. Structure-factor magnitudes, $|F_{\mathbf{h}}|$, and also normalized structure-factor magnitudes, $|E_{\mathbf{h}}|$

were derived. The variance to be associated with each $|F_{\mathbf{h}}|$ was evaluated in the first stages of data reduction, as described below.

The first step in the data reduction procedure consists of obtaining an uncorrected initial intensity value for each reflection from the counting measurements:

$$I=[P-t_f(B_1+B_2)]$$

where P, B_1, and B_2 refer to the peak (integrated scan) and two background measurements expressed in actual counts, and t_f is a time factor necessary to relate the fixed background counting time to the variable integrated peak scan time. The random error in the time factor is very small and is considered negligible. The variance of each counting measurement, whether peak or background, is taken to be:

$$\sigma^2(N)=N+(cN)^2$$

in which the first term is the counting error assuming Poisson statistics, while the second accounts for random intensity-dependent errors due to source or system instability. The parameter c is thus a characteristic of each particular diffraction experiment, and may be estimated from a consideration of the sample variances of the monitored standard reflections. It was calculated to be 0·01 for this particular data collection. The overall expression for the variance in the intensity is then:

$$\sigma_I^2=P+c^2P^2+(t_f)^2[B_1+B_2+c^2B_1^2+c^2B_2^2]\ .$$

The structure factor modulus is obtained from the intensity by:

$$|F_{\mathbf{h}}|=\left(\frac{Q}{\mathrm{Lp}}\,.\,I\right)^{1/2},\quad I>0$$

$$|F_{\mathbf{h}}|=0\,,\quad I\le 0$$

where Lp is the Lorentz–polarization factor and Q is an attenuation factor which must be used if the source was attenuated by a metal-foil filter for the measurement of intense diffraction peaks. The determination of the attenuator factors by repetitive scans of chosen peaks leads to a distribution of values with appreciable sample variances. Therefore, estimated values for σ_Q^2 were included as a source of error in the structure factor. The resultant expression for the estimate of the structure-factor variance is:

$$\sigma_{|F|}^2=\frac{Q\,.\,I}{4\,\mathrm{Lp}}\left[\left(\frac{\sigma_I}{I}\right)^2+\left(\frac{\sigma_Q}{Q}\right)^2\right].$$

In our experience, the two error terms in this equation are often similar in magnitude for very strong reflections. Of course, for the majority of the data, no attenuators are used, and the second term vanishes. If a reflection is very weak, the above expression may be unsuitable. If I approaches zero or is slightly negative, the first term diverges or goes negative. In practice, if $I<5\sigma_I$ the following numerical approximation gives reasonable values for $\sigma_{|F|}$ and has been applied:

$$3\sigma_{|F|}=\left[\frac{1}{\mathrm{Lp}}\,(I+3\sigma_I)\right]^{1/2}-[I/\mathrm{Lp}]^{1/2}\,,\quad I\ge 0$$

$$3\sigma_{|F|}=\left[\frac{1}{\mathrm{Lp}}\,(I+3\sigma_I)\right]^{1/2},\quad I<0$$

where the first quantity on the right hand side of the equation corresponds to a (3σ) upper limit on $|F|$, and the second quantity is the expected value for $|F|$. If the intensity, I, is less than $-3\sigma_I$ there is good reason to doubt the credibility of at least one of the counting measurements, so the data reduction program rejects such reflections. The numerical approximation for $\sigma_{|F|}$ gives results virtually indistinguishable from the analytic form if $I>5\sigma_I$ and could be used for all data. A similar expression was used by Sletten, Sletten & Jensen (1969) to estimate $\sigma_{|F|}$ throughout the entire intensity range.

Structure determination

Precession and Weissenberg photographs of this crystal indicated the space group to be either Cc (acentric) or $C2/c$ (centric). An examination of the statistical distribution of intensities did not resolve this ambiguity. For example, the value of $\langle|E|\rangle$ for the observed reflections was 0·82 *versus* theoretical values of 0·80 for a centric distribution and 0·89 for an acentric one. This would seem to indicate a centric crystal; however, the observed value of $\langle|E|^2-1\rangle$ was 0·84, and the theoretical values for this statistical measure are 0·97 (centric) and 0·74 (acentric). Also, since the density indicated $Z=4$, the asymmetric unit would be only half a molecule if the space group were $C2/c$, and the molecule would possess either an inversion center or a twofold axis. This did not appear to be likely from the chemical evidence.

Thus, the phase determination was begun in space group Cc by the symbolic addition procedure (Karle & Karle, 1966). However, choosing Cc as the most likely space group does not preclude the solution of a $C2/c$ structure when this method is used for phase determination. The origin can be set in a way that is compatible with either space group, and the initial symbolic phasing procedure is the same in either case.

In space group Cc, the $0k0$ reflections have real phases and are structure seminvariants. Such reflections are therefore useful for symbolic assignments but may not be used to assign the origin. Two reflections of any other type may be used to fix the origin, but a unique assignment is assured only if

$$\begin{vmatrix} h_1 l_1 \\ h_2 l_2 \end{vmatrix}=\pm 1\ .$$

This condition for origin setting was originally expressed by Karle & Hauptman (1961), but in terms of indices referred to a primitive cell. Above, all references are to indices of the conventional centered cell. In this determination, the 355 and the 243 reflections were assigned zero phases to fix the origin. This pair of reflections, which obeys the above criterion, necessarily obeys the less stringent requirements for fixing the origin of a $C2/c$ cell (Hauptman & Karle, 1959).

Maps were generated corresponding to the four most likely sets of phases. One map, corresponding to a set which contained both real and imaginary phases (thus, a Cc structure), contained a structural fragment which looked promising but not entirely satisfactory. A possible *s*-triazine ring was apparent, with the N atoms slightly heavier than the C atoms, but the S atom position was not apparent. However, the *s*-triazine ring and all atoms directly connected to it were used as a partial structure in a tangent-formula phasing procedure (Karle, 1968).

Each cycle of this procedure consists of phasing the reflections with strongest $|E|$ values from a structural fragment, refining those phases and determining additional phases with the tangent formula, and generating an improved E map from these phases. After three cycles, the full ring system and the amino N atoms were apparent, and the S atom appeared as the heaviest atom. All methyl carbon atoms were found in a conventional difference map. A re-examination of the original E map revealed that the peak for the S atom was indeed present, but was seventh in intensity, and could not be connected to the partial structure because C(2), the adjacent ring atom, was missing in that first map.

An examination of the coordinates of the refined structure revealed a pseudo-center in the molecule, which could explain some of the ambiguities encountered in the determination of this structure. A shift of $\Delta x = -0{\cdot}517$, $\Delta z = -0{\cdot}895$ (arbitrary shifts in x and z preserve the crystallographic symmetry in Cc) moves the center of the *s*-triazine ring to the origin. The positions of the atoms of the *s*-triazine ring, as well as N(1) and N(13), are now quite accurately related by an inversion center at the origin. [C(2) and C(14) also constitute an approximate inversion pair]. If the other

Table 2. *Observed and calculated structure factors for* 5,7-*bis*(*dimethylamino*)-2-(*methylthio*)-*s*-*triazolo*-[1,5-*a*]-*s*-*triazine* (II)

The columns are the index l, $10|F_o|$, and $10|F_c|$.

0	0	L
2	889	914
4	345	357
6	97	96
8	130	129
0	2	L
0	999	1049
1	374	361
2	389	403
3	127	128
4	158	161
5	134	140
6	126	122
7	106	109
8	56	62
9	70	73
0	4	L
0	117	112
1	345	349
2	93	99
3	600	603
4	131	130
5	344	346
6	95	94
7	132	129
8	100	94
9	44	40
0	6	L
0	32	35
1	492	495
2	116	114
3	395	392
4	425	407
5	67	72
6	86	86
7	93	91
8	91	85
9	69	61
0	8	L
0	236	232
1	487	459
2	579	564
3	172	165
4	131	143
5	23	25
6	67	57
7	75	80
8	10	24
0	10	L
0	86	88
1	246	249
2	137	133
3	200	198
4	150	150
5	41	43
6	212	207
7	103	107
8	24	31
0	12	L
0	210	207
1	307	313
2	294	295
3	167	172
4	89	88
5	143	139
6	79	86
7	110	107
8	18	22
0	14	L
0	176	176
1	38	43
2	312	304
3	186	193
4	53	52
5	75	70
6	83	82
7	21	25
0	16	L
0	302	299
1	81	81
2	58	65
3	106	109
4	107	108
5	52	48
6	45	43
0	18	L
0	10	36
1	74	79
2	46	56
3	133	143
4	55	55
5	62	51
0	20	L
0	84	83
1	69	69
2	13	18
3	63	57
4	24	29
0	22	L
0	0	4
1	0	25
2	49	47
1	1	L
-9	58	54
-8	12	8
-7	80	77
-6	146	149
-5	261	263
-4	126	133
-3	403	421
-2	704	688
-1	410	405
0	976	981
1	623	627
2	287	284
3	383	381
4	278	281
5	145	143
6	21	20
7	115	110
8	11	19
9	44	24
1	3	L
-9	79	81
-8	124	116
-7	82	79
-6	192	185
-5	64	58
-4	237	240
-3	260	268
-2	871	897
-1	445	457
0	1008	1019
1	541	554
2	522	524
3	97	90
4	328	322
5	150	149
6	188	184
7	149	148
8	58	53
1	5	L
-9	110	105
-8	32	31
-7	47	47
-6	143	147
-5	98	98
-4	209	209
-3	189	194
-2	297	302
-1	179	133
0	313	308
1	350	340
2	346	338
3	153	155
4	240	235
5	84	83
6	40	33
7	198	190
8	31	34
1	7	L
-9	23	24
-8	47	43
-7	109	105
-6	54	52
-5	205	205
-4	226	234
-3	251	258
-2	191	185
-1	357	351
0	264	263
1	331	327
2	339	319
3	340	345
4	81	76
5	212	209
6	75	78
7	13	25
8	43	35
1	9	L
-8	30	30
-7	179	182
-6	39	40
-5	65	65
-4	171	182
-3	373	389
-2	97	100
-1	114	109
0	137	141
1	578	588
2	257	249
3	102	98
4	46	39
5	300	306
6	73	72
7	36	25
8	52	51
1	11	L
-8	0	16
-7	128	128
-6	142	143
-5	28	34
-4	116	122
-3	141	139
-2	258	263
-1	152	153
0	266	265
1	157	157
2	165	160
3	60	58
4	208	219
5	189	189
6	31	29
7	77	69
1	13	L
-7	51	58
-6	46	45
-5	77	83
-4	86	84
-3	52	51
-2	353	354
-1	20	24
0	378	351
1	48	40
2	74	76
3	108	112
4	84	85
5	84	89
6	49	50
7	37	25
1	15	L
-7	60	60
-6	25	46
-5	32	31
-4	0	19
-3	319	319
-2	230	233
-1	65	65
0	246	256
1	384	392
2	11	27
3	33	33
4	66	71
5	107	103
6	18	21
1	17	L
-6	21	15
-5	93	87
-4	21	12
-3	52	57
-2	119	122
-1	108	106
0	123	139
1	52	62
2	23	4
3	123	123
4	41	43
5	72	75
1	19	L
-5	30	23
-4	80	83
-3	32	28
-2	30	13
-1	0	7
0	17	12
1	34	33
2	120	120
3	29	26
4	101	95
1	21	L
-3	26	26
-2	52	50
-1	78	73
0	50	52
1	40	37
2	36	40
3	65	60
2	0	L
-8	62	59
-6	177	180
-4	381	389
-2	3467	3407
0	893	898
2	568	566
4	137	134
6	215	218
8	49	54
2	2	L
-9	34	39
-8	62	58
-7	52	58
-6	58	79
-5	101	102
-4	233	230
-3	222	220
-2	847	847
-1	514	517
0	368	383
1	168	164
2	235	220
3	273	268
4	220	208
5	198	210
6	96	102
7	131	132
8	34	30
2	4	L
-9	73	70
-8	45	45
-7	174	178
-6	97	91
-5	319	315
-4	66	68
-3	151	142
-2	89	90
-1	360	354
0	70	66
1	732	737
2	100	108
3	549	539
4	163	163
5	193	189
6	178	174
7	62	61
8	58	54
2	6	L
-9	54	50
-8	47	47
-7	45	45
-6	222	216
-5	196	194
-4	106	111
-3	287	282
-2	36	30
-1	445	454
0	99	101
1	539	542
2	613	611
3	97	99
4	118	115
5	145	146
6	160	158
7	109	108
8	43	37
2	8	L
-9	41	37
-8	30	30
-7	22	25
-6	63	75
-5	84	79
-4	346	345
-3	289	294
-2	215	214
-1	412	390
0	657	651
1	214	210
2	201	204
3	28	14
4	78	73
5	136	136
6	56	50
7	29	33
8	65	54
2	10	L
-8	105	105
-7	18	11
-6	72	69
-5	134	132
-4	119	119
-3	191	193
-2	64	70
-1	198	201
0	106	114
1	197	199
2	231	228
3	83	89
4	318	317
5	172	170
6	58	60
7	67	66
2	12	L
-8	50	51
-7	96	94
-6	55	54
-5	108	107
-4	191	197
-3	200	198
-2	153	151
-1	324	327
0	299	302
1	174	184
2	108	108
3	187	184
4	110	114
5	177	166
6	33	36
7	41	31
2	14	L
-7	48	46
-6	16	28
-5	114	117
-4	278	228
-3	12	15
-2	139	142
-1	58	66
0	311	313
1	233	239
2	56	58
3	88	86
4	119	116
5	40	47
6	43	45
2	16	L
-7	27	26
-6	55	55
-5	76	77
-4	53	55
-3	70	71
-2	260	258
-1	68	71
0	66	68
1	126	132
2	152	150
3	63	66
4	68	69
5	48	53
2	18	L
-6	45	28
-5	98	90
-4	46	45
-3	56	55
-2	19	34
-1	84	87
0	56	57
1	147	153
2	85	81
3	82	80
4	71	60
5	76	65
2	20	L
-4	30	19
-3	52	48
-2	71	72
-1	67	68
0	13	15
1	70	65
2	42	35
3	31	40
2	22	L
-2	14	10
-1	16	18
0	50	50
1	26	17
3	1	L
-9	34	36
-8	67	71
-7	123	122
-6	62	57
-5	182	187
-4	336	331
-3	326	334
-2	848	842
-1	441	442
0	281	280
1	331	322
2	391	388
3	273	223
4	58	56
5	170	170
6	44	33
7	56	52
8	27	26
3	3	L
-9	46	36
-8	88	83
-7	44	46
-6	119	121
-5	80	83
-4	434	438
-3	170	170
-2	612	589
-1	410	422
0	581	594
1	87	91
2	406	408
3	226	224
4	248	246
5	215	220
6	92	92
7	59	60
8	33	26
3	5	L
-9	31	24
-8	74	72
-7	58	54
-6	102	106
-5	77	73
-4	192	190
-3	66	64
-2	259	253
-1	249	247
0	392	308
1	199	197
2	275	279
3	96	93
4	41	42
5	282	278
6	64	67
7	41	46
8	35	34
3	7	L
-9	45	44
-8	39	26
-7	104	101
-6	118	125
-5	141	151
-4	97	90
-3	330	340
-2	149	142
-1	276	284
0	356	339
1	399	399
2	75	81
3	377	327
4	108	108
5	14	19
6	60	58
7	35	41
3	9	L
-9	90	91
-8	32	30
-7	32	33
-6	99	103
-5	192	188
-4	37	36
-3	74	77
-2	90	80
-1	509	507
0	267	253
1	117	113
2	22	25
3	393	394
4	142	138
5	53	40
6	83	86
7	51	39
3	11	L
-8	79	75
-7	26	16
-6	65	70
-5	90	89
-4	160	165
-3	68	72
-2	181	184
-1	121	116
0	189	188
1	55	53
2	271	217
3	221	223
4	31	37
5	108	101
6	92	84
7	58	54
3	13	L
-8	25	16
-7	45	47
-6	58	64
-5	57	52
-4	268	264
-3	25	26
-2	219	217
-1	35	28
0	52	55
1	171	126
2	109	104
3	97	102
4	69	68
5	57	46
6	48	50
3	15	L
-7	16	15
-6	0	13
-5	192	198
-4	157	162
-3	58	66
-2	199	196
-1	336	337
0	19	22
1	0	16
2	76	80
3	140	132
4	78	34
5	90	89
3	17	L
-6	6	13
-5	59	51
-4	84	87
-3	87	87
-2	109	115
-1	81	65
0	28	15
1	130	134
2	54	59
3	99	102
4	70	65
3	19	L
-5	30	20
-4	18	9
-3	15	3
-2	12	10
-1	38	30
0	115	124
1	27	22
2	114	106
3	38	45
3	21	L
-3	61	53
-2	49	44
-1	34	26
0	49	40
1	80	61
2	98	50
4	0	L
-8	86	84
-6	147	141
-4	1372	1363
-2	333	331
0	486	494
2	150	153
4	295	293
6	97	96
4	2	L
-9	26	28
-8	0	24
-7	55	46
-6	114	109
-5	113	117
-4	419	421
-3	356	362
-2	230	240
-1	160	167
0	254	246
1	301	286
2	267	263
3	263	265
4	139	139
5	186	191
6	38	41
7	54	53
4	4	L
-9	74	74
-8	49	55
-7	143	139
-6	20	23
-5	77	75
-4	56	60
-3	161	165
-2	105	103
-1	487	489
0	45	68
1	592	575
2	207	213
3	211	215
4	242	240
5	82	81
6	83	85
7	27	34
4	6	L
-9	29	27
-8	105	101
-7	89	86
-6	58	64
-5	146	149
-4	21	15
-3	228	225
-2	123	129
-1	345	346
0	560	557
1	133	129
2	108	111
3	178	172
4	220	221
5	153	157
6	46	68
7	58	63
4	8	L
-9	15	19
-8	33	31
-7	32	33
-6	173	179
-5	137	146
-4	174	137
-3	206	210
-2	480	456
-1	136	138
0	202	197
1	43	40
2	74	77
3	166	171
4	73	72
5	58	55
6	91	90
7	36	29
4	10	L
-8	31	29
-7	66	64
-6	72	73
-5	109	111
-4	36	38
-3	112	117
-2	92	91
-1	135	141
0	223	217
1	124	122
2	353	355
3	273	228
4	87	84
5	98	97
6	65	58
4	12	L
-8	18	28
-7	50	48
-6	105	107
-5	116	118
-4	77	77
-3	224	220
-2	210	206
-1	138	142
0	97	97
1	185	194
2	115	112
3	208	202
4	49	42
5	50	45
6	40	51
4	14	L
-7	59	60
-6	124	128
-5	0	18
-4	75	73
-3	51	55
-2	250	249
-1	211	212
0	53	44
1	66	74
2	124	122
3	60	66
4	61	62
5	67	69
4	16	L
-7	47	46
-6	35	37
-5	60	51
-4	171	170
-3	42	47
-2	73	58
-1	135	138
0	146	146
1	65	69
2	59	68
3	56	68
4	58	58
4	18	L
-6	30	31
-5	36	38
-4	30	27
-3	75	68
-2	58	42
-1	129	125
0	93	80
1	88	88
2	74	65
3	41	81
4	20	L
-4	40	48
-3	47	43
-2	0	12
-1	57	54
0	33	30
1	42	49
2	38	34
5	1	L
-9	50	45
-8	24	22
-7	66	71
-6	128	134
-5	171	176
-4	481	477
-3	200	198
-2	119	128
-1	199	192
0	338	334
1	217	248
2	91	89
3	185	193
4	60	57
5	82	75
6	42	39
7	43	34
5	3	L
-9	24	31
-8	58	61
-7	26	21
-6	186	188
-5	59	56
-4	298	294
-3	168	169
-2	309	317
-1	16	8
0	334	328
1	227	225
2	244	252
3	240	242
4	117	116
5	81	83
6	42	43
7	39	30
5	5	L
-9	34	47
-8	45	47
-7	37	37
-6	92	91
-5	60	63
-4	145	146
-3	111	118
-2	169	163
-1	160	162
0	193	190
1	74	73
2	38	40
3	308	309
4	90	92
5	55	68
6	50	50
5	7	L
-9	47	36
-8	56	59
-7	63	69
-6	91	48
-5	153	151
-4	57	52
-3	155	157
-2	258	264
-1	285	263
0	59	64
1	334	349
2	113	107
3	31	32
4	70	67
5	54	60
6	28	34
5	9	L
-9	0	12
-8	48	50
-7	82	83
-6	27	22
-5	46	42
-4	48	43
-3	289	285
-2	196	199
-1	96	96
0	28	31
1	363	364
2	157	151
3	42	39
4	101	104
5	58	60
6	90	85
5	11	L
-8	26	29
-7	50	49
-6	72	72
-5	27	24
-4	105	108
-3	83	82
-2	166	167
-1	25	18
0	175	173
1	193	190
2	27	31
3	123	121
4	120	111
5	72	68
5	13	L
-8	28	35
-7	30	38
-6	151	152
-5	25	18
-4	116	113
-3	0	19
-2	46	35
-1	102	99
0	102	100
1	97	105
2	79	74
3	59	54
4	71	67
5	55	48
5	15	L
-7	99	102
-6	87	94
-5	45	47
-4	124	119
-3	218	214
-2	0	13
-1	22	20
0	76	70
1	125	129
2	32	43
3	98	98
4	38	42
5	17	L
-6	45	44
-5	55	51
-4	80	79
-3	52	57
-2	24	16
-1	114	113
0	54	57
1	99	102
2	64	68
3	42	38
5	19	L
-4	22	8
-3	19	23
-2	93	90
-1	15	16
0	89	86
1	38	45
2	31	42
6	0	L
-8	52	49
-6	551	556
-4	87	94
-2	243	245
0	121	123
2	299	297
4	127	129
6	30	35
6	2	L
-9	28	15
-8	49	45
-7	49	52
-6	185	187
-5	179	177
-4	170	119
-3	89	94
-2	176	179
-1	177	169
0	207	205
1	242	245
2	146	147
3	198	210
4	40	36
5	65	70
6	60	57
6	4	L
-9	42	48
-8	17	8
-7	31	33
-6	30	34
-5	68	59
-4	61	70
-3	244	241
-2	34	37
-1	429	427
0	159	161
1	167	181
2	240	241
3	93	94
4	93	95
5	60	51
6	36	27
6	6	L
-9	38	33
-8	27	37
-7	64	64
-6	0	6
-5	105	100
-4	97	97
-3	152	150
-2	337	331
-1	179	130
0	90	90
1	157	154
2	224	229
3	174	183
4	65	69
5	84	88
6	30	38
6	8	L
-9	24	12
-8	77	78
-7	62	63
-6	59	60
-5	85	90
-4	230	230
-3	62	67
-2	140	132
-1	61	65
0	82	79
1	157	162
2	67	72
3	61	67
4	107	106
5	48	39
6	10	L
-8	37	34
-7	56	58
-6	0	16
-5	49	51
-4	65	66
-3	73	73
-2	144	141
-1	115	112
0	290	286
1	222	235
2	86	65
3	109	109
4	68	65
5	65	65
6	12	L
-8	52	45
-7	57	66
-6	40	34
-5	113	113
-4	110	114
-3	63	66
-2	60	67
-1	139	136
0	104	94
1	162	185
2	37	36
3	49	51
4	45	56
6	14	L
-7	16	17
-6	26	21
-5	40	36
-4	154	153
-3	142	144
-2	30	30
-1	41	44
0	100	103
1	60	66
2	60	63
3	75	76
4	43	42
6	16	L
-6	89	90
-5	9	23
-4	54	42
-3	116	114
-2	102	100
-1	60	57
0	54	47
1	56	67
2	69	67
3	30	35
6	18	L
-5	42	42
-4	0	23
-3	77	79
-2	64	53
-1	75	68
0	55	52
1	75	72
7	1	L
-9	23	22
-8	53	57
-7	76	74
-6	227	237
-5	79	82
-4	59	52
-3	100	100
-2	197	195
-1	151	149
0	90	68
1	147	155
2	68	70
3	80	79
4	42	40
5	46	44
7	3	L
-9	0	1
-8	68	73
-7	10	20
-6	130	137
-5	77	73
-4	149	140
-3	31	37
-2	190	190
-1	153	149
0	178	180
1	182	191
2	103	107
3	88	94
4	60	56
5	38	37
7	5	L
-9	25	16
-8	42	40
-7	28	35
-6	70	67
-5	58	54
-4	72	71
-3	101	102
-2	94	88
-1	45	51
0	55	45
1	252	259
2	95	97
3	77	77
4	55	54
5	32	31
7	7	L
-9	28	25
-8	30	24
-7	59	52
-6	26	29
-5	71	64
-4	146	151
-3	155	154
-2	34	30
-1	247	253
0	100	94
1	30	36
2	57	60
3	66	73
4	41	39
5	53	49
7	9	L
-8	29	16
-7	25	23
-6	29	25
-5	140	139
-4	120	122
-3	70	69
-2	29	32
-1	250	246
0	177	178
1	73	18
2	87	95
3	74	69
4	97	92
7	11	L
-8	37	23
-7	21	13
-6	52	51
-5	51	52
-4	95	95
-3	22	15
-2	109	108
-1	134	127
0	0	14
1	106	110
2	106	104
3	63	64
4	40	40
7	13	L
-7	20	16
-6	47	47
-5	23	20
-4	13	12
-3	71	58
-2	71	66
-1	87	83
0	74	65
1	58	46
2	66	68
3	50	56
7	15	L
-6	61	62
-5	113	111
-4	0	7
-3	35	34
-2	53	48
-1	102	98
0	45	41
1	76	82
2	40	37
7	17	L
-5	43	39
-4	26	19
-3	53	78
-2	37	40
-1	80	76
0	56	57
1	75	29
8	0	L
-8	215	220
-6	22	13
-4	119	115
-2	92	90
0	278	227
2	117	127
4	37	35
8	2	L
-9	14	19
-8	85	88
-7	83	79
-6	64	56
-5	35	38
-4	76	79
-3	82	79
-2	126	126
-1	174	173
0	174	124
1	169	181
2	14	23
3	58	67
4	65	64
8	4	L
-9	0	12
-8	0	18
-7	0	11
-6	19	34
-5	106	102
-4	18	22
-3	233	231
-2	83	70
-1	106	107
0	190	189
1	77	80
2	71	81
3	57	57
4	28	26
8	6	L
-8	0	7
-7	45	43
-6	53	57
-5	71	69
-4	165	164
-3	94	90
-2	64	64
-1	106	107
0	174	171
1	154	162
2	48	55
3	80	92
4	42	45
8	8	L
-8	16	27
-7	43	37
-6	101	99
-5	6	27
-4	77	77
-3	47	50
-2	64	61
-1	115	116
0	56	54
1	49	62
2	81	90
3	37	40
8	10	L
-7	0	17
-6	45	36
-5	37	31
-4	71	71
-3	71	69
-2	178	173
-1	180	182
0	66	67
1	93	96
2	53	56
3	63	68
8	12	L
-7	45	44
-6	50	54
-5	39	40
-4	29	32
-3	76	72
-2	62	64
-1	138	133
0	30	25
1	56	42
2	46	47
8	14	L
-6	76	76
-5	79	82
-4	15	12
-3	35	21
-2	68	65
-1	51	47
0	46	48
1	63	64
8	16	L
-4	48	50
-3	36	36
-2	42	30
-1	42	50
0	68	59
9	1	L
-8	108	112
-7	33	31
-6	29	19
-5	36	38
-4	94	96
-3	84	81
-2	64	64
-1	103	98
0	99	98
1	67	68
2	32	31
3	35	40
9	3	L
-8	89	57
-7	42	35
-6	60	59
-5	35	32
-4	95	92
-3	81	81
-2	98	100
-1	114	108
0	66	66
1	89	86
2	92	54
3	44	33
9	5	L
-8	33	26
-7	28	21
-6	10	19
-5	51	52
-4	39	42
-3	26	24
-2	35	39
-1	171	169
0	80	76
1	62	69
2	49	45
3	32	33
9	7	L
-8	0	15
-7	21	10
-6	69	75
-5	67	68
-4	18	11
-3	131	135
-2	73	68
-1	18	24
0	48	42
1	55	67
2	0	32
9	9	L
-7	61	58
-6	60	61
-5	37	38
-4	36	24
-3	128	128
-2	170	123
-1	23	18
0	59	65
1	61	59
2	77	80
9	11	L
-6	41	39
-5	28	12
-4	53	53
-3	77	72
-2	0	5
-1	83	85
0	66	70
1	40	45
9	13	L
-5	39	30
-4	28	28
-3	56	52
-2	51	46
-1	32	30
0	55	52
9	15	L
-3	57	57
-2	39	30
10	0	L
-8	6	17
-6	47	51
-4	97	57
-2	126	124
0	86	79
2	0	28
10	2	L
-7	18	13
-6	25	26
-5	42	38
-4	76	70
-3	92	89
-2	78	80
-1	176	127
0	25	16
1	34	46
2	49	54
10	4	L
-7	42	38
-6	34	15
-5	102	95
-4	31	34
-3	58	47
-2	110	111
-1	56	58
0	60	53
1	46	47
2	25	19
10	6	L
-7	39	26
-6	72	68
-5	51	47
-4	32	36
-3	54	57
-2	98	98
-1	125	118
0	34	31
1	74	70
10	8	L
-6	89	42
-5	21	30
-4	36	34
-3	67	67
-2	31	34
-1	50	45
0	54	59
1	30	31
10	10	L
-5	42	28
-4	86	86
-3	103	110
-2	32	35
-1	63	64
0	35	39
10	12	L
-4	30	34
-3	77	76
-2	27	14
0	24	32
10	14	L
0	39	29
11	1	L
-6	43	42
-5	38	36
-4	39	37
-3	48	49
-2	44	38
-1	43	41
0	32	20
11	3	L
-6	48	39
-5	27	39
-4	46	45
-3	50	52
-2	30	26
-1	87	60
0	30	40
11	5	L
-6	0	21
-5	20	14
-4	25	15
-3	92	89
-2	47	45
-1	46	49
0	38	30
11	7	L
-5	58	57
-4	35	38
-3	22	14
-2	0	26
-1	54	47
0	11	21
11	9	L
-3	18	22
0	53	55
11	11	L
0	12	25
12	0	L
0	22	16
12	2	L
0	29	35
12	4	L
0	26	12
12	6	L
0	17	28

atoms were absent, this would be a true crystallographic center, and the space group would be $C2/c$. The initial phase determination gave phases which tended to reinforce this pseudo-center, and this led to an E map which emphasized those atoms that obeyed the pseudo symmetry. A re-examination of the first E map revealed that the largest spurious peak was a pseudo-inversion equivalent of the sulfur atom. This, of course, disappeared as the truly acentric portion of the structure was added and more of the phases were refined to their true acentric values.

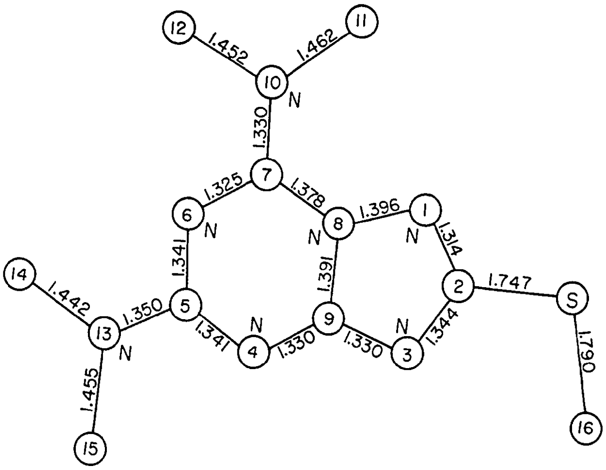


Fig. 1. Bond distances for (II). The standard deviations for bond distances indicated by the least-squares refinement are 0·005 Å for bonds to peripheral methyl carbons and 0·003–0·004 Å for all other bonds between non-hydrogen atoms.

Refinement

Isotropic and anisotropic full-matrix least-squares refinement of the non-hydrogen atoms led to an unweighted R of 0·069 at which time a difference Fourier map revealed the 15 hydrogen atoms of the structure. The hydrogen atom positions were subsequently varied, while their anisotropic thermal parameters were included in the refinement as constrained parameters; *i.e.*, the thermal parameters of all atoms of a methyl group were set equal, and varied in unison. Spherical atomic scattering factors for S, C, and N were taken from *International Tables for X-ray Crystallography* (1962), and the spherical scattering factors for bonded hydrogen of Stewart, Davidson & Simpson (1965) were used. Anomalous scattering contributions were included for S: $\Delta f' = 0{\cdot}110$, $\Delta f'' = 0{\cdot}124$ (Cromer & Liberman, 1970). An isotropic secondary extinction correction was applied to the calculated structure factors, as outlined by Larson (1967). Only three of the corrections were greater than 5%; the correction factors applied to F_c for the $20\bar{2}$, 110, and 020 reflections were 0·74, 0·93, and 0·91, respectively. The function minimized was $\sum w|F_o - F_c|^2$, and the final measures of agreement were

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|} = 0{\cdot}041$$

$$R_w = \frac{\sum w|F_o - F_c|^2}{\sum wF_o^2} = 0{\cdot}031$$

and

$$s = \left[\frac{\sum w|F_o - F_c|^2}{N_o - N_v}\right]^{1/2} = 2{\cdot}23$$

wherein N_o was 1358 and N_v, the total number of varied parameters, was 198. No reflections were considered 'unobserved' and omitted from the above summations. Final observed and calculated structure factors are given in Table 2. Final positions and thermal

Table 3. *Fractional coordinates and thermal parameters with standard deviations*

The thermal parameters are of the form:

$$T = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

Hydrogen atoms were assigned thermal factors equal to those of the adjoining carbon atom.
Standard deviations are those indicated by the full-matrix least-squares refinement.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0·87260	0·81602 (5)	1·25440	4·76 (4)	4·46 (4)	5·36 (4)	1·27 (4)	0·87 (3)	1·25 (4)
N(1)	0·77301 (31)	0·95264 (14)	1·16039 (38)	3·73 (13)	3·77 (13)	4·03 (13)	0·57 (10)	0·69 (10)	0·42 (10)
C(2)	0·74242 (36)	0·88173 (18)	1·12764 (41)	3·72 (14)	3·80 (14)	3·76 (14)	0·70 (11)	1·28 (12)	0·47 (11)
N(3)	0·61480 (31)	0·86382 (14)	0·99160 (37)	4·11 (13)	3·36 (12)	3·98 (13)	0·54 (10)	1·03 (10)	0·26 (11)
N(4)	0·42530 (30)	0·94303 (15)	0·79491 (35)	3·75 (13)	3·51 (13)	3·74 (13)	0·29 (9)	0·69 (10)	0·38 (10)
C(5)	0·39402 (43)	1·01559 (18)	0·76481 (54)	3·53 (17)	4·15 (14)	3·83 (13)	0·67 (13)	1·51 (13)	0·69 (13)
N(6)	0·47782 (34)	1·07262 (14)	0·85595 (41)	3·68 (12)	3·27 (12)	4·14 (12)	0·47 (11)	1·27 (10)	0·53 (11)
C(7)	0·60571 (40)	1·05855 (16)	0·99063 (47)	3·94 (14)	3·46 (14)	4·17 (15)	0·22 (12)	2·01 (13)	0·08 (13)
N(8)	0·64838 (31)	0·98545 (14)	1·02974 (37)	3·57 (12)	3·22 (12)	3·66 (11)	0·31 (10)	0·98 (9)	0·03 (10)
C(9)	0·55432 (41)	0·92957 (18)	0·92965 (47)	4·37 (16)	3·39 (13)	3·62 (13)	0·40 (11)	1·33 (12)	0·12 (11)
N(10)	0·68833 (31)	1·11439 (15)	1·08509 (38)	4·13 (13)	3·10 (12)	5·62 (15)	0·17 (11)	1·53 (11)	−0·32 (11)
C(11)	0·84109 (48)	1·10938 (25)	1·21865 (68)	4·11 (18)	4·80 (21)	6·59 (22)	−0·42 (15)	0·87 (16)	−1·40 (17)
C(12)	0·62784 (57)	1·18919 (23)	1·04606 (75)	5·26 (22)	3·87 (18)	8·70 (26)	0·14 (16)	1·64 (22)	−0·75 (17)
N(13)	0·26551 (34)	1·03384 (16)	0·62901 (40)	4·06 (14)	4·48 (14)	4·35 (14)	0·42 (11)	0·63 (12)	0·44 (11)
C(14)	0·22310 (57)	1·11051 (28)	0·58715 (68)	5·48 (24)	5·73 (21)	5·84 (22)	1·55 (18)	0·86 (20)	1·55 (21)
C(15)	0·16104 (52)	0·97669 (27)	0·52791 (66)	4·66 (19)	6·75 (25)	4·62 (17)	−0·46 (20)	0·25 (16)	1·11 (18)
C(16)	0·77394 (58)	0·73198 (22)	1·16325 (74)	7·26 (26)	3·48 (16)	8·35 (28)	1·18 (18)	2·45 (24)	1·10 (20)

Table 3 (*cont.*)

	x	*y*	*z*
H(11*A*)	0·9052 (36)	1·1442 (18)	1·1680 (46)
H(11*B*)	0·8854 (40)	1·0660 (18)	1·2035 (49)
H(11*C*)	0·8476 (38)	1·1349 (19)	1·3199 (50)
H(12*A*)	0·6376 (39)	1·2097 (17)	1·1598 (51)
H(12*B*)	0·7001 (42)	1·2190 (20)	1·0396 (58)
H(12*C*)	0·5375 (45)	1·1906 (19)	1·0200 (58)
H(14*A*)	0·1590 (43)	1·1168 (22)	0·6360 (49)
H(14*B*)	0·2000 (42)	1·1146 (20)	0·4771 (49)
H(14*C*)	0·2861 (44)	1·1449 (24)	0·6121 (53)
H(15*A*)	0·1843 (42)	0·9312 (23)	0·5578 (50)
H(15*B*)	0·0732 (41)	0·9740 (19)	0·5491 (47)
H(15*C*)	0·1171 (39)	0·9954 (21)	0·4145 (49)
H(16*A*)	0·6927 (43)	0·7312 (18)	1·2034 (51)
H(16*B*)	0·7635 (43)	0·7254 (18)	1·0390 (54)
H(16*C*)	0·8269 (46)	0·6909 (17)	1·2172 (58)

motion parameters are listed in Table 3; no corrections for librational motion were applied to the positions or to the bond distances and angles given. The linear absorption coefficient is small (2·48 cm^{-1}), and absorption corrections were not applied.

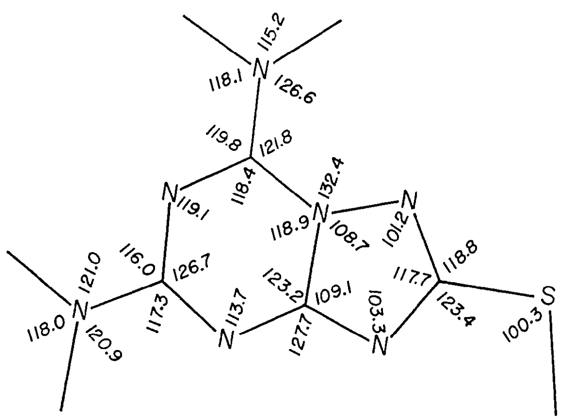


Fig. 2. Bond angles for (II). The standard deviations are 0·2° for angles involving the sulfur atom and 0·3° for all other angles involving non-hydrogen atoms.

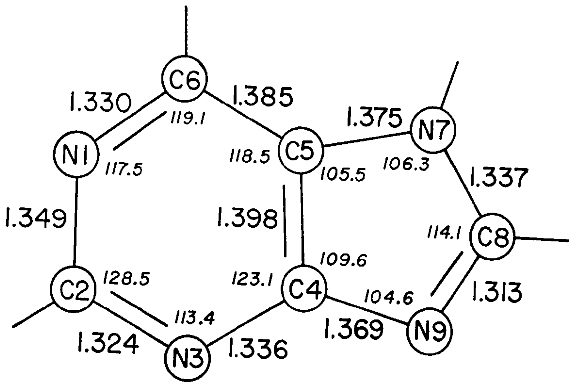


Fig. 3. Bond distances and angles of unsubstituted purine (Watson, Sweet & Marsh, 1965). Two sets of nearly identical parameters were presented by Watson, Sweet & Marsh; those of Sweet & Marsh are presented here.

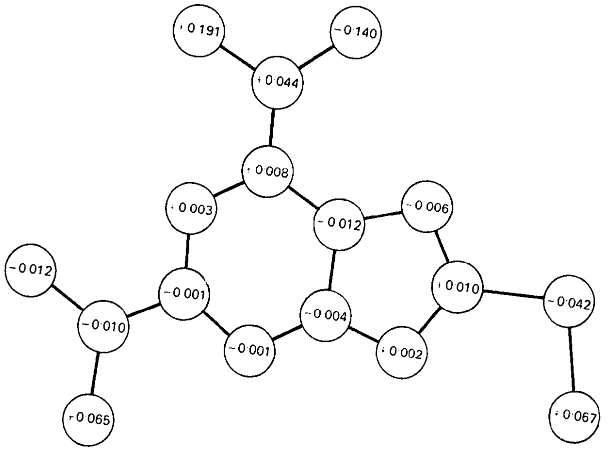


Fig. 4. Deviations of each atom in (II) from a best least-squares plane calculated through the atoms of the heterocyclic ring system.

Molecular structure

The triazolo-triazine ring system of (II) bears a strong resemblance to purine. Both are planar (to within approximately 0·01 Å), and in both cases the observed bond distances indicate that the ten π electrons available on ring atoms in either system are extensively delocalized. The bond distances and angles of (II) are presented in Figs. 1 and 2. For comparison, the bond distances, bond angles, and formal bonding diagram of unsubstituted purine (Watson, Sweet & Marsh, 1965) are presented in Fig. 3. Although formally purine has a pyrimidine ring with three double bonds, and the triazolo-triazine derivative has an *s*-triazine ring with two double bonds, there are actually no significant differences in the parameters of the six-membered rings of the two compounds. In the five-membered rings of each, there are shortened bonds which indicate some degree of localization of double bond character between atoms which are formally double-bonded in the structural diagrams (II and Fig. 3). However, none of the ring bonds is as short as an isolated double bond or as long as an isolated single bond. The dimethylamino nitrogen atoms, N(10) and N(13), apparently contribute to the π-bond system also; they are connected to the ring system with bonds of hybrid length, and their bonding geometry is essentially planar.

The deviations of all atoms from a best least-squares plane calculated through just the ring atoms are shown in Fig. 4. Most of the distortions from planarity are minor, and could reasonably be attributed to intermolecular forces and/or fairly distant intramolecular repulsions. However, in the linked region, N(1)–N(8)–C(7)–N(10)–C(11), van der Waals repulsion forces should be large, for there are two consecutive *cis* junctions along this chain. There is a close approach between N(1) and C(11) of 2·893 (5) Å compared to an estimated van der Waals approach of approximately 3·3 Å. Also, one of the hydrogen atoms on C(11),

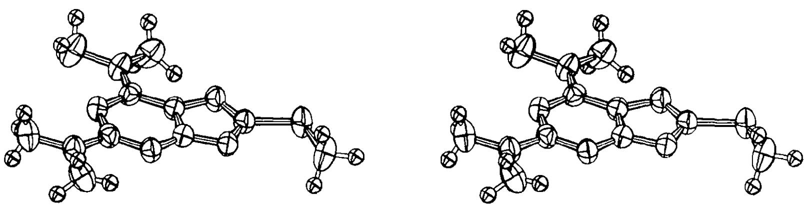


Fig. 5. A stereodrawing of (II), showing thermal vibration ellipsoids corresponding to the final thermal factors and isotropic hydrogen atoms at their refined positions.

H(11*B*), is situated only 2·27 (3) Å from N(1), compared to a van der Waals contact of 2·75 Å. The close approaches in this region would be considerably smaller if the N(10) dimethylamino group had exactly the same conformation as the N(13) dimethylamino group. The C(7)–N(10)–C(11) angle is 126·6 (3)°, more than 5° larger than the corresponding angles in the other dimethylamino group. Calculation of a plane through C(7), C(11), and C(12) reveals that N(10) is very slightly pyramidal; the N atom is 0·027 Å above the plane. The out-of-plane twist* of the N(10) dimethylamino group is 7·6° *versus* only 1·9° for the other one. Sundaralingam & Arora (1969) report that an out-of-plane twist of approximately 8° occurs in puromycin, which has a dimethylamino substituent in an analogous position on a purine ring system; full structural details were not published, so other structural adjustments in this vicinity cannot be compared.

Fig. 5 is a stereo-illustration which portrays the overall conformation of the molecule. The carbon, nitrogen and sulfur atoms are represented by thermal vibration ellipsoids calculated from the final thermal parameters, which are scaled to include 50% of the probability density.

Figs. 5, 6 and 7 were prepared with the help of the *ORTEP* computer program (Johnson, 1965).

Packing

The structure as viewed down **b** is shown in Fig. 6. The sheets of planar molecules are stacked parallel to the $(10\bar{1})$ planes, with an interplanar distance of 3·36 Å. This stacking distance is similar to values observed in a wide variety of purines; *e.g.*, in purine itself the distance is 3·39 Å (Watson, Sweet & Marsh, 1965). Two sheets of molecules are viewed down a direction which is perpendicular to their plane in Fig. 7, illustrating the overlap of the heterocyclic systems. Within each layer of this system, there is no opportunity for H-bond formation because each amino hydrogen has been replaced by a dimethylamino group. There is only one hydrogen–heavy atom approach that is shorter than a normal van der Waals contact. A methylthio hydrogen, H(16*C*), occurs only 2·58 (3) Å from N(4) of an adjacent coplanar molecule; the corresponding van der Waals approach is estimated to be about 2·74 Å. The shortest distance between stacked molecules is 3·360 Å, occurring between C(7) and N(4). There are, of course, several C–N and C–C contacts in the 3·4 to 3·5 Å range.

References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

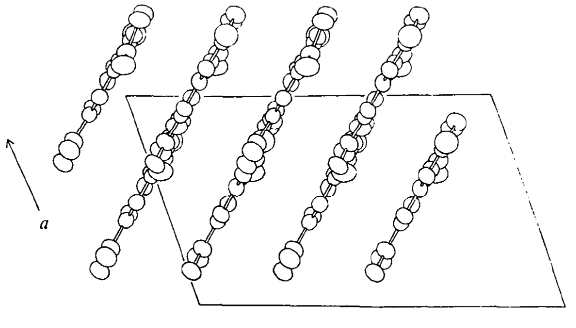


Fig. 6. A view of the packing down **b**. Hydrogen atoms are omitted for clarity; there are no hydrogen–hydrogen contacts between molecules less than 2·5 Å.

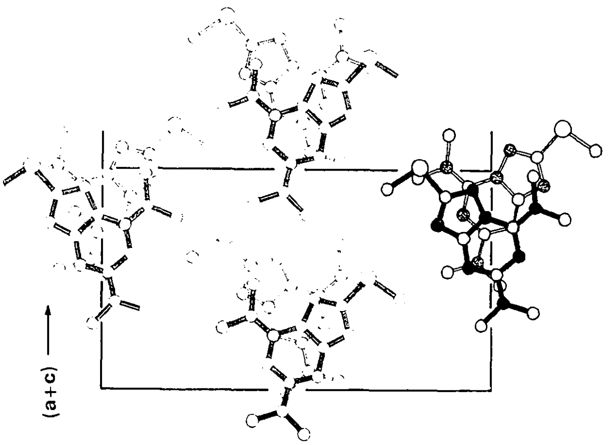


Fig. 7. A view of the packing normal to the layers shown in Fig. 6. Molecules from two layers are shown. In the pair of molecules at the right, nitrogen atoms are shaded and carbon atoms are left blank.

---

* The twist angle is defined as the average of two torsion angles; namely, ω(N6–C7–N10–C12) and ω(N8–C7–N10–C11). This is in accord with the twist angle defined by Winkler & Dunitz (1971) in their discussion of torsions in a semi-planar system.

DeMilo, A. B., Oliver, J. E. & Gilardi, R. D. (1973). *J. Heterocyclic Chem.* **10**, 231-233.

Hauptman, H. & Karle, J. (1959). *Acta Cryst.* **12**, 93–97.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Karle, J. (1968). *Acta Cryst.* B**24**, 182–186.

Karle, J. & Hauptman, H. (1961). *Acta Cryst.* **14**, 217–223.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Larson, A. (1967). *Acta Cryst.* **23**, 664–665.

Sletten, E., Sletten, J. & Jensen, L. H. (1969). *Acta Cryst.* B**25**, 1330–1338.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sundaralingam, M. & Arora, S. K. (1969). *Proc. Natl. Acad. Sci.* **64**, 1021–1026.

Watson, D. G., Sweet, R. M. & Marsh, R. E. (1965). *Acta Cryst.* **19**, 573–580.

Winkler, F. K. & Dunitz, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1973). B**29**, 2095

Structure Cristalline du Fluorosséléniure d'Yttrium Orthorhombique YSeF 1*O*

Par Nguyen Huy-Dung

Laboratoire de Physique, Faculté des Sciences Pharmaceutiques et Biologiques de Paris–Luxembourg 4, *Avenue de l'Observatoire*, 75270 *Paris Cedex* 06, *France*

(*Reçu le* 14 *mars* 1973, *accepté le* 3 *mai* 1973)

The 1*O* form of yttrium fluoroselenide, YSeF, crystallizes in the orthorhombic system, with the space group *Pnam* ($a = 9{\cdot}912$, $b = 6{\cdot}314$, $c = 4{\cdot}080$ Å, $Z = 4$). A single crystal was used for the structural determination by the heavy-atom method, and the atomic positions were refined by the least-squares method to $R = 0{\cdot}06$. The selenium atoms are at the vertex of a slightly deformed octahedron and have fourfold coordination while the three-coordinated fluorine atoms are at the centre of an yttrium isosceles triangle. The yttrium atoms have sevenfold coordination. The main feature in this structure is that there are plane groups of Y–F along two diagonals of the projected selenium hexagons. YSeF 1*O* is the basic structure of many polytype crystals in the Y–Se–F system.

Introduction

L'étude systématique des composés de lanthanides à deux anions a conduit récemment Dagron (1972) à isoler et décrire l'existence d'une famille de fluorosséléniures d'yttrium et de lanthanides lourds, de formule générale LSeF (L = Ho, Er, Y). Les multiples phases observées dans le système Y–Se–F ont pu être identifiées sans ambiguïté, grâce à des études sur monocristaux. Ces composés sont tous des polytypes, dont la structure de base orthorhombique (que nous appelons YSeF1*O*, d'après la notation de Ramsdell), était jusqu'à présent inconnue. Rappelons que Dagron a proposé un classement de ces polytypes en deux groupes. Le premier groupe de composés comprend, outre le monotype YSeF1*O*, les polytypes orthorhombiques 3*O* et 7*O*, dont les paramètres *b* sont des multiples 3 ou 7 du paramètre b_1 de la structure de base. Le deuxième groupe, en revanche, comprend les polytypes 2*M*, 3*M*,4*M*,5*M*,6*M*, monocliniques. Leurs paramètres *b* vérifient la relation

$$b = nb_1 \sin \gamma \quad (n = 2,3,4,5,6) \; .$$

Données expérimentales

Les cristaux de YSeF1*O* sont tranparents, de couleur jaune pâle. Le cristal utilisé a une forme parallélépipèdique de 80 μm de long sur 50 μm d'épaisseur et est allongé suivant l'axe **c**.

Les paramètres de la maille sont évalués à partir des clichés d'oscillation–rotation et de Weissenberg puis affinés par la méthode des moindres carrés à partir de quinze raies *hkl* d'un diffractogramme de Debye–Scherrer, avec un étalonnage donné par les raies du cuivre métallique: $a_1 = 9{,}912$ (4); $b_1 = 6{,}314$ (2); $c_1 = 4{,}080$ (1) Å. La densité expérimentale 4,86 g cm^{-3} conduit à placer quatre masses formulaires par maille, en accord avec la densité calculée (4,86 g cm^{-3}).

Les réflexions obéissent aux conditions suivantes: $0kl$: $k + l = 2n$; $h0l$: $h = 2n$. Les groupes spatiaux compatibles sont *Pnam* ou $Pna2_1$. Nous n'avons pas tenu compte de la présence de deux réflexions 902 et 052 d'intensité très faible dans la détermination du groupe spatial car leux existence observée dans le réseau réciproque d'un seul cristal est douteuse. Le calcul de la fonction de Patterson confirmera ultérieurement l'un de ces groupes spatiaux.