The Crystal Structure of Adenosine*

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The crystal structure of adenosine, $C_{10}H_{13}N_5O_4$, has been determined from the intensities of 1333 reflections, each measured at least four times on an automated diffractometer. The crystals are monoclinic, space group $P2_1$, with $a=4\cdot825$ (1), $b=10\cdot282$ (2), $c=11\cdot823$ (1) Å, $\beta=99\cdot30$ (1)°, and two molecules per cell. Least-squares refinement of coordinates and anisotropic temperature factors for all atoms, including hydrogen, led to an R index of 0·024 and standard deviations of about 0·003 Å for bond distances between pairs of heavy atoms. The anomalous scattering by nitrogen and oxygen was used to confirm the absolute configuration of the sugar ring. The conformation of the ribose ring is $C(3')$ *endo*; the torsion angle about the glycosidic bond is 9·9°. Intermolecular interactions include a full complement of hydrogen bonds, a relatively short $C(2)$–H$\cdots$O(2') contact (3·09 Å), and parallel stacking of adenine rings with an interplanar spacing of 3·57 Å.

Introduction

The determination of the crystal structure of adenosine was undertaken as part of a research program on the structures of compounds related to nucleic acids, and with a particular aim towards furnishing accurate details of the molecular geometry and obtaining further information concerning intermolecular forces such as hydrogen bonding and base stacking.

Experimental

Crystals of adenosine, in the form of colorless prisms, were kindly supplied by Dr C. E. Bugg. Preliminary oscillation and Weissenberg photographs showed them to be monoclinic. The absence of reflections 0*k*0 with *k* odd indicated the space group $P2_1$, $P2_1/m$ being ruled out since the nucleoside is optically active.

Accurate cell dimensions were obtained from a least-squares fit to 93 measurements made on *h*0*l* and 0*kl* Weissenberg photographs prepared in a Straumanis-type camera. The density was measured by

Table 1. *Crystal data*

Adenosine	$C_{10}H_{13}N_5O_4$
Space group: $P2_1$	$F(000)=280$
$a=~4\cdot825\pm0\cdot001$Å	F.W. 267·25
$b=10\cdot282\pm0\cdot002$	$Z=2$
$c=11\cdot823\pm0\cdot001$	$D_x=1\cdot533$g.cm.$^{-3}$
$\beta=99\cdot30\pm0\cdot01°$	$D_m=1\cdot54$g.cm.$^{-3}$
(λCu $K_\alpha=1\cdot5418$Å)	

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flotation. Crystallographic data are given in Table 1.

A cubic crystal of dimensions $0\cdot1\times0\cdot1\times0\cdot1$ mm was selected for intensity data collection and was mounted in an arbitrary orientation on a Datex-automated General Electric XRD-5 diffractometer. Intensities were measured using Ni-filtered copper radiation and $\theta-2\theta$ scans at a scanning speed of 1° (in 2θ) per min; the background was counted for 30 sec at each extremum. The scan ranges were adjusted to account for $\alpha_1-\alpha_2$ splitting. All reflections within one quadrant of the sphere of reflection extending to $2\theta=155°$ were measured four times; intensities of about 100 very strong reflections were measured a fifth time at a reduced current setting. A check reflection was monitored every twenty reflections; it showed no significant drift in intensity during nearly six weeks of data collection.

Of 5500 measurements, 56 were rejected because they differed distinctly from the other measurements in the set. These rejected measurements usually occurred in groups of two or more, leading us to suspect failures in the instrumentation. The remaining measurements were averaged, with appropriate weights, to yield 1333 intensities, of which 5 were less than one e.s.d. above background. Individual variances $\sigma^2(I_i)$ were calculated from counting statistics with an additional term $(0\cdot02~S)^2$, where S is the scan count; variances in the averaged intensities, $\sigma^2(I)$, were calculated from the expression

$$\sigma^{-2}(I)=\sum_i \sigma^{-2}(I_i).$$

Finally, the intensities and their standard deviations were placed on an absolute scale by Wilson's (1942) method. No correction was made for absorption ($\mu t\simeq 0\cdot1$). All calculations were carried out on an IBM 7094 computer under the *CRYRM* system (Duchamp, 1964).

Determination and refinement of the structure

The orientation of the planar adenine moiety was derived from a three-dimensional sharpened Patterson synthesis and approximate y and z coordinates for these atoms were deduced from packing and hydrogen bonding considerations. The ribose ring was located on subsequent electron density projections onto (100). Further packing studies and three-dimensional electron density maps then led to a set of approximate x coordinates. The hydrogen atoms were located from difference maps calculated during the course of the refinement.

Refinement was carried out mainly by least-squares methods. The quantity minimized was $\sum w(F_o^2 - F_c^{*2}/k^2)^2$, with weights w equal to $1/\sigma^2(F_o^2)$ and F_c^* as defined by Larson (1967), equation (3). Throughout the refinement the y coordinate of $O(1')$ was held fixed. The full matrix of normal equations was collected until it became too large (over 207 parameters) to fit into core memory. Atomic scattering factors for the non-hydrogen atoms were obtained from *International Tables for X-ray Crystallography* (1962), and those for hydrogen atoms were from Stewart, Davidson & Simpson (1965).

Eventually, a list of 289 parameters was adjusted: coordinates and anisotropic temperature parameters of all 32 atoms (including hydrogen), a scale factor, and a secondary extinction parameter g (Zachariasen, 1963; Larson, 1967). The anisotropic temperature factors for the heavy atoms, the scale factor and the secondary extinction parameter were kept in one matrix and the positional parameters in a second matrix; the anisotropic temperature parameters of the hydrogen atoms were adjusted during two least-squares
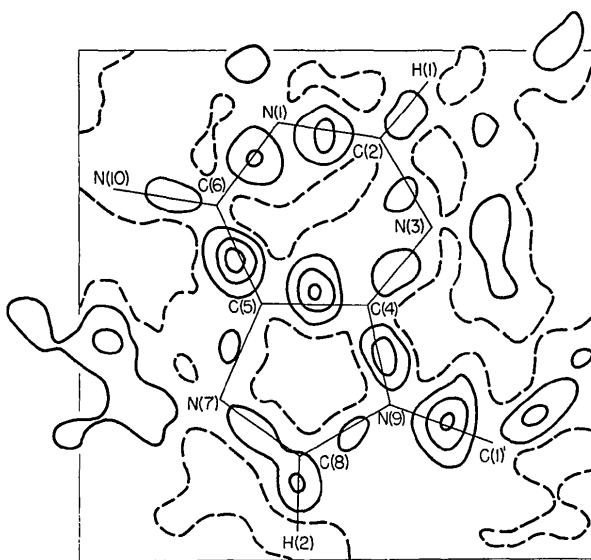

Fig. 1. A portion of the final difference map, evaluated in the plane of the adenine moiety. Contours are at intervals of 0·05 e.Å⁻³; the zero contour is dashed.

cycles in which the remaining parameters were held fixed. The refinement approached convergence at an R value of 0·025.

In view of the low R value attained it was thought that the accuracy of the intensity data must be sufficiently high that the anomalous scattering by oxygen and nitrogen could be used to check the absolute configuration of the ribose moiety. Accordingly, structure factors for both enantiomers were calculated, using the following correction terms (Hope, 1969):*

Atom	$\Delta f'$	$\Delta f''$
N	0·032	0·019
O	0·049	0·032

The R index was 0·0261 for the correct configuration and 0·0268 for the opposite enantiomer. (No adjustment for the change in scale factor k was made in these calculations, which accounts for the worsening of R for both alternatives.)

Refinement was concluded with two least-squares cycles based on the correct enantiomer and with the form factors of nitrogen and oxygen corrected for anomalous dispersion. Coordinates of all the atoms were included in one full matrix while the anisotropic temperature coefficients of the heavy atoms and the scale and extinction parameters were included in a second matrix; the anisotropic coefficients of the hydrogen atoms were not further adjusted. During the last cycles, two reflections 2,12,2 and 303 with residuals $|F_o^2 - F_c^2|$ over 15 times as large as the standard deviations $\sigma(F_o^2)$ were given zero weight. For the 2,12,2 reflection, which lies at the outer edge of the effective sphere of reflection, the second background count was appreciably higher than the first, suggesting that the entire $\alpha_1-\alpha_2$ doublet was not captured; we have no explanation (other than the standard apologia of double reflection) for the discrepancy in the 303 reflection. In the final cycle, no heavy-atom parameter shifted by as much as one-eighth of its e.s.d., nor any hydrogen parameter by 0·3 e.s.d. The final R index for 1333 independent reflections is 0·024 and the goodness-of-fit is 3·47. The final value of the extinction parameter g was $(5·6 \pm 0·2) \times 10^{-5}$.

At the conclusion of the refinement a three-dimensional difference map was calculated. A section passing through the best plane of the adenine moiety is shown in Fig. 1. Apart from regions between two bonded atoms, no peaks or troughs exceeded 0·10 e.Å⁻³ in magnitude.

Observed and calculated structure factors are listed in Table 2. Atomic parameters and their standard deviations are listed in Table 3. Since the parameters were partitioned into three separate matrices, these e.s.d.'s may be slightly underestimated. We make no claim that the e.s.d.'s of the anisotropic temperature

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* Slightly different values have more recently been reported by Cromer & Liberman (1970).

Table 2. *Observed and calculated structure factors* (×10) *and phase angles* (°)

1 K -0			
-1	455	442	276
-2	334	329	3
-3	217	215	97
-4	405	395	131
-5	89	88	53
-6	55	53	302
-7	38	36	42
-8	102	104	335
-9	198	203	242
-10	57	58	78
-11	37	36	207
-12	86	86	10
1 K -1			
-0	385	397	0
-1	170	173	324
-2	210	207	37
-3	162	161	293
-4	162	164	327
-5	29	25	341
-6	174	171	15
-7	78	77	83
-8	66	65	308
-9	45	46	26
-10	93	91	54
-11	52	52	214
-12	40	38	85
1 K -2			
-0	368	379	180
-1	432	435	76
-2	147	148	333
-3	41	40	288
-4	176	172	6
-5	173	169	237
-6	34	33	289
-7	60	61	80
-8	102	103	93
-9	40	37	12
-10	80	77	153
-11	78	77	309
1 K -3			
-0	217	215	180
-1	366	370	270
-2	141	143	41
-3	126	127	274
-4	194	200	320
-5	251	244	240
-6	44	43	355
-7	76	75	226
-8	101	101	170
-9	76	77	215
-10	13	11	187
-11	45	44	81
1 K -4			
-0	57	56	359
-1	30	34	265
-2	264	261	80
-3	286	287	91
-4	134	134	151
-5	166	167	11
-6	163	159	78
-7	88	90	14
-8	11	9	262
-9	77	76	248
-10	138	138	70
-11	75	74	45
1 K -5			
-0	202	205	0
-1	239	242	125
-2	101	101	9
-3	84	93	222
-4	191	187	208
-5	91	88	92
-6	55	56	61
-7	64	64	247
-8	170	173	277
-9	113	118	74
-10	61	62	45
-11	26	24	190
1 K -6			
-0	107	104	0
-1	286	281	16
-2	108	110	339
-3	138	140	270
-4	68	67	129
-5	78	80	296
-6	107	111	70
-7	17	18	175
-8	46	47	116
-9	106	105	53
-10	49	49	255
-11	77	75	293
1 K -7			
-0	109	100	0
-1	49	50	327
-2	54	52	312
-3	139	140	300
-4	146	144	5
-5	147	145	100
-6	70	68	71
-7	149	150	174
-8	86	90	51
-9	28	25	3
-10	17	19	16
1 K -8			
-0	35	35	181
-1	22	22	326
-2	25	18	247
-3	164	166	87
-4	42	43	336
-5	135	132	44
-6	49	48	276
-7	161	163	1
-8	90	92	22
-9	12	13	283
-10	44	44	53
1 K -9			
-0	72	73	1
-1	203	204	197
-2	153	154	13
-3	171	173	224
-4	43	45	4
-5	18	16	340
-6	80	83	339
-7	156	156	278
-8	9	10	58
-9	20	18	320
1 K-10			
-0	65	68	180
-1	119	121	357
-2	80	80	1
-3	111	113	170
-4	120	119	73
-5	116	118	293
-6	39	41	290
-7	20	20	290
-8	13	9	18
1 K-11			
-0	93	93	1
-1	114	116	329
-2	101	99	150
-3	107	109	315
-4	57	58	2
-5	29	33	18
-6	13	12	145
-7	56	56	164
1 K-12			
-0	43	42	1
-1	44	45	343
-2	40	40	234
-3	45	43	342
-4	32	29	49
-5	34	34	235
-6	52	52	232
1 K-13			
-0	29	30	0
-1	61	60	229
-2	30	31	206
-3	54	56	248
-4	33	32	277
1 K-14			
-0	21	17	182
-1	31	30	94
2 K -0			
-1	146	148	313
-2	82	79	115
-3	255	250	327
-4	79	79	27
-5	112	111	113
-6	106	108	35
-7	115	115	190
-8	55	56	161
-9	40	40	80
-10	50	51	154
-11	39	37	296
-12	81	82	80
2 K -1			
-0	185	194	0
-1	182	183	30
-2	139	137	357
-3	15	15	32
-4	54	54	317
-5	60	58	227
-6	89	92	328
-7	39	39	135
-8	92	93	314
-9	110	114	265
-10	39	38	46
-11	77	75	292
-12	28	30	165
2 K -2			
-0	8	7	188
-1	84	84	189
-2	85	84	66
-3	262	266	243
-4	65	64	242
-5	79	77	214
-6	113	110	84
-7	40	37	247
-8	18	21	152
-9	99	101	87
-10	75	72	44
-11	84	85	169
-12	41	42	239
2 K -3			
-0	205	205	180
-1	278	273	76
-2	31	30	136
-3	42	41	157
-4	69	71	354
-5	168	165	38
-6	89	86	95
-7	69	66	284
-8	144	152	130
-9	120	120	59
-10	47	46	136
-11	37	36	281
-12	28	26	178
2 K -4			
-0	62	61	179
-1	42	40	317
-2	125	123	300
-3	55	56	210
-4	108	101	59
-5	59	57	73
-6	154	153	265
-7	154	154	226
-8	89	94	35
-9	45	47	65
-10	35	33	243
-11	12	13	7
2 K -5			
-0	513	515	0
-1	73	72	6
-2	34	34	57
-3	164	162	108
-4	95	95	94
-5	50	51	359
-6	34	37	146
-7	71	70	59
-8	88	88	0
-9	24	24	244
-10	56	59	291
-11	61	58	43
2 K -6			
-0	59	57	0
-1	140	138	167
-2	103	100	272
-3	41	39	308
-4	172	175	120
-5	112	114	117
-6	111	111	126
-7	49	50	73
-8	90	93	35
-9	35	36	167
-10	14	13	199
-11	61	60	175
2 K -7			
-0	59	55	180
-1	157	162	349
-2	89	87	316
-3	89	90	72
-4	177	179	331
-5	86	85	344
-6	145	146	351
-7	148	148	26
-8	50	51	111
-9	24	25	285
-10	27	27	319
2 K -8			
-0	6	2	185
-1	40	41	246
-2	117	114	57
-3	92	92	209
-4	234	235	2
-5	22	13	187
-6	119	121	316
-7	105	107	201
-8	48	45	72
-9	41	43	297
-10	70	68	81
2 K -9			
-0	134	133	1
-1	13	19	72
-2	139	144	130
-3	72	75	119
-4	66	67	17
-5	101	100	264
-6	79	80	204
-7	56	56	343
-8	44	45	269
-9	19	14	171
2 K-10			
-0	140	145	0
-1	127	127	201
-2	6	8	354
-3	172	177	312
-4	73	69	122
-5	48	47	263
-6	63	63	101
-7	35	37	301
-8	37	37	51
-9	27	26	20
2 K-11			
-0	52	52	1
-1	19	20	357
-2	112	117	309
-3	70	70	22
-4	37	36	297
-5	51	51	224
-6	61	52	22
-7	53	52	100
-8	41	39	336
2 K-12			
-0	92	92	180
-1	59	61	254
-2	50	50	157
-3	69	67	300
-4	44	44	202
-5	42	39	176
-6	28	27	86
-7	44	42	219
2 K-13			
-0	4	6	179
-1	24	26	151
-2	45	45	49
-3	18	13	299
-4	32	31	97
-5	30	29	4
2 K-14			
-0	22	22	180
-1	27	26	166
-2	65	61	312
-3	23	24	137
3 K -0			
-1	114	115	51
-2	205	204	279
-3	34	34	43
-4	84	82	314
-5	39	43	127
-6	66	66	30
-7	76	77	181
-8	65	65	310
-9	23	23	103
-10	40	40	240
-11	40	39	283
3 K -1			
-0	134	137	180
-1	152	154	321
-2	87	85	175
-3	115	115	288
-4	140	142	115
-5	67	67	157
-6	41	44	214
-7	78	83	198
-8	114	117	104
-9	18	16	65
-10	60	61	172
-11	43	42	250
3 K -2			
-0	144	150	1
-1	114	113	67
-2	64	67	91
-3	72	72	116
-4	117	119	21
-5	48	49	334
-6	95	95	246
-7	74	76	75
-8	76	76	71
-9	59	57	279
-10	8	6	159
-11	11	10	168
3 K -3			
-0	9	1	212
-1	121	122	145
-2	97	99	237
-3	115	113	118
-4	46	45	333
-5	95	92	251
-6	55	59	176
-7	122	124	41
-8	86	90	23
-9	52	51	129
-10	30	29	356
-11	79	78	92
3 K -4			
-0	182	178	0
-1	124	121	178
-2	10	5	348
-3	85	83	77
-4	62	63	259
-5	37	39	162
-6	127	128	83
-7	32	30	323
-8	55	56	183
-9	21	23	223
-10	28	29	291
-11	56	55	61
3 K -5			
-0	50	49	180
-1	61	58	261
-2	88	87	38
-3	106	107	86
-4	160	161	111
-5	107	106	88
-6	17	13	40
-7	38	38	162
-8	33	33	0
-9	66	66	237
-10	44	45	66
3 K -6			
-0	229	225	0
-1	42	41	15
-2	93	92	77
-3	77	79	57
-4	193	191	332
-5	106	106	36
-6	106	106	345
-7	120	119	55
-8	79	78	261
-9	26	27	54
-10	32	35	32
3 K -7			
-0	97	98	181
-1	144	140	145
-2	32	30	276
-3	124	126	289
-4	109	111	11
-5	102	106	201
-6	26	25	17
-7	33	31	197
-8	78	77	64
-9	34	32	55
-10	70	69	118
3 K -8			
-0	25	25	180
-1	28	33	127
-2	74	74	351
-3	78	79	337
-4	53	55	299
-5	154	152	229
-6	60	62	15
-7	28	27	286
-8	20	20	85
-9	23	19	359
3 K -9			
-0	5	10	357
-1	19	14	232
-2	157	159	18
-3	43	43	12
-4	97	99	132
-5	50	50	16
-6	38	36	56
-7	16	15	152
-8	33	29	17
3 K-10			
-0	53	56	1
-1	51	54	277
-2	46	44	351
-3	57	60	167
-4	48	48	221
-5	28	28	8
-6	6	4	71
-7	25	24	280
-8	77	76	280
3 K-11			
-0	66	68	181
-1	61	63	282
-2	41	42	251
-3	71	70	251
-4	57	53	145
-5	29	30	265
-6	41	40	63
-7	40	40	274
3 K-12			
-0	37	33	1
-1	70	68	40
-2	35	35	339
-3	38	39	80
-4	36	38	357
-5	9	4	33
-6	43	40	77
3 K-13			
-0	31	32	181
-1	27	26	328
-2	27	29	130
-3	28	25	101
-4	33	30	243
3 K-14			
-0	35	34	1
4 K -0			
-1	24	25	242
-2	72	72	210
-3	20	22	103
-4	34	35	95
-5	74	75	265
-6	101	103	87
-7	61	59	60
-8	52	53	78
-9	32	32	230
4 K -1			
-0	32	32	0
-1	97	94	104
-2	48	48	248
-3	115	115	14
-4	67	70	294
-5	95	96	151
-6	82	83	85
-7	79	80	116
-8	37	37	224
-9	6	6	263
4 K -2			
-0	127	129	180
-1	12	12	260
-2	35	35	83
-3	48	48	7
-4	86	87	202
-5	38	39	153
-6	12	14	312
-7	46	46	3
-8	20	18	178
-9	17	18	87
4 K -3			
-0	44	43	1
-1	117	113	173
-2	129	129	41
-3	130	130	178
-4	12	15	328
-5	64	63	54
-6	31	33	343
-7	48	47	276
-8	17	17	178
-9	11	12	311
4 K -4			
-0	71	74	180
-1	89	90	103
-2	17	16	127
-3	160	159	110
-4	69	71	77
-5	84	87	63
-6	45	44	156
-7	44	42	36
-8	12	12	338
-9	27	26	117
4 K -5			
-0	67	66	1
-1	27	28	297
-2	55	56	5
-3	163	160	346
-4	70	69	336
-5	47	46	118
-6	65	66	3
-7	46	44	160
-8	41	41	213
-9	38	38	86
4 K -6			
-0	80	82	180
-1	80	80	28
-2	130	133	351
-3	43	44	326
-4	57	57	99
-5	69	68	219
-6	85	85	343
-7	88	89	142
-8	81	81	26
4 K -7			
-0	28	28	0
-1	67	71	45
-2	27	24	9
-3	90	90	179
-4	69	69	257
-5	42	41	288
-6	60	57	42
-7	34	31	38
-8	31	28	302
4 K -8			
-0	40	44	359
-1	19	16	27
-2	33	30	346
-3	65	65	189
-4	31	32	67
-5	66	64	12
-6	72	73	110
-7	66	63	300
-8	34	35	83
4 K -9			
-0	82	84	1
-1	74	74	283
-2	25	25	331
-3	28	26	216
-4	53	54	338
-5	18	17	171
-6	29	28	294
-7	64	64	226
4 K-10			
-0	16	6	2
-1	29	29	323
-2	66	64	142
-3	21	21	48
-4	37	35	132
-5	27	28	8
-6	18	16	133
4 K-11			
-0	43	41	1
-1	40	45	144
-2	12	13	148
-3	15	15	234
-4	8	11	5
-5	36	33	98
4 K-12			
-0	17	18	181
-1	15	12	291
-2	34	34	296
-3	12	12	238
5 K -0			
-1	34	33	159
-2	61	59	321
-3	51	49	217
-4	71	70	164
-5	25	26	84
-6	5	6	328
-7	35	34	235
5 K -1			
-0	29	28	181
-1	58	58	359
-2	53	52	268
-3	60	60	150
-4	21	20	291
-5	51	51	18
-6	39	38	30
-7	41	40	36
5 K -2			
-0	33	29	180
-1	35	37	99
-2	44	42	134
-3	25	24	149
-4	38	40	16
-5	61	63	117
-6	31	29	201
-7	43	43	167
5 K -3			
-0	58	60	180
-1	64	63	67
-2	85	83	90
-3	63	60	78
-4	33	33	91
-5	17	15	214
-6	71	73	250
-7	27	28	27
5 K -4			
-0	78	76	0
-1	14	16	29
-2	96	93	17
-3	18	19	246
-4	32	33	359
-5	27	27	350
-6	48	50	5
-7	38	38	138
5 K -5			
-0	41	40	0
-1	80	79	32
-2	83	83	257
-3	57	56	122
-4	14	13	286
-5	33	31	59
-6	82	78	83
5 K -6			
-0	73	76	0
-1	26	27	285
-2	70	71	212
-3	52	52	290
-4	27	30	279
-5	27	26	126
-6	31	33	70
5 K -7			
-0	77	75	0
-1	43	41	125
-2	62	62	26
-3	2	6	126
-4	79	78	37
-5	10	9	36
5 K -8			
-0	14	13	179
-1	47	46	201
-2	22	26	130
-3	32	33	179
-4	24	25	347
-5	26	29	210
5 K -9			
-0	17	19	181
-1	34	35	229
-2	23	23	189
-3	24	26	337
-4	20	22	151
5 K-10			
-0	16	17	2
-1	1	6	103
-2	50	51	335
6 K -1			
-0	59	59	180
-1	41	42	143
6 K -2			
-0	0	3	184
-1	72	73	53
-2	12	7	296
6 K -3			
-0	70	73	0
-1	13	18	55
-2	9	10	134
6 K -4			
-0	45	46	1
-1	24	25	177
-1 K 14			
2	31	31	206
3	27	29	298
-1 K 13			
5	82	80	122
-1 K 14			
4	10	10	277
-1 K 13			
6	15	13	306
-1 K 12			
7	6	6	329
-1 K 11			
8	30	30	161
-1 K 10			
9	16	17	167
-1 K 9			
10	12	12	46
-1 K 7			
11	36	36	178
-1 K 5			
12	58	56	180
-1 K 4			
12	29	28	252
-1 K 3			
12	18	15	64
-1 K 2			
12	33	32	60
0 K 0			
2	186	188	350
4	213	217	14
6	145	146	277
8	211	209	40
10	196	195	52
12	84	83	213
0 K 1			
0	4	0	274
1	292	291	180
2	206	208	107
3	316	318	43
4	279	275	249
5	168	167	200
6	91	89	185
7	84	83	284
8	173	174	332
9	57	57	191
10	22	23	6
11	104	101	171
12	44	45	327
0 K 2			
0	298	313	180
1	325	328	93
2	106	109	268
3	189	190	38
4	425	423	32
5	79	79	92
6	188	187	3
7	107	105	3
8	157	159	208
9	107	107	82
10	48	47	270
11	37	37	117
12	34	33	258
0 K 3			
0	186	190	180
1	191	192	178
2	283	287	325
3	79	79	242
4	273	264	334
5	95	94	287
6	100	96	54
7	133	132	115
8	89	89	280
9	131	133	71
10	90	89	266
11	13	13	6
12	55	50	42
0 K 4			
0	335	347	0
1	205	208	147
2	14	15	326
3	53	50	140
4	25	27	178
5	88	87	98
6	126	126	133
7	68	68	63
8	82	82	69
9	92	94	256
10	46	45	78
11	32	34	226
12	33	33	206
0 K 5			
0	146	149	180
1	121	122	178
2	74	73	134
3	123	117	53
4	330	325	234
5	193	185	84
6	94	91	238
7	86	86	346
8	150	153	280
9	9	6	152
10	70	71	179
11	23	22	296
12	105	103	292
0 K 6			
0	65	67	1
1	82	83	286
2	121	123	29
3	153	153	312
4	148	146	27
5	86	88	153
6	96	99	10
7	113	113	273
8	82	85	106
9	97	98	90
10	15	15	227
11	65	62	333
0 K 7			
0	93	91	181
1	161	157	29
2	149	149	309
3	159	155	341
4	35	37	201
5	43	43	188
6	42	43	300
7	91	96	284
8	40	39	146
9	1	4	95
10	62	62	291
11	47	46	354
0 K 8			
0	74	74	0
1	7	7	93
2	107	107	326
3	112	110	83
4	90	90	114
5	17	13	51
6	75	76	294
7	66	70	178
8	14	14	238
9	31	33	287
10	65	66	339
0 K 9			
0	60	60	181
1	59	58	319
2	103	101	82
3	89	89	215
4	16	14	87
5	116	117	43
6	57	55	308
7	69	66	14
8	110	111	334
9	35	34	334
10	45	44	352
0 K 10			
0	224	225	0
1	119	121	154
2	25	27	337
3	31	31	182
4	129	131	37
5	44	43	288
6	96	96	310
7	68	70	67
8	72	73	109
9	41	41	48
0 K 11			
0	81	83	180
1	106	107	116
2	68	67	321
3	38	38	64
4	121	124	233
5	37	38	246
6	31	31	147
7	71	71	75
8	37	35	74
0 K 12			
0	8	9	177
1	79	78	48
2	68	68	305
3	96	93	75
4	41	38	117
5	36	38	32
6	53	52	23
7	6	7	89
0 K 13			
0	93	90	181
1	88	85	314
2	26	27	59
3	35	34	113
4	39	36	338
5	30	29	36
6	15	16	115
0 K 14			
0	14	15	179
1	42	40	69
2	52	51	165
3	33	35	126
4	35	33	52
1 K 0			
0	270	276	180
1	467	463	264
2	336	329	357
3	217	214	84
4	406	396	230
5	89	89	127
6	56	54	57
7	38	37	139
8	102	104	26
9	199	203	299
10	57	58	283
11	38	37	331
12	87	86	350
1 K 1			
0	434	447	0
1	581	550	355
2	396	387	358
3	84	85	123
4	115	116	15
5	195	191	44
6	151	145	325
7	104	105	282
8	68	66	160
9	65	65	311
10	97	99	101
11	110	109	63
12	9	9	292
1 K 2			
0	103	103	0
1	468	459	64
2	241	230	87
3	266	263	106
4	177	171	356
5	138	137	268
6	44	40	269
7	226	228	167
8	197	202	330
9	114	118	116
10	63	65	9
11	86	82	135
12	42	40	53
1 K 3			
0	318	333	0
1	192	196	59
2	155	155	182
3	199	199	265
4	184	185	48
5	96	95	353
6	38	32	165
7	171	170	16
8	96	98	315
9	44	44	118
10	67	66	344
11	69	67	29
12	60	60	207
1 K 4			
0	49	49	180
1	299	301	184
2	149	144	285
3	162	157	135
4	112	112	265
5	106	103	79
6	15	17	224
7	144	142	80
8	95	99	224
9	35	32	58
10	42	41	213
11	40	39	259
12	39	38	262
1 K 5			
0	118	122	1
1	129	130	46
2	41	41	82
3	101	98	166
4	163	157	20
5	136	139	58
6	58	56	23
7	44	45	33
8	140	141	113
9	13	13	148
10	14	13	129
11	9	4	124
1 K 6			
0	71	73	0
1	107	106	79
2	173	170	191
3	158	156	50
4	119	117	250
5	135	133	264
6	95	98	253
7	60	62	141
8	60	62	290
9	47	45	333
10	33	33	254
11	40	40	147
1 K 7			
0	119	120	1
1	107	103	279
2	31	29	187
3	83	83	345
4	35	33	237
5	74	75	253
6	130	133	134
7	12	15	303
8	44	41	317
9	57	55	33
10	36	37	120
11	53	53	65
1 K 8			
0	73	71	181
1	53	54	133
2	51	49	320
3	84	85	49
4	99	101	329
5	112	115	100
6	89	91	97
7	53	54	318
8	64	62	289
9	28	28	259
10	12	12	94
1 K 9			
0	11	8	182
1	53	53	206
2	28	27	346
3	64	65	326
4	127	129	20
5	32	32	96
6	69	72	346
7	40	38	272
8	49	48	203
9	23	22	212
1 K 10			
0	95	96	180
1	24	24	121
2	81	80	83
3	34	32	324
4	108	111	203
5	23	21	143
6	14	16	293
7	39	39	81
8	54	58	338
1 K 11			
0	231	226	0
1	55	57	46
2	78	77	14
3	32	34	158
4	48	48	156
5	68	67	62
6	42	41	311
7	45	44	351
1 K 12			
0	17	18	359
1	39	39	130
2	2	4	202
3	38	39	122
4	38	38	288
5	25	23	115
6	34	35	208
1 K 13			
0	72	73	180
1	67	66	102
2	67	66	213
3	44	44	354
4	78	75	58
1 K 14			
0	82	82	181
1	40	41	146
2 K 0			
0	64	64	1
1	146	148	228
2	82	79	245
3	256	250	213
4	90	80	333
5	113	111	68
6	106	109	326
7	116	115	351
8	53	55	199
9	40	40	100
10	50	52	207
11	38	37	244
12	81	81	281
2 K 1			
0	44	46	0
1	170	175	146
2	51	51	283
3	228	227	58
4	132	129	346
5	115	112	185
6	58	60	285
7	53	49	155
8	74	77	86
9	88	88	59
10	47	47	309
11	37	34	223
12	60	66	13
2 K 2			
0	196	196	0
1	232	232	348
2	346	341	339
3	386	376	355
4	38	39	58
5	49	50	273
6	65	62	351
7	109	110	292
8	33	35	66
9	62	63	308
10	68	69	340
11	105	105	42
12	26*	33	74
2 K 3			
0	190	190	180
1	73	75	148
2	186	183	355
3	262	268	86
4	133	130	146
5	78	75	132
6	59	71	29
7	206	208	163
8	46	47	323
9	42	44	271
10	56	54	322
11	39	38	145
2 K 4			
0	149	151	180
1	138	132	50
2	123	119	82
3	198	201	187
4	20	20	36
5	222	224	44
6	61	60	309
7	153	157	47
8	67	69	313
9	31	30	72
10	40	40	229
11	43	44	59
2 K 5			
0	179	177	0
1	147	148	140
2	49	49	87
3	85	83	175
4	56	59	314
5	99	101	290
6	108	111	283
7	107	108	76
8	25	21	234
9	39	38	79
10	60	60	138
11	32	31	218
2 K 6			
0	17	17	176
1	98	97	26
2	35	37	64
3	44	46	327
4	138	143	198
5	8	2	73
6	96	97	136
7	57	55	321
8	49	50	75
9	48	48	106
10	33	33	133
2 K 7			
0	31	24	180
1	114	112	43
2	106	104	270
3	146	145	94
4	45	43	163
5	111	114	99
6	22	24	295
7	38	37	218
8	25	27	196
9	4	7	300
10	55	56	309
2 K 8			
0	52	53	181
1	124	125	295
2	39	40	229
3	77	75	233
4	100	101	24
5	92	90	324
6	26	23	265
7	12	8	336
8	45	46	184
9	40	38	340
2 K 9			
0	33	38	180
1	84	84	101
2	60	61	164
3	11	10	181
4	53	53	12
5	81	80	296
6	25	28	120
7	61	59	91
8	17	18	200
2 K 10			
0	98	100	0
1	19	20	69
2	12	14	245
3	16	15	22
4	32	34	324
5	27	25	27
6	19	21	47
7	20	19	101
2 K 11			
0	26	26	1
1	64	64	252
2	17	17	135
3	53	55	64
4	28	27	275
5	65	66	138
6	15	15	128
2 K 12			
0	31	29	0
1	27	26	318
2	22	24	44
3	52	52	29
4	15	15	123
2 K 13			
0	14	10	182
1	68	69	99
3 K 0			
0	107	107	1
1	115	115	129
2	206	204	82
3	33	34	138
4	83	82	47
5	39	42	53
6	65	66	332
7	76	77	0
8	64	64	50
9	25	23	77
10	40	40	122
11	39	39	259
3 K 1			
0	134	134	0
1	76	76	4
2	99	95	15
3	49	47	273
4	79	80	257
5	58	57	219
6	81	84	305
7	31	28	335
8	74	73	318
9	25	25	86
10	35	34	46
11	29	28	60
3 K 2			
0	40	40	2
1	28	29	22
2	142	139	268
3	48	47	81
4	51	49	315
5	14	13	184
6	127	132	116
7	59	57	219
8	29	28	132
9	32	31	50
10	37	35	9
3 K 3			
0	84*	63	181
1	79	78	59
2	117	117	261
3	62	60	342
4	168	166	353
5	148	152	63
6	69	67	89
7	109	108	334
8	34	37	229
9	24	26	118
10	57	57	272
3 K 4			
0	88	88	0
1	143	143	162
2	57	54	74
3	76	75	45
4	192	194	40
5	79	78	162
6	126	127	337
7	70	69	153
8	23	23	120
9	41	40	146
10	23	23	356
3 K 5			
0	82	86	180
1	30	27	84
2	103	104	89
3	79	77	3
4	177	182	192
5	53	55	116
6	77	75	259
7	45	44	73
8	34	37	341
9	40	39	38
3 K 6			
0	149	149	0
1	41	44	72
2	57	57	315
3	94	95	102
4	90	91	180
5	61	61	83
6	59	61	263
7	28	28	102
8	37	39	112
9	45	45	28
3 K 7			
0	60	57	180
1	35	37	235
2	11	8	199
3	21	22	121
4	22	22	332
5	36	36	314
6	57	54	134
7	35	32	359
8	32	28	45
3 K 8			
0	93	94	180
1	79	80	111
2	18	21	179
3	31	28	14
4	26	24	61
5	29	26	214
6	8	14	113
7	23	21	12
3 K 9			
0	70	68	181
1	11	5	7
2	25	25	351
3	47	47	292
4	66	63	200
5	20	19	346
6	15	17	259
3 K 10			
0	21	20	1
1	22	19	20
2	32	32	1
3	36	37	200
4	28	28	117
5	26	24	26
3 K 11			
0	9	9	181
1	25	25	300
2	23	22	240
3	31	32	173
4 K 0			
0	44	41	359
1	24	24	297
2	72	72	152
3	22	22	78
4	34	35	267
5	75	75	275
6	101	103	274
7	61	60	121
8	51	53	284
9	32	32	310
4 K 1			
0	75	74	1
1	74	75	306
2	31	32	87
3	60	62	9
4	15	20	171
5	38	39	259
6	77	79	115
7	36	37	272
8	49	49	49
9	61	61	334
4 K 2			
0	37	36	0
1	27	28	113
2	66	66	290
3	57	55	125
4	41	40	255
5	53	53	104
6	25	21	202
7	36	36	9
8	29	25	304
9	6	8	57
4 K 3			
0	15	11	358
1	66	66	158
2	43	43	12
3	37	39	166
4	81	80	28
5	73	75	301
6	28	28	7
7	48	48	70
8	9	6	68
4 K 4			
0	104	104	180
1	79	78	59
2	27	28	84
3	39	38	301
4	53	56	293
5	70	71	325
6	42	42	79
7	33	33	58
8	55	57	278
4 K 5			
0	86	87	1
1	41	43	28
2	34	35	236
3	31	30	118
4	57	58	7
5	70	70	103
6	58	61	71
7	48	46	161
4 K 6			
0	10	2	3
1	18	20	224
2	42	40	176
3	70	68	78
4	42	39	270
5	99	100	113
6	25	28	158
7	28	23	10
4 K 7			
0	39	37	0
1	1	1	216
2	18	20	87
3	33	31	19
4	34	34	142
5	26	28	117
6	47	48	262
4 K 8			
0	56	51	181
1	27	30	77
2	28	27	134
3	12	14	12
4	50	49	172
4 K 9			
0	35	32	1
1	39	38	76
2	27	25	236
5 K 0			
0	49	49	180
1	34	33	21
2	60	59	39
3	60	49	324
4	71	71	196
5	26	25	96
6	3	6	36
7	34	34	305
5 K 1			
0	3	8	181
1	25	25	28
2	58	57	258
3	50	49	164
4	66	64	189
5	37	36	89
6	41	41	261
5 K 2			
0	4	6	0
1	46	48	280
2	19	16	47
3	21	18	137
4	45	43	63
5	35	35	344
6	9	7	89
5 K 3			
0	10	10	357
1	30	28	32
2	27	25	43
3	13	13	356
4	16	14	354
5	6	7	205
5 K 4			
0	24	28	0
1	24	24	93
2	15	12	218
3	23	23	294
4	25	24	118
5	19	20	320
5 K 5			
0	2	7	180
1	62	61	124
2	15	16	309
3	26	26	136
4	0	3	286
5 K 6			
0	3	2	3
1	27	24	251
2	23	22	353
6 K 0			
0	19	19	2

coefficients of the hydrogen atoms are realistic. These parameters were not adjusted after the anomalous dispersion corrections were made; moreover, a few of them shifted by more than one e.s.d. during the final cycle in which they were adjusted, and it appeared as though convergence would be slow. Nevertheless, we are convinced that these parameters are of some significance. During the two least-squares cycles in which they were adjusted the goodness-of-fit dropped by about 15% below the value obtained with converged isotropic temperature parameters for the hydrogen atoms. In addition, the resulting thermal ellipsoids are quite reasonable.

The relatively large value of the goodness-of-fit deserves some comment. The individual values of the weighted residuals, $\sqrt{w}(F_o^2 - F_c^2)$, appear to be normally distributed, and independent of the magnitude of F_o^2. However, a disproportionate number of the larger residuals represent low-angle reflections; taken in conjunction with the final difference map (Fig. 1), this trend suggests that the assumption of spherically-symmetric atomic form factors may be an important

Table 3. Final parameters and their standard deviations (in parentheses)

The coordinates and temperature coefficients of the heavy atoms have been multiplied by 10^4; those of the hydrogen atoms by 10^3. The anisotropic temperature factor is expressed in the form

$$\exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right].$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	9236 (4)	−899 (2)	1862 (1)	484 (8)	49 (1)	53 (1)	109 (5)	140 (5)	12 (2)
C(2)	7928 (5)	−722 (2)	2767 (2)	625 (12)	54 (2)	56 (1)	139 (7)	198 (7)	39 (3)
N(3)	6384 (4)	282 (2)	3007 (1)	471 (8)	48 (1)	45 (1)	76 (5)	148 (5)	21 (2)
C(4)	6230 (3)	1189 (2)	2175 (1)	261 (7)	36 (1)	36 (1)	6 (5)	46 (4)	−11 (2)
C(5)	7504 (3)	1165 (2)	1210 (1)	261 (7)	40 (1)	33 (1)	−3 (5)	49 (4)	−2 (2)
C(6)	9096 (3)	41 (2)	1057 (1)	274 (7)	40 (1)	39 (1)	8 (5)	50 (5)	−11 (2)
N(7)	6857 (3)	2275 (2)	557 (1)	380 (8)	51 (1)	44 (1)	45 (5)	99 (4)	16 (2)
C(8)	5226 (4)	2930 (2)	1135 (1)	400 (9)	48 (1)	43 (1)	74 (6)	99 (5)	18 (2)
N(9)	4768 (3)	2340 (2)	2120 (1)	275 (6)	38 (1)	36 (1)	27 (4)	54 (4)	0 (2)
N(10)	10458 (4)	−147 (2)	176 (1)	407 (8)	57 (1)	46 (1)	59 (5)	116 (5)	1 (2)
C(1′)	3140 (3)	2782 (2)	2993 (1)	254 (7)	36 (1)	40 (1)	16 (5)	72 (5)	−4 (2)
C(2′)	5049 (4)	3161 (2)	4106 (1)	310 (8)	42 (1)	39 (1)	54 (5)	37 (5)	−5 (2)
C(3′)	5437 (4)	4616 (2)	3921 (1)	252 (7)	44 (1)	39 (1)	7 (5)	51 (4)	−9 (2)
C(4′)	2585 (3)	5024 (2)	3273 (1)	228 (7)	39 (1)	43 (1)	7 (5)	54 (4)	−8 (2)
C(5′)	2661 (4)	6177 (2)	2490 (2)	340 (8)	46 (2)	57 (1)	15 (6)	35 (5)	17 (2)
O(1′)	1583 (2)	3897	2590 (1)	263 (5)	42 (1)	50 (1)	39 (4)	8 (3)	−12 (2)
O(2′)	3579 (3)	3010 (2)	5037 (1)	668 (9)	44 (1)	42 (1)	17 (5)	152 (5)	0 (2)
O(3′)	6341 (3)	5337 (2)	4936 (1)	355 (6)	51 (1)	46 (1)	−46 (4)	37 (4)	−21 (2)
O(5′)	−83 (3)	6422 (2)	1890 (1)	411 (7)	48 (1)	59 (1)	88 (4)	1 (4)	10 (2)
H(1)	826 (5)	−136 (3)	336 (2)	62 (12)	13 (3)*	10 (2)	0 (11)*	27 (8)	2 (4)*
H(2)	441 (5)	376 (2)	92 (2)	60 (11)	8 (3)	5 (2)	13 (10)	6 (8)	2 (4)
H(3)	1128 (4)	−93 (2)	8 (2)	55 (12)	6 (3)	7 (2)	9 (9)	19 (8)	3 (4)
H(4)	1031 (6)	42 (2)	−40 (2)	72 (13)	8 (3)	7 (2)	17 (10)	18 (9)	−2 (5)
H(5)	183 (4)	206 (2)	313 (2)	19 (9)	3 (2)*	5 (1)	5 (7)	−9 (6)	0 (3)*
H(6)	671 (5)	267 (2)	421 (2)	44 (11)	7 (2)	4 (2)	2 (8)	8 (7)	−3 (3)
H(7)	330 (6)	217 (2)	514 (2)	81 (15)	4 (3)	8 (2)	7 (11)	5 (9)	−3 (5)
H(8)	683 (4)	474 (2)	346 (2)	28 (10)	3 (2)	4 (2)	6 (7)	3 (6)	1 (3)
H(9)	531 (7)	503 (3)	544 (2)	71 (16)	11 (4)	13 (3)	1 (14)	−13 (12)	1 (6)
H(10)	135 (4)	518 (4)	383 (1)	19 (8)	5 (2)	3 (1)	−3 (6)	2 (5)	−4 (3)
H(11)	323 (5)	693 (2)	294 (2)	55 (13)	5 (3)	8 (2)	4 (10)	−6 (9)	−1 (5)
H(12)	395 (4)	603 (2)	193 (2)	37 (11)	9 (2)	7 (2)	11 (9)	11 (7)	6 (4)
H(13)	−24 (6)	726 (3)	170 (3)	62 (19)	11 (5)	18 (3)	9 (15)	5 (13)	−3 (7)

* These parameters shifted by more than one e.s.d. during the last least-squares cycle in which the anisotropic temperature coefficients of the hydrogen atoms were adjusted. The largest shift was about 3·0 e.s.d. for b_{22} of H(1); the remaining shifts were less than 2·0 e.s.d.

Table 4. Hydrogen-bond distances and angles

Donor Atom	Acceptor Atom	Position of Acceptor Atom*	Distance D···A	H···A	Angle	
N(10)	N(7)	$-x+2, y-\frac{1}{2}, -z$	3·133 Å	2·32 Å	N(10)–H(3)—N(7)	167·1°
N(10)	O(5′)	$-x+1, y-\frac{1}{2}, -z$	2·908	2·03	N(10)–H(4)—O(5′)	169·0
O(2′)	O(3′)	$-x+1, y-\frac{1}{2}, -z+1$	2·749	1·90	O(2′)–H(7)—O(3′)	161·0
O(3′)	N(3)	$-x+1, y+\frac{1}{2}, -z+1$	2·947	2·15	O(3′)–H(9)—N(3)	149·3
O(5′)	N(1)	$x-1, y+1, z$	2·774	1·92	O(5′)–H(13)–N(1)	159·4

*Relative to parameters of Table 2.

source of error. In addition, it is probable that the weights *w*, which were derived by adding together the weights of four or five individual observations (see *Experimental*), do not adequately reflect experimental errors other than counting statistics.

Discussion

Hydrogen bonding and base stacking

Fig. 2 shows the structure viewed down the *a* axis. Each nucleoside is hydrogen bonded to six neighboring molecules; all nitrogen and oxygen atoms except N(9) and O(1′) participate in the three-dimensional hydrogen bonding system. The hydrogen bond lengths and angles are given in Table 4. Additional close intermolecular contacts of 3·09 Å between C(2) and O(2′) (at $1-x$, $y-\frac{1}{2}$, $1-z$) and 2·31 Å between H(1) and O(2′) suggest a weak C–H···O bond; the angle H–C···O is 29°. No other intermolecular contact appears to be incompatible with accepted van der Waals radii.

The stacking of the purine rings in adenosine has already been described and compared with that in other crystalline derivatives of purine by Bugg (1971). The stacking involves molecules related to one another by translation along the *a* axis; the interplanar spacing between adjacent adenine moieties is 3·57 Å. The stacking interactions appear to involve primarily the amino group, which lies approximately above the midpoint of the C(5)–C(6) bond of the neighboring molecule.

Molecular geometry

The bond distances and angles involving non-hydrogen atoms are shown in Fig. 3 and those involving hydrogen atoms are given in Table 5. The esti-

mated standard deviations in distances involving the heavy atoms are about 0·003 Å and slightly less than 0·2° in the angles; for bonds involving hydrogen atoms, the uncertainties are approximately ten times larger.
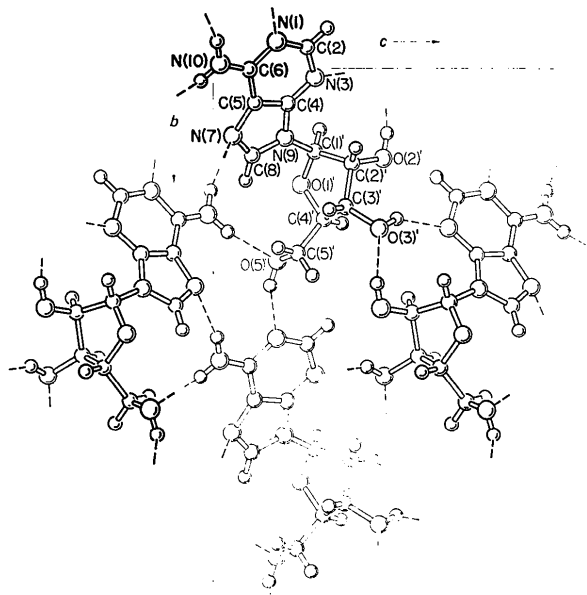

Fig. 2. The structure viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

Table 5. *Bond distances and angles involving hydrogen atoms*

Standard deviations are about 0·03 Å and 2·0°

C(2)—H(1)	0·96 Å	C(3′)–H(8)	0·94 Å
C(8)—H(2)	0·95	O(3′)–H(9)	0·89
N(10)–H(3)	0·92	C(4′)–H(10)	0·97
N(10)–H(4)	0·89	C(5′)–H(11)	0·95
C(1′)–H(5)	1·01	C(5′)–H(12)	0·99
C(2′)–H(6)	0·94	O(5′)–H(13)	0·89
O(2′)–H(7)	0·88		

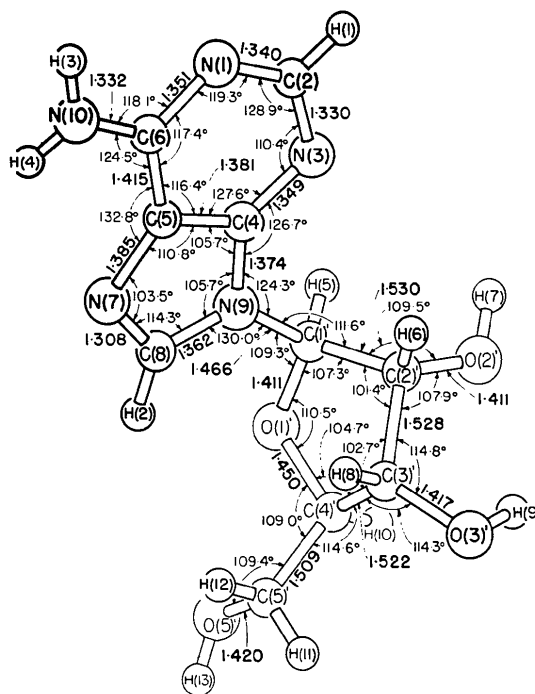|			
H(1)–C(2)—N(1)	116·6°	H(8)—C(3′)–C(2)	109·1°
H(1)–C(2)—N(3)	114·3	H(8)—C(3′)–C(4′)	110·2
H(2)–C(8)—N(7)	125·3	H(8)—C(3′)–O(3′)	105·8
H(2)–C(8)—N(9)	120·4	H(9)—O(3′)–C(3′)	104·5
H(3)–N(10)–H(4)	118·4	H(10)–C(4′)–C(3′)	108·0
H(3)–N(10)–C(6)	120·0	H(10)–C(4′)–O(1′)	108·7
H(4)–N(10)–C(6)	120·6	H(10)–C(4′)–C(5′)	111·6
H(5)–C(1′)–N(9)	108·2	H(11)–C(5′)–C(4′)	108·9
H(5)–C(1′)–C(2′)	110·6	H(11)–C(5′)–O(5′)	107·4
H(5)–C(1′)–O(1′)	109·8	H(11)–C(5′)–H(12)	110·1
H(6)–C(2′)–C(1′)	111·3	H(12)–C(5′)–C(4′)	111·6
H(6)–C(2′)–C(3′)	114·9	H(12)–C(5′)–O(5′)	109·4
H(6)–C(2′)–O(2′)	111·3	H(13)–O(5′)–C(5′)	109·2
H(7)–O(2′)–C(2′)	108·9		

Fig. 3. Bond distances and angles involving the heavy atoms. Standard deviations are about 0·003 Å in the distances and 0·2° in the angles.

The reports of the crystal structures of ten compounds containing a neutral adenine ring substituted at the N(9) position have come to our attention: the pure compounds 9-methyladenine (Stewart & Jensen, 1964); deoxyadenosine (Watson, Sutor & Tollin, 1965); 3'-*O*-acetyladenosine (Rao, Sundaralingam & Arora, 1970); α-D-2'-amino-2'-deoxyadenosine monohydrate (Rohrer & Sundaralingam, 1970); 1:1 complexes between 9-methyladenine and 1-methylthymine (Hoogsteen, 1963); 9-ethyladenine and 1-methyluracil (Mathews & Rich, 1964); 9-ethyladenine and 5-bromouracil (Katz, Tomita & Rich, 1966); 9-methyladenine and 1-methyl-5-bromouracil (Baklagine, Volkenstein & Kondrashev, 1966); 9-ethyladenine and 1-methyl-5-fluorouracil (Tomita, Katz & Rich, 1967); and a 2:1 complex between 8-bromo-9-ethyladenine and phenobarbital (Kim & Rich, 1968).

Within their uncertainties, the bond distances and angles in these other compounds are in satisfactory agreement with our values. In the five most accurate of the earlier analyses – the four uncomplexed compounds and the 9-methyladenine:1-methylthymine complex – the e.s.d.'s were in the range 0·005–0·010 Å and 0·3–0·5°; for these five determinations, the average values of the bond distances agree with ours within an r.m.s. deviation of 0·005 Å, and the angles within 0·6°. A common feature of all the structures is the relatively large difference between the bond angles N(1)–C(6)–N(10) and C(5)–C(6)–N(10) to the amino nitrogen atom.

Similarly, the bond lengths in the ribose moiety are in statistical agreement with those found in other nucleosides, including guanosine dihydrate and inosine dihydrate (Thewalt, Bugg & Marsh, 1970), adenosine-3'-phosphate (Sundaralingam, 1966), and 3'-*O*-acetyladenosine (Rao et al., 1970) where the e.s.d.'s are in the range 0·004–0·006 Å and 0·2–0·3°. (The C(3')–O(3') distances are about 0·02 Å longer in the latter two

compounds, reflecting the effects of the attached phosphate and ester groups.) The bond angles, which are probably more sensitive to the conformations in the ribose rings, show larger differences; of particular note in the present structure are the relatively large values of the angles C(2')–C(3')–O(3') and C(4')–C(3')–O(3').

Average values for the C–H, N–H, and O–H distances are 0·96, 0·91, and 0·89 Å. These are typical for X-ray diffraction investigations, being somewhat shorter than the standard values for the internuclear separations.

A stereoscopic view of the molecule is shown in Fig. 4. Deviations from least-squares planes through the purine and the ribose moieties are listed in Table 6. It is interesting to note that the amino hydrogen atoms H(3) and H(4) are displaced from the plane of the adenine rings toward the hydrogen-bond acceptor atoms N(7) and O(5'). Similar, but statistically more significant, out-of-plane displacements of hydrogen atoms, presumably dictated by hydrogen bonding, have been noted in crystals of ethylenebis(biguanidine)-nickel(II) dichloride monohydrate (Holian & Marsh, 1970). On the other hand, atom H(1), which is involved in the intermolecular C(2)–H(1)···O(2') interaction, is displaced from the plane in a direction opposite from O(2').

A view of the molecule along the glycosidic bond C(1')–N(9) is shown in Fig. 5. Torsion angles in adenosine and in four related compounds are given in Table 7. The furanose ring is puckered with C(3') *endo*. The small value of the torsion angle φ(CN) about the glycosidic bond, 9·9°, is characteristic of purine nucleosides and nucleotides with 3' puckering of the ribose ring. Further discussions of torsion angles in related compounds are given by Sundaralingam (1969), among others.

The absolute configuration of the molecule has been
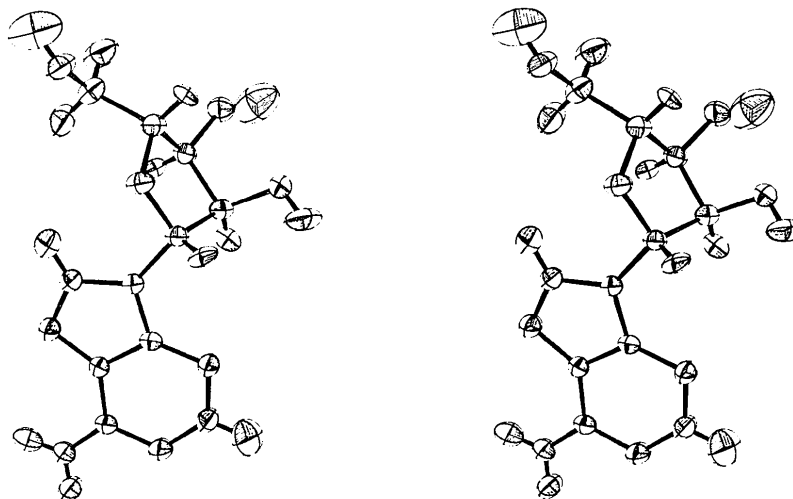

Fig. 4. A stereoscopic view of the molecule (Johnson, 1965).

confirmed by the use of anomalous scattering of Cu $K\alpha$ radiation by oxygen and nitrogen atoms. Other reports in which the anomalous scattering by oxygen has been successfully used for this purpose are given by Hope & de la Camp (1969), Thiessen & Hope (1970), and Moncrief & Sims (1969).

Temperature ellipsoids

Ellipsoids representing the anisotropic temperature parameters are shown in Fig. 4. Thermal motions are reasonably small and isotropic for the heavy atoms, and in most instances the motions of the hydrogen atoms satisfactorily reflect those of the heavy atoms to which they are attached. Some of the hydrogen atoms have relatively large apparent motions parallel to the covalent bond, perhaps representing the delocalization of the bonding electron; we emphasize again, however, that the temperature parameters of the hydrogen atoms have not been determined with high precision.

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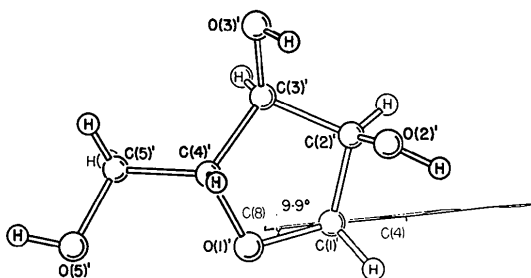Moncrief, J. W. & Sims, S. P. (1969). *Acta Cryst.* A25, supplement, page S74.

Table 6. *Deviations of the atoms from the least-squares planes*

The direction cosines of the planes, q_i, are relative to the crystallographic axes; D is the origin-to-plane distance.

Ribose		Adenine	
C(1')	−0·039* Å	N(1)	0·021* Å
O(1')	0·041*	C(2)	−0·003*
C(2')	0·023*	N(3)	0·015*
C(3')	−0·554	C(4)	0·006*
C(4')	−0·025*	C(5)	0·019*
O(2')	1·371	C(6)	0·002*
O(3')	−0·240	N(7)	0·008*
C(5')	−0·897	C(8)	−0·016*
O(5')	−0·341	N(9)	−0·011*
N(9)	−1·290	N(10)	0·009
		C(1')	0·000
q_a = −0·8156		H(1)	0·09
q_b = −0·1853		H(2)	−0·02
q_c = 0·6727		H(3)	−0·10
D = 0·654 Å		H(4)	−0·04
		q_a = 0·7395	
		q_b = 0·4471	
		q_c = 0·3772	
		D = 3·773	

* Atoms included in the calculation of the least-squares plane.

Fig. 5. The molecule as viewed along the glycosidic bond C(1')–N(9).

Table 7. *Torsion angles in adenosine and related compounds*

Angle	(a)	(b)	(c)	(d)	(e)
C(8)—N(9)–C(1')–O(1')	9·9°	12·4°	−139·9°	25·7°	3·8°
C(2')–C(1')–O(1')–C(4')	7·4	5·0	−26·4	4·8	−3·4
C(3')–C(2')–C(1')–O(1')	−27·3	−28·7	37·1	−29·8	−19·1
C(4')–C(3')–C(2')–C(1')	35·7	38·5	−33·2	42·3	34·6
O(1')–C(4')–C(3')–C(2')	−32·5	−36·9	18·8	−40·0	−37·6
C(1')–O(1')–C(4')–C(3')	16·0	20·7	4·8	22·8	25·6
C(3')–C(4')–C(5')–O(5')	177·0	40·9	58·0	40·0	171·2

(a) Adenosine; this investigation.
(b) Adenosine-5-bromouridine (Haschemeyer & Sobell, 1963; Sundaralingam, 1969).
(c) 3'-O-Acetyladenosine (Rao, Sundaralingam & Arora, 1970).
(d) Adenosine-5'-phosphate (Kraut & Jensen, 1963; Sundaralingam, 1969).
(e) Adenosine-3'-phosphate dihydrate (Sundaralingam, 1966; 1969).

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The Crystal Structure of Diiodoacetylene; an Example of Pseudosymmetry

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Diiodoacetylene, C_2I_2, forms tetragonal crystals with $a=15\cdot68$ (3), $c=4\cdot30$ (1) Å, eight molecules in the unit cell, space group $P4_2/n$. The structure was determined from three-dimensional diffractometer data, and the refinement carried to a conventional R of 0·145. The problem was complicated by decomposition of the crystals, twinning and pseudosymmetry in the diffraction pattern. The linear molecules are in general positions, but each molecule points, at both ends, towards the middles of two adjacent molecules to give four $C\cdots I$ distances of about 3·4 Å, which we interpret as donor($C\equiv C$)–acceptor(I) interactions. The intramolecular $I\cdots I$ distance is 5·16 Å.

Introduction

Several years ago Professor Jerry Donohue pointed out to one of us an apparently anomalous situation in the structure of crystalline diiodoacetylene, C_2I_2. Flannery & Nixon (Flannery, 1966) had made X-ray diffraction photographs that showed Laue symmetry $4/mmm$ and systematic extinctions corresponding to an n glide plane perpendicular to the c axis. This evidence would require the space group to be $P4/nmm$, although there was also an indication of a 4_2 axis parallel to c. The cell dimensions, $a=b=15\cdot65$, $c=4\cdot29$ Å, and measured density suggested eight molecules in the unit cell. No hypothetical structure consistent with the $P4/nmm$ space group with $Z=8$ could be found, and an examination of the $hk0$ reflexions (Patterson projection along the short c axis) did not provide a solution. The possibility of twinning was raised but not explored further. Additional complications are caused by gradual decomposition of the compound in the X-ray beam.

We have studied the problem further and report here our results.

Experimental

A sample of diiodoacetylene was supplied to us by Dr E. Kloster-Jensen (Kloster-Jensen, 1969). Crystals

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suitable for X-ray diffraction studies were prepared by sublimation at 50°C under reduced pressure; since the crystals are light-sensitive it was necessary to work in a darkened room. Precession photographs (Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å) showed the crystals to be tetragonal with $a=15\cdot68(3)$ and $c=4\cdot30(1)$ Å, in agreement with Flannery's values of 15·65 and 4·29 Å. Careful scrutiny of the photographs shows that the $P4/mmm$ symmetry is only approximate; about 20% of the reflexion-pairs hkl and khl show small but significant intensity differences that cannot be explained away as absorption effects. The intensity differences vary from crystal to crystal but they affect the same reflexion pairs. The true Laue symmetry is only $P4/m$. Systematic extinctions: $0k0$, $k=2n+1$; $hk0$, $h+k=2n+1$ show the space group to be $P4_2/n$. (The following discussion is based on the second arrangement of $P4_2/n$ given in International Tables for X-ray Crystallography (1959) with the origin at $\bar{1}$.) The density of 3·43(3) g.cm^{-3} measured by flotation in thallous formate–thallous malonate solution agrees with the value of 3·49(1) g.cm^{-3} calculated for $Z=8$.

Intensity data were collected using the Hilger and Watts linear diffractometer (Mo $K\alpha$ radiation, balanced filters, crystal mounted with c as the rotation axis, two cycles per reflexion). At room temperature, at which all the measurements were made, the crystals decomposed in the X-ray beam at such a rate that it was necessary to use three different crystals to collect the data; one for $hk0$, one for $hk1$ and $hk2$, and one for $hk3$ and $hk4$. All the crystals were prisms elongated