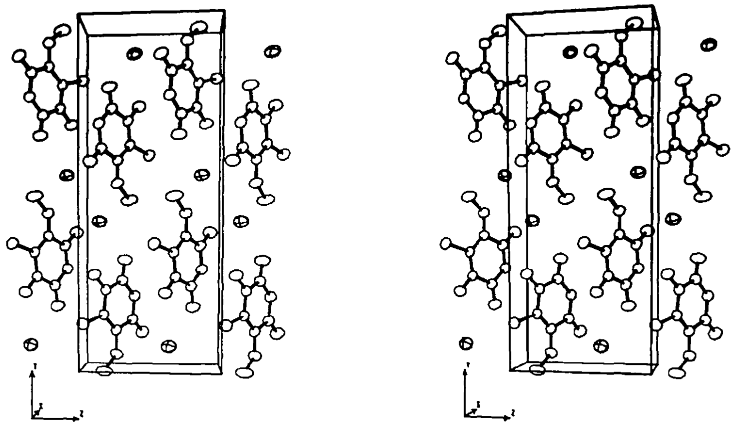

Fig. 2. Three-dimensional view of the crystal structure of 4-chloro-5-methylamino-2,3,6-pyridinetrione monohydrate.

The O–H···O distances are 3·001, 3·011, and 2·864 Å to O(1), O(2) and O(3) respectively. In addition, the amine [N(2)] hydrogen of a molecule related by $1-x,\frac{1}{2}+y,\frac{1}{2}-z$ forms an N–H···O bond of 2·808 Å to the H_2O oxygen. The basic molecule and that related by $x-1,\frac{1}{2}-y,z-\frac{1}{2}$ may also interact weakly through an N(1)–H···O(2) contact of 3·117 Å. We note that these hydrogen-bonded interactions are not only critical in determining the crystal structure of the monohydrate, but also may play an important role in stabilizing the valence structures inferred from the molecular bond lengths.

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The Crystal and Molecular Structure of the Tetraphenylarsonium Salt of the Monoanion of Adenine, $[C_{24}H_{20}As]^+[C_5N_5H_4]^-. 3H_2O$*

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The tetraphenylarsonium salt of the monoanion of adenine crystallizes from aqueous solution as the trihydrate. The crystals are monoclinic, space group $P2_1/n$, with $a=9·878$ (4), $b=21·347$ (7), $c=13·407$ (4) Å, $\beta=103·19$ (3)° and $Z=4$. 2982 independent intensities (2418 above zero) were collected by counter methods. A structural solution was obtained by the heavy-atom method. The adenine anion is disordered in the crystal and accurate values for its bond lengths and angles have not been obtained. Full-matrix least-squares refinement based on the 2418 non-zero *F*'s led to an *R* value of 0·103 with all atoms treated isotropically.

Introduction

Our recent interest in the coordination chemistry of purines and pyrimidines (Kistenmacher, Marzilli & Chang, 1973) has led to the synthesis and structural investigation of several cobalt(III) complexes containing the monoanion of adenine (I) as a coordinated ligand. In an effort to compare the bond lengths and angles in the free anion *versus* those in the complexed anion, we have undertaken a structural study of the tetraphenylarsonium salt of the monoanion of adenine. Our efforts to obtain accurate dimensions have been thwarted by a disordering of the adenine anions.

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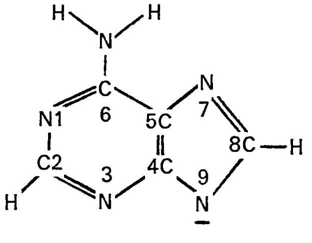
We are presently investigating other cations in an attempt to obtain crystals free of disorder.



Experimental

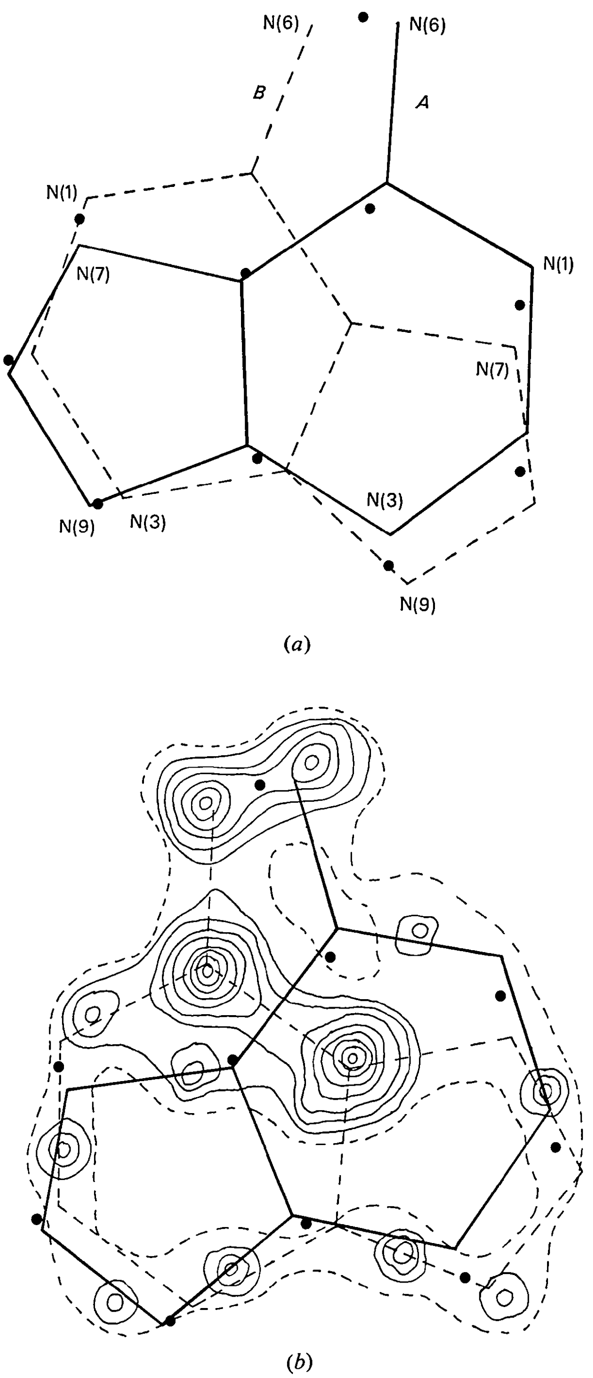
The crystals used in this study were prepared by Professor L. G. Marzilli and Mr C.-H. Chang. Clear, colorless crystals of the salt were obtained by slowly evaporating an aqueous solution. The crystals are approximately hexagonal prisms with the *a* axis coincident with the prism axis. Preliminary unit-cell constants and the space group were determined from Weissenberg photographs.

Intensities (*hkl* and *hk$\bar{l}$*) were measured on a Syntex

Table 1. *Coordinates* ($\times 10^4$) *and isotropic temperature parameters of the heavy atoms*

Estimated standard deviations are in parentheses.

	x	*y*	*z*	*B*
Tetraphenylarsonium ion				
As	2736 (1)	220 (1)	1615 (1)	3·45 (3)
C(11)	2910 (12)	−409 (5)	655 (8)	4·0 (3)
C(12)	2463 (12)	−286 (6)	−374 (9)	4·8 (3)
C(13)	2526 (14)	−763 (7)	−1105 (10)	5·7 (3)
C(14)	3027 (13)	−1348 (6)	−792 (10)	5·5 (3)
C(15)	3471 (13)	−1473 (6)	267 (10)	5·6 (3)
C(16)	3429 (13)	−1014 (6)	1006 (9)	5·0 (3)
C(21)	1341 (12)	−19 (5)	2315 (9)	4·0 (3)
C(22)	1131 (12)	383 (5)	3113 (9)	4·4 (3)
C(23)	94 (13)	203 (7)	3617 (9)	5·5 (3)
C(24)	−627 (14)	−373 (6)	3412 (10)	5·8 (3)
C(25)	−358 (13)	−754 (6)	2624 (9)	5·0 (3)
C(26)	627 (13)	−588 (6)	2069 (9)	4·6 (3)
C(31)	2221 (11)	965 (5)	845 (8)	3·6 (2)
C(32)	3137 (14)	1199 (6)	307 (10)	5·5 (3)
C(33)	2707 (14)	1753 (6)	−346 (10)	5·5 (3)
C(34)	1437 (14)	1988 (6)	−390 (10)	5·3 (3)
C(35)	520 (13)	1763 (6)	157 (9)	5·0 (3)
C(36)	912 (12)	1223 (5)	805 (9)	4·1 (3)
C(41)	4413 (12)	349 (5)	2647 (8)	4·1 (2)
C(42)	4832 (13)	−143 (7)	3326 (10)	6·0 (3)
C(43)	6065 (16)	−44 (7)	4120 (11)	6·8 (4)
C(44)	6754 (14)	534 (6)	4200 (10)	5·5 (3)
C(45)	6274 (13)	1015 (6)	3512 (10)	5·0 (3)
C(46)	5104 (13)	926 (6)	2713 (9)	5·0 (3)
Adenine anion				
N(1)	1870 (11)	2069 (5)	3461 (8)	5·2 (2)
N(3)	3450 (11)	2525 (5)	2600 (8)	5·7 (2)
N(6)	−848 (13)	2282 (6)	2966 (9)	7·3 (3)
N(7)	−204 (11)	3072 (4)	1453 (7)	4·8 (2)
N(9)	2068 (11)	3173 (5)	1269 (8)	5·3 (2)
C(2)	3156 (15)	2159 (6)	3327 (10)	5·5 (3)
C(4)	2224 (14)	2779 (6)	2078 (10)	4·7 (3)
C(5)	758 (21)	2705 (9)	2204 (15)	9·8 (5)
C(6)	640 (21)	2365 (9)	2833 (15)	10·7 (5)
C(8)	688 (14)	3318 (6)	983 (10)	5·1 (3)
Water molecules				
O(1)	4033 (9)	3328 (4)	−11 (7)	6·8 (2)
O(2)	6071 (9)	2573 (4)	2078 (7)	6·8 (2)
O(3)	7015 (9)	3371 (4)	504 (7)	7·3 (2)



(*a*)

(*b*)

Fig. 1. (*a*) A schematic diagram of the proposed disorder model. The solid circles mark the final least-squares atomic positions. (*b*) Final difference Fourier map in the plane of the adenine ring.

$P\bar{1}$ automated diffractometer with monochromated Mo $K\alpha$ radiation. The crystal studied was 0·20mm along the prism axis and varied from 0·16 to 0·18mm in cross section. A θ–2θ scan technique was used in the data collection ($2\theta_{\max}=45°$). Cell constants, based on the complete angular setting of 12 reflections, and other crystal data are as follows: $a=9{\cdot}878$ (4), $b=21{\cdot}347$ (7), $c=13{\cdot}407$ (4) Å, $\beta=103{\cdot}19$ (3)°, space group $P2_1/n$ (systematic absences; $h0l$, $h+l=2n+1$; $0k0$, $k=2n+1$), $V=2752{\cdot}5$ Å^3, $Z=4$, $D_c=1{\cdot}38$, $D_m=1{\cdot}38$ (1) g cm^{-3} $\mu=13{\cdot}5$ cm^{-1}.

2982 independent intensities (2418 above zero) were collected. Each reflection was assigned a variance, $\sigma^2(F)$, based on counting statistics plus a term $(0{\cdot}03I)^2$ where I is the scan count. The 564 reflections with net intensities less than zero were assigned F and $\omega(F)$ of zero. The intensities were corrected for Lorentz and polarization effects. The calculated linear absorption coefficient (Mo $K\bar{\alpha}$) is 13·5 cm^{-1}; the maximum error due to neglect of absorption effects was estimated to be 5% in the intensities, which we considered to be sufficiently small to be ignored.

Determination and analysis of the structure

The coordinates of the As atom were determined from an unsharpened Patterson map. An electron density map based on signs derived from the known arsenic

Table 2. *Observed and calculated structure factors*

The three columns contain values of l, $10F$(obs) and $10\lvert F(\text{calc})\rvert$.

l	$10F$(obs)	$10\lvert F(\text{calc})\rvert$
0	0	L
2	927	990
4	0	218*
6	567	563
8	152	160
10	466	425
12	384	364
0	1	L
1	809	848
2	551	535
3	288	252
4	353	345
5	106	68
6	161	185
7	178	166
8	168	144
9	529	487
10	0	38*
11	135	103
12	0	2*
13	116	140
0	2	L
0	751	835
1	455	410
2	248	328
3	92	92
4	1272	1142
5	376	315
6	403	350
7	70	71
8	318	257
9	86	93
10	404	411
11	216	213
12	450	421
13	0	104*
0	3	L
1	384	377
2	523	465
3	1575	1492
4	242	152
5	489	461
6	116	136
7	545	519
8	468	452
9	397	380
10	230	227
11	82	69
12	0	14*
13	278	226
0	4	L
0	1934	1952
1	1133	1107
2	2676	2477
3	939	856
4	0	167*
5	0	107*
6	755	835
7	171	184
8	189	247
9	200	222
10	416	387
11	98	101
12	225	204
0	5	L
1	923	806
2	156	157
3	591	409
4	869	727
5	614	575
6	217	198
7	339	330
8	607	580
9	419	414
10	147	85
11	135	126
12	0	6*
0	6	L
0	921	934
1	347	381
2	1598	1296
3	255	223
4	629	511
5	771	765
6	1051	761
7	446	385
8	0	2*
9	166	155
10	406	351
11	275	231
12	164	197
0	7	L
1	496	457
2	867	850
3	1048	981
4	861	766
5	653	618
6	554	535
7	84	112
8	675	647
9	250	249
10	131	129
11	118	65
12	110	100
0	8	L
0	364	359
1	448	429
2	801	670
3	461	410
4	0	13*
5	457	418
4	294	287
5	0	41*
6	78	77
7	63	110
8	244	188
0	18	L
0	374	295
1	98	31
2	220	208
3	231	198
4	161	202
5	73	125
6	266	252
7	175	161
0	19	L
1	254	271
2	301	246
3	217	195
4	87	65
5	0	43*
6	0	65*
0	20	L
0	328	316
1	0	74*
2	0	79*
3	0	81*
4	0	132*
0	21	L
1	149	130
2	0	23*
3	297	285
1	0	L
1	1746	1814
3	424	380
5	649	634
7	501	517
9	0	7*
11	376	350
1	1	L
0	141	130
1	464	530
2	1564	1500
3	774	669
4	729	746
5	132	159
6	82	116
7	121	111
8	433	427
9	0	15*
10	484	467
11	164	82
12	100	112
1	2	L
0	0	81*
1	772	698
2	79	84
3	164	140
4	543	453
5	787	729
6	399	454
7	1022	1042
8	253	279
9	130	155
10	237	199
11	390	354
12	108	60
1	3	L
0	34	62
1	855	846
2	2062	1924
3	62	35
4	358	410
5	65	84
6	254	253
7	351	323
8	344	314
9	430	432
10	303	291
11	69	94
12	65	70
1	4	L
0	121	60
1	1289	1336
2	324	314
3	1257	1130
4	222	164
5	747	686
6	290	254
7	386	393
8	139	71
9	157	106
10	105	50
11	445	413
12	93	67
1	5	L
0	225	183
1	593	574
2	311	226
3	333	326
4	1038	948
5	152	175
6	286	253
7	317	302
8	168	168
9	471	448
10	289	283
11	0	113*
12	0	20*
0	486	458
1	248	223
2	338	295
3	0	83*
4	318	336
5	32	24
6	353	346
7	146	124
8	145	143
9	0	111*
1	15	L
0	0	35*
1	0	17*
2	205	232
3	581	563
4	0	55*
5	159	234
6	306	272
7	157	115
8	243	203
9	293	223
1	16	L
0	457	441
1	485	487
2	425	416
3	0	20*
4	328	283
5	329	249
6	324	353
7	241	187
8	213	167
1	17	L
0	172	175
1	88	139
2	84	90
3	217	190
4	0	36*
5	0	16*
6	143	123
7	203	192
8	207	201
1	18	L
0	257	210
1	298	267
2	177	136
3	82	79
4	67	19
5	243	259
6	218	190
1	19	L
0	126	11
1	323	283
2	152	123
3	169	175
4	318	334
5	171	191
1	20	L
0	147	170
1	262	261
2	0	22*
3	0	70*
4	0	58*
1	21	L
0	29	31
1	0	18*
2	66	92
2	0	L
0	1296	1327
2	846	768
4	1150	1083
6	759	805
8	846	868
10	184	176
12	213	190
2	1	L
0	1128	1131
1	1551	1539
2	138	142
3	1193	1191
4	333	244
5	359	396
6	283	309
7	129	186
8	0	41*
9	629	633
10	0	37*
11	106	67
12	0	28*
13	234	176
2	2	L
0	605	589
1	240	213
2	540	581
3	511	465
4	242	249
5	357	373
6	382	385
7	122	77
8	166	169
9	120	144
10	85	34
11	235	213
12	191	214
2	3	L
0	501	404
1	1052	978
2	577	507
2	373	359
3	382	369
4	413	379
5	0	34*
6	160	89
7	0	33*
8	302	281
9	76	114
10	116	161
2	12	L
0	224	229
1	495	526
2	161	144
3	103	152
4	0	81*
5	472	430
6	0	68*
7	689	652
8	0	76*
9	0	95*
10	100	73
2	13	L
0	0	142*
1	0	192*
2	631	645
3	70	85
4	337	299
5	0	36*
6	122	90
7	135	125
8	314	331
9	235	236
10	325	272
2	14	L
0	191	144
1	393	365
2	0	24*
3	71	59
4	93	72
5	370	377
6	0	35*
7	173	208
8	94	67
9	0	82*
2	15	L
0	218	187
1	0	38*
2	416	434
3	300	301
4	382	372
5	166	86
6	0	51*
7	89	100
8	136	126
2	16	L
0	350	357
1	446	434
2	184	164
3	0	17*
4	106	68
5	207	206
6	219	208
7	317	285
2	17	L
0	141	172
1	88	141
2	227	228
3	245	302
4	180	234
5	0	5*
6	0	78*
7	0	52*
2	18	L
0	289	255
1	284	272
2	173	133
3	0	70*
4	42	64
5	0	58*
6	168	145
2	19	L
0	125	172
1	0	60*
2	184	190
3	340	264
4	0	155*
5	256	203
2	20	L
0	279	253
1	191	194
2	86	75
3	0	38*
3	0	L
1	1569	1506
3	164	142
5	674	739
7	592	609
9	134	131
11	376	302
3	1	L
0	854	831
1	635	598
2	612	650
3	568	495
4	1018	945
5	62	38
6	130	175
9	231	267
10	0	4*
3	10	L
0	219	257
1	220	203
2	584	665
3	0	48*
4	359	334
5	172	103
6	547	461
7	202	154
8	178	111
9	0	3*
10	91	116
3	11	L
0	262	260
1	176	174
2	0	15*
3	524	525
4	102	123
5	359	391
6	0	93*
7	159	87
8	0	51*
9	355	343
3	12	L
0	480	465
1	0	14*
2	396	363
3	0	16*
4	202	214
5	138	103
6	209	203
7	58	70
8	210	233
9	0	92*
3	13	L
0	99	85
1	46	40
2	0	155*
3	446	427
4	122	190
5	310	265
6	0	87*
7	0	19*
8	88	55
3	14	L
0	649	654
1	240	212
2	157	104
3	0	34*
4	146	89
5	99	131
6	281	283
7	0	19*
8	89	106
3	15	L
0	151	125
1	88	50
2	328	270
3	276	311
4	308	244
5	266	303
6	151	121
7	0	28*
3	16	L
0	273	230
1	302	338
2	397	410
3	0	33*
4	0	157*
5	173	160
6	212	254
3	17	L
0	0	33*
1	57	69
2	192	202
3	319	239
4	216	243
5	169	163
6	0	110*
3	18	L
0	171	144
1	324	302
2	252	243
3	218	164
4	52	81
5	119	148
3	19	L
0	127	147
1	0	87*
2	158	122
3	0	144*
3	20	L
0	294	273
1	251	261
4	0	L
0	652	694
2	853	835
4	229	282
6	400	362
8	298	282
10	179	200
4	1	L
9	79	119
4	10	L
0	207	269
1	436	416
2	131	127
3	262	275
4	0	7*
5	280	233
6	224	168
7	291	256
8	0	107*
9	0	97*
4	11	L
0	238	285
1	0	56*
2	524	542
3	126	126
4	545	558
5	0	7*
6	288	319
7	109	111
8	268	190
4	12	L
0	127	58
1	585	613
2	229	240
3	278	242
4	0	27*
5	0	24*
6	0	46*
7	313	333
8	0	0*
4	13	L
0	480	459
1	102	105
2	243	196
3	183	127
4	347	309
5	163	153
6	0	75*
7	0	21*
4	14	L
0	89	141
1	465	494
2	0	43*
3	0	33*
4	0	18*
5	0	79*
6	61	58
7	153	175
4	15	L
0	135	174
1	189	197
2	116	132
3	124	204
4	373	357
5	236	221
6	136	165
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1	310	283
2	258	240
3	203	150
4	137	93
5	152	167
4	17	L
0	208	252
1	0	23*
2	128	86
3	240	230
4	184	107
4	18	L
0	308	328
1	269	314
2	216	168
3	0	66*
4	19	L
0	266	193
1	0	27*
5	0	L
1	824	837
3	0	17*
5	522	530
7	310	355
9	373	343
5	1	L
0	858	936
1	263	224
2	68	98
3	51	62
4	568	628
5	0	91*
6	289	302
7	0	34*
8	104	128
9	143	81
5	2	L
0	334	345
1	827	833
2	162	164
3	523	551
4	0	95*
5	229	239
2	648	645
3	0	85*
4	68	45
5	150	143
6	319	350
7	121	83
5	13	L
0	0	200*
1	0	112*
2	275	268
3	175	161
4	210	182
5	265	238
6	0	7*
5	14	L
0	335	318
1	179	169
2	227	236
3	0	29*
4	0	155*
5	0	39*
5	15	L
0	123	128
1	115	71
2	129	52
3	261	259
4	0	88*
5	253	253
5	16	L
0	174	144
1	187	205
2	425	411
3	238	200
4	0	23*
5	17	L
0	0	37*
1	71	57
2	86	99
3	207	191
5	18	L
0	80	102
1	79	150
6	0	L
0	459	496
2	156	245
4	216	266
6	330	317
8	315	347
6	1	L
0	158	123
1	341	347
2	0	160*
3	356	379
4	54	43
5	241	343
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5	0	50*
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8	0	40*
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8	183	115
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3	223	210
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5	336	349
6	0	37*
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3	0	5*
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-3	0	110*
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-12	247	228
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-10	231	227
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-7	411	489
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-2	193	148
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-2	230	190
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-4	91	144
-3	133	103
-2	79	69
-1	242	201
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-2	208	208
-1	0	55*
2	0	L
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-8	0	178*
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-7	633	696
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-12	322	355
-11	208	61
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-7	0	37*
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-6	133	174
-5	141	129
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-1	374	381
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-7	111	110
-6	348	273
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-2	115	71
-1	168	171
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-6	233	168
-5	150	58
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-2	164	155
-1	345	406
2	20	L
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-1	266	242
3	0	L
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-7	265	310
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-3	118	58
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-8	553	574
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-6	333	369
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-7	139	125
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-1	0	38*
3	15	L
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-3	76	83
-2	0	32*
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-5	0	36*
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-3	216	214
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-1	396	407
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-5	293	252
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-3	200	245
-2	0	17*
-1	188	175
3	19	L
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-3	54	47
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-2	0	72*
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-7	0	12*
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-4	0	166*
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-2	437	422
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8	3	L
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-8	0	108*
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-3	128	73
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-6	0	24*
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-5	41	136
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-2	382	353
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-3	0	47*
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-1	108	78
8	8	L
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-5	263	294
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-3	343	369
-2	0	48*
-1	0	16*
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-8	136	113
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-1	0	60*

Table 2 (*cont.*)

atom position clearly revealed the carbons of the four phenyl rings of the arsonium ion. The position of the adenine anion was also indicated, but coordinates of individual atoms in the residue were unclear. A second electron density map based on the arsenic plus the 24 phenyl ring carbon atoms gave approximate positions for the atoms in the adenine ring system. Particular difficulty was encountered in finding suitable positions for atoms C(5) and C(6). This second map also gave coordinates for the three water molecules. Several cycles of isotropic, fullmatrix least-squares refinement, the quantity minimized being $\sum\omega(F_o-F_c)^2$, led to an R value, $\sum||F_o|-|F_c||/\sum|F_o|$, of 0·103 (excluding rejects), and 0·142 (including rejects). The final weighted R value, $[\sum\omega(F_o-F_c)^2/\sum\omega F_o^2]^{1/2}$ is 0·091; the goodness of fit, $[\sum\omega(F_o-F_c)^2/(n-p)]^{1/2}$ for $n=2418$ observations of non-zero weight and $p=153$ parameters, is 2·3. The maximum shift over error for any parameter was 0·6. The scattering factors for all atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The final positional and thermal parameters are given in Table 1, and the observed and calculated structure factors in Table 2.

The least-squares refinement has led to a final set of thermal parameters and derived bond lengths and angles for the adenine ring which contain several anomalies. In particular, the thermal parameters for atoms C(5) and C(6) are about 10 Å^2 (Table 1), and the bond

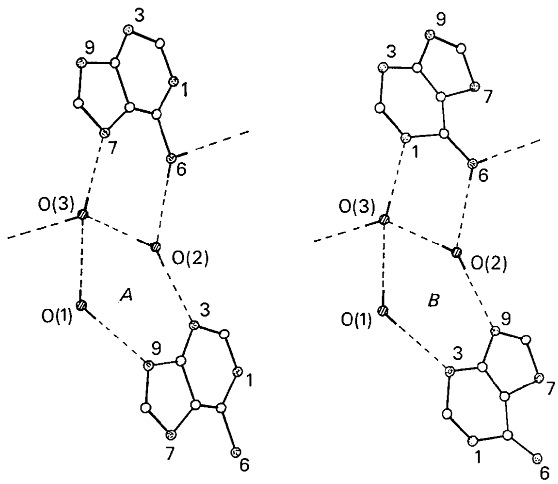

Fig. 2. Hydrogen bonding between the water molecules and translationally equivalent anions. Schemes *A* and *B* differ only in the orientation of the adenine ring system, see text.

lengths C(5)–C(6), 1·14 Å, C(4)–C(5), 1·50 Å, and N(6)–C(6), 1·53 Å, differ significantly from the expected values of about 1·4 Å (see Table 3). In an attempt to understand the reason for these anomalies, a difference Fourier map was computed with the atoms of the adenine ring removed. While several of the adenine anion atoms appeared as reasonably well-defined peaks, only broad maxima, about 2·9 e Å^{-3}, were found for atoms C(5) and C(6) (all the maxima agreed within 2σ of the final least-squares values). The broad maxima were surrounded by diffuse density of the order of 1·5–2·0 e Å^{-3}. A good account of the electron density could be made if the adenine system were assumed to be disordered such that the observed density is a 1:1 superposition of two adenine rings with their five- and six-membered rings interchanged. Fig. 1 contains (*a*) a schematic of the proposed disorder model, and (*b*) a final difference Fourier in the plane of the adenine molecule. The proposed disorder is very similar to that by Sletten (1969) in a dimeric copper complex containing a disordered adenine anion ligand. The near superpositioning of N(6) and the effective interchangeability of the sites occupied by atoms N(1) and N(7), and N(3) and N(9) in the two orientations of the disorder anion is obviously important in maintaining the hydrogen bonding in the structure. The hydrogen bonds which couple translationally related anions, along the *a* axis, are illustrated in Fig. 2. The hydrogen bonding is not markedly affected by whether the constituent rings of the adenine moiety are orientated imidazole-pyrimidine, *A* in Fig. 2, or pyrimidine-imidazole, *B* in Fig. 2. The hydrogen-bond distances are given in Table 4; the heavy-atom distances are the basis of the schematic positioning of the hydrogens in Fig. 2. The other important stabilizing force in the structure is the sandwiching of the adenine between screw-related tetraphenylarsonium cations, Fig. 3. A careful examination of Fig. 3 and the interatomic contacts indicates that the interactions involved in this stacking are, like the hydrogen bonding, reasonably insensitive to the two different orientations of the adenine ring system.

Table 3. *Bond lengths and angles in the adenine anion*

Estimated standard deviations are in parentheses.

N(1)–C(2)	1·34 (2) Å	C(2)–N(1)–C(6)	124 (1)°
N(1)–C(6)	1·45 (2)	C(2)–N(3)–C(4)	107 (1)
N(3)–C(2)	1·33 (2)	C(5)–N(7)–C(8)	98 (1)
N(3)–C(4)	1·36 (2)	C(4)–N(9)–C(8)	107 (1)
N(6)–C(6)	1·53 (3)	N(1)–C(2)–N(3)	124 (1)
N(7)–C(5)	1·45 (2)	N(3)–C(4)–N(9)	126 (1)
N(7)–C(8)	1·31 (2)	N(3)–C(4)–C(5)	132 (1)
N(9)–C(4)	1·35 (2)	N(9)–C(4)–C(5)	103 (1)
N(9)–C(8)	1·36 (2)	N(7)–C(5)–C(4)	111 (1)
C(4)–C(5)	1·50 (2)	N(7)–C(5)–C(6)	134 (1)
C(5)–C(6)	1·14 (3)	C(4)–C(5)–C(6)	114 (2)
		N(1)–C(6)–N(6)	125 (1)°
		N(1)–C(6)–C(5)	119 (2)
		N(6)–C(6)–C(5)	115 (2)
		N(7)–C(8)–N(9)	121 (1)

Table 4. *Hydrogen-bond distances*

Donor atom	Acceptor atom	Symmetry†			Distance (donor–acceptor)
O(2)	N(3)*	x	y	z	2·83 Å
O(3)	N(7)*	$1+x$	y	z	2·83
O(1)	O(3)*	x	y	z	2·87
O(3)	N(1)*	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	2·87
O(1)	N(9)*	x	y	z	2·89
O(2)	O(3)*	x	y	z	3·02
N(6)*	O(1)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	3·03
N(6)*	O(2)	$1+x$	y	z	3·07

† Transformation to be applied to the coordinates of the asterisked atom as listed in Table 1.

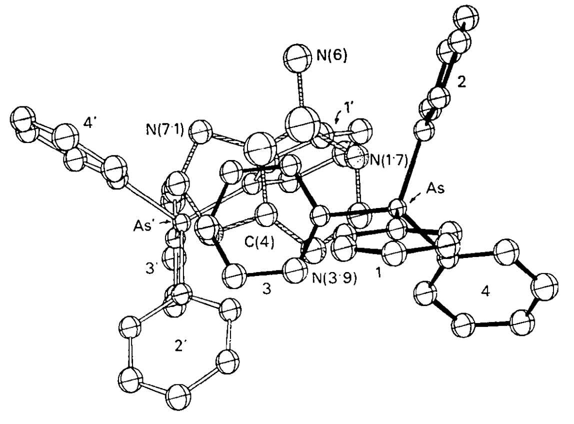

Fig. 3. Stacking of the adenine anion between two screw-related tetraphenylaronsium cations. The thermal ellipsoids are drawn at the 25% probability level [*ORTEP*; Johnson (1965)].

The dimensions of the tetraphenylarsonium cation are similar to those found in other crystal structure analyses. The ranges of bond lengths and angles are as follows:

As–C 1·90 (1)–1·92 (1) Å; C–As–C 106·2 (6)–113·2 (6)°; C–C 1·34 (2)–1·47 (2) Å; C–C–C 116·5 (15)–124·7 (15)°.

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The Prediction of the Stereochemistry of Polysulphate and Hydrogen Sulphate Ions

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The angles in nine polysulphate and hydrogen sulphate ions are predicted to within 1·5° using two empirical relations, one involving the lengths of the bonds which define the angle, the other involving the configuration of the bonds around the bridging oxygen atom. Using, in addition, the bond strength relations of Brown & Shannon it is possible to predict *a priori* the complete geometry of the $S_2O_7^{2-}$ ion to an accuracy of 0·013 Å and 0·8°. The variations in angle can be understood equally well by assuming that they are caused by O–O repulsion or by variation in the strengths of the S–O bonds.

In most crystals the sulphate ion, SO_4^{2-}, shows a remarkable regularity, variations from $\bar{4}3m$ (Td) symmetry usually being quite small, but in the polysulphate and hydrogen sulphate ions much larger variations are found. The bond lengths can range from 1·36 to 1·83 Å and the angles from 97 to 128°. This paper shows that it is possible to make quantitative predictions of these effects.

The variations in bond length in SO_4 groups have been discussed in terms of π bonding by Cruickshank (1961), but they can also be understood in terms of the bond strength or bond valence theory by which it is assumed that the formal valence of an atom is shared among the bonds it forms. Thus in a regular SO_4^{2-} ion the valence, 6, of sulphur is shared equally between the four S–O bonds, each having a bond strength of 1·5 valence units (v.u.). The oxygen atoms have a valence of 2 and consequently form additional bonds with a total strength of 0·5 v.u. to other atoms in the crystal. Where the sulphur valence is shared unequally between the bonds the effect is manifest in the unequal lengths of the S–O bonds. Brown & Shannon (1973) have recently determined an empirical relationship between bond length (R) and bond strength (s) of the form:

$$s=(R/R_0)^{-N} \qquad (1)$$

where $R_0=1{\cdot}622$ and $N=4{\cdot}290$ for S–O bonds.

This relationship can be used either to determine bond strengths when the bond lengths are known or, if an *a priori* estimate of the bond strengths can be made, it can be used to predict the bond lengths. The regularity of most SO_4^{2-} ions arises because the very weak bonds ($s\sim0{\cdot}15$) formed between most metallic cations and oxygen cause only small variations in the S–O bond strengths.

In the case of the polysulphate and hydrogen sulphate ions, at least one of the oxygen atoms (here designated as bridging) is bonded to two sulphur atoms or one sulphur and one hydrogen atom. Consequently its valence is more nearly equally shared between these two bonds giving rise to bonds of strength close to 1 v.u. with lengths of about 1·62 Å. The remaining oxygen atoms (here designated as terminal) are correspondingly more strongly bound with the bond-length shortening from the normal 1·47 to 1·43 Å. The effect is less marked in the hydrogen sulphate ions since the O–H bond typically has a bond strength of 0·85 v.u. (Brown & Shannon, 1973) so that the strength of the S–O bond will be 1·15 v.u. corresponding to a length of 1·57 Å.

Two different theories have been offered to explain the wide range of angles found in the SO_4 group. Baur (1970) assumes that the contact repulsion between the O atoms is sufficiently large to ensure that the oxygen atoms remain at the corners of a regular tetrahedron and the variation in angle is the result of the sulphur atom moving away from the centre of the tetrahedron. Thus the shortening of an S–O bond results in the increase of the angles between it and neighbouring bonds. On the other hand Louisnathan & Gibbs (1972) associate the increase in O–S–O angle with an increase