hétérocycle glucidique à cinq chaînons. Ce composé présente le double intérêt d'être à la fois un précurseur extrêmement utile à la synthèse d'analogues des nucléosides glucofuranosidiques et de présenter une conformation du cycle tout à fait originale.

Les auteurs remercient M. J. Defaye de leur avoir fourni le sujet de ce travail.

Références

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM 360 system, *World List of Crystallographic Computer Programs*, 2nd ed. Appendix, p. 52.

Ashmawy, A. E., Horton, D., Magbanua, L. G. & Tronchet, S. M. S. (1968). *Carbohyd. Res.* **6**, 299.

Baur, E. H. (1965). *Acta Cryst.* **19**, 909.

Brown, G. M. & Levy, H. A. (1965). *Science*, **141**, 921.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS. A Fortran Crystallographic Least-squares Program.* Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Defaye, J., Horton, D., Nakamura, T. & Philips, K. D. (1970). *Carbohyd. Res.* **16**, 133.

Dickerson, R. E. (1959). *Acta Cryst.* **12**, 610.

Hall, L. D. (1964). *Advanc. Carbohyd. Chem.* **19**, 51.

Hauptman, H. & Karle, J. (1953). A.C.A. Monograph No. 3. Pittsburg: Polycrystal Book Service.

Horton, D., Magbanua, L. G. & Tronchet, J. M. J. (1966). *Chem. & Ind.* (*Lond.*), p. 1718.

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

Jeffrey, G. A. & Rosenstein, R. D. (1964). *Advanc. Carbohyd. Chem.* **19**, 7.

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

Karle, J. & Hauptman, H. (1956). *Acta Cryst.* **9**, 635.

Lipson, H. & Cochran, W. (1966). *The Determination of Crystal Structures.* (*The Crystalline State,* Vol. 3). p. 167. London: Bell.

McDowell, J. J. H. (1970). *Acta Cryst.* **B26**, 954.

Munns, A. R. I. & Tollin, P. (1970). *Acta Cryst.* **B26**, 1101.

Parthasarathy, R. & Davis, R. E. (1967). *Acta Cryst.* **23**, 1049.

Shefter, E. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 1067.

Spencer, M. (1959). *Acta Cryst.* **12**, 59.

Strah (1970). *Advanc. Carbohyd. Chem.* **25**, 53.

Sundaralingam, M. (1965). *J. Amer. Chem. Soc.* **87**, 599.

Acta Cryst. (1972). B**28**, 1201

The Crystal and Molecular Structure of Catechol Cyclic Phosphate

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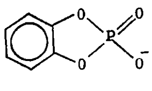
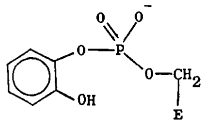
The crystal structure of catechol cyclic phosphate, $C_6H_5PO_4$, has been determined from three-dimensional X-ray diffraction data. The orthorhombic unit cell, space group $Pbca\,(D_{2h}^{15})$ has lattice parameters $a = 8{\cdot}549$ (2), $b = 15{\cdot}041$ (3), and $c = 11{\cdot}053$ (2) Å, giving a calculated density of 1·608 g.cm^{-3} for M.W. 172·078 and $Z = 8$. The intensities of 1211 unique reflections were measured using the θ–2θ scan mode of a Picker automatic 4-circle diffractometer and Cu $K\alpha$ radiation. The structure was solved from the Patterson function, and the positions and anisotropic temperature factors of the P, O, and C atoms were refined by full-matrix least-squares methods. Hydrogen atoms were located, and in some cases refined. The final R values were $R_1 = 0{\cdot}063$ and $R_2 = 0{\cdot}052$ for the 851 reflections above background. The ring system is essentially planar. The O–P–O bond angle in the highly strained five-membered ring is $98{\cdot}4 \pm 0{\cdot}2°$. Some distortion occurs in the six-membered ring as indicated by bond angles of 115·2 and 115·9° at the α-carbon atoms. The crystal structure contains infinite hydrogen bonded chains, proceeding in the x direction and generated by the a glide, linking the phosphoryl and hydroxyl oxygen atoms of adjacent molecules with an O–H···O distance of 2·464 Å.

Introduction

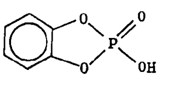
The observation that catechol cyclic phosphate (I) can phosphorylate α-chymotrypsin *reversibly*, whereby the phenolic hydroxyl groups of the phosphoryl-enzyme species (II) are shown to carry out nucleophilic attack at the phosphoryl phosphorus far more effectively than the external nucleophile water, resulting in reformation of (I) (Kaiser, Lee & Boer 1971), is remarkable in view of the anticipated ring strain in this cyclic five-membered diester. Indeed, the demonstration of reversibility is particularly dramatic when it is remembered that (I) is attacked by hydroxide ion nearly 10^7 times faster than its acyclic analog, diphenyl phosphate (Kaiser & Kudo, 1967).



(I)



(II)



(III)

Similar kinetic acceleration has been documented in the case of hydrolysis of aliphatic five-membered cyclic diesters (Kumamoto, Cox & Westheimer, 1956; Covitz & Westheimer, 1963). These results may provide a useful clue to the action mechanism of adenosine 3′,5′-monophosphate (cyclic AMP). The importance of cyclic AMP in the regulation of metabolism is well established, and is believed to derive from its function as a second messenger in the action of many hormones (Robison, Butcher & Sutherland, 1968). However, the action mechanism of cyclic AMP has not yet been demonstrated, and the possibility that it may occur by similar reversible phosphorylation reactions at the active or allosteric sites of proteins is intriguing. In fact, re-formation of the six-membered cyclic diester, cyclic AMP, should be considerably more favorable from the thermodynamic point of view (Usher, Dennis & Westheimer, 1965) than the cyclization of (I). The demonstration of a protein phosphorylation mechanism would also be of considerable interest (Greengard & Kuo, 1970), because of an accumulating array of evidence linking cyclic AMP and other cyclic nucleotides to the neuronal function and suggesting that these compounds may play a key role in the molecular biology of learning and memory.

Experimental

A sample of catechol cyclic phosphate (III) was received from E. T. Kaiser. The crystals were colorless and showed evidence of extensive fragmentation. The most commonly occurring form appeared to be a thick plate, or fragment thereof, in which the {010} faces were well-developed. Because catechol cyclic phosphate hydrolyzes readily (Kaiser *et al.*, 1971) and may be light-sensitive, precautions were taken to minimize decomposition of the sample. Several of the most promising crystalline fragments were selected under the polarizing microscope and sealed in thin-walled Lindemann glass capillaries. Oscillation photographs, taken on a Weissenberg goniometer, confirmed that most of these crystals were significantly fragmented; a more detailed examination of the better crystals using ω scans of 'φ-independent' ($\chi = 90°$) reflections on a four-circle diffractometer showed that the diffraction maxima of *all* crystals examined could, in some orientation, be resolved into distinct peaks. The crystal selected for data collection was the one where this effect was smallest, amounting to a maximum peak separation of $\Delta\omega = 0{\cdot}2°$. This crystal was an irregularly shaped fragment 0·11 mm thick, 0·41 mm long, and with a transverse dimension ranging from 0·08 to 0·19 mm. Variations in intensity of the 'φ-independent' 002 reflection were of the order of 1 % at varied φ settings.

A preliminary survey of the reciprocal lattice on a precession camera showed diffraction symmetry D_{2h} and the systematic absence of $0kl$ reflections for k odd, $h0l$ for l odd, and $hk0$ for h odd, establishing the space group uniquely as *Pbca*. The crystal was then carefully centered on the Picker four-circle goniostat, and the alignment on **c*** was refined. Lattice constants were computed by a least-squares fit to the setting angles of 12 reflections (Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å). As often occurs, the precision of fit given by the least-squares analysis was considerably better than the intrinsic accuracy of the measurement, which is subject to systematic instrumental errors. The errors assigned in Table 1 were obtained by multiplying the least-squares-calculated errors by an arbitrary factor of 10, to bring the values in line with our experience in trying to

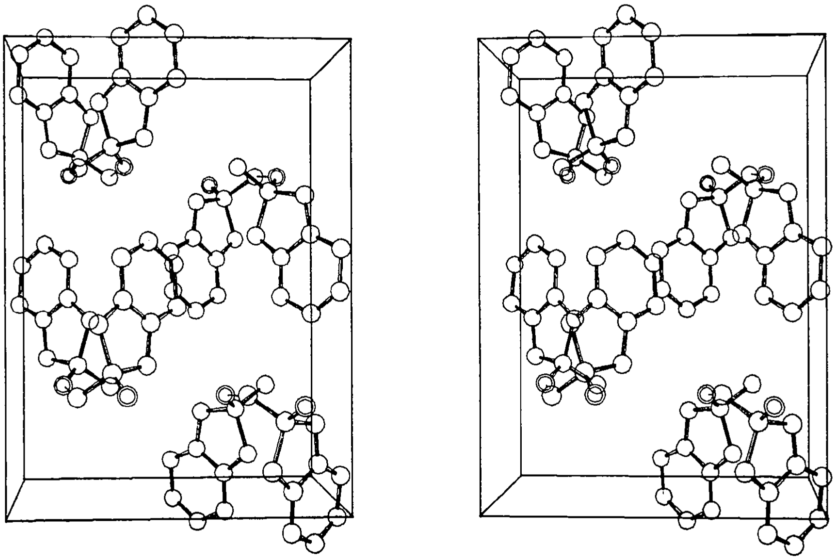


Fig. 1. Three-dimensional stereopair drawing of the crystal structure of catechol cyclic phosphate. The view is down x, with y vertical and z horizontal. The narrow line represents a hydrogen bond between molecules related by the a glide. The phosphoryl oxygen atom O(4) is distinguished by a double circle.

reproduce cell constants with different crystals or under a different set of experimental conditions. An experimental density measurement was not attempted because of the hydrolysis problem.

Table 1. *Crystal data*

Molecular formula	$C_6H_5PO_4$
Molecular weight	172·078
Crystal habit	Plate: {010}
Space group	*Pbca* (D_{2h}^{15})
Cell constants: *a*	$8\cdot549 \pm 0\cdot001_5$ Å
25°C) *b*	$15\cdot041 \pm 0\cdot003$
c	$11\cdot053 \pm 0\cdot002_4$
Volume	$1421\cdot1 \pm 0\cdot2$ Å^3
Density (calc)	1·608 g.cm^{-3} ($Z = 8$)
Density (obs)	–
Absorption coefficient	31·45 cm^{-1}
Number of independent reflections measured	1211

The intensities of all unique reflections in the range $0 < \sin\theta < 0\cdot909$ were measured, using the θ–2θ scan mode of the Picker diffractometer and Ni-filtered Cu $K\alpha$ radiation. The X-ray tube was at a 3° take-off angle, and the scintillation detector was placed 31·6 cm from the crystal and screened with a 6 mm square aperture. Incident- and exit-beam collimators, 1·5 mm in diameter, served to limit stray radiation. Attenuators were available to keep the count rate from exceeding 12,000 per sec, but were needed for only three reflections. The scan speed was 2°. min^{-1} over 2θ angles of $2° + \Delta$, where Δ is the calculated separation of the $K\alpha$ doublet. Examination of the strip chart recorder record showed that this range was sufficient to allow for the observed mosaic spread of the crystal. Stationary-crystal stationary-counter background counts of 10 sec were taken at each end of the scan. The 122 reflection was monitored after every 50 measurements and it showed a net loss in intensity of 11 %, with the largest changes occurring near the end of the data set. Accordingly, a decomposition (rescaling) correction was applied to the data. An error $\sigma(I) = [(0\cdot02\,I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_0 - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\sum w(|F_0| - |F_c|)^2$ was minimized. Here, N_0 is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities corrected for Lorentz and polarization effects. The 360 reflections for which $I < 0$ or $I/\sigma(I) < 2$ were denoted absent and were not used in refinement, but they were subsequently checked against their calculated values. Absorption corrections were not applied, since the differences in transmission coefficients were small and the accuracy of the data set was clearly limited by other factors originating in the nature of the crystal. An overall temperature factor ($B_0 = 4\cdot59$ Å^2) was calculated by Wilson's (1942) method. The distribution of intensities is quite close to the theoretical (parentheses) distribution for a

Table 2. *Structure factors* (e$^-$ × 10)

H	K	FOBS	FCAL
** L = 0 **			
2	0	662	713
4	0	266	277
6	0	389	392
8	0	253	262
10	0	121	125
2	1	349	343
4	1	371	376
6	1	69	88
8	1	75	75
10	1	69	62
0	2	450	374
2	2	1116	1191
4	2	130	134
6	2	434	429
8	2	221	222
10	2	42	28
2	3	143	139
4	3	415	443
6	3	263	249
8	3	97	116
0	4	903	842
2	4	210	211
4	4	251	254
6	4	154	151
2	5	156	158
4	5	386	389
6	5	200	185
0	6	1103	1090
2	6	104	95
4	6	33	38
8	6	113	100
2	7	270	268
4	7	160	169
6	7	80	76
0	8	699	691
2	8	178	170
4	8	295	300
6	8	104	94
8	8	216	199
2	9	127	115
4	9	115	123
6	9	309	309
8	9	77	83
0	10	309	319
2	10	386	392
4	10	362	367
6	10	462	480
8	10	152	145
2	11	130	121
4	11	224	236
0	12	117	122
2	12	230	228
4	12	140	137
2	13	85	86
4	13	88	76
0	14	101	213
2	14	50	65
4	14	152	155
6	14	51	34
2	15	79	78
0	16	61	67
2	16	44	48
2	17	36	25
** L = 1 **			
1	1	688	696
2	1	704	743
3	1	86	60
5	1	161	158
6	1	109	106
7	1	125	128
8	1	111	98
9	1	57	53
10	1	72	55
0	2	1483	1322
1	2	283	289
2	2	934	963
3	2	159	161
4	2	362	370
5	2	146	145
6	2	382	370
8	2	179	168
1	3	521	520
2	3	163	165
3	3	252	251
4	3	195	205
5	3	238	242
6	3	66	71
7	3	125	111
8	3	56	19
9	3	89	74
0	4	887	919
1	4	190	192
2	4	298	301
3	4	158	159
4	4	219	217
5	4	98	102
6	4	312	307
7	4	65	60
8	4	233	224
1	5	322	327
2	5	41	13
3	5	222	224
4	5	241	241
5	5	105	104
6	5	45	21
7	5	143	147
9	5	109	96
0	6	592	607
1	6	81	94
2	6	378	392
3	6	108	116
4	6	229	231
5	6	42	55
6	6	245	249
7	6	97	90
8	6	158	147
1	7	411	400
2	7	126	115
3	7	85	83
4	7	41	13
5	7	95	94
6	7	41	7
7	7	94	92
0	8	618	618
1	8	138	128
2	8	395	396
3	8	73	64
4	8	243	240
5	8	46	42
6	8	270	295
9	8	132	126
2	9	257	249
3	9	61	49
4	9	100	100
5	9	154	159
2	10	95	98
1	11	108	108
3	11	87	94
4	11	209	215
5	11	111	105
0	12	345	342
1	12	83	74
2	12	231	233
3	12	106	117
4	12	157	153
5	12	140	147
6	12	120	124
7	12	52	5
1	13	149	157
2	13	153	156
3	13	62	58
4	13	46	33
6	13	74	82
0	14	175	179
1	14	92	103
2	14	158	159
4	14	108	116
6	14	52	56
3	15	86	84
4	15	39	4
0	16	89	80
1	16	55	35
2	16	131	124
4	16	90	86
** L = 2 **			
0	0	972	885
1	0	690	766
2	0	2199	2291
3	0	86	92
4	0	358	345
5	0	109	107
6	0	308	299
7	0	116	110
8	0	142	153
9	0	99	84
1	1	976	1015
2	1	123	129
3	1	168	161
4	1	188	184
5	1	208	221
6	1	130	110
7	1	402	402
8	1	96	100
9	1	93	80
0	2	1318	1357
1	2	781	752
2	2	172	161
3	2	401	409
4	2	467	479
5	2	52	36
6	2	171	170
8	2	102	88
9	2	50	43
1	3	274	279
2	3	230	225
3	3	208	210
4	3	323	331
5	3	170	183
6	3	116	93
7	3	210	213
8	3	72	75
9	3	114	118
0	4	470	449
1	4	558	516
2	4	93	97
3	4	53	51
4	4	262	267
5	4	187	190
7	4	84	73
1	5	112	105
2	5	119	113
3	5	78	80
4	5	215	220
6	5	97	85
7	5	66	60
0	6	361	339
1	6	129	123
2	6	415	399
3	6	336	337
4	6	140	144
5	6	52	64
6	6	67	66
7	6	87	80
9	6	45	39
1	7	307	306
2	7	170	164
3	7	270	279
4	7	71	69
7	7	73	26
8	7	81	77
9	7	76	81
0	8	134	125
1	8	484	474
2	8	350	343
3	8	316	310
4	8	191	189
5	8	75	78
6	8	223	219
7	8	75	89
8	8	75	59
1	9	449	448
2	9	108	101
3	9	212	217
4	9	201	207
5	9	93	78
7	9	140	145
8	9	71	61
0	10	183	179
1	10	165	169
2	10	267	270
4	10	465	483
5	10	163	175
6	10	190	193
7	10	62	41
8	10	166	157
1	11	276	289
2	11	142	140
3	11	133	123
5	11	136	148
6	11	104	85
0	12	132	132
1	12	55	51
2	12	102	101
3	12	191	192
4	12	66	75
5	12	62	43
6	12	90	88
1	13	55	46
2	13	72	67
3	13	153	149
4	13	57	43
5	13	56	44
0	14	68	61
1	14	55	44
3	14	63	52
5	14	61	56
1	15	48	46
3	15	60	53
4	16	38	9
1	17	54	40
** L = 3 **			
1	1	971	1013
2	1	540	567
3	1	85	81
4	1	146	160
5	1	122	115
6	1	47	36
7	1	73	78
8	1	80	59
9	1	105	105
0	2	301	301
1	2	187	186
2	2	415	411
4	2	656	664
5	2	72	69
6	2	129	113
8	2	80	76
9	2	53	48
1	3	259	261
2	3	405	403
3	3	450	469
4	3	47	13
5	3	323	320
6	3	68	70
7	3	325	326
9	3	61	54
0	4	347	338
1	4	74	76
2	4	241	229
3	4	69	81
4	4	233	230
6	4	151	151
7	4	67	54
1	5	571	577
2	5	52	44
3	5	204	208
4	5	169	159
5	5	276	290
6	5	171	182
7	5	210	209
8	5	76	80
9	5	113	107
0	6	105	97
2	6	56	57
3	6	43	19
4	6	255	261
6	6	134	131
9	6	55	44
1	7	566	561
2	7	231	223
3	7	162	175
4	7	69	61
5	7	187	194
7	7	133	132
0	8	211	220
1	8	196	190
2	8	286	276
3	8	48	34
4	8	276	278
6	8	65	61
8	8	76	70
3	9	86	81
5	9	135	139
6	9	60	45
7	9	117	128
8	9	49	22
0	10	52	35
1	10	61	58
3	10	71	86
4	10	89	97
5	10	99	102
2	11	222	219
3	11	170	171
4	11	90	90
5	11	146	136
7	11	92	86
1	12	120	126
2	12	213	203
3	12	98	94
4	12	178	186
1	13	245	240
2	13	46	62
3	13	143	147
4	13	43	21
5	13	69	50
6	13	59	67
0	14	51	40
1	14	50	67
3	14	55	51
4	14	56	57
1	15	73	87
2	15	42	23
3	15	133	129
0	16	142	109
2	16	42	43
1	17	67	58
** L = 4 **			
0	0	75	82
1	0	708	717
2	0	253	252
3	0	106	102
4	0	838	836
5	0	67	91
6	0	40	10
7	0	153	141
8	0	73	53
9	0	76	71
1	1	317	336
2	1	52	54
3	1	503	522
5	1	530	536
7	1	281	273
9	1	156	140
0	2	427	428
1	2	493	461
2	2	447	439
3	2	641	600
6	2	63	66
7	2	75	86
8	2	81	57
1	3	62	61
2	3	275	268
3	3	34	23
4	3	116	111
5	3	247	265
6	3	57	55
7	3	273	293
8	3	65	58
9	3	47	37
0	4	137	135
2	4	239	279
3	4	114	114
4	4	56	50
6	4	64	57
8	4	80	63
1	5	44	46
2	5	283	273
3	5	191	190
4	5	75	72
6	5	62	57
7	5	64	54
0	6	110	105
1	6	302	290
2	6	239	223
3	6	48	40
4	6	143	147
6	6	74	69
7	6	73	78
1	7	255	243
2	7	176	171
3	7	300	300
5	7	162	171
6	7	102	111
0	8	87	75
1	8	51	38
2	8	105	97
3	8	180	181
4	8	157	157
6	9	58	37
1	9	344	375
2	9	233	226
3	9	463	437
4	9	47	52
5	9	260	259
7	9	87	49
8	9	61	8
0	10	86	80
1	10	116	114
2	10	257	257
3	10	97	95
1	11	281	281
2	11	69	76
3	11	335	341
4	11	49	32
5	11	148	136
6	11	50	67
7	11	88	81
1	12	170	162
2	12	101	85
3	12	141	146
6	12	57	48
1	13	173	172
3	13	45	47
4	13	46	30
5	13	62	43
2	14	42	19
3	14	58	51
4	14	86	72
1	15	67	50
2	15	47	41
0	16	43	21
3	16	59	65
** L = 5 **			
1	1	196	206
2	1	138	139
3	1	563	578
4	1	237	236
5	1	99	88
7	1	104	105
0	2	173	164
1	2	107	97
2	2	190	180
3	2	267	272
4	2	101	111
6	2	97	98
7	2	76	64
9	2	52	50
1	3	240	231
2	3	277	266
3	3	465	453
4	3	58	51
5	3	428	432
7	3	98	89
9	3	125	114
0	4	216	218
1	4	244	231
2	4	162	165
3	4	40	23
4	4	56	57
6	4	170	182
7	4	77	70
1	5	313	306
2	5	37	13
3	5	279	288
4	5	79	83
6	5	330	347
7	5	146	147
8	5	63	42
0	6	317	309
1	6	83	81
2	6	124	122
3	6	61	56
4	6	94	99
5	6	63	71
6	6	72	65
1	7	291	291
3	7	401	407
4	7	118	111
5	7	152	147
7	7	146	130
8	7	45	44
1	8	62	58
2	8	79	85
3	8	71	70
4	8	83	72
5	8	63	48
1	9	92	93
2	9	143	136
3	9	110	94
4	9	60	45
0	10	85	101
1	10	75	85
2	10	48	35
3	10	155	159
4	10	50	56
5	10	64	44
1	11	42	26
2	11	150	146
3	11	223	229
4	11	64	59
5	11	111	110
0	12	156	161
1	12	203	205
1	13	130	132
2	13	64	61
3	13	149	157
5	13	120	123
2	14	61	43
4	14	48	51
1	15	90	88
3	15	82	90
** L = 6 **			
0	0	327	313
1	0	105	110
2	0	66	66
3	0	246	234
4	0	112	114
5	0	83	81
6	0	133	145
1	1	197	183
2	1	301	312
3	1	426	435
4	1	102	111
5	1	339	343
6	1	111	121
7	1	183	163
8	1	84	69
0	2	36	17
1	2	66	56
2	2	219	227
3	2	99	67
4	2	148	150
5	2	94	73
6	2	277	285
8	2	59	36
1	3	114	119
2	3	135	139
3	3	182	186
5	3	125	133
7	3	87	78
0	4	735	738
2	4	48	52
3	4	70	69
5	4	52	41
6	4	105	107
7	4	61	37
1	5	196	184
4	5	70	87
5	5	66	68
6	5	59	61
7	5	42	32
8	5	45	35
0	6	74	52
2	6	65	63
3	6	109	111
4	6	194	203
5	6	91	99
6	6	129	142
1	7	182	182
2	7	48	26
3	7	147	143
4	7	116	130
5	7	74	62
7	7	61	39
0	8	85	66
1	8	44	7
2	8	132	130
4	8	199	203
5	8	83	94
1	9	343	353
2	9	106	105
3	9	247	252
5	9	138	127
7	9	81	73
0	10	322	343
1	10	50	27
2	10	94	73
3	10	59	44
4	10	159	159
5	10	59	26
6	10	79	64
1	11	216	225
3	11	167	167
5	11	105	110
0	12	227	224
1	12	54	27
2	12	71	54
4	12	65	56
5	12	62	53
1	13	70	79
3	13	49	54
3	14	53	47
4	14	35	20
2	15	53	50
** L = 7 **			
1	1	196	159
3	1	38	18
4	1	166	167
5	1	261	257
2	2	70	62
3	2	74	72
4	2	113	109
5	2	171	164
1	3	356	333
2	3	203	202
3	3	182	191
4	3	53	44
7	3	116	110
0	4	226	229
1	4	163	157
2	4	296	286
3	4	65	65
4	4	274	265
5	4	95	105
6	4	142	145
7	4	57	36
8	4	101	90
1	5	114	118
3	5	188	191
7	5	72	63
0	6	237	231
1	6	42	29
2	6	279	271
3	6	62	73
4	6	216	224
6	6	133	127
1	7	184	185
3	7	131	176
4	7	78	68
5	7	132	145
0	8	75	61
3	8	79	77
4	8	65	37
5	8	58	63
6	8	60	23
1	9	128	128
2	9	44	41
0	10	50	31
1	10	113	107
3	10	62	68
4	10	43	26
5	10	68	48
2	11	132	134
3	11	51	28
4	11	53	52
0	12	68	67
1	12	78	88
3	12	63	60
4	12	74	80
1	13	61	53
0	14	51	50
2	14	100	98
** L = 8 **			
0	0	280	276
1	0	138	136
2	0	332	338
3	0	110	112
4	0	54	34
5	0	227	207
6	0	96	92
1	1	136	121
2	1	82	89
3	1	105	105
5	1	74	75
7	1	97	94
0	2	351	347
1	2	160	150
2	2	177	184
3	2	136	144
4	2	252	256
5	2	54	34
6	2	101	82
1	3	89	97
4	3	60	77
6	3	59	10
0	4	124	130
1	4	58	56
2	4	242	246
4	4	82	78
1	5	133	128
2	5	61	47
3	5	48	60
6	5	58	22
7	5	57	20
0	6	52	30
1	6	54	37
2	6	113	112
3	6	98	105
4	6	98	110
5	6	76	84
6	6	57	45
1	7	77	80
2	7	102	101
3	7	56	47
4	7	47	14
0	8	122	124
2	8	193	178
4	8	100	102
6	8	79	94
1	9	190	201
3	9	45	26
4	9	62	60
0	10	118	98
1	10	121	124
3	10	73	77
4	10	108	110
1	11	137	136
2	11	55	50
3	11	43	13
0	12	69	57
1	12	76	78
2	12	120	111
4	12	48	63
** L = 9 **			
2	1	85	83
3	1	89	91
4	1	64	80
7	1	93	87
0	2	151	149
1	2	60	36
2	2	82	71
3	2	49	35
6	2	87	73
7	2	47	34
1	3	140	131
2	3	79	83
6	3	56	50
0	4	286	287
2	4	234	240
3	4	100	103
4	4	138	153
6	4	98	87
1	5	52	43
3	5	60	41
5	5	70	32
6	5	55	47
0	6	181	194
1	6	69	68
2	6	192	194
4	6	157	156
6	6	92	92
2	7	58	56
3	7	49	27
0	8	69	75
1	8	45	36
2	8	64	70
1	9	89	94
2	9	45	33
0	10	61	35
3	10	53	57
4	10	47	38
1	11	75	79
2	11	48	51
0	12	94	103
1	12	41	47
** L = 10 **			
0	0	252	247
1	0	99	101
2	0	62	46
3	0	80	86
4	0	156	150
6	0	66	68
2	1	94	112
0	2	162	167
1	2	50	52
2	2	236	248
3	2	56	55
4	2	52	40
1	3	66	73
2	3	75	102
3	3	76	80
5	3	60	68
0	4	65	69
1	4	51	45
2	4	65	85
4	4	80	97
0	6	71	56
1	6	52	40
2	6	68	60
1	7	63	52
2	7	55	29
3	7	65	85
0	8	119	115
2	8	43	35
3	8	41	30
4	8	68	85
1	9	47	31
2	9	39	13
0	10	111	117
1	10	54	30
2	10	68	70
3	10	41	35
** L = 11 **			
2	1	81	84
4	1	51	16
5	1	48	28
1	2	62	47
1	3	80	61
2	3	48	43
5	3	61	49
0	4	118	125
2	4	83	94
3	4	39	6
4	4	66	74
1	5	99	99
3	5	101	111
0	6	81	75
2	6	74	69
3	6	38	22
4	6	53	65
1	7	58	39
** L = 12 **			
0	0	99	116
2	0	79	88
2	1	41	4
3	1	50	49
0	2	116	135
2	2	42	31
1	3	72	72
3	3	42	57
2	4	39	23
1	6	48	3

centric space group: $\langle|E|\rangle$, 0·802 (0·798); $\langle E^2\rangle$, 1·000 (1·000); $\langle|E^2-1|\rangle$, 0·953 (0·968); percentage >1, 28·4 (32·0); percentage >2, 5·0 (5·0); percentage >3, 0·3 (0·3).

Solution and refinement of the structure

The location of the phosphorus atom was apparent in a normal-sharpened Patterson map; subsequently, we were able to identify all vectors between phosphorus and the carbon and oxygen atoms. Inasmuch as the solution of the Patterson synthesis was straightforward, it is interesting to note that our first attempt to solve the structure by symbolic addition (Dewar & Stone, 1969) failed because of the weakness of the reflections of the class $h+k$ odd. Since the structure (Fig. 1) is by no means pseudo-*C*-centered, this result is somewhat unexpected. Apparently, the location of the phosphorus atom and one oxygen atom near $x=0$, where the *b* glide causes their contribution to $h+k$ odd reflections to vanish, had the effect of skewing the intensity distribution sufficiently to thwart a direct solution without resorting to a renormalization of subsets of data.

A structure-factor calculation on the model derived from the Patterson function gave $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}31$ and $R_2=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}=0{\cdot}38$. Six cycles of full-matrix least-squares refinement (Boer & van Remoortere, 1969) of atomic positions and isotropic temperature factors on a small computer reduced R_1 to 0·131 and R_2 to 0·132. An electron density difference map, calculated at this stage, failed to give peaks at the inferred hydrogen positions, except for a fairly broad peak where the hydroxyl hydrogen was expected. An inspection of the calculated structure factors indicated that intense low-order reflections appeared to be affected by secondary extinction. Accordingly, the Zachariasen (1963) correction, $F_o^{\text{corr}}=F_o(1+c\beta I_{\text{obs}})$, was applied to 16 reflections. The constant *c*, referred to the properly scaled intensities, was found to be $2{\cdot}43\times10^{-8}$, and the maximum correction was 17% for the 202 reflection. The structure factors are listed in Table 2.

From this point, refinement (Gvildys, 1965*a*) proceeded with anisotropic temperature factors for the P, O, and C atoms. During the course of the refinement, however, several different sets of assumptions were made about the hydrogen atoms. In the first cycle all five hydrogen atoms were placed in calculated positions (with the hydroxyl hydrogen placed on a line connecting O(3) and O(4) of adjacent molecules related by the *a* glide), but their positional parameters were not refined. During this cycle R_1 was lowered from 0·127 to 0·084 and R_2 from 0·131 to 0·083. In the next two cycles we varied the hydrogen position and temperature factors. Three of these atoms, H(4), H(5), and H(6), behaved reasonably. H(3) developed a very high temperature factor and moved 1·7 Å away from C(3), while the hydroxyl hydrogen atom moved within 0·36 Å of O(4). The *R* values at this point were 0·074 (R_1) and 0·069 (R_2). We then decided to stop varying position coordinates of H(3), fix it at its chemically calculated position, and vary only its temperature factor. The hydroxyl hydrogen atom was omitted from the calculation altogether to facilitate its location in the final difference map. With these restrictions, refinement converged smoothly to give final values of $R_1=0{\cdot}063$ and $R_2=0{\cdot}052$ for the 851 reflections above background. In the final cycle no parameter shift exceeded 0·03σ. The final difference Fourier synthesis showed a peak of 0·40 e.Å^{-3}, approximately 1·1 Å from O(3) and on a direct line to O(4). This peak is attributed to the hydroxyl hydrogen atom which forms a hydrogen bond to a phosphoryl oxygen atom, 2·464 Å distant from a neighbouring molecule related by the *a* glide (see Fig. 2). The highest remaining peaks in the map were all less than 0·30 e.Å^{-3}, and the largest negative amplitude was −0·32 e.Å^{-3}. Table 3 lists the final structure parameters and their errors as calculated in the last least-squares cycle. The atom numbering

Table 3. *Final structure parameters with standard deviations in parentheses*

Anisotropic thermal parameters are in the form:

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

	x	y	z	10 β_{11}	10 β_{22}	10 β_{33}	10 β_{12}	10 β_{13}	10 β_{23}
P	−0·0013 (2)	0·3008 (1)	0·3049 (1)	133 (2)	48 (1)	116 (1)	−12 (1)	−17 (2)	−1 (1)
O(1)	0·1266 (3)	0·3119 (2)	0·4071 (3)	185 (5)	37 (2)	128 (3)	−5 (3)	−4 (4)	8 (2)
O(2)	−0·0168 (4)	0·4023 (2)	0·2665 (3)	179 (6)	56 (2)	105 (3)	0 (3)	−43 (4)	7 (2)
O(3)	0·0715 (3)	0·2480 (2)	0·2008 (3)	194 (6)	67 (2)	140 (4)	−13 (3)	3 (4)	−40 (2)
O(4)	−0·1477 (4)	0·2620 (2)	0·3459 (3)	163 (5)	79 (2)	158 (4)	−3 (3)	11 (4)	5 (2)
C(1)	0·1655 (5)	0·4024 (3)	0·4193 (4)	113 (7)	42 (2)	98 (5)	2 (4)	9 (6)	0 (3)
C(2)	0·0832 (5)	0·4538 (3)	0·3382 (4)	131 (7)	47 (2)	91 (5)	1 (4)	9 (6)	4 (3)
C(3)	0·0994 (6)	0·5437 (3)	0·3332 (5)	219 (10)	46 (3)	119 (6)	7 (5)	30 (7)	14 (3)
C(4)	0·2045 (7)	0·5806 (4)	0·4149 (6)	229 (11)	47 (3)	153 (7)	−25 (5)	54 (8)	−10 (4)
C(5)	0·2861 (6)	0·5287 (4)	0·4942 (6)	175 (10)	69 (4)	134 (7)	−27 (5)	6 (7)	−32 (5)
C(6)	0·2704 (5)	0·4375 (3)	0·4989 (5)	143 (9)	60 (3)	109 (6)	−5 (4)	−21 (6)	7 (4)
H(3)	0·039	0·582	0·273	8·8 (1·5)*					
H(4)	0·218 (6)	0·647 (3)	0·409 (4)	9·0 (1·5)*					
H(5)	0·350 (5)	0·556 (3)	0·548 (4)	4·7 (1·2)*					
H(6)	0·324 (4)	0·394 (3)	0·560 (4)	5·9 (1·2)*					
H(0)	0·19$_8$	0·25$_8$	0·17$_2$						

* Isotropic temperature factors are in Å^2.

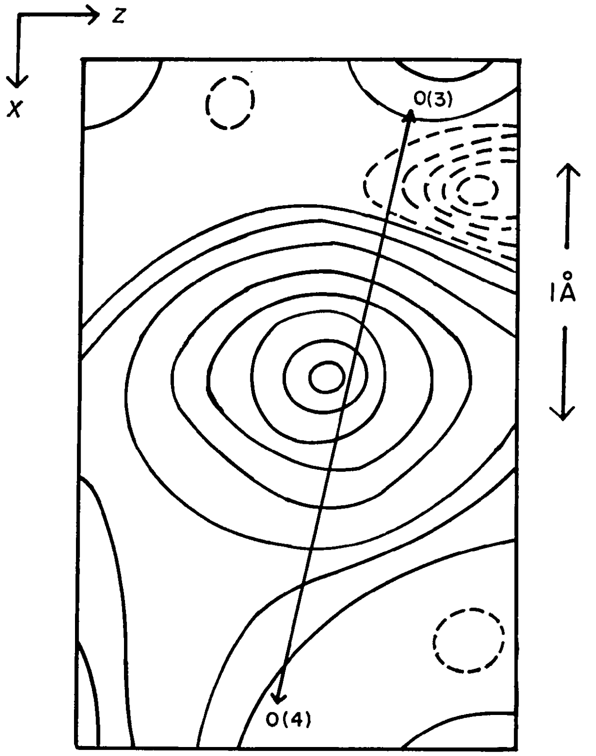


Fig. 2. Electron density difference map showing the region containing the hydroxyl hydrogen atom. The positions of O(3) and O(4) are indicated on the Figure. Contour intervals are 0·05 e.Å^{-3}, with dotted lines indicating negative density.

system, bond distances, bond angles, and standard errors, as calculated (Gvildys, 1967) from the variance–covariance obtained in the final least-squares cycle, are shown in Fig. 3.

The atomic scattering factors for P, O, and C were taken from *International Tables for X-ray Crystallography* (1962). The scattering factor for hydrogen is that given by Stewart, Davidson, & Simpson (1965). Fourier summations, least-squares refinements, and error analysis were based on adaptations of standard programs by Gvildys (1964, 1965*a,b,* 1967), and illustrations were prepared using our own adaptation of the thermal ellipsoid plot program of Johnson (1965).

Discussion

The results confirm that catechol cyclic phosphate closely observes the structural principles established in previous crystal structures of organic phosphates. The O–P–O bond angle internal to the ring, 98·4 ± 0·2°, was of special interest and was found to be very similar to the corresponding angle in five-membered cyclic triesters, *i.e.* methyl ethylene phosphate, 99·1° (Steitz & Lipscomb, 1965); methyl pinacol phosphate, 98·4° (Newton, Cox & Bertrand, 1966); and the unsaturated triester acetoinenediol cyclophosphate, 98·5°(Swank, Caughlan, Ramirez, Madan & Smith, 1967). By comparison, the corresponding O(C)–P–O(C) bond angle in a six-membered cyclic phosphate system, namely the nucleotide uridine 3′,5′-monophosphate (Coulter, 1969), was found to be 103·1° (average of two values). In acyclic systems, O(C)–P–O(C) bond angles are in general very close to this value, as can be seen for tris-*p*-nitrophenyl phosphate, 103·1° (average of three angles) (Mazhar-ul-Haque & Caughlan, 1970); bis-*p*-nitrophenyl phosphate (procaine complex), 103·3° (Sax, Pletcher & Gustaffson, 1970); dibenzylphosphoric acid, 103·8° (Dunitz & Rollett, 1956); L-α-glycerylphosphorylcholin, 103·1° (Abrahamsson & Pascher, 1966); and triphenyl phosphate, 101·5° (average of two values) (Svetich & Caughlan, 1965). The value of 108·1° reported for bis-*p*-chlorophenyl phosphate (Calleri & Speakman, 1964) appears to be above the normal range. The above data give us confidence that the O–P–O angle in catechol cyclic phosphate is not unusual and can be expected to be about 5° less than that in cyclic AMP, for which a crystal structure has been reported (Watenpaugh, Dow, Jensen & Furberg, 1968) but for which accurate bond distance and angles are probably not available.

The endocyclic P–O–C and O–C–C angles of (III) (Fig. 3) average 109·3 and 111·4° respectively. These values are reasonably close to the corresponding average angles of 107·9 and 112·7°, respectively, reported for acetoinenediol cyclophosphate, a system in which the C atoms are also sp^2 hybridized and which is known to be very reactive hydrolytically (Swank *et al.*, 1967). In catechol cyclic sulfate, the S–O–C angles averaged 108·7°, while the O–C–C angles in the five-membered ring averaged 111·6° (Boer & Flynn, 1969).

The six-membered ring is evidently distorted from an ideal hexagon by the presence of the strained five-membered system, which supplies a force tending to increase the C(2)–C(1)–C(6) and C(1)–C(2)–C(3) bond angles [122·6 (5) and 122·2 (5)° respectively]. The internal angles at C(4) and C(5) are also larger than 120°, with the consequence that the angles at C(3) and C(6) [115·9 (5) and 115·2 (5)°, respectively] are considerably diminished. Very similar distortions have been observed previously in other ring systems where the *o*-phenylenedioxy moiety chelates a heteroatom. For example, in catechol cyclic sulfate (Boer & Flynn, 1969) the ring angles corresponding to the C(3) and C(6) positions averaged 116·1° (two values); in tetramethylammonium bis-*o*-phenylenedioxyphenylsiliconate (Boer, Flynn & Turley, 1968) the angles averaged 115·5° (two values); and in pyridinium tris-*o*-phenylenedioxysiliconate (Flynn & Boer, 1969) an average angle of 117·9° (three values) was found. Bond distances in catechol cyclic phosphate are also regular. Calleri & Speakman (1964) have observed that the sum of the four P–O bond lengths in phosphates is generally about 6·177 ± 0·030 Å. In catechol cyclic phosphate, the sum is 6·153 prior to correction (see below) for rigid-body thermal motion; after correction, the sum is

6·197 Å. (In subsequent discussion we shall use the corrected values for bond distances, as listed in Table 4*D*, rather than the uncorrected values shown in Fig. 3). The P–O bond lengths within the ring, 1·593 (3) and 1·602 (3) Å, appear slightly longer than those observed for the triester tris-*p*-nitrophenyl phosphate (Mazhar-ul-Haque & Caughlan, 1970), where the average of three P–O(C) bonds is 1·572 Å. Our P=O and P–OH bond distances, 1·462 and 1·540 Å respectively, are very close to the respective values of 1·469 and 1·545 Å reported for dibenzyl phosphoric acid by Dunitz & Rollett (1956). Both systems are diesters and form intermolecular hydrogen bonds of similar lengths. In catechol cyclic phosphate, the O–H···O distance is 2·464 *versus* 2·422 Å in dibenzylphosphoric acid. The O–C distances of (III), 1·406 (5) and 1·414 (5) Å, are close to those found in tris-*p*-nitrophenyl phosphate (1·413 Å average for three values). The C–C distances range from 1·366 to 1·396 Å and are normal.

Table 4. *Rigid body thermal analysis**†

A. Principal axes of **T**

	Magnitude (Å)	Direction cosines‡		
$T_{11}^{1/2}$	0·235	−0·0249	−0·5516	−0·8837
$T_{22}^{1/2}$	0·217	−0·1456	−0·8233	0·5485
$T_{33}^{1/2}$	0·202	−0·9893	0·1344	−0·0556

B. Principal axes of **ω**

	Magnitude (°)	Direction cosines‡		
$\omega_{11}^{1/2}$	7·34	−0·4165	−0·7990	−0·4335
$\omega_{22}^{1/2}$	4·58	−0·7844	0·0750	0·6156
$\omega_{33}^{1/2}$	3·15	−0·4594	0·5964	−0·6581

C. S Matrix‡ (× 10⁵)

185	211	232
−140	235	71
−19	−111	420

D. Corrected bond distances

P——O(1)	1·593 Å	C(1)–C(2)	1·391 Å
P——O(2)	1·602	C(2)–C(3)	1·366
P——O(3)	1·540	C(3)–C(4)	1·396
P——O(4)	1·462	C(4)–C(5)	1·378
O(1)–C(1)	1·414	C(5)–C(6)	1·385
O(2)–C(2)	1·406	C(6)–C(1)	1·369

* Program *TLS* (Shomaker & Trueblood, 1968).
† Center of mass is 0·0861, 0·3885, 0·3552.
‡ Referred to the **a**, **b**, and **c** directions.

The ring system in catechol cyclic phosphate is essentially planar; the least-squares plane fit (Gvildys, 1965*b*) to the nine heavier atoms is defined by the equation $6{\cdot}242x-1{\cdot}640y-7{\cdot}455z=0{\cdot}386$. Individual atoms deviate* from this plane by −0·017 Å (P), 0·001 Å [O(1)], 0·007 Å [O(2)], 0·005 Å [C(1)], 0·011 Å [C(2)], 0·003 Å [C(3)], −0·011 Å [C(4)], −0·007 Å [C(5)], and 0·009 Å [C(6)]. Hydrogen atoms are all within 0·06 Å of this plane. The planarity of (III) is of some interest, since the five-membered ring of the sulfur analog, catechol cyclic sulfate (Boer & Flynn, 1969), was unexpectedly found to be nonplanar in the solid state, with the plane of the sulfur atom and the two oxygen atoms bound to it forming a sizable dihedral angle of 13·7° with the *o*-phenylenedioxy plane.

The atoms of catechol cyclic sulfate show fairly large amplitudes of thermal motion. A least-squares analysis (Schomaker & Trueblood, 1968) was performed to test the degree to which the motion could be described using the rigid-body assumption. The degree of fit was fair, with a root-mean-square ΔU_{ij}, of 0·0044 Å² and a maximum ΔU_{ij} of 0·0103 Å², for U_{11} of O(1). The translational and librational tensors are summarized in Table 4.

The molecular packing is illustrated in three-dimensions in Fig. 1. The crystal is held together by infinite hydrogen-bonded chains proceeding in the *x* direction and generated *via* the *a* glide. Interactions between chains do not seem to be especially strong; the shortest intermolecular C–C contact is 3·64 Å, the shortest O–C contact is 3·40 Å, and the shortest O–O distance (excepting the hydrogen bond) is 3·40 Å.

The author is pleased to thank Professor E. T. Kaiser for supplying the sample and for many interesting discussions.

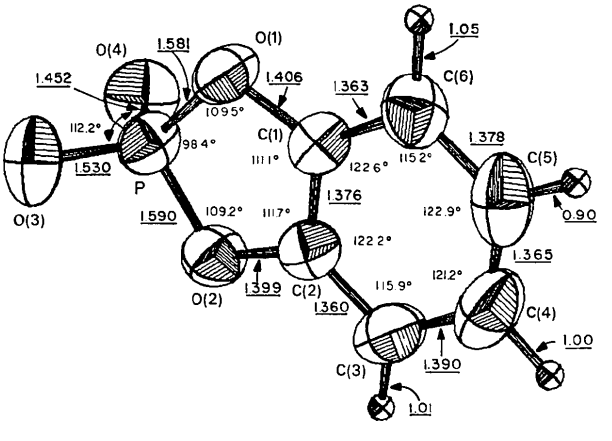


Fig. 3. A molecule of catechol cyclic phosphate with ellipsoids of thermal motion drawn at 50% probability. Hydrogen atoms are represented by 0·10 Å radius spheres. Standard errors for bond distances and angles were calculated (Gvildys, 1967) from the variance–covariance matrix obtained in the final least-squares cycle and are: P–O, ±0·003; C–O, ±0·005; C–C, ±0·006 Å; O–P–O, ±0·2; P–O–C, ±0·3; O–C–C, ±0·4; C–C–C, ±0·5°. The four angles, O(1)–P–O(3), 108·1; O(1)–P–O(4), 114·5; O(2)–P–O(3), 109·3; O(2)–P–O(4), 113·4°, are not shown.

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* A preliminary communication of these results (Kaiser *et al.*, 1971) contains a misprint. The maximum deviation from plane is 0·017, not 0·17 Å.

References

ABRAHAMSSON, S. & PASCHER, I. (1966). *Acta Cryst.* **21**, 79.

BOER, F. P. & FLYNN, J. J. JR (1969). *J. Amer. Chem. Soc.* **91**, 6604.

BOER, F. P., FLYNN, J. J. JR & TURLEY, J. W. (1968). *J. Amer. Chem. Soc.* **90**, 6793.

BOER, F. P. & VAN REMOORTERE, F. P. (1969). *A Full-Matrix Fortran Crystallographic Least-Squares Program for the IBM* 1130 *Computer*. The Dow Chemical Company, Midland, Michigan.

CALLERI, M. & SPEAKMAN, J. C. (1964). *Acta Cryst.* **17**, 1097.

COULTER, C. L. (1969). *Acta Cryst.* B**25**, 2055.

COVITZ, F. & WESTHEIMER, F. H. (1963). *J. Amer. Chem. Soc.* **85**, 1773.

DEWAR, R. B. K. & STONE, A. L. (1969). *Program MAGIC and Auxiliary Links*. Univ. of Chicago, Chicago, Illinois.

DUNITZ, J. D. & ROLLETT, J. S. (1956). *Acta Cryst.* **9**, 327.

FLYNN, J. J. JR & BOER, F. P. (1969). *J. Amer. Chem. Soc.* **91**, 5756.

GREENGARD, P. & KUO, J. F. (1970). *Adv. Biochem. Psychopharmacol.* **3**, 287.

GVILDYS, J. (1964). *A Fortran Crystallographic Least-Squares Refinement Program*, based on *ORFLS*, Argonne National Laboratory, Argonne, Illinois.

GVILDYS, J. (1965*a*). *Two- and Three-Dimensional Crystallographic Fourier Summation Program*, based on *MIFRI*. Argonne National Laboratory, Argonne, Illinois.

GVILDYS, J. (1965*b*). *Least-Squares Line and Plane Fitter* (see SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600), Argonne National Laboratory, Argonne, Illinois.

GVILDYS, J. (1967). *A Fortran Crystallographic Function and Error Program*, based on *ORFFE*. Argonne National Laboratory, Argonne, Illinois.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202 ff. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KAISER, E. T. & KUDO, K. (1967). *J. Amer. Chem. Soc.* **89**, 6725.

KAISER, E. T., LEE, T. W. S. & BOER, F. P. (1971). *J. Amer. Chem. Soc.* **93**, 2351.

KUMAMOTO, J., COX, J. K. JR & WESTHEIMER, F. H. (1956). *J. Amer. Chem. Soc.* **78**, 4858.

MAZHAR-UL-HAQUE & CAUGHLAN, C. L. (1970). *Acta Cryst.* B**26**, 1528.

NEWTON, M. G., COX, J. R. JR & BERTRAND, J. A. (1966). *J. Amer. Chem. Soc.* **88**, 1503.

ROBISON, G. A., BUTCHER, R. W. & SUTHERLAND, E. W. (1968). *Ann. Rev. Biochem.* **37**, 149.

SAX, M., PLETCHER, M. S. J. & GUSTAFFSON, B. (1970). *Acta Cryst.* B**26**, 114.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63.

STEITZ, T. A. & LIPSCOMB, W. N. (1965). *J. Amer. Chem. Soc.* **87**, 2488.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

SVETICH, G. W. & CAUGHLAN, C. N. (1965). *Acta Cryst.* **19**, 645.

SWANK, D., CAUGHLAN, C. N., RAMIREZ, F., MADAN, O. P. & SMITH, C. P. (1967). *J. Amer. Chem. Soc.* **89**, 6503.

USHER, D. A., DENNIS, E. A. & WESTHEIMER, F. H. (1965). *J. Amer. Chem. Soc.* **87**, 2320.

WATENPAUGH, K., DOW, J., JENSEN, L. H. & FURBERG, S. (1968). *Science*, **159**, 206.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1972). B**28**, 1207

The Crystal and Molecular Structure of 3-(2-Diethylammoniumethoxy)-1,2-benzisothiazole Tetrachlorocobaltate

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Crystals of $(C_{13}H_{19}N_2OS)_2^+[CoCl_4]^{2-}$ are triclinic ($P\bar{1}$): $a=8\cdot92(2)$, $b=13\cdot57(2)$, $c=14\cdot47(1)$ Å, $\alpha=88\cdot1(2)^\circ$, $\beta=84\cdot6(2)^\circ$, $\gamma=69\cdot2(3)^\circ$, $Z=2$. The structure was solved by three-dimensional Patterson and Fourier methods and refined by least-squares calculations (final $R=8\cdot7$ %). The organic cation shows no coordinative interaction with metal, which forms a slightly distorted tetrahedral tetrachlorocobaltate ion [Co–Cl = 2·230(8), 2·271(3), 2·317(6), 2·245(8) Å]. Packing is mainly determined by hydrogen bonding interactions (NH···Cl = 3·13, 3·22 Å) and by the S···Cl = 3·52 Å van der Waals contact.

The crystal structure of 3-(2-diethylammoniumethoxy)-1,2-benzisothiazole tetrachlorocobaltate has been determined as part of a study concerning the compounds 3-(2-diethylammoniumethoxy)-1,2-benzisothiazole forms with transition metal halides, MCl_2 (M = Mn, Co, Cu). The corresponding Cu compound has been recently studied (Corradi Bonamartini, Nardelli, Palmieri & Pelizzi, 1971).