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The Crystal Structure of, and the Hydrogen Bonding in, Di-*p*-chlorophenyl Hydrogen Phosphate

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Di-*p*-chlorophenyl hydrogen phosphate $(ClC_6H_4O)_2PO(OH)$ crystallizes in the orthorhombic system with four molecules in a cell belonging to the space group *Pnaa*, with

$$a = 12{\cdot}43,\ b = 4{\cdot}61 \text{ and } c = 23{\cdot}78\ \text{Å}\ .$$

The molecule therefore has the symmetry 2, with the two oxygen atoms of the PO(OH) group crystallographically equivalent. Successive molecules in the **b** direction are related by an intervening twofold axis, across which they are joined by a hydrogen bond. A three-dimensional least-squares analysis, based on 672 independent observed reflexions with an *R* value of 11·1%, leads to an $O \cdots H \cdots O$-distance of $2{\cdot}398 \pm 0{\cdot}018$ Å. The possibility that this may represent a genuinely symmetrical hydrogen bond is discussed. The P–O distances are 1·579 and 1·497 ($\pm 0{\cdot}009$) Å.

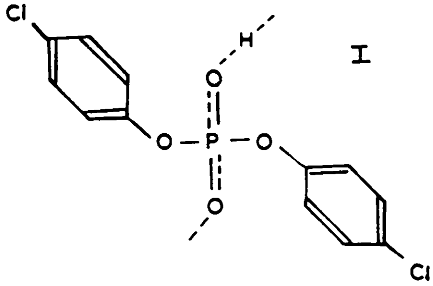
The shortest and strongest known hydrogen bond is in the bifluoride anion, HF_2^-; and it is probably symmetrical with the proton in a single potential-energy well, midway between the fluorine atoms. This anion has been studied in crystalline compounds, such as $LiHF_2$ (Frevel & Rinn, 1962), where it occupies a crystallographically symmetrical site. These solid bifluorides have an unusual type of infrared spectrum (*e.g.* Newman & Badger, 1951).

Between oxygen atoms, crystal-structure analysis has revealed many examples of hydrogen bonding. This usually occurs in situations where the oxygen atoms of a particular bond are not crystallographically related; the $O \cdots O$ distance usually lies in the range 2·5–2·8 Å, within which the hydrogen atom will be more closely linked to one oxygen atom than to the other (*e.g.* $R\text{–O–H} \cdots O = R'$ between carboxyl groups). The covalent distances *R*–O and $O = R'$ then differ in the sense required by this formulation, though the hydrogen atom may not have been located definitively. Where it has been, either by careful X-ray analysis or preferably by neutron diffraction (*e.g.* in α-resorcinol by Bacon & Curry, 1956), the non-central position of the proton has been verified. The infrared spectra of such hydrogen-bonded solids are normal in the sense that there is a fairly sharp absorption band in the region 2800–3500 cm^{-1}, which can be ascribed to the O–H stretching frequency.

However, the neutron-diffraction work shows that the O–H distance tends to increase as $O \cdots O$ diminishes overall (*e.g.* Pimentel & McClellan, 1960), so that a truly symmetrical hydrogen bond might result if the distance $O \cdots O$ were short enough. Interest therefore attaches to very short bonds, with $O \cdots O \leq 2{\cdot}5$ Å, and particularly to those exceptional cases where the two oxygen atoms are related by crystallographic symmetry. Examples of this are found amongst some of the acid salts (*e.g.* MHY_2, where M is a univalent metal) of monocarboxylic acids (HY). These have been termed Type *A* acid salts (Blinc, Hadži & Novak, 1960; Shrivastava & Speakman, 1961); and they have notably anomalous infrared spectra. An example is sodium hydrogen diacetate, $NaH(C_2H_3O_2)_2$ (Speakman & Mills, 1961) in which the acidic hydrogen atom links two oxygen atoms related by a digonal axis of the crystal. The $O \cdots O$ distance was originally given as $2{\cdot}444 \pm 0{\cdot}010$ Å; application by Dr Cruickshank of his correction for torsional oscillation of the acetate groups changes the atomic coordinates in such a way as to lead to a rather shorter distance 2·434 Å. Another well-authenticated instance is potassium hydrogen maleate (Darlow & Cochran, 1961), with $O \cdots O = 2{\cdot}437 \pm 0{\cdot}004$ Å; and in this crystal neutron-diffraction analysis provides evidence that the proton may genuinely lie on the mirror-plane midway between the two oxygen atoms (Peterson & Levy, 1958). Bacon & Curry (1957, 1960) have come to a similar, if more tentative, conclusion from their studies of potassium hydrogen bisphenylacetate, another acid salt of Type *A*.

Hadži & Novak (1960) observed that crystalline di-*p*-chlorophenyl hydrogen phosphate (hereinafter DPCPHP, formula (I) has an infrared spectrum reminiscent of those of Type *A* acid salts, and they predicted that it would have similarly symmetrical hydrogen bonding. We undertook a structural study of DPCPHP at Prof. Hadži's suggestion, and our results confirm the prediction. The structure is of additional interest because the chemically similar molecule of dibenzyl hydrogen phosphate (II), studied by Dunitz & Rollett (1956), crystallizes with normal hydrogen bonding: a chain of type $\cdots O = P\text{–OH} \cdots O = P\text{–OH} \cdots$ spirals round a 2_1-

axis, an arrangement similar to that occurring in α-resorcinol or, with interposition of water molecules, in oxalic acid dihydrate. These phosphate structures are of still further interest because of Cruickshank's theoretical work (1961) on the role of π-bonding in phosphate and other XO_4-type groups.



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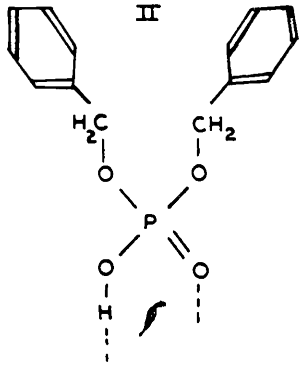

II

Experimental

Crystal data

Our specimen of DPCPHP, kindly provided by Prof. Hadži, consisted of colourless needles elongated in the **b** direction. All X-ray measurements were made with Cu *Kα* radiation (λ taken as 1·5418 Å, or 1·5443 and 1·5405 Å when α_1, α_2 separation occurred). Unit-cell dimensions were found by superposing on zero-layer Weissenberg photographs lines due to aluminum wire, for which *a* was taken as 4·04907 Å); the positions of a number of diffraction spots were found with respect to neighbouring Al-lines, so as to yield sin θ values for the spots; these, with the appropriate indices, were treated by a least-squares procedure.

Di-p-chlorophenyl hydrogen phosphate,
$(ClC_6H_4O)_2PO(OH)$.

F.W., 321·1. *Orthorhombic dipyramidal,*

$a = 12{\cdot}433 \pm 12,\ b = 4{\cdot}611 \pm 5,\ c = 23{\cdot}784 \pm 20$ Å;

unit-cell volume, 1363·3 Å^3; $D_m = 1{\cdot}55$, $Z = 4$, $D_x = 1{\cdot}564$, $F(000) = 656$; absorption coefficient for Cu radiation, 54 cm^{-1}. *Absent reflexions*: *hk*0 with *h* odd, *h*0*l* with *h* odd, and 0*kl* with (*k*+*l*) odd, unambiguously indicating the *space group Pnaa* (No. 56), with eightfold equivalent positions, $\pm(x, y, z;\ x, \tfrac{1}{2}-y, \tfrac{1}{2}-z;\ \tfrac{1}{2}+x, y, \tfrac{1}{2}-z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, z)$. The implication is that the molecular symmetry is either $\bar{1}$ or 2, only the latter being chemically acceptable. The phosphorus and acidic hydrogen atoms effectively occupy special positions (*c*) and (*d*) on twofold axes.

Intensity measurements

These were made visually from multiple-film exposures. In the first place data were collected for the nets *h*0*l*, *h*1*l*, and *h*2*l*. As the crystal used had a cross-section of ~ 0·08 × 0·06 mm^2, absorption, though not negligible, was moderate and largely independent of crystal azimuth, and would vary monotonically with sin θ; the neglect of absorption corrections would therefore appear chiefly as a small lowering of the apparent vibrational parameters. At a late stage of the analysis extra data were collected, about the *a* axis, for the nets 0*kl*–5*kl*. Owing to the crystal habit, absorption is more serious for these; absorption was again neglected, but only the reflexions additional to those already recorded in *h*0*l*–*h*2*l* were used in the refinement. Some statistical details of our intensity data are collected in Table 1. Data-processing and all other computations were done on the Glasgow University DEUCE, with the crystallographic programs developed by Rollett & Sime (1961).

Table 1. *Summary of reflexions used in the analysis*

	Number	*R*
*h*0*l*	123	9·15%
*h*1*l*	185	11·82
*h*2*l*	159	9·99
Other *hkl*	205	14·04

Determination of the structure

A projection of the structure along the short *b* axis was easily obtained by applying the minimum function to the sharpened Patterson function. The *x* axis and *z* coordinates were refined, by several cycles of electron-density and difference syntheses, to an *R* value of 18% for some 120 *h*0*l* terms. In this projection there is an ambiguity between centres of inversion and 2_1 axes. This was resolved and approximate *y* coordinates were established by trial, and then by generalized projections based on *h*1*l* and *h*2*l* terms. With an isotropic vibrational parameter of $B = 2{\cdot}3$ Å^2, *R* was thereby reduced to 22% for these terms.

Refinement

Refinement was by three-dimensional least-squares analysis, with anisotropic vibrational parameters. The weighting system was: $\sqrt{w} = |F^*|/|F_o|$ when $|F_o| > |F^*|$, $|F^*|$ being the average structure amplitude,

Table 2. *Final coordinates*

x, y, z, fractional $\times 10^4$; X, Y, Z, in 10^{-4} Å, with standard deviations in parentheses

	x	y	z	X	Y	Z
Cl	3382	9248	0378	42046(42)	42645(41)	8986(37)
O(1)	5452	1433	2004	67777(92)	6609(79)	47668(88)
O(2)	6834	5084	2313	84950(78)	23443(93)	55022(86)
C(1)	3999	6981	0862	49714(125)	32189(131)	20507(111)
C(2)	5034	6019	0747	62583(139)	27754(151)	17769(143)
C(3)	5513	4113	1146	68539(150)	18965(153)	27261(132)
C(4)	4990	3436	1620	62025(114)	15845(116)	38530(124)
C(5)	3986	4443	1726	49555(133)	20487(156)	41049(131)
C(6)	3499	6350	1346	43495(135)	29282(147)	32013(136)
P	6198	2500	2500	77045(44)	11528(—)	59460(—)
H–C(2)	5450	6610	0370	67800	30500	8900
H–C(3)	6250	3270	1070	77700	15100	25400
H–C(5)	3590	3870	2090	44700	17800	49600
H–C(6)	2750	7210	1430	34200	33200	33900
H–O(2)	6830	7500	2500	84900	34600	59500

Table 3. *Vibrational parameters* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
Cl	0·082	0·066	0·051	0·000	0·015	−0·017
O(1)	0·042	0·035	0·074	−0·001	0·006	−0·012
O(2)	0·042	0·035	0·075	−0·012	−0·009	−0·001
C(1)	0·064	0·045	0·038	−0·009	0·003	−0·016
C(2)	0·060	0·069	0·063	0·004	0·004	0·013
C(3)	0·054	0·079	0·052	0·009	−0·012	0·002
C(4)	0·048	0·034	0·053	−0·002	−0·005	−0·009
C(5)	0·048	0·083	0·051	−0·002	0·018	0·004
C(6)	0·051	0·069	0·060	0·004	0·001	0·007
P	0·025	0·020	0·052	—	−0·003	—
All H's	0·063	0·063	0·063	—	—	—

and $\sqrt{w}=|F_o|/|F^*|$ when $|F_o|<|F^*|$; 'half shifts' were generally used. In the earlier stages only the 467 *h0l–h2l* terms were introduced. Later the 205 additional reflexions in the *0kl–5kl* nets were added. After some dozen cycles of least-squares refinement, structure factors were calculated for all unobserved reflexions accessible to Cu radiation in the reciprocal nets photographed; those terms for which $|F_c|$ implied that a reflexion should have been observable were then included in a final cycle, with $|F_o|$ put equal to half the minimum locally observable. In the later cycles, hydrogen atoms were included in the structure-factor calculations, though their parameters were not refined: the four benzenoid hydrogen atoms were placed 1·05 Å from their respective carbon atoms; the acidic hydrogen atom was placed on the twofold axis at x', $\frac{3}{4}$, $\frac{1}{4}$, where x' is the value found for atom O(2). The atomic scattering functions were substantially those now recommended in *International Tables for X-ray Crystallography.* The numbering of atoms is included in Fig. 1, except for the hydrogen atoms, which were numbered by reference to their respective carbon or oxygen atoms. Final coordinates are listed in Table 2, with their standard deviations as derived from the least-squares residuals; vibrational parameters are given in Table 3 in the form of the matrix elements for the tensor representing their mean-square amplitudes of vibration. Structure factors based on the final parameters are compared with the observed structure amplitudes in Table 4. Final R values are included in Table 1. The parameters in Table 2 are given with more figures than are significant; this has been done to avoid discrepancies, in derived quantities, which might result from rounding off the primary parameters.

An attempt was made to correct the atomic coordinates for the effects of torsional oscillation of the molecule, considered as a rigid body. This is not straightforward in the present structure. The environment of the DPCPHP molecule is of uneven quality: the *p*-chlorophenyl groups react with their neighbours only by weak van der Waals forces, whilst the phosphate groups are more firmly linked to other such groups by hydrogen bonds. Consequently the model of a rigid molecule oscillating torsionally about its centre of mass is inadequate. We therefore, tentatively, postulated an effective centre of vibration, moved by 0·5 Å from the actual centre of mass towards the phosphate group, hoping to improve the agreement between observed and calculated vibrational anisotropy. This hope was not fulfilled. For the true centre of mass, the r.m.s. amplitudes found for libration about the three principal molecular axes were all about 2°, though one of these amplitudes only just exceed its standard deviation. We conclude that our thermal parameters are not accurate enough

Table 4. *Observed structure amplitudes and calculated structure factors*

(2·5 times the true values for the whole unit cell)

HKL	F_c	$\|F_o\|$
00L		
2	-132	80
4	72	77
6	-138	121
8	-21	25
10	-176	164
12	-32	38
14	-167	166
16	-48	51
18	-87	82
24	94	96
26	34	34
28	30	23
20L		
0	221	229
1	-76	95
2	-74	88
3	479	447
4	-238	237
5	-71	71
6	39	40
7	265	255
8	-147	135
9	36	44
10	147	149
11	62	59
12	99	99
13	-18	20
14	51	53
15	50	56
16	36	30
17	-90	81
18	9	17
19	-44	43
21	-132	135
22	-68	66
40L		
0	-214	244
1	-68	73
2	-4	12
3	-201	216
4	-136	149
5	-22	23
6	69	69
7	-156	167
8	-119	111
9	-82	75
10	118	105
11	-171	159
13	71	88
14	-142	129
15	78	80
18	86	79
19	83	84
22	-33	33
23	45	43
24	-41	38
26	19	24
28	-28	23
60L		
0	223	244
1	-142	144
2	81	81
3	-75	64
4	90	92
5	58	59
7	-72	78
9	77	70
10	-139	148
11	-127	150
12	-96	88
13	40	42
14	-20	15
15	-51	52
16	-66	65
17	31	27
21	43	41
25	23	18
26	36	31
80L		
0	21	26
1	-43	50
3	44	41
4	-25	30
5	70	75
7	48	62
8	27	29
9	146	141
10	-63	59
12	127	140
15	-34	36
18	-39	43
19	-43	42
22	-35	38
26	-31	17
10,0L		
1	-37	41
2	48	45
5	70	79
6	-40	39
8	-15	42
9	-43	46
10	-28	36
11	18	22
12	126	113
15	42	40
19	48	42
23	29	23
12,0L		
2	74	66
3	33	39
4	-31	39
5	-43	43
6	36	38
7	27	31
8	-48	43
9	-58	52
16	-40	36
20	-28	18
14,0L		
0	-30	27
1	64	60
2	35	19
3	-18	19
4	-34	32
5	36	31
6	27	28
7	-11	24
9	32	30
14	19	15
16,0L		
2	-31	20
01L		
1	-187	177
3	375	282
5	113	107
7	54	69
9	12	27
11	47	50
13	-60	65
15	92	88
17	-25	36
19	-22	33
21	-113	101
23	26	27
25	-23	30
11L		
1	99	96
2	-25	32
3	-212	202
4	-174	172
5	-155	153
6	-210	199
7	33	36
8	-41	50
9	22	42
10	-167	149
11	60	70
12	23	35
13	126	117
14	-20	31
15	-7	13
16	93	88
17	75	69
18	45	45
19	-11	18
20	53	48
21	-36	39
22	20	13
24	33	35
28	-19	22
21L		
0	-386	299
1	-183	164
2	7	15
3	57	66
4	-44	58
5	93	83
6	131	128
7	-89	88
8	-86	81
9	-57	60
10	58	53
11	-55	54
12	7	9
13	7	17
14	76	78
15	29	34
16	-15	19
17	33	41
18	102	89
21L(contd.)		
19	14	17
20	-34	43
21	-15	18
22	10	18
23	20	17
24	-43	43
31L		
1	207	195
2	63	65
3	226	217
4	-135	133
5	-71	76
6	87	89
7	30	33
8	-18	30
9	-167	167
10	-62	64
11	-31	29
12	-18	21
13	-110	105
14	15	10
15	-69	60
17	-50	54
19	16	21
20	-12	17
24	21	23
25	44	41
26	13	10
27	39	34
41L		
0	-39	41
1	-13	11
2	114	118
3	-134	124
4	9	11
5	106	107
6	63	59
7	-114	122
8	14	27
9	31	28
10	-100	109
11	-95	89
12	-29	32
13	43	47
14	-33	34
15	-67	62
16	-31	37
17	59	62
20	-16	21
21	45	57
22	23	37
25	12	14
27	-20	20
28	14	14
51L		
1	-28	34
2	19	24
3	-25	35
4	30	36
6	230	192
7	-36	44
8	58	53
9	62	68
10	50	62
11	-23	28
13	87	81
16	-31	38
18	-52	48
20	-53	43
61L		
0	50	56
1	37	36
3	19	28
4	56	60
5	68	65
6	-96	92
7	23	30
8	93	84
9	65	63
10	-90	81
11	34	34
12	85	82
13	-16	26
14	-46	45
15	-40	38
18	-53	48
71L		
1	-31	37
2	-77	86
3	-74	81
4	-53	54
6	-61	56
8	-29	34
10	-41	43
11	36	36
71L(contd.)		
13	59	56
14	-33	38
15	61	48
16	78	68
81L		
0	-51	64
1	-46	56
3	74	71
5	-49	57
6	-64	62
9	-86	75
11	75	73
12	-76	68
13	-53	53
15	39	39
91L		
1	72	70
4	-38	43
5	46	45
7	-24	38
8	-36	38
9	-85	71
10	24	39
12	-39	44
10,1L		
0	-43	52
2	73	71
4	-44	51
6	47	45
8	-51	46
9	-78	68
12	-38	39
11,1L		
5	41	39
6	35	44
7	-33	44
8	32	34
12,1L		
1	57	47
3	-27	47
5	62	38
6	33	38
7	-33	30
14,1L		
1	18	35
02L		
0	66	65
2	86	73
4	46	52
6	51	49
8	-67	73
10	-23	29
12	-122	112
14	-27	30
16	-54	54
18	67	65
20	-45	46
22	49	41
24	-16	20
26	40	54
12L		
1	76	69
3	87	79
4	-16	24
5	130	111
6	38	35
7	-47	45
8	-154	135
9	-64	65
10	-49	48
11	-44	32
12	-29	28
13	-72	69
14	-37	47
15	-68	69
16	106	97
17	-31	30
18	23	19
20	-18	14
22	23	26
25	22	31
27	21	21
22L		
0	-110	111
1	53	61
2	44	52
3	-34	30
4	-87	86
5	82	74
6	24	28
7	89	79
22L(contd.)		
9	104	91
10	42	48
11	-32	21
12	14	11
13	46	45
15	-98	92
16	28	33
19	-57	60
21	15	12
22	-16	12
23	-40	30
24	-15	22
25	20	19
27	-21	11
32L		
1	-9	8
2	14	22
3	-32	42
4	111	107
5	128	122
6	213	185
7	-27	24
8	27	24
9	-34	42
10	22	14
11	14	10
12	48	50
13	-20	30
14	-26	27
17	-13	12
18	-40	43
20	-46	46
22	-30	37
24	-30	36
42L		
0	20	25
1	75	74
2	-62	60
3	-153	155
4	32	35
6	-141	146
7	-57	47
8	87	85
10	-11	13
11	-32	41
12	83	84
15	17	12
16	55	56
17	26	30
18	-48	49
19	32	37
20	31	38
22	-24	30
23	15	20
26	-21	19
27	-12	9
52L		
1	-60	68
3	-117	113
5	21	28
8	-48	49
11	48	44
13	42	46
15	85	72
18	38	44
62L		
0	103	96
1	-99	98
3	89	83
4	83	77
5	-75	77
6	-83	88
7	60	71
9	-87	87
10	-44	60
11	48	64
12	-24	29
13	-58	59
15	52	55
18	-25	27
72L		
1	52	54
5	52	54
6	-70	77
7	-66	67
8	-51	56
11	-19	27
12	-33	34
13	-28	35
17	-45	42
18	37	41
82L		
0	-113	112
2	79	83
3	55	65
4	-70	70
5	32	20
6	80	76
7	36	33
8	-71	72
10	61	64
11	27	35
12	-36	35
14	44	42
92L		
4	104	101
7	-31	35
10,2L		
0	-20	27
1	65	63
2	-25	30
3	-77	69
5	44	46
7	-65	60
9	36	46
11	-38	45
13	33	36
11,2L		
3	-33	34
4	46	42
12,2L		
0	53	46
2	-29	23
4	49	39
6	-37	32
10	-34	29
03L		
1	47	49
5	187	178
7	15	13
9	148	150
11	-34	26
13	20	15
15	-44	44
17	12	15
19	-69	73
21	-23	27
23	-34	33
04L		
2	-75	75
4	84	93
6	-97	93
8	69	75
10	-50	61
12	64	63
14	-34	21
16	35	21
20	22	21
05L		
3	33	32
5	-19	15
7	69	87
9	-31	24
11	36	26
13	-34	26
15	21	19
13L		
1	-45	49
2	-52	63
3	-12	9
4	7	9
5	79	90
6	-33	37
7	-46	52
8	36	33
9	48	55
10	-33	36
12	38	32
13	-33	19
15	19	13
20	22	17
23	-18	18
14L		
1	57	74
2	-30	41
3	25	29
4	-26	23
5	11	13
6	-27	23
7	-13	13
9	-24	23
14L(contd.)		
10	-18	13
11	-28	18
12	-27	22
14	14	12
15	-34	21
17	-15	11
18	18	15
20	20	18
21	10	11
15L		
3	3	12
4	28	33
5	15	16
8	20	15
12	22	16
23L		
0	-11	11
1	-42	43
2	-143	156
3	-19	20
4	26	26
6	-81	99
7	-43	38
8	53	46
9	-28	31
11	-48	52
12	141	118
15	22	23
16	53	41
17	33	33
19	16	12
20	18	29
22	-22	30
24L		
0	-61	62
1	-65	64
2	42	42
3	57	55
5	-69	65
7	52	47
9	-91	81
11	41	32
13	-39	31
15	21	24
17	-22	26
18	-11	10
19	20	23
25L		
0	-32	38
1	18	11
3	-11	11
4	-44	37
5	-25	16
6	41	41
8	-29	26
10	46	45
12	-18	13
14	40	28
33L		
1	8	11
2	-30	32
3	16	20
5	-18	17
6	-11	12
8	23	21
10	15	13
12	-16	13
13	-57	56
15	48	47
16	-33	29
17	-23	22
18	21	18
19	10	12
21	24	22
23	15	13
34L		
2	39	37
4	44	37
6	32	29
8	62	59
9	-13	13
11	12	13
13	17	12
15	-16	11
16	-20	16
17	-7	10
18	-25	20
19	-16	13
20	-20	13
35L		
1	-26	20
2	10	11
3	-15	11
4	12	10
7	18	15
9	-9	14
11	18	13
15	21	16
43L		
0	55	67
1	-73	85
2	64	85
3	59	78
4	37	42
5	-80	91
7	18	13
8	-18	15
9	-120	115
10	-67	67
13	-29	22
14	-41	47
15	51	47
16	-29	46
18	-24	28
19	51	52
21	-12	20
22	21	33
23	27	34
24	26	33
44L		
0	-73	78
1	55	57
2	64	63
3	-16	16
4	-37	35
5	18	17
6	51	53
8	-17	16
10	30	28
11	29	36
12	-54	55
14	24	22
16	-26	35
18	12	18
20	-24	28
45L		
0	18	14
1	53	59
3	-40	37
6	10	14
7	-25	24
8	-26	29
9	22	18
11	-36	33
12	-17	15
13	26	27
53L		
4	33	41
6	-24	27
7	-48	60
9	61	67
12	-35	28
16	-24	23
19	-22	20
21	14	18
54L		
1	-48	63
2	29	28
5	-21	28
10	-32	27
11	31	26
13	33	26
14	28	25
15	23	20
55L		
5	22	15
6	-16	13
8	-19	14

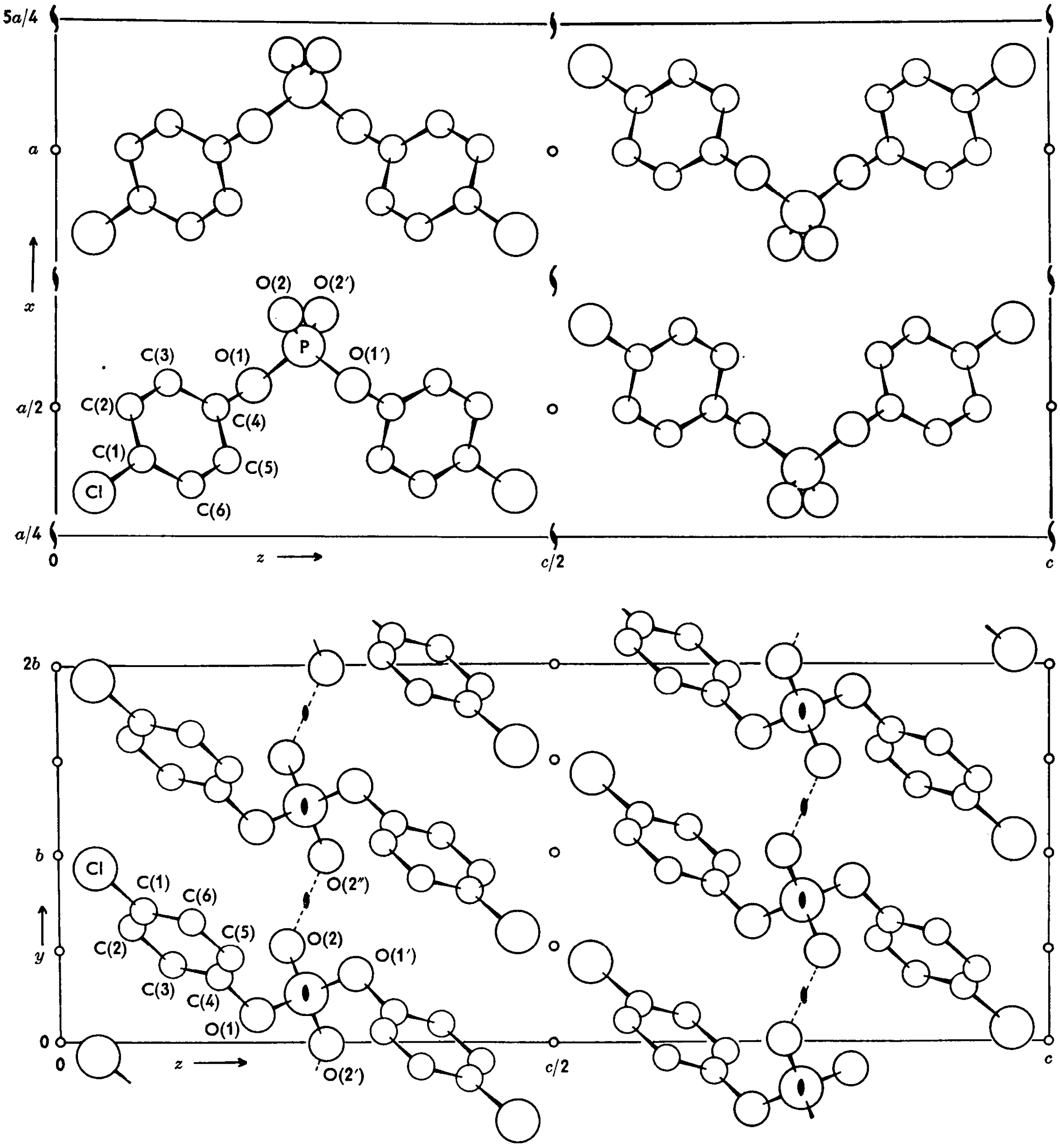

Fig. 1. The structure of di-*p*-chlorophenyl hydrogen phosphate seen in projection along the *b* and *a* axes. (In the latter, two unit cells are covered, but only the front half of each is shown — between $x = a/4$ and $x = 3a/4$.)

to warrant a sophisticated analysis of molecular vibrations, but that the torsional part of the vibration is small and any corrections to the lengths of radially directed bonds [such as Cl–C(1)] would not exceed 0·001 Å, which is not significant.

Discussion

Description of the structure

General views of the structure, in two directions, are shown in Fig. 1. Table 5 gives the important bond lengths and angles. Apart from the hydrogen

Table 5. *Bond-lengths and bond-angles*

Cl–C(1)	1·735 Å	C(1)–C(2)	1·388 Å
C(4)–O(1)	1·421	C(2)–C(3)	1·424
P–O(1)	1·579	C(3)–C(4)	1·338
P–O(2)	1·497	C(4)–C(5)	1·354
		C(5)–C(6)	1·399
O(2) · · · O(2″)	2·398	C(6)–C(1)	1·340
Cl–C(1)–C(2)	118·1°	C(3)–C(4)–O(1)	119·8°
Cl–C(1)–C(6)	119·8	C(5)–C(4)–O(1)	118·4
C(1)–C(2)–C(3)	117·0	C(4)–O(1)–P	121·0
C(2)–C(3)–C(4)	120·1	O(1)–P–O(2)	109·7
C(3)–C(4)–C(5)	121·7	O(1)–P–O(2′)	106·5
C(4)–C(5)–C(6)	119·6	O(1)–P–O(1′)	108·1
C(5)–C(6)–C(1)	119·4	O(2)–P–O(2′)	116·3
C(6)–C(1)–C(2)	122·0	P–O(2) · · · O(2″)	129·0

bonds, to be discussed later, there are no abnormal intermolecular contacts. We may note a distance of $3{\cdot}655 \pm 0{\cdot}008$ Å between two chlorine atoms related by a screw axis, and one of 4·459 Å between two related by a centre of inversion. The latter is not a genuine 'contact'. Rather the chlorine atom of one molecule makes contact with the carbon atoms C(1) and C(2) of the next molecule in the **b** direction, the distances to each being about 3·80 Å. The closest approach between carbon atoms belonging to different benzenoid rings of the same molecule is one of 4·09 Å between two C(5) atoms; the hydrogen atoms joined to these carbons are about 2·33 Å apart.

A standard value of 1·70 Å has been given for the distance between chlorine and a covalently linked aromatic carbon atom (*e.g. International Tables*, 1962). As has been stressed by Gafner & Herbstein (1962), significantly longer C–Cl bonds are common. With $1{\cdot}735 \pm 0{\cdot}013$ Å, DPCPHP probably provides yet another example.

The standard deviations were assessed in the usual way from the least-squares residuals. For C–C bonds they are all about ±0·019 Å; for C–O, ±0·017; and for P–O, ±0·009; whilst for angles they are ±0·5° for O–P–O; ±0·8° for C–O–P; and ±1·3° for C–C–C.

The mean plane through the six carbon atoms of the benzenoid ring is represented by the equation,

$$4{\cdot}9959x + 3{\cdot}6510y + 10{\cdot}9391z = 5{\cdot}5149 \text{ Å} .$$

None of the six atoms deviates significantly from this plane, the mean deviation being 0·014 Å, though the Cl atom lies 0·035 Å from it. Though apparently significant, this deviation is probably not really so, since the mean plane through the seven atoms of the chlorophenyl group is

$$4{\cdot}9588x + 3{\cdot}6698y + 10{\cdot}8332z = 5{\cdot}4928 ,$$

from which the mean deviation is 0·015 Å, with none of the individual deviations of certain significance. However, O(1) is 0·075 Å from the former of these planes and 0·092 from the latter; this represents a significant deviation, attributable to the conflicting claims of hydrogen bonding between the phosphate groups and of van der Waals packing of successive chlorophenyl groups in the *y* direction.

The phosphate group

Cruickshank (1961) has considered the rôle of π-bonding in phosphate and other XO_4 derivatives, and has surveyed the more reliable published data on such structures. He gives 'an empirical rule' which can be alternatively stated: though the individual P–O bond lengths in any phosphate group may range from 1·40 to 1·69 Å, their sum is nearly constant. (With the assumption of a linear relationship between bond length and bond order, this rule carries the implication that a constant dividend of π-bond character has to be allocated between the four bonds). Consideration of sixteen structures in which P–O distances have been determined with a standard deviation of ±0·01 Å or better gives a mean value for this sum of $6{\cdot}177 \pm 0{\cdot}030$ Å. In the DPCPHP molecule the sum is $6{\cdot}15_1$ Å.

The hydrogen bonding

This is the most interesting feature of the DPCPHP structure. Bonds, roughly parallel to the *b* axis, link successive molecules into infinite chains. With the twofold axis which relates the two halves of the standard molecule located at $x, \frac{1}{4}, \frac{1}{4}$, O(2) atoms of neighbouring molecules make a close approach across the axis at $x, \frac{3}{4}, \frac{1}{4}$. The bond is therefore formally symmetrical.

Like the hydrogen bond in sodium hydrogen diacetate, which also involves a twofold axis, or like that in potassium hydrogen maleate, which involves a plane of symmetry, but unlike that in potassium hydrogen bisphenylacetate, which involves a centre of inversion, the hydrogen bond in DPCPHP is not strictly required to have its proton midway between the oxygen atoms. The formal symmetry would be satisfied by a proton on the twofold axis but off the line of centres of the oxygen atoms. Granting the symmetry, such an off-centring seems unlikely.

With $O(2) \cdots O(2') = 2{\cdot}398$ Å, this is perhaps the shortest hydrogen bond between oxygen atoms to have been measured with any accuracy; but the relatively large standard deviation (±0·018 Å) affecting a bond lying across a symmetry element renders it uncertain that the bond is significantly shorter than those recorded in some acid salts. Nevertheless a survey of $O \cdots H \cdots O$ bonds between phosphorus atoms suggests that they tend to be distinctly shorter than corresponding bonds between carbon atoms. Many examples of the latter have been well studied, and their $O \cdots O$-distances range uniformly over the range from 2·42 to 2·90 Å or more. Table 6, which lists most of the well measured $O \cdots H \cdots O$ distances in phosphate systems, evidences a tendency towards shortness. Furthermore a number of contacts between oxygen atoms linked to different phosphorus atoms are as low as 2·8 Å and yet cannot represent hydrogen bonds. Such contact distances barely exceed twice the formal van der Waals radius of oxygen. Possibly the π-bonding within the PO_4 group, and its stronger potential acidity, make the effective radius of the oxygen atom rather shorter than in carboxyl groups. Any such contraction would be reflected in a shortening of otherwise comparable hydrogen bonds.

Only in one other case has a crystallographically symmetrical hydrogen bond between two phosphate groups been reported. This is monetite, $CaHPO_4$ (MacLennan & Beevers, 1955; Jones & Cruickshank, 1961), which has an infrared spectrum reminiscent of an acid salt of Type *A*. According to the refinement

Table 6. *Some hydrogen bonds between* PO_4 *groups*

Compound	O · · · O-distance	P–(OH) · · · O angle	Authors
H_3PO_4	2·53 ± 0·02 Å 2·53 ± 0·02 2·84 ± 0·02	117° 123 —	Furberg, 1955
Serine phosphate	2·55 ± 0·01	—	Sim, 1959
KH_2PO_4	2·49 ± 0·01	114	Bacon & Pease, 1953
Dibenzyl phosphate	$2{\cdot}49_5$ ± 0·01	119	Dunitz & Rollett, 1956
Monetite	*2·44 ± 0·03 2·58 ± 0·02 2·66 ± 0·02	108 119 140	Jones & Cruickshank, 1961
2-Aminoethanol phosphate	2·557 ± 0·01	118	Kraut, 1961
DPCPHP	2·398 ± 0·018	129	(Present paper)

carried out by the latter workers, this bond, lying across a centre of symmetry, has O · · · O = 2·44 ± 0·03 Å. This structure has the peculiarity (found also, for instance, in potassium hydrogen di-*p*-hydroxybenzoate hydrate by Skinner & Speakman, 1951) of possessing more presumptive hydrogen bonds than available protons; the unit cell includes only four hydrogen atoms, but has five short O · · · O-contacts; three are crystallographically independent and are listed in Table 6, where the contact in question, marked with an asterisk, is in a special position of reduced multiplicity.

As was pointed out by Donohue (1951), hydrogen bonding seems to be favoured if the angle X–O(H) · · · O is close to the tetrahedral value. This is certainly true for short bonds between carboxyl groups: for example 110·8° in sodium hydrogen diacetate, or within the maleate anion. Though a similar angle (108°) obtains in monetite, the P–O · · · O angle in DPCPHP is much wider (129·4° ± 0·5°). Table 6 has been extended to include information about corresponding angles. Evidently large variations in this angle are possible, even in short bonds between, phosphate groups.

There is a *prima facie* case for supposing that the short, and crystallographically symmetrical, hydrogen bonds found in some Type *A* salts may be genuinely symmetrical. The bond in DPCPHP clearly qualifies for consideration also. On the other hand, in one rather short bond between phosphate groups the proton has been located by neutron diffraction. This is in the tetragonal form of KH_2PO_4, where the O · · · O distance is 2·49 Å; and Bacon & Pease (1955) have located the proton at about 1·07 Å from one oxygen atom and therefore 1·42 Å from the other. Thus, if the hydrogen bond in DPCPHP is truly symmetrical, a decrease of 0·08 Å in the O · · · O-distance must have resulted in an increase of 0·13 Å in the O–H-distance. This would be surprising.

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References

Bacon, G. E. & Pease, R. S. (1953). *Proc. Roy. Soc.* A **220**, 397.

Bacon, G. E. & Pease, R. S. (1955). *Proc. Roy Soc.* A **230**, 359.

Bacon, G. E. & Curry, N. A. (1956). *Proc. Roy. Soc.* A **235**, 552.

Bacon, G. E. & Curry, N. A. (1957). *Acta Cryst.* **10**, 524.

Bacon, G. E. & Curry, N. A. (1960). *Acta Cryst.* **13**, 717.

Blinc, R., Hadži, D. & Novak, A. (1960). *Z. Elektrochem.* **64**, 567.

Cruickshank, D. W. J. (1961). *J. Chem. Soc.* p. 5486.

Darlow, S. F. & Cochran, W. (1961). *Acta Cryst.* **14**, 1256.

Donohue, J. (1952). *J. Phys. Chem.* **56**, 502.

Dunitz, J. D. & Rollett, J. S. (1956). *Acta Cryst.* **9**, 327.

Frevel, L. K. & Rinn, H. W. (1962). *Acta Cryst.* **15**, 286. (See also Ibers, J. A. (1963). *J. Chem. Phys.* **40**, 402).

Furberg, S. (1955). *Acta Chem. Scand.* **9**, 1557.

Gafner, G. & Herbstein, H. F. (1962). *Acta Cryst.* **15**, 1081.

Hadži, D. & Novak, A. (1960). *Proc. Chem. Soc.* p. 241.

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

Jones, D. W. & Cruickshank, D. W. J. (1961). *Z. Kristallogr.* **116**, 101.

Kraut, J. (1961). *Acta Cryst.* **14**, 1146.

MacLennan, G. & Beevers, C. A. (1955). *Acta Cryst.* **8**, 579.

Newman. R. L. & Badger, R. M. (1951). *J. Chem. Phys.* **19**, 1207.

Peterson, S. E. & Levy, H. A. (1958). *J. Chem. Phys.* **29**, 1193.

Pimentel, C. G. & McClellan, A. L. (1960). *The Hydrogen Bond.* San Francisco: Freeman.

Rollett, J. S. & Sime, J. G. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Oxford: Pergamon Press.

Shrivastava, H. N. & Speakman, J. C. (1961). *J. Chem. Soc.* p. 1151.

Sim, G. A. (1959). *Nature, Lond.* **184**, 1863.

Skinner, J. M. & Speakman, J. C. (1951). *J. Chem. Soc.* p. 185.

Speakman, J. C. & Mills, H. H. (1961). *J. Chem. Soc.* p. 1164. (See also 1963, p. 4355).