

ment Statistician, J.V.T. Baker, in providing time on the IBM 1620 computer is gratefully acknowledged.

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## The Crystal Structure of 2 $\alpha$ -Bromo-5 $\beta$ -bromomethyl-5 $\alpha$ -methyl-2 $\beta$ -oxo-1,3,2-dioxaphosphorinane\*

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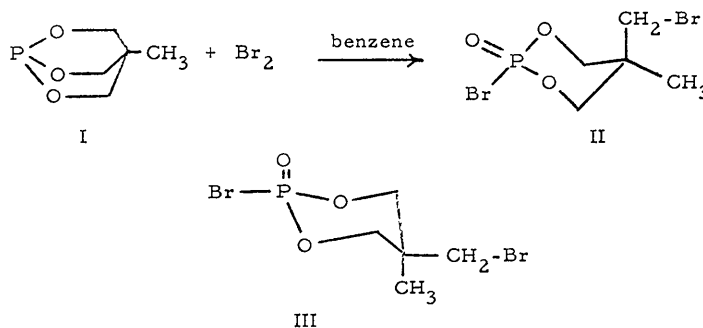
(Received 23 September 1966 and in revised form 15 February 1968)

The crystal structure of 2 $\alpha$ -bromo-5 $\beta$ -bromomethyl-5 $\alpha$ -methyl-2 $\beta$ -oxo-1,3,2-dioxaphosphorinane has been determined by three-dimensional single-crystal X-ray diffraction techniques. The crystals are orthorhombic, space group  $P2_12_12_1$  with unit-cell dimensions  $a=13.415$ ,  $b=11.407$ ,  $c=6.215$  Å and four molecules per unit cell. The final  $R$  for 478 reflections is 0.045. The molecular conformation is a distorted chair with the bromo and bromomethyl groups in axial positions. The interior O–P–O angle is 104.9° which is similar to the corresponding angle in acyclic phosphate esters and explains the similarity in the rates of hydrolysis of six-membered cyclic and acyclic phosphate esters as opposed to the strained five-membered cyclic esters.

### Introduction

In the course of nuclear magnetic resonance studies on the mechanism of long range phosphorus–hydrogen spin–spin interactions, 2 $\alpha$ -bromo-5 $\beta$ -bromomethyl-5 $\alpha$ -methyl-2 $\beta$ -oxo-1,3,2-dioxaphosphorinane (II, hereafter referred to as BBMOD) was prepared by reaction in benzene of the bicyclic phosphite ester (I) with bromine (Bertrand, Verkade & McEwen, 1968). Prior to the

present work neither the conformation of BBMOD nor the mechanism of the reaction had been established. The dipole moment of BBMOD in dioxane is 6.59D which agrees favorably with the 6.40D moment calculated for conformation II from individual bond moments. An identical treatment of individual bond moments for the other, sterically more favorable chair conformation (III) yielded a calculated moment of 1.57 D.



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In order to provide the structural parameters necessary for the interpretation of both the <sup>31</sup>P and the proton spectra of BBMOD, and to confirm the conformation tentatively assigned on the basis of the dipole

moment, the crystal structure of BBMOD was investigated by single-crystal X-ray diffraction techniques. A preliminary report on this work has been published elsewhere (Beineke, 1966).

### Experimental

A sample of BBMOD, m.p. 81–82°C, which had been recrystallized from hexane was kindly supplied by Professor Verkade. Because BBMOD reacts slowly with water vapor in the atmosphere, all crystals used in this investigation were sealed under vacuum in thin-walled glass capillaries. The crystals are colorless needles.

#### Crystal data

BBMOD = C<sub>5</sub>H<sub>9</sub>PO<sub>3</sub>Br<sub>2</sub>, *M* = 307.9. Orthorhombic, *a* = 13.415 ± 0.003, *b* = 11.407 ± 0.004, *c* = 6.215 ± 0.005 Å. These data were obtained from oscillation and Weissenberg photographs about the needle (*c*) axis. The photographs taken with Cu *K* $\alpha$  radiation,  $\lambda$  = 1.5418 Å, were corrected for film shrinkage by calibration with aluminum powder patterns (*a* = 4.0331 Å at 22°C). The systematic absences are: *h*00 when *h* is odd; 0*k*0 when *k* is odd; 00*l* when *l* is odd. The space group is *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. BBMOD is soluble in all of the organic solvents in which flotation was initially attempted. The reaction with water, however, was found to proceed slowly enough to permit flotation in an aqueous silver nitrate solution.  $\rho_m$  = 2.00 g.cm<sup>-3</sup>;  $\rho_x(z=4)$  = 2.15 g.cm<sup>-3</sup>. The linear absorption coefficient for Mo *K* $\alpha$  radiation is 87.9 cm<sup>-1</sup>.

A needle 0.10 × 0.15 mm in cross section and 0.5 mm long was used for the measurement of intensity data. A General Electric XRD-5 X-ray unit equipped with a single-crystal orienter and scintillation counter was used with Mo *K* $\alpha$  radiation in the moving crystal-moving-counter mode ( $\theta$ , 2 $\theta$  coupling) to measure intensities. A 100 sec scan covering 3.33° was used for each reflection. Backgrounds were obtained from a curve based on about 60 background measurements which were made at various values of 2 $\theta$  with  $\omega$  offset by 1.8°. Strong peaks were corrected for non-linearity

of the counting system by assuming a dead time of 10<sup>-5</sup> sec. The intensity of a reference reflection decreased linearly by fourteen per cent during the process of intensity measurement. A linear decomposition correction was therefore applied to all intensity data. One octant of data was collected out to 2 $\theta$  = 45° (sin  $\theta/\lambda$  = 0.558) beyond which few reflections could be distinguished above the background. A total of 755 reflections were recorded. A streak correction (Williams & Rundle, 1964) was applied to 60 reflections which occurred along densely packed radial reciprocal lattice rows. The approximate crystal dimensions were used to compute absorption corrections (Busing & Levy, 1957), and the resulting transmission factors which ranged from 0.286 to 0.401 were applied along with the usual Lorentz-polarization corrections to reduce the intensities to structure factors.

A standard deviation was computed for each intensity by means of the expression:

$$\sigma(I) = \frac{1}{A} [C_T + C_B + C_S + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2 + (K_A I)^2]^{\frac{1}{2}},$$

where *C<sub>T</sub>*, *C<sub>B</sub>*, *C<sub>S</sub>*, *I*, and *A* are, respectively, the total counts, background counts, streak counts, intensity corrected for Lorentz-polarization and absorption effects, and the transmission factor. *K<sub>T</sub>*, *K<sub>B</sub>*, *K<sub>S</sub>*, and *K<sub>A</sub>* are, respectively, the estimated systematic errors in the total counts, background counts, streak counts, and the transmission factor. Based on experience in this laboratory *K<sub>T</sub>* was assigned a value of 0.02; *K<sub>B</sub>* and *K<sub>S</sub>*, 0.10; and *K<sub>A</sub>*, 0.03.  $\sigma(F)$  was computed from  $\sigma(I)$  for each reflection by the method of finite differences (Williams & Rundle, 1964):

$$\sigma(F) = (Lp)^{-\frac{1}{2}} [(I + \sigma(I))^{\frac{1}{2}} - I^{\frac{1}{2}}].$$

Reflections were considered observed if in addition to giving a definite peak on the recorder trace,  $F_o > 3\sigma(F_o)$ . It was felt that the latter criterion was not too severe since even at this level a number of reflections with  $F_o > 3\sigma(F_o)$  were classed as unobserved because of the absence of a clearly defined peak on the recorder trace.

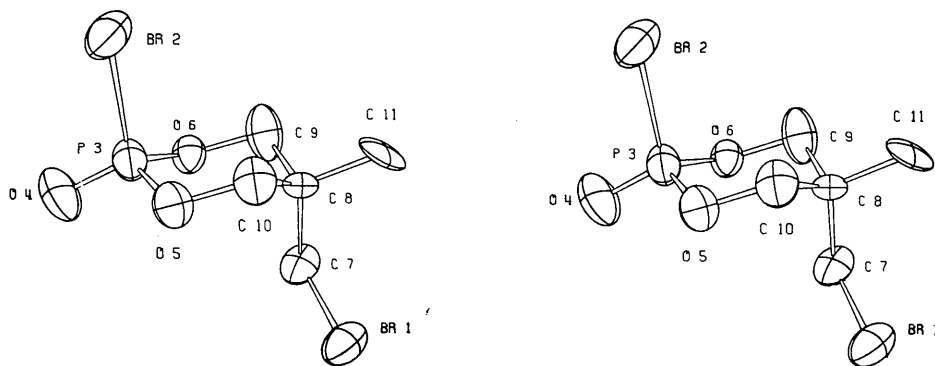


Fig. 1. Stereoscopic (Johnson, 1965) illustration of the BBMOD molecule. Anisotropic thermal vibration is indicated by 50% probability ellipsoids.

Of the 755 reflections only 470 were considered observed. Unobserved reflections were assigned a threshold value of  $3\sigma(F_o)$  or  $F_o$ , whichever was the larger, and were included in the least-squares refinement only if this threshold value was exceeded by  $F_c$ . Only eight unobserved reflections had  $F_c > F_o$  and were included in the final cycle of refinement.

#### Determination and refinement of the structure

The bromine positions were located directly from a sharpened three-dimensional Patterson synthesis. Successive structure-factor Fourier syntheses yielded the remaining atoms. The structure which resulted is illustrated in Fig. 1. All of the calculations were performed on an IBM 360 model 50 computer with the crystallographic programs of the National Research Council of Canada (Ahmed, Hall, Pippy, & Saunderson, 1966) unless otherwise noted. The structure was refined by block-diagonal least-squares minimization of the function  $\sum w(|F_o| - |F_c|)^2$ . Two blocks were used for each anisotropic atom. The first was a  $3 \times 3$  block of positional parameters; the second, a  $6 \times 6$  block of anisotropic temperature factors. The weighting scheme was  $\sqrt{w} =$

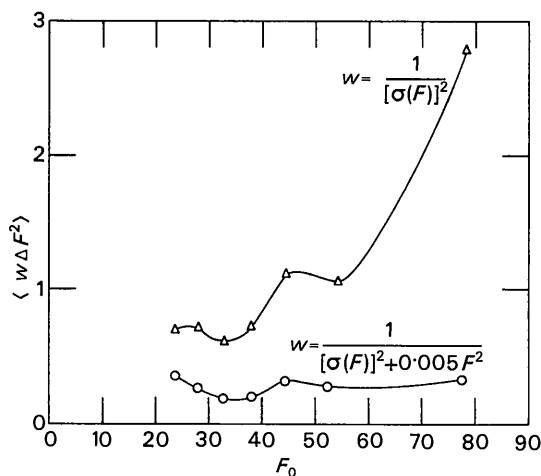


Fig. 2. Plot of  $\langle w(|F_o| - |F_c|)^2 \rangle$  vs.  $|F_o|$ . Between 75 and 127 reflections are averaged for each point.  $\triangle$ —: the unmodified weighting scheme;  $\circ$ —: the modified weighting scheme.

$\sigma(F)^{-1}$ . Unobserved reflections were weighted in exactly the same way as observed reflections if  $F_c \geq F_o$ . They were, however, given weights of zero if  $F_c < F_o$ . The scattering factors which were used are those of Hanson, Herman, Lea & Skillman (1964). The real and imaginary anomalous dispersion corrections from Table 3.3.2C of *International Tables for X-ray Crystallography* (1962) were included for both bromines and the phosphorus. Since the space group is acentric, both enantiomorphs were tried. After convergence with all atoms given anisotropic temperature factors, the conventional  $R$  index  $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$  was 0.055 and 0.050 for the two enantiomorphs. The enantiomorph which yielded the lower  $R_1$  was selected; however, since the only difference between the two enantiomorphs is rotation of the C(7)–Br(1) bond by  $120^\circ$  about the C(7)–C(8) bond, no effort was made rigorously to establish absolute configuration. An attempt was made to locate the hydrogens in a difference-Fourier synthesis computed with low-angle data, but the noise level,  $\pm 0.4 \text{ e.}\text{\AA}^{-3}$ , was too high.

The standard deviation of a reflection of unit weight was 1.14 which indicated that the weights were properly scaled. However, when average values of  $w(F_o - |F_c|)^2$  were plotted as a function of  $|F_o|$  as in Fig. 2, a striking dependence on  $|F_o|$  was observed. In constructing this plot, overlapping regions containing from 75 to 127 reflections were used for each point. A modified weighting scheme,  $\sqrt{w} = [\sigma(F)^2 + PF^2]^{-\frac{1}{2}}$ , was subsequently used with the value of  $P$  chosen to minimize the dependence of  $\langle w(|F_o| - |F_c|)^2 \rangle$  on  $|F_o|$ . In this case independence was achieved with a value of 0.005 for  $P$  as illustrated in Fig. 2. In the final least-squares cycle, the average shift was  $0.05\sigma$  with the maximum shift,  $0.17\sigma$ . The final weighted  $R$ ,  $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{\frac{1}{2}}$  was 0.057 with  $R_1 = 0.045$ . The standard deviation of a reflection of unit weight was 0.59. Apparently the modified weights are not on an absolute scale, but this is of little consequence since they have been made independent of  $|F_o|$ .

The final positional and thermal parameters along with their estimated standard deviations are listed in Table 1. Experience in this laboratory indicates that the block-diagonal approximation leads to standard

Table 1. Final parameters and standard deviations (in parentheses)

All values have been multiplied by  $10^4$ . The temperature factor expression is:

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

	$x$	$y$	$z$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Br(1)	8268 (2)	8797 (2)	7509 (4)	68 (1)	85 (2)	419 (8)	-36 (3)	-52 (8)	112 (9)
Br(2)	5528 (2)	4224 (2)	9602 (4)	86 (2)	69 (2)	455 (8)	-41 (3)	-61 (8)	56 (8)
P(3)	5715 (4)	5656 (4)	7338 (9)	62 (3)	66 (4)	230 (16)	2 (7)	-36 (17)	-32 (19)
O(4)	5326 (12)	5360 (14)	5243 (22)	104 (13)	144 (17)	241 (46)	8 (26)	-93 (45)	-74 (50)
O(5)	6863 (8)	5907 (11)	7353 (21)	65 (8)	83 (12)	277 (41)	7 (17)	1 (40)	-42 (52)
O(6)	5242 (9)	6730 (11)	8447 (20)	56 (9)	58 (10)	253 (40)	8 (16)	-17 (34)	-13 (36)
C(7)	6891 (14)	8426 (17)	8243 (33)	66 (15)	50 (16)	336 (72)	10 (26)	-94 (60)	106 (58)
C(8)	6837 (14)	7467 (16)	10008 (31)	54 (12)	61 (14)	153 (49)	-26 (24)	35 (48)	50 (47)
C(9)	5686 (16)	7240 (19)	10429 (37)	82 (16)	96 (20)	381 (77)	51 (34)	-49 (75)	-174 (79)
C(10)	7342 (14)	6358 (18)	9314 (34)	63 (14)	68 (17)	300 (67)	30 (29)	-46 (55)	9 (68)
C(11)	7331 (21)	7843 (22)	12200 (30)	158 (23)	122 (25)	101 (62)	-44 (44)	-58 (71)	152 (75)

deviations which are consistently underestimated by a factor of 0.8. Consequently the standard deviations listed in Table 1, as well as all estimated errors derived from them, should be multiplied by 1.2 to correspond

with values derived from the more conventional full-matrix least-squares techniques. The structure factors listed in Table 2, as well as all estimated errors derived from these parameters are compared with the observed values in Table 2. An examination of the

Table 2. Observed and calculated structure factors

Each group of data is headed with values for *h* and *k*. Within each group of data are listed *l*, 10*F*<sub>0</sub>, 10 $\sigma$ (*F*<sub>0</sub>), and 10*F*<sub>c</sub> respectively. Reflections for which *F*<sub>0</sub> is negative are unobserved.

2 0 0 L	1 407 22 415	0 734 17 744	2 201 32 247	0 -220* 73 128	1 237 27 231	4 -191* 64 41	4 197 47 161
2 525 17 406	2 208 35 217	1 564 11 400	3 517 76 513	1 -109* 136 58	2 -160* 53 111	0 599 29 610	0 474 23 441
4 1160 34 1176	3 338 23 334	2 -205 85 263	4 -274 45 263	2 -105* 135 80	3 186 40 112	1 184 23 353	1 -231 50 546
6 235 39 207	4 306 23 418	3 262 75 333	5 -422* 144 73	3 -213* 111 135	4 -148* 45 127	2 -90* 100 58	2 -140 40 144
1 0 0 L	0 -144* 62 110	4 -254 62 251	4 -254 62 251	4 -220* 139 44	5 279 30 277	3 327 31 317	3 272 32 272
1 958 18 590	4 1 1 1	5 -177* 75 98	5 581 21 644	4 -11 4 4	0 307 15 413	4 284 19 213	4 -127* 55 190
2 291 24 250	4 1 1 1	1 1 1 1	1 355 25 346	0 126 4 198	0 126 4 198	0 126 4 198	0 126 4 198
3 456 17 507	0 182 40 164	6 2 1 1	2 161 47 159	1 222 30 236	1 511 17 503	8 7 1 1	5 0 0 0
4 228 29 213	1 201 35 195	0 226 31 228	3 757 29 362	2 -409* 135 51	2 433 19 423	0 247 75 225	0 -192* 64 70
4 180 39 203	2 767 17 492	1 516 19 513	4 -202 45 456	2 227 40 210	3 -193* 44 306	1 331 29 333	2 204 32 207
6 -259* 86 38	3 629 18 651	2 -154* 51 145	5 -430* 144 58	4 181 40 168	4 181 40 168	1 218 30 218	1 -171* 57 111
0 231 33 301	4 -154* 88 76	4 657 21 488	0 166 4 198	5 -168* 55 100	3 252 37 224	3 252 37 224	3 252 37 224
1 951 19 905	6 -170* 59 128	5 175 45 212	0 -165 49 157	0 126 4 198	3 6 1 1	4 184 49 164	4 184 49 164
2 1221 19 1281	5 1 1 1	7 2 1 1	1 355 25 346	1 -192* 64 125	0 126 4 198	0 126 4 198	0 126 4 198
3 343 20 342	0 1754 17 400	0 314 24 336	3 229 39 236	2 227 40 210	2 635 19 602	0 173 46 163	0 173 46 163
4 -248* 83 84	1 503 17 492	1 516 19 513	4 -418* 139 120	3 -420* 139 54	1 -178* 59 107	1 331 29 333	2 204 32 207
5 -239* 80 3	2 219 30 230	2 222 32 228	0 174 45 171	0 13 4 1	2 635 19 602	2 196 44 178	1 -228* 76 84
6 -208* 70 117	3 -152 51 124	4 1093 39 195	5 -192* 65 142	0 -141* 139 101	4 437 24 412	2 196 44 178	1 -228* 76 84
0 231 33 301	4 -154* 88 76	4 657 21 488	0 166 4 198	0 -141* 139 101	4 -150* 53 138	3 -162* 54 140	3 -162* 54 140
1 1147 17 1202	5 192 41 224	5 192 41 224	0 240 33 264	0 5 1 1	0 126 4 198	0 126 4 198	0 126 4 198
2 174 35 191	6 -237* 79 91	6 -237* 79 91	1 339 27 341	0 5 1 1	0 126 4 198	0 126 4 198	0 126 4 198
3 319 28 348	0 154* 88 76	0 154* 88 76	1 339 27 341	0 5 1 1	0 126 4 198	0 126 4 198	0 126 4 198
4 251 27 233	6 1 1 1	6 1 1 1	4 -418* 139 77	1 687 15 670	0 -340* 135 50	0 126 4 198	0 126 4 198
5 382 23 375	1 524 17 558	2 -153* 51 125	1 151 50 180	3 -197* 65 153	1 600 19 602	1 -760* 86 73	2 204 32 207
6 -387* 127 27	2 222 30 236	3 505 10 510	2 -174 45 171	2 -189 46 166	2 174 41 157	2 179 47 177	3 -223* 74 39
0 390 40 367	3 -269* 90 49	4 -157 53 168	4 -157 53 168	5 -224* 74 36	3 248 33 216	0 284 33 261	0 284 33 261
1 695 15 692	4 191 39 196	5 -176* 58 141	2 271 42 207	1 5 1 1	5 6 1 1	2 -228* 76 108	2 171 50 154
2 919 16 848	5 262 27 285	0 154* 88 76	3 376 38 344	1 691 15 709	0 547 20 534	3 8 1 1	3 8 1 1
3 255 25 292	6 -190* 96 36	0 154* 88 76	0 154 39 187	2 538 14 534	1 342 25 339	0 -462* 146 115	0 -462* 146 115
4 -157* 82 94	7 1 1 1	2 753 24 749	12 3 1 1	4 -147* 45 127	4 393 28 384	1 -147* 49 105	1 -147* 49 105
5 -150* 72 86	0 -348* 117 126	2 753 24 749	0 -402* 135 19	4 -147* 45 127	4 393 28 384	2 396 20 406	0 0 10 10
6 -215* 72 86	1 237 27 285	3 -104* 131 89	3 -104* 131 89	5 -125* 53 127	5 -432* 144 69	3 157 44 180	3 157 44 180
0 450 17 470	2 659 18 711	4 204 41 225	2 728 39 221	6 -162* 48 140	0 324 29 305	4 -364* 123 31	0 -147* 49 20
1 311 21 355	3 439 21 464	5 -239* 80 105	3 -203* 68 117	0 4 1 1	0 324 29 305	1 361 24 370	1 361 24 370
2 451 18 494	5 -394* 131 57	0 110 2 1	11 3 1 1	0 4 1 1	0 324 29 305	3 464 24 474	3 464 24 474
3 259 28 285	8 1 1 1	0 716 35 211	0 -225* 74 96	1 905 19 906	2 -273* 82 70	0 315 32 318	0 315 32 318
4 186 40 180	0 377 23 380	2 235 34 236	1 121 45 179	2 405 17 623	3 424 26 408	1 1 10 10	1 1 10 10
5 -237* 79 36	1 177 17 190	4 -201* 94 84	14 3 1 1	1 321 21 318	4 -420* 139 73	2 327 24 328	0 386 23 397
0 448 17 408	3 -372* 123 50	0 413 2 1	0 -306* 100 79	5 359 27 381	5 -167* 55 194	1 220 37 180	1 220 37 180
1 727 16 752	4 113 28 133	0 413 2 1	0 413 2 1	6 193 44 168	7 6 1 1	5 264 35 227	5 -147* 45 121
2 451 18 494	5 -241* 80 92	0 413 2 1	0 413 2 1	0 203 30 204	2 8 1 1	2 8 1 1	2 8 1 1
3 246 27 258	9 1 1 1	1 -204* 68 108	0 1475 21 1421	1 228 36 218	2 8 1 1	2 8 1 1	2 8 1 1
4 186 40 180	0 -140 46 153	2 -154* 51 125	2 826 16 857	4 -160* 53 150	1 211 53 220	1 -147* 49 105	1 -147* 49 105
5 -237* 79 36	1 338 23 354	3 -307* 131 52	3 402 38 229	4 -160* 53 150	2 -165* 49 75	2 196 39 180	2 196 39 180
6 -190* 131 22	2 184 37 194	4 234 34 229	4 320 24 316	0 676 24 670	4 311 28 316	3 192 38 192	3 192 38 192
0 502 16 528	3 243 32 272	0 216 2 1	5 -153* 55 34	0 676 24 670	4 311 28 316	3 192 38 192	3 192 38 192
1 237 27 248	4 -264* 86 100	0 216 2 1	6 275 30 212	0 676 24 670	4 311 28 316	3 192 38 192	3 192 38 192
2 -271* 102 132	5 -400* 139 71	1 216 39 208	0 532 16 525	2 -215* 72 95	0 468 20 465	0 155 46 160	0 155 46 160
3 -183* 85 116	0 276 27 263	2 167 46 188	1 456 17 452	3 289 33 286	1 380 32 390	1 286 29 271	1 286 29 271
4 -235* 82 94	0 276 27 263	3 177 46 162	2 176 17 169	4 247 30 235	2 146* 49 126	3 -155* 50 118	3 -155* 50 118
5 253 32 350	0 13 2 1	1 456 17 452	3 349 19 352	0 283 32 264	4 374 25 372	0 221* 73 39	0 221* 73 39
0 1339 28 1375	0 13 2 1	4 154 16 156	4 154 16 156	1 211 53 220	4 205 40 180	1 211 53 220	1 211 53 220
1 219 29 245	11 1 1 1	0 -260* 94 75	0 -260* 94 75	2 327 24 328	4 205 40 180	1 211 53 220	1 211 53 220
2 170 20 232	0 -205* 69 63	1 216 39 208	0 516 17 467	3 195 40 183	0 269 32 263	1 156 49 122	1 156 49 122
3 -362* 120 44	1 266 30 237	2 167 46 188	0 516 17 467	4 205 40 183	1 349 25 368	3 -196* 65 79	3 -196* 65 79
4 401 22 426	2 640 17 619	3 177 46 162	0 516 17 467	5 -181* 53 121	2 273 40 292	0 -224* 74 75	0 -224* 74 75
5 -222* 74 83	3 193 40 185	4 178 46 162	2 4 1 1	0 516 17 467	3 194 41 212	5 10 10 10	5 10 10 10
0 450 17 408	4 -398* 131 32	0 13 2 1	0 516 17 467	0 516 17 467	4 -142* 61 112	0 164 44 187	0 164 44 187
1 727 16 752	12 1 1 1	1 1454 70 1450	0 516 17 467	0 516 17 467	0 10 6 1	1 380 32 390	1 380 32 390
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3 246 27 258	1 338 23 354	3 592 16 538	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
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5 -237* 79 36	3 243 32 272	5 -396* 131 62	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
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0 502 16 528	5 -400* 139 71	0 11 2 1	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
1 237 27 248	0 276 27 263	14 2 1 1	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
2 -271* 102 132	0 276 27 263	0 -407* 135 23	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
3 -183* 85 116	0 276 27 263	1 219 37 189	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
4 -235* 82 94	0 276 27 263	2 235 34 236	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
5 253 32 350	0 276 27 263	4 -201* 94 84	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
0 1339 28 1375	0 276 27 263	3 -372* 123 50	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
1 219 29 245	0 276 27 263	4 113 28 133	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
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3 -362* 120 44	0 276 27 263	1 216 39 208	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
4 401 22 426	0 276 27 263	2 167 46 188	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
5 -222* 74 83	0 276 27 263	3 177 46 162	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
0 450 17 408	0 276 27 263	4 178 46 162	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
1 727 16 752	0 276 27 263	5 178 46 162	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
2 451 18 494	0 276 27 263	6 167* 47 125	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	3 196 39 180
3 246 27 258	0 276 27 263	0 516 17 467	0 516 17 467	0 516 17 467	1 380 32 390	3 196 39 180	

observed and calculated  $F$ 's for the more intense reflections indicated the absence of extinction effects. Consequently, no extinction correction was made.

### Results

Prior to this work, conformation III with the bulky bromo and bromomethyl groups in equatorial positions, was considered to be sterically more favorable than II. The actual conformation of BBMOD, however, is best described as II in agreement with the dipole moment measurements. Bond distances and angles are listed in Table 3 along with their standard deviations. The interior C—O—P angles which are larger by nine degrees than the ring angles in cyclohexane (Davis & Hassel, 1963) cause the phosphate end of the ring to assume a somewhat planar configuration with the resultant loss of distinction between equatorial and axial positions at P(3). This is best illustrated by considering the angle between the normal to the least-squares plane through O(5), O(6), C(9), and C(10) (from which the atoms deviate by  $\pm 0.01$  Å) and the normal to the plane defined by O(5), P(3), and O(6). It is  $36.7^\circ$ , whereas the corresponding angle with the plane of C(8), C(9), and C(10) is  $52.5^\circ$ . The net result is a reduction of the steric interactions between Br(2) and the hydrogens of C(9) and C(10). The intramolecular interactions of Br(1) also involve the methylene groups C(9) and C(10), but because of the tetrahedral arrangement of bonds about C(8), these interactions are independent of the conformation of the ring. Thus, there is very little, if any, preference for either conformation on the basis of steric considerations. By way of comparison, it should be noted that axial halogens have been observed in a number of *trans*-dihalodioxanes (Altona, Knobler, & Romers, 1963*a* and *b*; Altona & Romers, 1963). The torsion angles about the ring bonds are listed in Table 4. When each bond is viewed in Newman projection in the direction indicated, a clockwise rotation of the ring atom farthest from the viewer has arbitrarily been given a positive sign; a counterclockwise rotation, a negative sign.

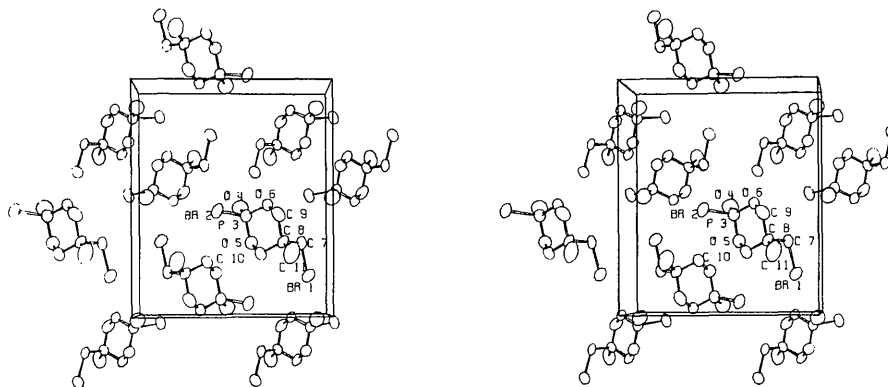


Fig. 3. Packing diagram. The  $c$  axis points out of the plane of the paper; the  $a$  axis, from top to bottom; and the  $b$  axis from left to right.

Table 3. Bond distances and angles

Distances (Å)			
Standard deviations ( $\times 10^3$ ) are given in parentheses.			
P(3)—Br(2)	2.171 (6)	C(9)—O(6)	1.487 (25)
O(4)—P(3)	1.443 (16)	C(9)—C(8)	1.588 (29)
O(5)—P(3)	1.566 (13)	C(10)—O(5)	1.471 (24)
O(6)—P(3)	1.543 (13)	C(10)—C(8)	1.498 (27)
C(7)—Br(1)	1.949 (20)	C(11)—C(8)	1.575 (30)
C(8)—C(7)	1.551 (27)		

Angles ( $^\circ$ )			
Standard deviations in degrees are given in parentheses.			
Br(2)—P(3)—O(4)	111.5 (0.7)	C(7)—C(8)—C(9)	106.1 (1.5)
O(5)—P(3)—Br(2)	104.4 (0.5)	C(7)—C(8)—C(10)	111.8 (1.6)
O(5)—P(3)—O(4)	113.8 (0.8)	C(7)—C(8)—C(11)	113.6 (1.6)
O(5)—P(3)—O(6)	104.9 (0.7)	C(9)—C(8)—C(10)	110.5 (1.6)
O(6)—P(3)—Br(2)	105.1 (0.5)	C(9)—C(8)—C(11)	108.1 (1.6)
O(6)—P(3)—O(4)	116.1 (0.8)	C(10)—C(8)—C(11)	106.8 (1.6)
C(10)—O(5)—P(3)	119.9 (1.1)	C(8)—C(9)—O(6)	108.5 (1.6)
C(9)—O(6)—P(3)	121.0 (1.2)	C(8)—C(10)—O(5)	109.6 (1.5)
Br(1)—C(7)—C(8)	111.3 (1.3)		

Table 4. Torsion angles in the ring

See text for sign convention.

Bond	Torsion angle
O(6)→P(3)	-43.2°
P(3)→O(5)	+44.6
O(5)→C(10)	-56.1
C(10)→C(8)	+58.4
C(8)→C(9)	-63.1
C(9)→O(6)	+55.8

The way in which BBMOD packs is illustrated in Fig. 3. All intermolecular distances less than the sum of the pertinent van der Waals radii (Pauling, 1960) are listed in Table 5. All of these short distances involve methylene or methyl groups for which reliable van der Waals radii are not available. In the absence of accurate positions for the hydrogens, little can be said about these distances.

### Discussion

Five-membered cyclic phosphate esters exhibit anomalously high rates of hydrolysis when compared with

Table 5. *Short intermolecular distances*

Listed below are all distances which are less than the sum of the van der Waals radii (Pauling, 1960).

From	to	in molecule at	Distance
Br(1)	C(9)	$\frac{1}{2} + x, \frac{3}{2} - y, 2 - z$	3.683 Å
Br(1)	C(11)	$x, y, z - 1$	3.695
Br(1)	C(11)	$\frac{3}{2} - x, 2 - y, z - \frac{1}{2}$	3.920
Br(2)	C(7)	$1 - x, y - \frac{1}{2}, \frac{3}{2} - z$	3.806
O(5)	C(10)	$\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$	3.373
C(7)	C(11)	$x, y, z - 1$	3.859

their six-membered and cyclic analogues (Kumamoto, Cox, & Westheimer, 1956; Khorana, Tener, Wright, & Moffat, 1957). It has been suggested (Westheimer, 1957; Cox, Wall, & Westheimer, 1959) that a major factor in this rate enhancement is strain in the five-membered ring. According to this proposal, these hydrolysis reactions proceed through a trigonal-bipyramidal activated complex (Haake & Westheimer, 1961) in which one ring oxygen occupies an axial position and the other, an equatorial position. This trigonal-bipyramidal geometry has been observed in 2,2,2-triisopropoxy-4,5-(2',2''-biphenyleno)-1,3,2-dioxaphospholene (Hamilton, LaPlaca, Ramirez, & Smith, 1967; Spratley, Hamilton, & Ladell, 1967) in which the internal O-P-O bond angle is 89.3°. One would therefore expect the energy of activation for hydrolysis to be directly related to the deviation of the O-P-O angle in phosphate esters from the ideal of 90°. In Table 6 the pertinent molecular dimensions are compared for the three kinds of phosphates. It is immediately evident that the O-P-O angle in the five-membered ring is much closer to 90° than in either the six-membered cyclic or acyclic phosphate. The similar reactivity of these latter compounds is, therefore, attributable to their equal O-P-O bond angles.

A theoretical interpretation of the relationship between ring strain and chemical reactivity in phosphate esters has been given by Collin (1966). In that study  $\pi$ -electron energies which arise from  $2p-3d$  orbital

interactions were calculated from the known geometries of acyclic and five-membered cyclic phosphate esters, by a self-consistent molecular orbital method. In the absence of structural data for six-membered cyclic phosphate esters estimates were made from molecular models. That the geometry of the BBMOD ring is almost exactly that used for these calculations lends credence to this interpretation. The  $\pi$ -electron energies of acyclic and six-membered cyclic phosphates were seen to be very nearly the same, while that of the five-membered ring was significantly higher. Assuming a similar energy level for the activated complex in the hydrolyses of all three types of phosphates, the energy of activation is clearly smaller in the case of the five-membered cyclic phosphate which explains its enhanced rate of reaction.

The author wishes to express his thanks to Professor Verkade for suggesting this research and supplying samples of BBMOD and to Mr Fred H. Hollenbeck for assistance in measuring the intensity data.

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Table 6. *Comparison of molecular dimensions*

The values in parentheses are the standard deviations in the last significant digit.

	BBMOD	Methyl ethylene phosphate (Steitz & Lipscomb, 1965)	Dibenzylphosphoric acid (Dunitz & Rollett, 1956)
Bond distances (Å)			
P=O	1.44 (2)	1.44 (1)	1.469 (4)
P-O (ring)*	1.57 (1)	1.57 (1)	1.545 (4)
	1.54 (1)	1.57 (1)	1.566 (4)
Bond angles (°)			
O-P-O (ring)*	104.9 (7)	99.1 (6)	103.8 (2)
O=P-O	113.8 (8)	116.0 (6)	112.8 (2)
	116.1 (8)	117.3 (6)	108.3 (2)
C-O-P (ring)*	120 (1)	112.0 (9)	118.8 (3)
	121 (1)	112.0 (9)	122.3 (3)

\* These dimensions refer to the distances and angles within the five and six-membered rings and the analogous dimensions in the acyclic compound.

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## Structures Cristallines des Dérivés 2 et 2,3 de la Naphtoquinone-1,4. IX. Amino-3-naphtoquinone-1,4

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(Reçu le 3 janvier 1968)

The crystalline structure of 3-amino-1,4-naphthoquinone has been determined by X-ray diffraction methods. The crystals are monoclinic ( $P2_1/c$ ). Three-dimensional integrated intensity data were collected on retigrams and operated by computers. The hydrogen bonds were deduced both from the location of the hydrogen atoms and from the distance between possible acceptors and donors. The distances between N(3) and the nearest oxygen atoms are 2.89<sub>9</sub> Å and 3.05<sub>2</sub> Å. The structure consists of piles of parallel molecules; the interplanar spacing within the column is short (3.49 Å).

### Données expérimentales

Nous avons utilisé l'amino-3-naphtoquinone-1,4 pure des laboratoires Eastman Kodak. Cristallisé par sublimation très lente au voisinage de sa température de fusion ( $F=210^\circ$ ) ce composé forme de belles aiguilles rouge-orangées de section propre à une étude radiocristallographique (0,1 mm<sup>2</sup>).

Le groupe spatial et les dimensions de la maille ont été déterminés respectivement sur diagrammes de De Jong et de Bragg, la rotation du cristal s'effectuant autour de l'axe d'allongement  $b$ .

#### Données cristallographiques

Système monoclinique.

$$\begin{aligned} a &= 17,03 \pm 0,02 \text{ \AA} , \\ b &= 3,96 \pm 0,01 , & \beta &= 125^\circ 30' . \\ c &= 14,72 \pm 0,02 . \end{aligned}$$

Volume de la maille: 808 Å<sup>3</sup>,

Groupe spatial:  $P2_1/c$ ,

Nombre de molécule par maille: 4,

Densité calculée: 1,42 g.cm<sup>-3</sup>,

$F(000) = 360$ .

Nous avons obtenu au moyen du rétigraphe de De Jong (radiation Cu  $K\alpha$ ) les quatre plans réciproques

contenus dans la sphère de résolution et portant les réflexions  $h0l$ ,  $h1l$ ,  $h2l$ ,  $h3l$ . Les intensités de 953 réflexions ont été retenues et mesurées par comparaison visuelle avec une échelle étalon. Ce nombre représente 50% environ du nombre total de réflexions contenues dans la sphère de rayon  $2/\lambda_{Cu K\alpha}$ .

Les facteurs de diffusion atomiques employés ont été calculés à partir des coefficients donnés par Brusentsev (1963).

### Détermination de la structure

La détermination a pu être effectuée uniquement à partir des projections de la fonction de Patterson réalisées au moyen du photosommateur harmonique de von Eller.

#### Etude de la projection (010)

La projection (010) est de type  $P2$  et contient deux molécules centrosymétriques dans la demi maille  $a$ ,  $c/2$ .

La projection de la fonction de Patterson 'sur ponctualisée' par l'application des fonctions modifiées\* fait apparaître au voisinage de l'origine quelques pseudo

\* James (1948), Abrahamson & Maslen (1963), Waser & Schomaker (1953).