*Contribution from the Institute for Atomic Research*
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# The Crystal Structure of a Hydrolysis Product of 2, 8, 9-Trioxa -1-Phospha-Adamantane[*]

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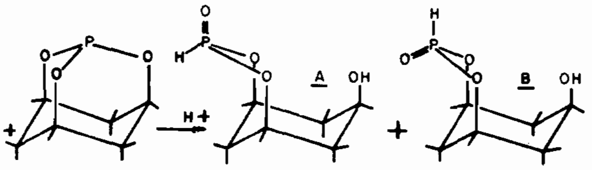
*The structure determination by X-ray diffraction of one of the two isomers formed in the hydrolysis of 2,8,9-trioxa-1-phospha-adamantane is reported. The conformation of the isomer 3-α-oxo-3-β-hydrido-7-β-hydroxy-2,4-dioxa-3-phosphabicyclo[3.3.1]nonane, predicted earlier on the basis of infrared and pnmr spectral evidence, is fully confirmed. The structures of both isomeric hydrolysis products are discussed in terms of conformational stability and a proposed mechanism for the reaction.* $PO_4C_5H_{11}$ *crystallizes in space group* $P2_12_12_1$ *with unit cell dimensions 5.84×11.67×10.91 Å with four molecules per unit cell* ($\rho = 1.59$ g/cm$^3$). *The intensities of 1007 reflections were measured by counter methods and refined by least squares to a conventional R factors of 6.3%.*

## Introduction

The acid-catalyzed hydrolysis of $P(OCH)_3(CH_2)_3$ (2,8,9-trioxa-1-phospha-adamantane) was recently reported to produce two isomeric hydrolysates: isomer A (3-α-oxo-3-β-hydrido-7-β-hydroxy-2,4-dioxa-3-phosphabicyclo[3.3.1]nonane) and isomer B (3β-oxo-3-α-hydrido-7-β-hydroxy-2,4-dioxa-3-phosphabicyclo-[3.3.1]nonane).[1]



The configuration and conformation of isomer A was previously predicted on the basis of an assumed structure for isomer B.[1] It was reasoned from earlier work[2] that the presence of a long-range coupling over five bonds of the P–H proton to a methylene proton in the carbon ring could take place only if the proton-phosphorus and carbon-hydrogen bonds involved were opposing and colinear. Thus, the only conformation which would allow such a geometry is that shown for isomer B in which the methylene axial carbon-hydrogen bond is colinearly opposed to that of the phosphorus-proton bond. Moreover, the P–O stretching frequency was lower than that in isomer A and was thought to be due to hydrogen bonding with the equatorial methylene hydrogen. The position of the OH group was determined from the lack of *trans* vicinal coupling of the methine and methylene protons which would have been expected if the OH group were equatorial. The near identity of the pnmr spectrum of isomer A to that of B, except for the presence of the long-range coupling, made it attractive to postulate that only reversal of the phosphoryl oxygen and hydrogen groups on phosphorus differentiated isomer A from B. The structure of isomer A reported herein fully confirms this prediction.

The structures of these isomers are of importance because of the paucity of structural knowledge concerning the stereochemical course of nucleophilic reactions of phosphites in general and of polycyclic phosphites in particular. Since bond cleavage reactions in polycyclic phosphites do not result in their fragmentation, significant information concerning the stereochemistry of these reactions can be deduced from configurational and conformational analyses of their products.[3]

## Experimental Section

*Preparation.* Crystals of the hydrolysis product were kindly supplied by Dr. J. M. Jenkins. Single crystals suitable for X-ray analysis were grown from acetone by allowing the acetone to evaporate slowly. Both the film data and the intensity data were obtained from single crystals glued to the end of a glass fiber. No protection from the atmosphere was found necessary.

*Crystal Data.* Photographs from a Weissenberg camera with $CuK_\alpha$ radiation dictated the space group assignment of $P2_12_12_1$. Lattice parameters were obtained from three crystals with Weissenberg photographs taken with $CuK_\alpha$ radiation at room temperature. Calibration was achieved by replacing the crystal with an aluminum powder sample after each photograph was taken but before the film was removed from the camera. The port was then reopened and the powder

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(*) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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(1) J. M. Jenkins, T. J. Huttemann, and J. G. Verkade, "Advances in Chemistry Series", R. F. Gould, Ed., American Chemical Society, Vol. 62, p. 604 (1967).

(2) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Am. Chem. Soc.*, *88*, 1140 (1966).

(3) R. D. Bertrand, G. K. McEwen, E. J. Boros, and J. G. Verkade, submitted for publication.

lines were recorded on the same film. Two of the crystals examined were mounted about the *c* axis and the third was mounted about the *a* axis. The lattice parame ers and their standard deviations ($a = 5.836 \pm 0.012$ Å, $b = 11.671 \pm 0.010$ Å, $c = 10.908 \pm 0.020$ Å) were obtained by a least-squares extrapolation treatment[4] of the calibrated data. It is not understood why the method did not yield more accurate lattice constants.

The calculated density for four molecules per unit cell is 1.59 g/cm$^3$. All atoms reside in general positions with one molecule per asymmetric unit.

*Collection and Treatment of Data.* Three-dimensional X-ray diffraction intensity data were gathered at room temperature with zirconium-filtered molybdenum radiation on a General Electric XRD-5 X-ray unit equipped with a single crystal orienter and scintillation counter. All reflections within a 2θ sphere of 55° of one octant were scanned using a 100 sec., 3.33°-2θ moving-crystal-moving-counter scan technique with a 3° take-off angle and a 1.8° aperture of the counter. In addition, the same 2θ ranges for 160 reflections were scanned with an omega off-set of 1.8° for establishing tables for background correction. A chi dependence in addition to the usual 2θ dependence was observed and taken into account.

Each peak, at the time it was taken, was marked as to whether it was clearly above background, questionably above or indistinguishable from background for use in the refinement.

Three standard reflections (0.0.6, 0.6.0, and 3.0.2) were periodically measured to monitor crystal shifting and decomposition. The two primary lattice row reflections decreased in intensity linearly with X-ray exposure time by about 8%. The 3.0.2 reflection, however, did not decrease in intensity. Independent refinements of the structure using data with and without decomposition suggested that no correction for decomposition should be made. Corrections for Lorentz-polarization and noncharacteristic radiation[5] were applied to the intensities. Because of the small linear absorption coefficient (3.35 cm$^{-1}$) and the regular shaped crystal (0.2×0.2×0.3 mm), no absorption correction was made. No correction was made for extinction, nor were the form factors corrected for anomalous dispersion.

A standard deviation was calculated for the intensity of each reflection using the following expression:

$$\sigma_I = (TC + (0.03\ TC)^2 + (0.03\ Bg)^2 + (0.05\ St)^2)^{1/2}$$

where TC = total counts, Bg = background, and St = streak correction. The last three terms of the expression represent estimates of nonstatistical systematic errors in their values. Its propagation into the structure factor was computed with the following expression:

$$\sigma_F = \left(\frac{I + \sigma_I}{LP}\right)^{1/2} - F_{obs}$$

where I = corrected intensity, LP = Lorentz-polarization factor, and Fobs = the observed structure factor $= \left(\frac{I}{LP}\right)^{1/2}$.

*Structure Determination.* A sharpened and an unsharpened Patterson map were calculated. Examination of the three Harker layers led to the postulation of a phosphorus position consistent with the possible P–P peaks on the sharpened Patterson. Spheres of 1.5 Å radius were contoured about each of the P–P peaks for locating P–O vectors. In this manner an oxygen location was found consistent with all P–O and O–O

**Table I.** Final positional and thermal parameters and standard errors (in parentheses) for isomer A. The anisotropic temperature factor expression is $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2h\beta_{13} + 2k\beta_{23}))$

| Atom | x/a | y/b | z/c | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| P | 0.2446 (4) | 0.1492 (1) | 0.1140 (2) | 0.0290 (6) | 0.0042 (1) | 0.0066 (1) | 0.0018 (4) | −0.0004 (4) | −0.0006 (2) |
| $O_1$ | 0.0396 (10) | 0.1914 (4) | 0.1680 (5) | 0.0390 (22) | 0.0091 (5) | 0.0115 (6) | 0.0051 (9) | 0.0008 (10) | −0.0036 (5) |
| $O_2$ | 0.2061 (8) | 0.0671 (4) | 0.0045 (4) | 0.0299 (19) | 0.0052 (3) | 0.0069 (4) | 0.0033 (7) | −0.0008 (8) | −0.0000 (3) |
| $O_3$ | 0.4096 (9) | 0.0885 (4) | 0.2043 (4) | 0.0341 (18) | 0.0058 (4) | 0.0061 (4) | 0.0006 (8) | −0.0018 (9) | −0.0013 (4) |
| $O_4$ | 0.0912 (10) | −0.1230 (4) | 0.1825 (6) | 0.0283 (18) | 0.0065 (4) | 0.0110 (6) | 0.0010 (8) | 0.0031 (10) | 0.00183(5) |
| $C_1$ | 0.3831 (14) | −0.0143 (6) | −0.0354 (6) | 0.0315 (27) | 0.0061 (6) | 0.0045 (6) | 0.0025 (11) | 0.0013 (11) | −0.0005 (5) |
| $C_2$ | 0.3023 (12) | −0.1337 (5) | −0.0047 (6) | 0.0277 (28) | 0.0049 (5) | 0.0058 (6) | 0.0009 (10) | 0.0005 (10) | −0.0013 (5) |
| $C_3$ | 0.3002 (12) | −0.1608 (6) | 0.1333 (7) | 0.0282 (29) | 0.0048 (5) | 0.0091 (9) | 0.0017 (11) | 0.0049 (12) | 0.0024 (6) |
| $C_4$ | 0.5061 (12) | −0.1145 (6) | 0.1993 (7) | 0.0246 (25) | 0.0055 (6) | 0.0068 (7) | 0.0030 (10) | −0.0006 (12) | 0.0011 (6) |
| $C_5$ | 0.5818 (12) | 0.0046 (6) | 0.1619 (6) | 0.0142 (20) | 0.0065 (6) | 0.0085 (7) | 0.0028 (11) | −0.0032 (11) | −0.0005 (6) |
| $C_6$ | 0.6060 (13) | 0.0137 (5) | 0.0253 (7) | 0.0231 (24) | 0.0053 (6) | 0.0090 (8) | −0.0008 (11) | 0.0054 (13) | 0.0006 (6) |
| H(P) | 0.36607 | 0.23236 | 0.06841 | | | | | | |
| H($O_4$) | 0.07135 | −0.18462 | 0.22544 | | | | | | |
| H($C_1$) | 0.40409 | −0.01039 | −0.12661 | | | | | | |
| H($C_2$) | 0.14261 | −0.14546 | −0.03625 | | | | | | |
| H($C_2$) | 0.40564 | −0.19195 | −0.04519 | | | | | | |
| H($C_3$) | 0.31698 | −0.24734 | 0.13566 | | | | | | |
| H($C_4$) | 0.46979 | −0.11241 | 0.28968 | | | | | | |
| H($C_4$) | 0.63742 | −0.16846 | 0.18607 | | | | | | |
| H($C_5$) | 0.73546 | 0.02002 | 0.20071 | | | | | | |
| H($C_6$) | 0.65353 | 0.09400 | 0.00307 | | | | | | |
| H($C_6$) | 0.72733 | −0.04116 | −0.00350 | | | | | | |

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[4] D. E. Williams, USAEC Rept. IS-876, Ames Laboratory, Ames, Iowa.

[5] Streak was calculated by the method of J. E. Benson and D. R. Fitzwater, Iowa State University, Ames, Iowa. The method is essentially the same as that reported by D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, *86*, 1660 (1964).

vectors. Several other potential oxygen positions were discovered, but none were completely consistent with all of the possible vector combinations. These potential oxygen positions were rejected or established with alternating least-squares position refinement and electron density computations. Subsequent Fourier syntheses in conjunction with a scale model of the postulated molecule suggested the positions of the remainder of the atoms.

Refinement of the model was achieved by a least-squares minimization of $\Sigma w(|F_0|-|F_c|)^2$, where $w = \frac{1}{\sigma_F^2}$, on an IBM 360/50 computer by means of OR FLS

**Table II.** Comparison of calculated and observed structure factors based upon the parameters given in Table I. The three columns consist of k, $F_{obs}$ (×10) and $F_{calcd}$ (×10). Negative values of $F_{obs}$ denote reflections which were not clearly distinguishable from their backgrounds

| K | FO | FC |
|---|---|---|
| 0 K 0 | | |
| 2 | 893 | 859 |
| 4 | 1187 | 1201 |
| 6 | 753 | 788 |
| 8 | 457 | 455 |
| 10 | 147 | 129 |
| 12 | 172 | 161 |
| 14 | 273 | 251 |
| 0 K 1 | | |
| 1 | 370 | 330 |
| 2 | 327 | 255 |
| 3 | 314 | 291 |
| 4 | 123 | 100 |
| 5 | 319 | 295 |
| 6 | 446 | 418 |
| 7 | 251 | 241 |
| 8 | 139 | 134 |
| 9 | 106 | 107 |
| 10 | 137 | 171 |
| 11 | 256 | 265 |
| 12 | 120 | 104 |
| 13 | -81 | 41 |
| 14 | 161 | 144 |
| 0 K 2 | | |
| 0 | 221 | 220 |
| 1 | 1891 | 1835 |
| 2 | 692 | 660 |
| 3 | 1512 | 1508 |
| 4 | 602 | 615 |
| 5 | -0 | 19 |
| 6 | 264 | 255 |
| 7 | 606 | 605 |
| 8 | -37 | 32 |
| 9 | 126 | 112 |
| 10 | 239 | 248 |
| 11 | 63 | 95 |
| 12 | -34 | 33 |
| 13 | 219 | 214 |
| 14 | 196 | 144 |
| 0 K 3 | | |
| 1 | 342 | 310 |
| 2 | 720 | 752 |
| 3 | 352 | 337 |
| 4 | 289 | 287 |
| 5 | 341 | 334 |
| 6 | 281 | 285 |
| 7 | 197 | 224 |
| 8 | 392 | 380 |
| 9 | -0 | 66 |
| 10 | 242 | 235 |
| 11 | -0 | 11 |
| 12 | 118 | 130 |
| 13 | -30 | 1 |
| 14 | -58 | 39 |
| 0 K 4 | | |
| 0 | -145 | 75 |
| 1 | 1122 | 1091 |
| 2 | 998 | 976 |
| 3 | 361 | 340 |
| 4 | 286 | 310 |
| 5 | 169 | 153 |
| 6 | 683 | 696 |
| 7 | -107 | 42 |
| 8 | 132 | 112 |
| 9 | 301 | 307 |
| 10 | 315 | 313 |
| 11 | 152 | 143 |
| 12 | 93 | 69 |
| 13 | 112 | 100 |
| 14 | 59 | 81 |
| 0 K 5 | | |
| 1 | 433 | 406 |
| 2 | -94 | 82 |
| 3 | -66 | 25 |
| 4 | 311 | 310 |
| 5 | 898 | 922 |
| 6 | -73 | 23 |
| 7 | 146 | 148 |
| 8 | -40 | 32 |
| 9 | 588 | 582 |
| 10 | -78 | 58 |
| 11 | -81 | 26 |
| 12 | -77 | 64 |
| 13 | 180 | 158 |
| 0 K 6 | | |
| 0 | 1131 | 1107 |
| 1 | -113 | 60 |
| 2 | 364 | 359 |
| 3 | 397 | 375 |
| 4 | -62 | 34 |
| 5 | 383 | 392 |
| 6 | -92 | 7 |
| 7 | 468 | 463 |
| 8 | -51 | 84 |
| 9 | 270 | 266 |
| 10 | 177 | 148 |
| 11 | 229 | 195 |
| 12 | -69 | 50 |
| 13 | 230 | 191 |
| 0 K 7 | | |
| 1 | -57 | 45 |
| 2 | 296 | 297 |
| 3 | -80 | 48 |
| 4 | 208 | 208 |
| 5 | 64 | 95 |
| 6 | 508 | 501 |
| 7 | -0 | 46 |
| 8 | 213 | 175 |
| 9 | -23 | 11 |
| 10 | -45 | 65 |
| 11 | -76 | 41 |
| 12 | 279 | 249 |
| 0 K 8 | | |
| 0 | 274 | 266 |
| 1 | 92 | 151 |
| 2 | -34 | 54 |
| 3 | 183 | 165 |
| 4 | 154 | 149 |
| 5 | 222 | 218 |
| 6 | 232 | 224 |
| 7 | -155 | 82 |
| 8 | -0 | 33 |
| 9 | -68 | 36 |
| 10 | 344 | 337 |
| 11 | -66 | 27 |
| 12 | -88 | 55 |
| 0 K 9 | | |
| 1 | 227 | 212 |
| 2 | 119 | 131 |
| 3 | 288 | 298 |
| 4 | -0 | 68 |
| 5 | 112 | 106 |
| 6 | -89 | 49 |
| 7 | -13 | 18 |
| 8 | -77 | 59 |
| 9 | 100 | 112 |
| 10 | 246 | 203 |
| 11 | 216 | 181 |
| 0 K 10 | | |
| 0 | 409 | 422 |
| 1 | -35 | 51 |
| 2 | -0 | 21 |
| 3 | 186 | 151 |
| 4 | 411 | 418 |
| 5 | -0 | 71 |
| 6 | 115 | 99 |
| 7 | -65 | 52 |
| 8 | -46 | 22 |
| 9 | 178 | 149 |
| 10 | 110 | 98 |
| 0 K 11 | | |
| 1 | -0 | 2 |
| 2 | 259 | 258 |
| 3 | -0 | 18 |
| 4 | -61 | 14 |
| 5 | 90 | 101 |
| 6 | -95 | 88 |
| 7 | 159 | 120 |
| 8 | 160 | 165 |
| 9 | 63 | 79 |
| 0 K 12 | | |
| 0 | 138 | 139 |
| 1 | 147 | 128 |
| 2 | -80 | 21 |
| 3 | 151 | 145 |
| 4 | 76 | 80 |
| 5 | -82 | 57 |
| 7 | 96 | 80 |
| 0 K 13 | | |
| 1 | 109 | 91 |
| 2 | -0 | 53 |
| 3 | -75 | 15 |
| 4 | -27 | 40 |
| 5 | 212 | 183 |
| 0 K 14 | | |
| 0 | -37 | 63 |
| 1 | -34 | 62 |
| 2 | -0 | 6 |
| 1 K 0 | | |
| 1 | 1747 | 1688 |
| 2 | 243 | 199 |
| 3 | 1655 | 1668 |
| 4 | 567 | 554 |
| 5 | 494 | 494 |
| 6 | 237 | 228 |
| 7 | 391 | 384 |
| 8 | 147 | 112 |
| 9 | 346 | 352 |
| 10 | -66 | 29 |
| 11 | 262 | 266 |
| 12 | -44 | 11 |
| 13 | 269 | 261 |
| 14 | 138 | 79 |
| 1 K 1 | | |
| 0 | 343 | 305 |
| 1 | 833 | 802 |
| 2 | 790 | 747 |
| 3 | 653 | 640 |
| 4 | 155 | 138 |
| 5 | 303 | 300 |
| 6 | 270 | 267 |
| 7 | 277 | 302 |
| 8 | 122 | 126 |
| 9 | 183 | 188 |
| 10 | 224 | 254 |
| 11 | 159 | 178 |
| 12 | 297 | 301 |
| 13 | 105 | 80 |
| 14 | -79 | 20 |
| 15 | 146 | 112 |
| 1 K 2 | | |
| 0 | 1279 | 1260 |
| 1 | 507 | 473 |
| 2 | 821 | 784 |
| 3 | 424 | 414 |
| 4 | 1054 | 1096 |
| 5 | 153 | 170 |
| 6 | 300 | 327 |
| 7 | 176 | 175 |
| 8 | -64 | 87 |
| 9 | 150 | 176 |
| 10 | 404 | 413 |
| 11 | 93 | 109 |
| 12 | -69 | 92 |
| 13 | -95 | 87 |
| 14 | 138 | 138 |
| 1 K 3 | | |
| 0 | 336 | 310 |
| 1 | 429 | 441 |
| 2 | 349 | 349 |
| 3 | 365 | 361 |
| 4 | 398 | 402 |
| 5 | 567 | 577 |
| 6 | 302 | 307 |
| 7 | 168 | 167 |
| 8 | 165 | 181 |
| 9 | 303 | 312 |
| 10 | 159 | 182 |
| 11 | 131 | 136 |
| 12 | -0 | 20 |
| 13 | 134 | 126 |
| 1 K 4 | | |
| 0 | 397 | 373 |
| 1 | 130 | 121 |
| 2 | 147 | 143 |
| 3 | 769 | 784 |
| 4 | 171 | 172 |
| 5 | 265 | 266 |
| 6 | 148 | 143 |
| 7 | 583 | 594 |
| 8 | 103 | 80 |
| 9 | 171 | 183 |
| 10 | 148 | 149 |
| 11 | 117 | 141 |
| 12 | -0 | 44 |
| 13 | 153 | 156 |
| 1 K 5 | | |
| 0 | 138 | 132 |
| 1 | 354 | 349 |
| 2 | 446 | 453 |
| 3 | 256 | 265 |
| 4 | 512 | 527 |
| 5 | 198 | 172 |
| 6 | 460 | 479 |
| 7 | 60 | 75 |
| 8 | 432 | 434 |
| 9 | 155 | 188 |
| 10 | 275 | 273 |
| 11 | -85 | 73 |
| 12 | 170 | 157 |
| 13 | -64 | 62 |
| 1 K 6 | | |
| 0 | 595 | 589 |
| 1 | 253 | 243 |
| 2 | 174 | 164 |
| 3 | 186 | 187 |
| 4 | 247 | 234 |
| 5 | 244 | 258 |
| 6 | 548 | 573 |
| 7 | 192 | 178 |
| 8 | 163 | 177 |
| 9 | -0 | 6 |
| 10 | 282 | 273 |
| 11 | -90 | 57 |
| 12 | 109 | 67 |
| 13 | -68 | 70 |
| 1 K 7 | | |
| 0 | 79 | 74 |
| 1 | 254 | 248 |
| 2 | 181 | 169 |
| 3 | 150 | 166 |
| 4 | 123 | 109 |
| 5 | 394 | 406 |
| 6 | -74 | 117 |
| 7 | 206 | 213 |
| 8 | 88 | 80 |
| 9 | 241 | 246 |
| 10 | -73 | 42 |
| 11 | 197 | 124 |
| 12 | -89 | 72 |
| 1 K 8 | | |
| 0 | 354 | 367 |
| 1 | 320 | 322 |
| 2 | 180 | 179 |
| 3 | 348 | 335 |
| 4 | 119 | 120 |
| 5 | -0 | 26 |
| 6 | 202 | 200 |
| 7 | 205 | 224 |
| 8 | 98 | 124 |
| 9 | 280 | 262 |
| 10 | -89 | 18 |
| 11 | 185 | 166 |
| 12 | 114 | 80 |
| 1 K 9 | | |
| 0 | 145 | 127 |
| 1 | -53 | 46 |
| 2 | 338 | 337 |
| 3 | 178 | 198 |
| 4 | -0 | 55 |
| 5 | 85 | 78 |
| 6 | 133 | 122 |
| 7 | -18 | 56 |
| 8 | 169 | 153 |
| 9 | -95 | 65 |
| 10 | 74 | 72 |
| 1 K 10 | | |
| 0 | 164 | 158 |
| 1 | 249 | 241 |
| 2 | 100 | 100 |
| 3 | 180 | 183 |
| 4 | 211 | 189 |
| 5 | 126 | 136 |
| 6 | 91 | 92 |
| 7 | -82 | 106 |
| 8 | -2 | 56 |
| 9 | -2 | 73 |
| 10 | 165 | 149 |
| 1 K 11 | | |
| 0 | 91 | 96 |
| 1 | 228 | 215 |
| 2 | -47 | 40 |
| 3 | 128 | 154 |
| 4 | 108 | 106 |
| 5 | -153 | 166 |
| 6 | -157 | 139 |
| 7 | -0 | 15 |
| 8 | -0 | 38 |
| 9 | 109 | 110 |
| 1 K 12 | | |
| 0 | 80 | 101 |
| 1 | -100 | 74 |
| 2 | -58 | 54 |
| 3 | -77 | 60 |
| 4 | 121 | 116 |
| 5 | 80 | 46 |
| 6 | -2 | 51 |
| 7 | 142 | 108 |
| 1 K 13 | | |
| 0 | 47 | 90 |
| 1 | 57 | 72 |
| 2 | 125 | 128 |
| 3 | -0 | 27 |
| 4 | 140 | 143 |
| 6 | 145 | 147 |
| 2 K 0 | | |
| 0 | 389 | 386 |
| 1 | 145 | 108 |
| 2 | 155 | 159 |
| 3 | 176 | 184 |
| 4 | 486 | 513 |
| 5 | 177 | 177 |
| 6 | 250 | 285 |
| 7 | 455 | 474 |
| 8 | 96 | 46 |
| 9 | 203 | 203 |
| 10 | 614 | 624 |
| 11 | -74 | 27 |
| 12 | 120 | 101 |
| 13 | -50 | 0 |
| 14 | 233 | 219 |
| 2 K 1 | | |
| 0 | 268 | 254 |
| 1 | 381 | 386 |
| 2 | 463 | 482 |
| 3 | 433 | 415 |
| 4 | 91 | 92 |
| 5 | 328 | 321 |
| 6 | 458 | 478 |
| 7 | 275 | 263 |
| 8 | 176 | 191 |
| 9 | 210 | 203 |
| 10 | 179 | 190 |
| 11 | 196 | 208 |
| 12 | 148 | 141 |
| 13 | 115 | 104 |
| 14 | -90 | 35 |
| 2 K 2 | | |
| 0 | 1239 | 1220 |
| 1 | 459 | 464 |
| 2 | 214 | 208 |
| 3 | 905 | 888 |
| 4 | 615 | 598 |
| 5 | 104 | 134 |
| 6 | 238 | 234 |
| 7 | 436 | 440 |
| 8 | 119 | 138 |
| 9 | 338 | 358 |
| 10 | 0 | 34 |
| 11 | 191 | 212 |
| 12 | -0 | 42 |
| 13 | 266 | 252 |
| 14 | 68 | 40 |
| 2 K 3 | | |
| 0 | 242 | 241 |
| 1 | 351 | 353 |
| 2 | 374 | 375 |
| 3 | 394 | 359 |
| 4 | 159 | 160 |
| 5 | 487 | 502 |
| 6 | 339 | 339 |
| 7 | 191 | 191 |
| 8 | 357 | 375 |
| 9 | 406 | 431 |
| 10 | 8 | 84 |
| 11 | -26 | 80 |
| 12 | 225 | 234 |
| 13 | 103 | 98 |
| 14 | 104 | 75 |
| 2 K 4 | | |
| 0 | 248 | 258 |
| 1 | 518 | 515 |
| 2 | 495 | 483 |
| 3 | 410 | 399 |
| 4 | 447 | 454 |
| 5 | 135 | 126 |
| 6 | 497 | 489 |
| 7 | -105 | 104 |
| 8 | 216 | 219 |
| 9 | 34 | 108 |
| 10 | 227 | 234 |
| 11 | 54 | 64 |
| 12 | 110 | 106 |
| 2 K 5 | | |
| 0 | 240 | 228 |
| 1 | 292 | 317 |
| 2 | -0 | 36 |
| 3 | 164 | 170 |
| 4 | 113 | 117 |
| 5 | 451 | 466 |
| 6 | 207 | 227 |
| 7 | 145 | 165 |
| 8 | -74 | 97 |
| 9 | 233 | 240 |
| 10 | 65 | 71 |
| 11 | 130 | 135 |
| 12 | -97 | 88 |
| 2 K 6 | | |
| 0 | 225 | 223 |
| 1 | 444 | 470 |
| 2 | 384 | 376 |
| 3 | 541 | 553 |
| 4 | 78 | 80 |
| 5 | 171 | 193 |
| 6 | 306 | 295 |
| 7 | 344 | 374 |
| 8 | 34 | 115 |
| 9 | 106 | 97 |
| 10 | -19 | 53 |
| 11 | -89 | 98 |
| 12 | -47 | 36 |
| 2 K 7 | | |
| 0 | 212 | 201 |
| 1 | 333 | 346 |
| 2 | 332 | 326 |
| 3 | 171 | 173 |
| 4 | 295 | 282 |
| 5 | 233 | 236 |
| 6 | 107 | 121 |
| 7 | 153 | 152 |
| 8 | 221 | 225 |
| 9 | 108 | 113 |
| 10 | 35 | 90 |
| 11 | 114 | 126 |
| 12 | 108 | 124 |
| 2 K 8 | | |
| 0 | 723 | 729 |
| 1 | 222 | 235 |
| 2 | 107 | 120 |
| 3 | 300 | 296 |
| 4 | 430 | 447 |
| 5 | 124 | 151 |
| 6 | 125 | 149 |
| 7 | 176 | 179 |
| 8 | 66 | 98 |
| 9 | -59 | 67 |
| 10 | 190 | 175 |
| 2 K 9 | | |
| 0 | 102 | 119 |
| 1 | 271 | 298 |
| 2 | -0 | 31 |
| 3 | 212 | 221 |
| 4 | 42 | 73 |
| 5 | 157 | 149 |
| 6 | -0 | 31 |
| 7 | 82 | 97 |
| 8 | -59 | 39 |
| 9 | -82 | 88 |
| 2 K 10 | | |
| 0 | 179 | 183 |
| 1 | 197 | 185 |
| 2 | -69 | 54 |
| 3 | 204 | 214 |
| 4 | -76 | 55 |
| 5 | -0 | 49 |
| 6 | 152 | 133 |
| 7 | 177 | 155 |
| 8 | -0 | 38 |
| 9 | -34 | 76 |
| 2 K 11 | | |
| 0 | 139 | 129 |
| 1 | -0 | 32 |
| 2 | 235 | 240 |
| 3 | -105 | 64 |
| 4 | 102 | 108 |
| 5 | -0 | 59 |
| 6 | 111 | 119 |
| 7 | 2 | 68 |
| 8 | 61 | 99 |
| 2 K 12 | | |
| 0 | -70 | 39 |
| 1 | -45 | 46 |
| 2 | 117 | 89 |
| 3 | -75 | 81 |
| 4 | -2 | 3 |
| 5 | -0 | 44 |
| 6 | 153 | 155 |
| 2 K 13 | | |
| 0 | -73 | 42 |
| 1 | 166 | 164 |
| 2 | 102 | 80 |
| 3 K 0 | | |
| 1 | 275 | 283 |
| 2 | 81 | 69 |
| 3 | 124 | 96 |
| 4 | 101 | 109 |
| 5 | 183 | 197 |
| 6 | -62 | 21 |
| 7 | 469 | 489 |
| 8 | 178 | 183 |
| 9 | 261 | 262 |
| 10 | -0 | 27 |
| 11 | 128 | 132 |
| 12 | 172 | 165 |
| 13 | 285 | 262 |
| 3 K 1 | | |
| 0 | 75 | 65 |
| 1 | 156 | 166 |
| 2 | 461 | 469 |
| 3 | 151 | 151 |
| 4 | 167 | 164 |
| 5 | 459 | 463 |
| 6 | 163 | 150 |
| 7 | 180 | 193 |
| 8 | 336 | 348 |
| 9 | 327 | 347 |
| 10 | -95 | 76 |
| 11 | 0 | 70 |
| 12 | 104 | 133 |
| 13 | 134 | 100 |
| 3 K 2 | | |
| 0 | 425 | 442 |
| 1 | 514 | 517 |
| 2 | 480 | 477 |
| 3 | 292 | 294 |
| 4 | 159 | 161 |
| 5 | 297 | 307 |
| 6 | 532 | 554 |
| 7 | 50 | 71 |
| 8 | 139 | 171 |
| 9 | -58 | 61 |
| 10 | 259 | 257 |
| 11 | 98 | 121 |
| 12 | 172 | 152 |
| 13 | -105 | 44 |
| 3 K 3 | | |
| 0 | 94 | 98 |
| 1 | 275 | 288 |
| 2 | 105 | 81 |
| 3 | 259 | 299 |
| 4 | 278 | 283 |
| 5 | 264 | 257 |
| 6 | 421 | 439 |
| 7 | 221 | 243 |
| 8 | 179 | 217 |
| 9 | 242 | 268 |
| 10 | 144 | 166 |
| 11 | 148 | 157 |
| 12 | 139 | 147 |
| 13 | -59 | 57 |
| 3 K 4 | | |
| 0 | 642 | 633 |
| 1 | 280 | 268 |
| 2 | -77 | 39 |
| 3 | 340 | 348 |
| 4 | 295 | 290 |
| 5 | 127 | 107 |
| 6 | 134 | 138 |
| 7 | 329 | 362 |
| 8 | -0 | 28 |
| 9 | 112 | 143 |
| 10 | -0 | 12 |
| 11 | -0 | 60 |
| 12 | -24 | 19 |
| 13 | 170 | 146 |
| 3 K 5 | | |
| 0 | 180 | 187 |
| 1 | 83 | 95 |
| 2 | 329 | 318 |
| 3 | 152 | 160 |
| 4 | 279 | 238 |
| 5 | 160 | 162 |
| 6 | 216 | 218 |
| 7 | 119 | 120 |
| 8 | 138 | 134 |
| 9 | 143 | 135 |
| 10 | 27 | 49 |
| 11 | -39 | 41 |
| 12 | 123 | 126 |
| 3 K 6 | | |
| 0 | 468 | 472 |
| 1 | 177 | 189 |
| 2 | 172 | 186 |
| 3 | 359 | 369 |
| 4 | 496 | 508 |
| 5 | 88 | 103 |
| 6 | 54 | 88 |
| 7 | 61 | 57 |
| 8 | -25 | 52 |
| 9 | 98 | 107 |
| 10 | 190 | 184 |
| 11 | -94 | 83 |
| 12 | 79 | 85 |
| 3 K 7 | | |
| 0 | -62 | 55 |
| 1 | 223 | 231 |
| 2 | 162 | 182 |
| 3 | 171 | 179 |
| 4 | 169 | 190 |
| 5 | 161 | 195 |
| 6 | -0 | 47 |
| 7 | 143 | 159 |
| 8 | -48 | 38 |
| 9 | -111 | 89 |
| 10 | -0 | 44 |
| 11 | 113 | 111 |
| 3 K 8 | | |
| 0 | -0 | 76 |
| 1 | 358 | 366 |
| 2 | 380 | 394 |
| 3 | 314 | 335 |
| 4 | 233 | 231 |
| 5 | 106 | 113 |
| 6 | 40 | 89 |
| 7 | 183 | 183 |
| 8 | -73 | 64 |
| 9 | -81 | 77 |
| 10 | 141 | 145 |
| 3 K 9 | | |
| 0 | -0 | 62 |
| 1 | 25 | 74 |
| 2 | 146 | 150 |
| 3 | 54 | 81 |
| 4 | 123 | 127 |
| 5 | -0 | 34 |
| 6 | -0 | 26 |
| 7 | -75 | 49 |
| 8 | 91 | 121 |
| 9 | -0 | 31 |
| 3 K 10 | | |
| 0 | 255 | 274 |
| 1 | -70 | 77 |
| 2 | -78 | 24 |
| 3 | 120 | 119 |
| 4 | 83 | 100 |
| 5 | -62 | 68 |
| 6 | 162 | 165 |
| 7 | -33 | 83 |
| 8 | 2 | 66 |
| 3 K 11 | | |
| 0 | 86 | 107 |
| 1 | 137 | 136 |
| 2 | -61 | 28 |
| 3 | -64 | 67 |
| 4 | -0 | 69 |
| 5 | 141 | 150 |
| 6 | -25 | 12 |
| 3 K 12 | | |
| 0 | -71 | 93 |
| 1 | -66 | 67 |
| 2 | -33 | 55 |
| 3 | 132 | 147 |
| 4 | 2 | 53 |
| 4 K 0 | | |
| 0 | 219 | 189 |
| 1 | 296 | 312 |
| 2 | 408 | 393 |
| 3 | 471 | 463 |
| 4 | 450 | 500 |
| 5 | 132 | 122 |
| 6 | 119 | 139 |
| 7 | 159 | 169 |
| 8 | 196 | 76 |
| 9 | -94 | 63 |
| 10 | 280 | 293 |
| 11 | 123 | 103 |
| 12 | -87 | 3 |
| 4 K 1 | | |
| 0 | 141 | 147 |
| 1 | 288 | 296 |
| 2 | 208 | 203 |
| 3 | 174 | 136 |
| 4 | 290 | 269 |
| 5 | 298 | 302 |
| 6 | 243 | 243 |
| 7 | 144 | 140 |
| 8 | 239 | 239 |
| 9 | 100 | 93 |
| 10 | -0 | 38 |
| 11 | 124 | 133 |
| 12 | 124 | 128 |
| 4 K 2 | | |
| 0 | -53 | 4 |
| 1 | 185 | 176 |
| 2 | 246 | 249 |
| 3 | 400 | 413 |
| 4 | 230 | 229 |
| 5 | -0 | 52 |
| 6 | 218 | 247 |
| 7 | 234 | 251 |
| 8 | 76 | 100 |
| 9 | 168 | 169 |
| 10 | 89 | 81 |
| 11 | 127 | 112 |
| 12 | -83 | 54 |
| 4 K 3 | | |
| 0 | 308 | 325 |
| 1 | 151 | 172 |
| 2 | 297 | 297 |
| 3 | -15 | 62 |
| 4 | 103 | 132 |
| 5 | 257 | 262 |
| 6 | 185 | 214 |
| 7 | 61 | 92 |
| 8 | 96 | 109 |
| 9 | 81 | 144 |
| 10 | 21 | 44 |
| 11 | 42 | 76 |
| 12 | 137 | 136 |
| 4 K 4 | | |
| 0 | 370 | 372 |
| 1 | 148 | 143 |
| 2 | 145 | 160 |
| 3 | 117 | 122 |
| 4 | 192 | 195 |
| 5 | 66 | 139 |
| 6 | 305 | 317 |
| 7 | 76 | 65 |
| 8 | -63 | 85 |
| 9 | 30 | 95 |
| 10 | 133 | 137 |
| 11 | -87 | 5 |
| 12 | 59 | 57 |
| 4 K 5 | | |
| 0 | 95 | 60 |
| 1 | 241 | 254 |
| 2 | 214 | 206 |
| 3 | 153 | 145 |
| 4 | -48 | 69 |
| 5 | 216 | 219 |
| 6 | 138 | 166 |
| 7 | -71 | 37 |
| 8 | 204 | 220 |
| 9 | 138 | 137 |
| 10 | 0 | 47 |
| 11 | -59 | 56 |
| 4 K 6 | | |
| 0 | 121 | 113 |
| 1 | 191 | 189 |
| 2 | -0 | 41 |
| 3 | 315 | 321 |
| 4 | 138 | 122 |
| 5 | 71 | 55 |
| 6 | 143 | 140 |
| 7 | 162 | 158 |
| 8 | 158 | 161 |
| 9 | 145 | 113 |
| 10 | -0 | 39 |
| 11 | 98 | 85 |
| 4 K 7 | | |
| 0 | 146 | 144 |
| 1 | 134 | 144 |
| 2 | 187 | 195 |
| 3 | 100 | 102 |
| 4 | -0 | 43 |
| 5 | -57 | 76 |
| 6 | 141 | 121 |
| 7 | -100 | 109 |
| 8 | 207 | 184 |
| 9 | 110 | 83 |
| 10 | -38 | 71 |
| 4 K 8 | | |
| 0 | 243 | 251 |
| 1 | 85 | 112 |
| 2 | -0 | 48 |
| 3 | -73 | 77 |
| 4 | 164 | 168 |
| 5 | -6 | 58 |
| 6 | -85 | 87 |
| 7 | 162 | 144 |
| 8 | -46 | 44 |
| 9 | -0 | 32 |
| 4 K 9 | | |
| 0 | 120 | 123 |
| 1 | 82 | 86 |
| 2 | 6 | 77 |
| 3 | -0 | 34 |
| 4 | -0 | 19 |
| 5 | 109 | 112 |
| 6 | -28 | 81 |
| 7 | -47 | 42 |
| 8 | -0 | 74 |
| 4 K 10 | | |
| 0 | 174 | 177 |
| 1 | 90 | 107 |
| 2 | -0 | 41 |
| 3 | 130 | 143 |
| 4 | -0 | 48 |
| 5 | -0 | 19 |
| 6 | 76 | 110 |
| 7 | 115 | 112 |
| 4 K 11 | | |
| 0 | -0 | 29 |
| 1 | -47 | 65 |
| 2 | -0 | 50 |
| 3 | -0 | 33 |
| 4 | 123 | 87 |
| 4 K 12 | | |
| 0 | -0 | 8 |
| 1 | -0 | 52 |
| 5 K 0 | | |
| 1 | 165 | 150 |
| 2 | 538 | 533 |
| 3 | 409 | 397 |
| 4 | 78 | 100 |
| 5 | -82 | 42 |
| 6 | 159 | 162 |
| 7 | 124 | 105 |
| 8 | -71 | 39 |
| 9 | 125 | 121 |
| 10 | -62 | 57 |
| 11 | -112 | 65 |
| 5 K 1 | | |
| 0 | -48 | 23 |
| 1 | 283 | 272 |
| 2 | 272 | 266 |
| 3 | 285 | 286 |
| 4 | 160 | 156 |
| 5 | 191 | 181 |
| 6 | -79 | 59 |
| 7 | 56 | 52 |
| 8 | 112 | 121 |
| 9 | -70 | 43 |
| 10 | -49 | 31 |
| 11 | 114 | 90 |
| 5 K 2 | | |
| 0 | 327 | 322 |
| 1 | 219 | 222 |
| 2 | 153 | 148 |
| 3 | 155 | 166 |
| 4 | 216 | 227 |
| 5 | 98 | 108 |
| 6 | 197 | 191 |
| 7 | -31 | 31 |
| 8 | 54 | 70 |
| 9 | -68 | 78 |
| 10 | 138 | 133 |
| 11 | -85 | 32 |
| 5 K 3 | | |
| 0 | -0 | 31 |
| 1 | 164 | 198 |
| 2 | 103 | 130 |
| 3 | -18 | 99 |
| 4 | 119 | 133 |
| 5 | 187 | 177 |
| 6 | -0 | 32 |
| 7 | -0 | 46 |
| 8 | 91 | 96 |
| 9 | 95 | 107 |
| 10 | -87 | 22 |
| 5 K 4 | | |
| 0 | -51 | 74 |
| 1 | 170 | 191 |
| 2 | 95 | 119 |
| 3 | 264 | 267 |
| 4 | 158 | 159 |
| 5 | 74 | 94 |
| 6 | 0 | 95 |
| 7 | 174 | 188 |
| 8 | 101 | 104 |
| 9 | 123 | 79 |
| 10 | 0 | 17 |
| 5 K 5 | | |
| 0 | -73 | 32 |
| 1 | 106 | 135 |
| 2 | 128 | 118 |
| 3 | 171 | 183 |
| 4 | 163 | 148 |
| 5 | 106 | 130 |
| 6 | 85 | 101 |
| 7 | 115 | 122 |
| 8 | 157 | 156 |
| 9 | 104 | 91 |
| 10 | -88 | 59 |
| 5 K 6 | | |
| 0 | 120 | 125 |
| 1 | 88 | 63 |
| 2 | 209 | 204 |
| 3 | 158 | 119 |
| 4 | 175 | 153 |
| 5 | 113 | 88 |
| 6 | -112 | 91 |
| 7 | 157 | 126 |
| 8 | -89 | 46 |
| 9 | -75 | 35 |
| 5 K 7 | | |
| 0 | -0 | 7 |
| 1 | 121 | 120 |
| 2 | -66 | 60 |
| 3 | 134 | 130 |
| 4 | 103 | 95 |
| 5 | 149 | 129 |
| 6 | -96 | 30 |
| 7 | -82 | 35 |
| 8 | 92 | 65 |
| 5 K 8 | | |
| 0 | -13 | 42 |
| 1 | -67 | 78 |
| 2 | -18 | 35 |
| 3 | 105 | 82 |
| 4 | -73 | 63 |
| 5 | -33 | 25 |
| 6 | -50 | 62 |
| 7 | 172 | 132 |
| 5 K 9 | | |
| 0 | -0 | 46 |
| 1 | -0 | 11 |
| 2 | 119 | 119 |
| 3 | 0 | 19 |
| 4 | -0 | 43 |
| 5 | -59 | 73 |
| 5 K 10 | | |
| 0 | 79 | 93 |
| 1 | -90 | 57 |
| 2 | 108 | 120 |
| 3 | 33 | 64 |
| 6 K 0 | | |
| 0 | 330 | 320 |
| 1 | 170 | 175 |
| 2 | 114 | 92 |
| 3 | 93 | 73 |
| 4 | -73 | 21 |
| 5 | 89 | 111 |
| 6 | 142 | 158 |
| 7 | -64 | 21 |
| 8 | 121 | 100 |
| 9 | -59 | 8 |
| 6 K 1 | | |
| 0 | 0 | 25 |
| 1 | 140 | 127 |
| 2 | 164 | 156 |
| 3 | 62 | 64 |
| 4 | -0 | 31 |
| 5 | 132 | 107 |
| 6 | 128 | 84 |
| 7 | -67 | 43 |
| 8 | 91 | 70 |
| 9 | 135 | 86 |
| 6 K 2 | | |
| 0 | -0 | 22 |
| 1 | 195 | 184 |
| 2 | 118 | 102 |
| 3 | 95 | 97 |
| 4 | 0 | 72 |
| 5 | -26 | 22 |
| 6 | 81 | 54 |
| 7 | 179 | 150 |
| 8 | -56 | 35 |
| 9 | -105 | 19 |
| 6 K 3 | | |
| 0 | -0 | 18 |
| 1 | 59 | 93 |
| 2 | 85 | 92 |
| 3 | -0 | 66 |
| 4 | 108 | 100 |
| 5 | 96 | 76 |
| 6 | -70 | 61 |
| 7 | -64 | 18 |
| 8 | 145 | 134 |
| 6 K 4 | | |
| 0 | 151 | 150 |
| 1 | -0 | 60 |
| 2 | -0 | 51 |
| 3 | 96 | 100 |
| 4 | 147 | 123 |
| 5 | -0 | 47 |
| 6 | 95 | 95 |
| 7 | -88 | 44 |
| 8 | -98 | 59 |
| 6 K 5 | | |
| 0 | -0 | 36 |
| 1 | 67 | 78 |
| 2 | -0 | 55 |
| 3 | 92 | 61 |
| 4 | -43 | 61 |
| 5 | 148 | 131 |
| 6 | -0 | 32 |
| 7 | 88 | 62 |
| 6 K 6 | | |
| 0 | -75 | 27 |
| 1 | -102 | 75 |
| 2 | 92 | 106 |
| 3 | -122 | 100 |
| 4 | 133 | 112 |
| 5 | -0 | 22 |
| 6 | 95 | 30 |
| 6 K 7 | | |
| 0 | -57 | 19 |
| 1 | -47 | 40 |
| 2 | 120 | 95 |
| 3 | 90 | 57 |
| 4 | -59 | 72 |
| 5 | -49 | 41 |
| 6 K 8 | | |
| 0 | -0 | 50 |
| 1 | 68 | 51 |
| 2 | -0 | 21 |
| 3 | 130 | 101 |
| 7 K 0 | | |
| 1 | -73 | 20 |
| 2 | -103 | 19 |
| 3 | 134 | 111 |
| 4 | -83 | 31 |
| 5 | 121 | 85 |
| 7 K 1 | | |
| 0 | -65 | 8 |
| 1 | -82 | 41 |
| 2 | 74 | 84 |
| 3 | -89 | 13 |
| 4 | 127 | 109 |
| 5 | 101 | 77 |
| 7 K 2 | | |
| 0 | 93 | 51 |
| 1 | -111 | 56 |
| 2 | 134 | 109 |
| 3 | -85 | 30 |
| 4 | 164 | 135 |
| 7 K 3 | | |
| 0 | -0 | 3 |
| 1 | 106 | 84 |
| 2 | -41 | 28 |
| 3 | 118 | 95 |
| 4 | -44 | 2 |
| 7 K 4 | | |
| 0 | -76 | 24 |
| 1 | -83 | 65 |
| 2 | 90 | 58 |
| 3 | 119 | 89 |
| 7 K 5 | | |
| 0 | -2 | 35 |
| 1 | -2 | 24 |
| 2 | 126 | 90 |

least-squares program[6] employing Hartree-Fock-Slater scattering factor tables.[7] With the inclusion of the last of the atoms, the reliability index $\left(R=\frac{\Sigma||F_0|-|F_c||}{\Sigma|F_0|}\right)$ for this acentric structure with more than ten reflections per variable and isotropic temperature factors dropped from 0.191 to 0.084 in two cycles. All atoms were eventually given anisotropic thermal parameters. Positions for the nine cyclohexane hydrogens were calculated, and the atoms were included but were not allowed to vary. The phosphoryl and hydroxyl hydrogens were located on a difference Fourier synthesis. Their positions were adjusted to conform with typical bond distances and were not varied.

Independent refinements with the 706 clearly observed reflections and with the total 1007 reflections were carried out. The parameters and their standard deviations refined to very nearly the same values. The final positional and thermal parameters (listed in Table I) for the observed data yielded an unweighted R-factor of 0.063 and a weighted R factor $\left(Rwt=\frac{(\Sigma w(|F_0|-|F_c|)^2)^{1/2}}{(\Sigma wF_0^2)^{1/2}}\right)$ of 0.052. Table II contains a listing of the structure factors calculated from these parameters as well as the observed structure factors.

A final difference Fourier using all data and the final parameters of Table I was computed. No peaks or holes corresponding to more than 0.5 electrons /A$^3$ were found. The standard error of an observation of unit weight was computed to be 1.28 from the relation-

NO—NV

observations and NV is the number of variables.

*Structure.* A stereoscopic drawing of the molecular structure of isomer A with 50% probability thermal ellipsoids was computed with OR TEP.[8] The plotted result is given in Figure 1 Interatomic distances and angles and their standard deviations were computed with OR FFE[9] on the basis of the complete variance-covariance matrix of the last least-squares cycle and are listed in Table III.

A stereoscopic drawing of the packing of the molecules in the unit cell was computed and plotted and is shown in Figure 2. A weak hydrogen bond presumably exists between the hydroxyl hydrogen and $O_1$ of the neghboring molecule related by the two-fold screw

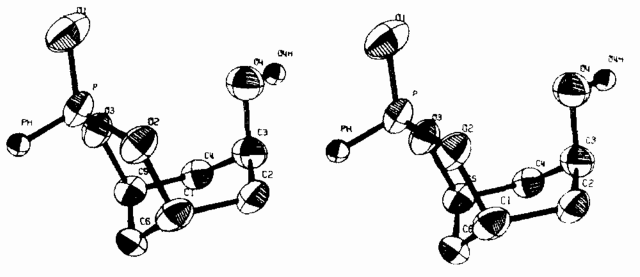

Figure 1. The molecular structure of isomer A with 50% probability thermal ellipsoids.

**Table III.** Interatomic distances and angles and their standard errors

| Bond Distances | | Bond Angles | |
|---|---|---|---|
| Atoms | Distance | Atoms | Angle |
| $O_1$—P | 1.420 (6) | $O_1PO_2$ | 114.4 (3) |
| $O_1$—P [a] | 1.446 (6) | $O_1PO_3$ | 114.6 (3) |
| P—$O_2$ | 1.550 (5) | $O_2PO_3$ | 107.5 (2) |
| P—$O_3$ | 1.549 (5) | $PO_2C_1$ | 121.8 (4) |
| $O_2$—$C_1$ | 1.468 (8) | $PO_3C_5$ | 121.6 (4) |
| $O_3$—$C_5$ | 1.476 (8) | $O_2C_1C_2$ | 108.1 (5) |
| $O_4$—$C_3$ | 1.403 (9) | $O_3C_5C_4$ | 108.9 (5) |
| $C_1$—$C_2$ | 1.507 (9) | $O_2C_1C_6$ | 109.8 (5) |
| $C_2$—$C_3$ | 1.541 (9) | $O_3C_5C_6$ | 109.2 (6) |
| $C_3$—$C_4$ | 1.501 (10) | $O_4C_3C_2$ | 108.5 (6) |
| $C_4$—$C_5$ | 1.512 (9) | $O_4C_3C_4$ | 113.4 (6) |
| $C_5$—$C_6$ | 1.503 (9) | $C_1C_2C_3$ | 114.2 (5) |
| $C_6$—$C_1$ | 1.495 (10) | $C_2C_3C_4$ | 113.0 (6) |
| $O_4$—$O_1'$ [b] | 2.816 (7) | $C_3C_4C_5$ | 115.6 (6) |
| | | $C_4C_5C_6$ | 111.2 (6) |
| | | $C_5C_6C_1$ | 110.1 (6) |
| | | $C_6C_1C_2$ | 112.6 (6) |

[a] Interatomic distances averaged over thermal motion. $O_1$ is assumed to ride on P.[10] The effects of thermal motion on all other interatomic distances was never more than 0.007 Å. The actual $O_1$–P distance undoubtedly is somewhere between the extreme in which independent motions of $O_1$ and P are assumed (1.420 Å) and the extreme in which the motion of $O_1$ follows that of P (1.4460 Å). [b] $O_1'$ is related to $O_1$ by the screw axis y.

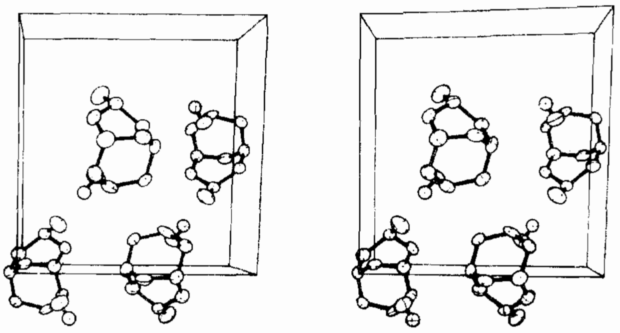

Figure 2. Stereoscopic drawing of the thermal ellipsoids and packing of isomer A. The z axis is horizontal and the y axis is vertical.

The final value of the z coordinate of $C_3$ appears to be anomalous. A shift from this parameter of several standard deviations tends to equalize the $C_3$–$C_2$ and $C_3$–$C_4$ distances with the average C$\simeq$C distance as well as the $O_4$–$C_3$–$C_2$ and $O_4$–$C_3$–$C_4$ angles. No data analysis or chemical reasoning, however, could be found to explain its refined position.

## Results and Discussion

The structure of isomer A strongly suggests that the postulated structure of B is also correct. The some-

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[6] W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Rept. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennesse.

[7] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, *17*, 1040 (1964).

[8] C. K. Johnson, USAEC Rept. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

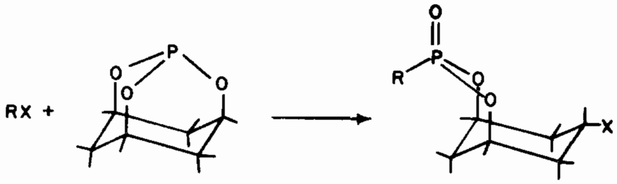
[9] W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Rept. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

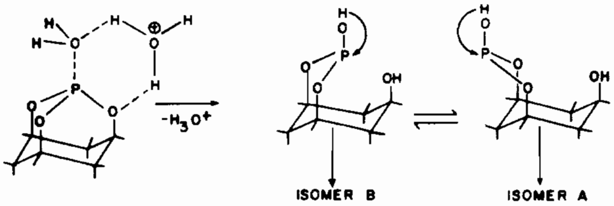
[10] W. R. Busing and H. A. Levy, *Acta Cryst.*, *17*, 142 (1964).

what unusual boat conformation of the phosphorus-containing ring would be preferred because of steric interference of the phosphoryl oxygen with that of the OH group in the chair conformation of this ring. The flexing of the phosphorus-containing ring in both isomers rather than the carbon ring upon cleaving the parent phosphite could be due to two factors. Not only are the accompanying hybridization changes more permissible for phosphorus and oxygen than for carbon, but flexing of the carbon ring would necessitate unfavorable eclipsing interactions among seven carbon protons and the OH group. Interatomic distance calculations based upon the POC and OPO angles found in isomer A give a $O_1$–$C_6$ distance for isomer B of 3.4 Å. It appears, therefore, that stabilization of the boat form of the ring in isomer B is not achieved by hydrogen bonding.

The OPO (107.5°) and average POC (121.7°) bond angles in isomer A are larger than those averaged bond angles in the parent caged phosphite in the coordination compound $[Ni(P(OCH)_3(CH_2)_3)_5](ClO_4)_2$ (104 and 116°, respectively).[11,12] If bond angle changes are small on coordination of the parent phosphite, its hydrolysis to isomer A would allow a release of some strain in these angles since the POC angles of uncyclized alkoxy moieties in phosphates tend to be 120°.[13] That some degree of pi bonding exists between phosphorus and the ring oxygens is suggested by the nearly 120° POC bond angles (indicative of $sp^2$ oxygens) and the shortening of all three P–O bond distances over the sum of the oxygen and phosphorus covalent radii (1.76 Å).

The structure of isomer A (and that of B by implication) is clear evidence that hydrolysis of the parent phosphite occurs by a different mechanism than its reaction with alkyl halides. From earlier dipole moment and spectral studies it was shown that only one isomer was obtained in the Michealis-Arbuzov reaction and that the halide was equatorially disposed on the carbon ring.[14] The reaction of alkyl halides with phosphites generally involves carbonium attack on phosphorus followed by $SN_2$ attack of halide on an oxygen-bearing carbon,[15] thus predicting the formation of an equatorial halide as shown in the reaction with $P(OC)_3(CH_2)_3$. To explain the formation of isomer A and B in the acid-catalyzed hydrolysis reaction, it seems reasonable at this time to postulate a mechanism similar to the one proposed by Aksnes and Aksnes[16] with the added feature of two possible rearrangement modes at phosphorus in an intermediate stage to account for the isomerism.





Kinetic studies and $O^{18}$ labelling experiments are in progress to test the validity of this mechanism.

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