

Conclusions

A series of radical-radical dimerization reactions have been studied using nuclear magnetic resonance techniques. Two different reactions, involving rearrangement of the dimer and dissociation of the dimer, were observed. A mechanism involving a common

intermediate for the two reactions was proposed. Rate and thermodynamic data were determined for a series of different dimers. Solvent effects were also studied. The dominant factor in these reactions appeared to be the steric hindrance of groups substituted near the reaction site.

The Crystal Structure of the Bicyclic Phosphate $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ ^{1a}

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Abstract: The structure of 1-oxo-4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$, has been determined by three-dimensional Fourier synthesis and full-matrix least-squares refinement of X-ray diffraction counter data. The crystals are orthorhombic, space group $\text{Pmc}2_1$, with unit cell dimensions $a = 6.74 \text{ \AA}$, $b = 5.96 \text{ \AA}$, $c = 17.77 \text{ \AA}$, four molecules per unit cell ($\rho_{\text{calcd}} = 1.53$, $\rho_{\text{obsd}} = 1.51 \text{ g/cm}^3$). The data reveal that some strain is probably present in the bicyclic structure. The bonding of the oxygens to the phosphorus appears to be similar to that found in other trialkyl phosphates whose structures are known. The terminal $\text{O}=\text{P}$ bond distance is $1.46 \pm 0.02 \text{ \AA}$, and the bridging P—O distances average $1.57 \pm 0.02 \text{ \AA}$. The $\text{O}=\text{P}—\text{O}$ angle is $115.0 \pm 1.1^\circ$ and the $\text{O}—\text{P}—\text{O}$ angle is $103.7 \pm 0.6^\circ$. The $\text{O}=\text{P}$ stretching frequency is compared with similar modes in open-chain phosphates and correlated qualitatively with the basicity of the oxygen.

Bicyclic alkoxy phosphites of the type $\text{P}(\text{OCH}_2)_3\text{CR}$ (where $\text{R} = \text{CH}_3$, C_2H_5 , and $n\text{-C}_5\text{H}_{11}$) have been shown to function as strong ligands in the presence of transition metal ions,² transition metal carbonyls,³ and boron-containing Lewis acids.⁴ Although the general bicyclic structure of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ and $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ was deduced from their H^1 and P^31 nmr spectra,⁵ it was of interest to determine an accurate structure of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ for several reasons. In addition to the fact that this study represents the first structural analysis of a bicyclic phosphate, the geometry of this molecule should closely approximate that of coordinated $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ in transition metal complexes and adducts. Moreover, it should have structural parameters similar to that of stable phosphonium cations of the type $[\text{RP}(\text{OCH}_2)_3\text{CCH}_3]^+$,⁶ as well as the phosphonium intermediates in the Michaelis-Arbuzov reactions of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$.⁷ It was also of interest to determine whether any of the structural features could account for the lack of extraction properties of the analogous $\text{OP}(\text{OCH}_2)_3\text{C}(\text{CH}_3)_4\text{CH}_3$ and the abnormally high $\text{O}=\text{P}$ stretching frequency in compounds of the type $\text{OP}(\text{OCH}_2)_3\text{CR}$.⁸

(1) (a) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2125. (b) Author to whom inquiries should be addressed at the Department of Chemistry, Iowa State University, Ames, Iowa.

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Experimental Section

Preparation. The preparation of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ has been described elsewhere.⁶ Crystals suitable for X-ray analysis were obtained by slow sublimation at 100° inside a water-cooled sublimation apparatus. The resulting long, needle-like, soft crystals were severed with a razor blade into near cubes. Torsional distortion of the resulting crystal was checked by examining Weissenberg photographs for drawn-out spots along the axis of rotation. A good single crystal for the collection of intensity data was obtained by this method, but later attempts to obtain suitable fresh crystals for the purpose of obtaining accurate lattice constants and for retaking part of the intensity data were not successful.

Crystal Data. Weissenberg and precession photographs with $\text{Cu K}\alpha$ radiation revealed mmm Laue symmetry (orthorhombic). Observed systematic extinctions ($h0l$, $l \neq 2n$) were compatible with space groups Pmcm , P2cm , and $\text{Pmc}2_1$. The lattice parameters were calculated from precession and Weissenberg photographs using $\text{Cu K}\alpha$ radiation and from measurements using a General Electric single-crystal orienter with $\text{Mo K}\alpha$ and $\text{Cr K}\alpha$ radiation. A least-squares lattice constant refinement program of Williams⁹ was employed to obtain the following values and estimated standard deviations: $a = 6.736 (0.003) \text{ \AA}$, $b = 5.96 (0.017) \text{ \AA}$, $c = 17.768 (0.004) \text{ \AA}$. The calculated density for four molecules per unit cell, 1.53 g/cm^3 , agrees favorably with the observed value of 1.51 g/cm^3 obtained by the flotation method in a mixture of benzene and carbon tetrachloride. On the basis of observed systematic extinctions not required by the space group symmetry along the a axis, together with a moderately well-grounded knowledge of the molecular structure, the Pmcm and P2cm space groups were eliminated as possibilities. (Elimination of Pmcm assumes that there is no disorder.)

Space requirements for the packing of the molecules also suggest the $\text{Pmc}2_1$ space group. Four molecules can be arranged in this space group and can account for the extra systematic extinction by placing a molecule on the $x = 0$ mirror and a crystallographically independent one on the $x = \frac{1}{2}$ mirror.

Collection and Treatment of Data. A full octant of three-dimensional X-ray diffraction intensity data was gathered at room

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Table I. Comparison of Calculated and Observed Structure Factors^a

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|-------|------|-----|----|------|------|----|-----|-----|----|------|-----|----|-----|-----|----|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|-----|----|----|----|----|----|----|
| L | FO | FC | 8 | 11 | 6 | 5 | 1 | L | 0 | 24 | 17 | 3 | 200 | 216 | 9 | 20 | 25 | 3 | 87 | 84 | 16 | 24 | 24 | 7 | 26 | 42 | 6 | 45 | 42 | | | | |
| 0 | 0 | 1 | 0 | 1 | 1 | 0 | 334 | 363 | 4 | 1158 | 148 | 6 | 2 | L | 4 | 5 | 125 | 126 | 11 | 55 | 45 | 5 | 40 | 72 | 18 | 13 | 11 | 9 | 0 | 15 | 8 | 32 | 22 |
| 4 | 424 | 433 | 0 | 25 | 1 | 0 | 76 | 73 | 5 | 179 | 162 | 0 | 45 | 46 | 6 | 84 | 78 | 12 | 0 | 16 | 6 | 44 | 35 | 19 | 35 | 40 | 10 | 33 | 30 | 6 | 34 | 29 | |
| 8 | 779 | 650 | 0 | 0 | 4 | 2 | 0 | 4 | 6 | 279 | 285 | 2 | 18 | 17 | 7 | 100 | 98 | 13 | 19 | 9 | 7 | 73 | 61 | 20 | 11 | 13 | 11 | 55 | 44 | 10 | 25 | 21 | |
| 14 | 73 | 78 | 2 | 937 | 939 | 4 | 111 | 107 | 8 | 55 | 65 | 4 | 75 | 72 | 9 | 155 | 153 | 8 | 3 | 1 | 9 | 79 | 73 | 2 | 5 | L | 13 | 26 | 14 | 12 | 0 | 7 | |
| 16 | 120 | 125 | 4 | 85 | 83 | 5 | 17 | 13 | 9 | 46 | 54 | 5 | 27 | 22 | 11 | 126 | 121 | 0 | 24 | 7 | 12 | 60 | 57 | 10 | 19 | 18 | 0 | 41 | 32 | 15 | 16 | 14 | |
| 18 | 0 | 30 | 5 | 140 | 117 | 6 | 0 | 0 | 10 | 140 | 134 | 6 | 0 | 31 | 21 | 12 | 57 | 56 | 13 | 19 | 13 | 45 | 30 | 2 | 59 | 60 | 17 | 27 | 16 | 1 | 7 | L | 0 |
| 20 | 60 | 55 | 6 | 274 | 284 | 7 | 29 | 36 | 11 | 134 | 141 | 7 | 40 | 37 | 13 | 126 | 121 | 0 | 15 | 7 | 12 | 53 | 50 | 4 | 31 | 17 | 11 | 55 | 44 | 10 | 25 | 21 | |
| 24 | 36 | 29 | 8 | 78 | 62 | 8 | 160 | 171 | 12 | 111 | 118 | 8 | 81 | 74 | 16 | 36 | 30 | 2 | 23 | 22 | 14 | 23 | 16 | 3 | 97 | 98 | 1 | 6 | 1 | 0 | 40 | 34 | |
| 1 | 0 | 1 | 10 | 458 | 448 | 9 | 0 | 2 | 13 | 110 | 106 | 9 | 40 | 33 | 15 | 41 | 40 | 3 | 20 | 23 | 15 | 55 | 41 | 4 | 5 | 118 | 121 | 1 | 6 | 1 | 0 | 40 | 34 |
| 0 | 0 | 5 | 12 | 112 | 106 | 10 | 0 | 8 | 14 | 143 | 147 | 10 | 15 | 11 | 16 | 16 | 4 | 0 | 3 | 16 | 3 | 17 | 5 | 118 | 121 | 1 | 6 | 1 | 0 | 40 | 34 | | |
| 21186 | 1082 | 16 | 67 | 70 | 13 | 28 | 26 | 17 | 56 | 61 | 13 | 17 | 13 | 19 | 25 | 20 | 7 | 7 | 13 | 19 | 46 | 36 | 8 | 0 | 10 | 2 | 50 | 45 | 4 | 75 | 31 | | |
| 4 | 56 | 53 | 17 | 61 | 84 | 14 | 32 | 33 | 18 | 45 | 40 | 14 | 26 | 17 | 20 | 15 | 8 | 11 | 5 | 4 | 1 | 10 | 42 | 42 | 4 | 20 | 27 | 5 | 0 | 20 | 0 | 20 | |
| 6 | 170 | 180 | 18 | 58 | 56 | 15 | 69 | 68 | 19 | 22 | 21 | 15 | 53 | 47 | 21 | 31 | 29 | 9 | 20 | 20 | 5 | 4 | 1 | 10 | 42 | 42 | 4 | 20 | 27 | 5 | 0 | 20 | |
| 8 | 86 | 76 | 19 | 23 | 6 | 16 | 39 | 42 | 15 | 12 | 16 | 39 | 27 | 22 | 0 | 16 | 10 | 0 | 4 | 0 | 11 | 10 | 11 | 29 | 35 | 5 | 32 | 32 | 7 | 25 | 22 | | |
| 10 | 442 | 438 | 20 | 23 | 15 | 17 | 0 | 9 | 21 | 30 | 31 | 17 | 0 | 15 | 23 | 30 | 27 | 0 | 4 | L | 0 | 11 | 10 | 12 | 0 | 29 | 7 | 28 | 31 | 9 | 22 | 4 | |
| 12 | 52 | 39 | 11 | 32 | 12 | 18 | 24 | 12 | 22 | 45 | 48 | 18 | 11 | 7 | 3 | 3 | 1 | 0 | 80 | 84 | 3 | 11 | 4 | 14 | 33 | 27 | 8 | 26 | 10 | 0 | 11 | | |
| 18 | 67 | 76 | 23 | 33 | 23 | 20 | 18 | 30 | 24 | 0 | 3 | 2 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 20 | 10 | 16 | 24 | 37 | 23 | 21 | 13 | 5 | 2 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 22 | 93 | 102 | 25 | 53 | 47 | 6 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| 24 | 36 | 23 | 1 | 1 | L | 0 | 11 | 12 | 0 | 99 | 84 | 2 | 24 | 21 | 0 | 5 | 0 | 158 | 168 | 1 | 161 | 141 | 2 | 11 | 10 | 12 | 0 | 11 | 10 | 12 | 0 | 11 | 10 |
| 2 | 0 | 1 | 0 | 1328 | 1262 | 0 | 11 | 12 | 0 | 119 | 116 | 3 | 15 | 18 | 4 | 88 | 82 | 3 | 131 | 129 | 6 | 21 | 19 | 18 | 0 | 22 | 20 | 5 | 12 | 20 | 5 | 12 | 20 |
| 0 | 839 | 818 | 1 | 187 | 176 | 2 | 117 | 122 | 3 | 357 | 344 | 5 | 16 | 22 | 6 | 0 | 12 | 7 | 80 | 63 | 10 | 26 | 29 | 0 | 29 | 8 | 16 | 8 | 13 | 1 | 13 | 3 | |
| 2 | 135 | 118 | 2 | 18 | 5 | 3 | 35 | 37 | 5 | 105 | 105 | 6 | 56 | 51 | 7 | 100 | 95 | 8 | 39 | 25 | 11 | 67 | 63 | 0 | 29 | 8 | 17 | 14 | 24 | 2 | 25 | 27 | |
| 6 | 46 | 52 | 3 | 214 | 200 | 4 | 0 | 9 | 6 | 70 | 84 | 7 | 36 | 18 | 8 | 72 | 72 | 9 | 7 | 189 | 185 | 12 | 25 | 18 | 2 | 23 | 17 | 2 | 6 | 1 | 4 | 7 | 25 |
| 12 | 380 | 391 | 6 | 34 | 34 | 6 | 95 | 93 | 6 | 187 | 186 | 9 | 18 | 25 | 10 | 68 | 65 | 10 | 57 | 52 | 13 | 24 | 28 | 2 | 23 | 17 | 2 | 6 | 1 | 4 | 7 | 25 | |
| 14 | 100 | 108 | 8 | 444 | 425 | 7 | 21 | 12 | 9 | 41 | 45 | 10 | 29 | 24 | 12 | 0 | 12 | 53 | 48 | 15 | 30 | 24 | 4 | 44 | 38 | 0 | 47 | 44 | 6 | 3 | 30 | | |
| 16 | 121 | 128 | 10 | 32 | 21 | 8 | 0 | 10 | 10 | 106 | 98 | 11 | 16 | 17 | 13 | 39 | 36 | 13 | 75 | 78 | 14 | 14 | 12 | 5 | 68 | 68 | 1 | 14 | 7 | 0 | 7 | 0 | |
| 18 | 33 | 27 | 11 | 22 | 22 | 11 | 2 | 27 | 28 | 10 | 11 | 12 | 27 | 28 | 14 | 33 | 32 | 14 | 74 | 65 | 17 | 11 | 24 | 6 | 13 | 12 | 2 | 9 | 14 | 8 | 11 | 15 | |
| 20 | 57 | 72 | 13 | 108 | 103 | 10 | 78 | 76 | 12 | 188 | 178 | 13 | 22 | 17 | 15 | 37 | 42 | 15 | 59 | 49 | 7 | 55 | 60 | 3 | 20 | 23 | 9 | 31 | 21 | 9 | 31 | 21 | |
| 22 | 0 | 16 | 14 | 62 | 51 | 11 | 0 | 15 | 13 | 61 | 59 | 14 | 51 | 36 | 16 | 43 | 42 | 16 | 40 | 36 | 6 | 4 | 1 | 5 | 26 | 32 | 4 | 38 | 37 | 10 | 21 | 20 | |
| 24 | 39 | 36 | 15 | 157 | 161 | 12 | 20 | 19 | 14 | 48 | 59 | 15 | 13 | 21 | 17 | 24 | 11 | 18 | 18 | 10 | 0 | 17 | 7 | 11 | 29 | 24 | 6 | 17 | 6 | 12 | 0 | 2 | |
| 3 | 0 | 1 | 17 | 35 | 20 | 14 | 66 | 62 | 16 | 69 | 73 | 17 | 21 | 22 | 22 | 48 | 40 | 20 | 25 | 32 | 2 | 16 | 6 | 14 | 13 | 9 | 8 | 28 | 11 | 0 | 7 | 1 | |
| 0 | 0 | 2 | 18 | 24 | 15 | 15 | 29 | 25 | 17 | 22 | 18 | 4 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 175 | 174 | 20 | 25 | 24 | 17 | 28 | 24 | 19 | 32 | 39 | 0 | 31 | 29 | 22 | 26 | 17 | 22 | 16 | 22 | 16 | 2 | 16 | 6 | 14 | 13 | 9 | 8 | 28 | 11 | 0 | 7 | 1 |
| 4 | 108 | 113 | 21 | 22 | 10 | 18 | 21 | 21 | 20 | 62 | 64 | 1 | 0 | 5 | 4 | 3 | 1 | 4 | 1 | 5 | 10 | 17 | 17 | 32 | 26 | 11 | 26 | 19 | 0 | 28 | 31 | 1 | 0 |
| 6 | 168 | 162 | 22 | 21 | 23 | 19 | 0 | 2 | 21 | 22 | 19 | 2 | 0 | 5 | 3 | 4 | 3 | 1 | 4 | 1 | 6 | 10 | 3 | 18 | 0 | 9 | 12 | 24 | 4 | 1 | 0 | 12 | |
| 8 | 119 | 121 | 23 | 44 | 43 | 7 | 1 | L | 3 | 20 | 23 | 5 | 0 | 10 | 1 | 76 | 74 | 0 | 0 | 13 | 8 | 0 | 7 | 4 | 5 | 1 | 14 | 21 | 6 | 3 | 11 | 4 | |
| 10 | 155 | 158 | 24 | 29 | 32 | 7 | 1 | L | 5 | 0 | 10 | 1 | 76 | 74 | 0 | 1 | 103 | 115 | 9 | 45 | 45 | 10 | 0 | 6 | 6 | 6 | 16 | 19 | 5 | 0 | 4 | 4 | |
| 14 | 301 | 298 | 2 | 1 | 1 | 0 | 77 | 85 | 3 | 2 | 1 | 6 | 10 | 7 | 2 | 75 | 75 | 2 | 79 | 89 | 10 | 0 | 0 | 6 | 6 | 6 | 16 | 19 | 5 | 0 | 4 | 4 | |
| 16 | 65 | 64 | 0 | 75 | 67 | 1 | 18 | 15 | 0 | 111 | 113 | 8 | 17 | 26 | 3 | 174 | 161 | 3 | 16 | 144 | 11 | 44 | 4 | 1 | 38 | 47 | 17 | 0 | 12 | 6 | 22 | 19 | |
| 18 | 76 | 65 | 0 | 175 | 167 | 2 | 17 | 6 | 0 | 111 | 113 | 8 | 17 | 26 | 4 | 49 | 49 | 4 | 15 | 29 | 12 | 0 | 13 | 2 | 2 | 17 | 2 | 9 | 14 | 8 | 11 | 15 | |
| 20 | 13 | 9 | 1 | 574 | 555 | 3 | 36 | 30 | 1 | 346 | 367 | 9 | 13 | 7 | 5 | 62 | 63 | 5 | 133 | 146 | 13 | 16 | 18 | 3 | 47 | 50 | 3 | 6 | L | 8 | 41 | 29 | |
| 22 | 90 | 93 | 4 | 113 | 98 | 5 | 0 | 5 | 3 | 9 | 9 | 11 | 42 | 33 | 6 | 67 | 68 | 6 | 33 | 38 | 14 | 20 | 17 | 4 | 0 | 5 | 0 | 5 | 10 | 0 | 13 | 2 | |
| 4 | 0 | 1 | 5 | 57 | 64 | 6 | 2 | 2 | 4 | 6 | 6 | 12 | 34 | 20 | 8 | 20 | 19 | 8 | 32 | 35 | 9 | 68 | 69 | 7 | 27 | 30 | 1 | 7 | 17 | 11 | 23 | 7 | |
| 0 | 532 | 555 | 8 | 27 | 20 | 8 | 62 | 65 | 6 | 164 | 148 | 9 | 2 | 1 | 10 | 16 | 21 | 10 | 69 | 68 | 0 | 0 | 5 | 9 | 28 | 31 | 4 | 6 | 1 | 4 | 7 | 1 | |
| 2 | 58 | 62 | 9 | 85 | 85 | 9 | 13 | 2 | 7 | 63 | 69 | 0 | 0 | 6 | 11 | 101 | 105 | 11 | 138 | 139 | 0 | 0 | 5 | 9 | 28 | 31 | 4 | 6 | 1 | 4 | | | |

Table II. Final Parameters and Standard Errors (in Parentheses) for $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$

| Atom | x/a | y/b | z/c | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|----------------|--------------------|---------------------|---------------------|--------------------|--------------------|--------------------|---------------------|--------------------|---------------------|
| Molecule 1 | | | | | | | | | |
| O ₁ | 0.0 | 0.1183 (0.0017) | -0.0816 (0.0005) | 0.0608 (0.0037) | 0.0601 (0.0043) | 0.0029 (0.0002) | 0.0 | 0.0 | 0.0011 (0.0008) |
| P | 0.0 | 0.0598 (0.0006) | 0.0 | 0.0279 (0.0007) | 0.0383 (0.0013) | 0.0026 (0.0001) | 0.0 | 0.9 | 0.0010 (0.0003) |
| O ₂ | 0.0 | 0.2632 (0.0011) | 0.0566 (0.0004) | 0.0336 (0.0022) | 0.0272 (0.0021) | 0.0035 (0.0002) | 0.0 | 0.0 | 0.0027 (0.0005) |
| O ₃ | 0.1829 (0.0009) | -0.0807 (0.0011) | 0.0253 (0.0003) | 0.0414 (0.0020) | 0.0528 (0.0023) | 0.0034 (0.0002) | 0.0097 (0.0018) | 0.0042 (0.0004) | 0.0010 (0.0006) |
| C ₁ | 0.0 | 0.2006 (0.0018) | 0.1341 (0.0006) | 0.0400 (0.0036) | 0.0249 (0.0031) | 0.0030 (0.0003) | 0.0 | 0.0 | -0.0012 (0.0008) |
| C ₂ | 0.1858 (0.0012) | -0.1473 (0.0015) | 0.1048 (0.0004) | 0.0340 (0.0024) | 0.0562 (0.0036) | 0.0032 (0.0002) | 0.0155 (0.0023) | 0.0020 (0.0006) | 0.0031 (0.0007) |
| C ₃ | 0.0 | -0.0538 (0.0019) | 0.1430 (0.0005) | 0.0212 (0.0021) | 0.0352 (0.0034) | 0.0021 (0.0002) | 0.0 | 0.0 | -0.0013 (0.0008) |
| C ₄ | 0.0 | -0.1217 (0.0021) | 0.2280 (0.0006) | 0.0377 (0.0034) | 0.0527 (0.0055) | 0.0031 (0.0003) | 0.0 | 0.0 | 0.0050 (0.0010) |
| Molecule 2 | | | | | | | | | |
| O | 0.5 | 0.3946 (0.0017) | 0.1672 (0.0004) | 0.0451 (0.0029) | 0.0703 (0.0046) | 0.0023 (0.0002) | 0.0 | 0.0 | -0.0003 (0.0081) |
| P | 0.5 | 0.4392 (0.0006) | 0.2466 (0.0002) | 0.0247 (0.0007) | 0.0396 (0.0012) | 0.0022 (0.0001) | 0.0 | 0.0 | -0.0001 (0.0003) |
| O ₂ | 0.5 | 0.6960 (0.0013) | 0.2681 (0.0004) | 0.0414 (0.0028) | 0.0336 (0.0025) | 0.0041 (0.0003) | 0.0 | 0.0 | 0.0042 (0.0007) |
| O ₃ | 0.3157 (0.0010) | 0.3443 (0.0011) | 0.2913 (0.0003) | 0.0369 (0.0019) | 0.0655 (0.0029) | 0.0043 (0.0002) | -0.0232 (0.0019) | 0.0009 (0.0005) | -0.0024 (0.0006) |
| C ₁ | 0.5 | 0.7475 (0.0022) | 0.3500 (0.0006) | 0.0430 (0.0041) | 0.0401 (0.0044) | 0.0033 (0.0003) | 0.0 | 0.0 | 0.0014 (0.0010) |
| C ₂ | 0.3185 (0.0011) | 0.3868 (0.0015) | 0.3710 (0.0004) | 0.0302 (0.0021) | 0.0481 (0.0033) | 0.0036 (0.0003) | -0.0172 (0.0022) | 0.0006 (0.0006) | -0.0001 (0.0007) |
| C ₃ | 0.5 | 0.5230 (0.0017) | 0.3902 (0.0006) | 0.0239 (0.0024) | 0.0286 (0.0032) | 0.0037 (0.0003) | 0.0 | 0.0 | 0.0003 (0.0008) |
| C ₄ | 0.5 | 0.5726 (0.0025) | 0.4769 (0.0005) | 0.0336 (0.0030) | 0.0678 (0.0059) | 0.0022 (0.0002) | 0.0 | 0.0 | -0.0051 (0.0010) |

istic radiation,¹⁰ and crystal decomposition. No absorption correction was applied because of the small linear absorption coefficient (2.18 cm^{-1}) and the corresponding small difference between the transmission extremes.

An estimate of the standard deviation of the intensity for each reflection was computed by means of the following expression

$$\sigma_I^2 = \text{TC} + \text{Bg} + (0.05\text{TC})^2 + (0.05\text{Bg})^2 + (0.10\text{St})^2$$

TC, Bg, and St refer to total counts, background, and streak, respectively. The last three terms represent estimates of nonstatistical systematic errors in their values.¹⁰ For those reflections for which the corrected intensity was greater than zero, a standard deviation

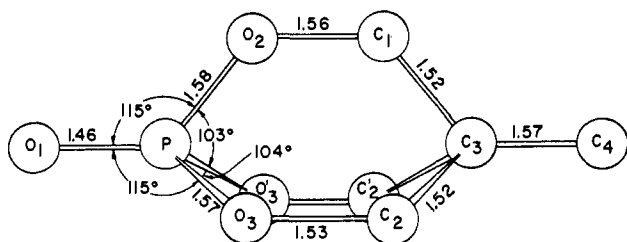


Figure 1. The molecular configuration of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$. The distances and angles are averages of the two crystallographically independent molecules of the asymmetric unit.

for the observed structure factor was computed by means of the expression, $\sigma_F = \sigma_I F_o / 2I$. The rest of the unobserved reflections were given σ_F values which were representative of the small but nonzero F_o values.

(10) Streak was calculated using 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).

Structure Determination. The space group $\text{Pmc}2_1$ permits an arbitrary origin with respect to z . Assuming the molecules lie on the mirrors at $x = 0$ and $x = 1/2$, by the reasoning referred to previously, a phosphorus of one of the molecules was fixed with respect to x and z . A sharpened Patterson map and packing considerations aided in proposing an orientation for each of the independent molecules which was substantiated in subsequent refinement of the structure. A full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, using a program of Fitzwater¹¹ on an IBM 7074 computer was initiated on part of the proposed model. Subsequent electron density computations with a program of Ledet¹² and further least-square refinement gradually suggested the inclusion of the remainder of the atoms. The structure factor calculations used Hartree-Fock-Slater atomic scattering factors.¹³ Final refinement was done anisotropically on all atoms. The final residual factor ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) for relating 108 positional and thermal parameters to 781 observed reflections was 0.082. The weighted R factor ($R_{wt} = \sum |F_o/\sigma| - |F_c/\sigma| / \sum |F_o/\sigma|$) was 0.078. The total 1191 reflections used in the refinement yielded an unweighted R factor of 0.121 and a weighted R factor of 0.105. A list of these calculated and observed structure factors is given in Table I. The final positional and thermal parameters and their standard errors are given in Table II.

Structures. The molecular structure of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ is shown in Figure 1. The interatomic distances, angles, and their errors were computed using the complete variance-covariance matrix with a program of Busing, Martin, and Levy.¹⁴ The results of these computations are listed in Tables III and IV. The two molecules in the asymmetric unit are crystallographically independent. It is felt, however, that the molecules are structurally equivalent, and that averaging corresponding distances and angles

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Table III. Individual and Averaged Interatomic Distances and Their Standard Errors

| Atoms | Molecule 1 | | Molecule 2 | | Av dist, Å | Av std error |
|--------------------------------|------------|-----------|------------|-----------|------------|--------------|
| | Dist, Å | Std error | Dist, Å | Std error | | |
| P-O ₁ | 1.491 | 0.017 | 1.436 | 0.015 | 1.464 | 0.016 |
| P-O ₂ | 1.575 | 0.016 | 1.577 | 0.018 | | |
| P-O ₃ | 1.556 | 0.012 | 1.578 | 0.012 | 1.574 | 0.015 |
| O ₂ -C ₁ | 1.425 | 0.022 | 1.488 | 0.024 | | |
| O ₃ -C ₂ | 1.467 | 0.017 | 1.439 | 0.017 | 1.455 | 0.020 |
| C ₁ -C ₃ | 1.524 | 0.028 | 1.516 | 0.030 | | |
| C ₂ -C ₃ | 1.528 | 0.018 | 1.506 | 0.018 | 1.519 | 0.024 |
| C ₃ -C ₄ | 1.565 | 0.023 | 1.569 | 0.024 | | |
| P-C ₃ | 2.629 | 0.017 | 2.599 | 0.019 | 2.614 | 0.018 |

Table IV. Individual and Averaged Bond Angles and Their Standard Errors^a

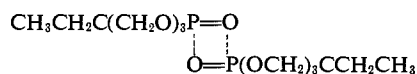
| Atoms ^b | Molecule 1 | | Molecule 2 | | Av angle | Av std error |
|--|------------|-----------|------------|-----------|----------|--------------|
| | Angle | Std error | Angle | Std Error | | |
| O ₁ -P-O ₂ | 116.2 | 1.0 | 114.6 | 0.9 | 115.0 | 0.8 |
| O ₁ -P-O ₃ | 114.0 | 0.5 | 115.3 | 0.7 | | |
| O ₂ -P-O ₃ | 103.3 | 0.6 | 103.1 | 0.6 | 103.7 | 0.6 |
| O ₃ -P-O ₃ ' | 104.7 | | 103.8 | | | |
| P-O ₂ -C ₁ | 114.5 | 1.2 | 115.9 | 1.2 | 115.2 | 1.1 |
| P-O ₃ -C ₂ | 115.7 | 0.9 | 114.9 | 0.9 | | |
| O ₂ -C ₁ -C ₃ | 111.1 | 1.4 | 106.1 | 1.8 | 108.7 | 1.4 |
| O ₃ -C ₂ -C ₃ | 108.5 | 1.2 | 109.2 | 1.2 | | |
| C ₁ -C ₃ -C ₂ | 108.5 | 1.2 | 111.6 | 1.2 | 109.6 | 1.2 |
| C ₂ -C ₃ -C ₂ ' | 109.9 | | 108.5 | | | |
| C ₁ -C ₃ -C ₄ | 111.0 | 1.6 | 107.2 | 1.9 | 109.2 | 1.5 |
| C ₂ -C ₃ -C ₄ | 109.5 | | 108.9 | 1.1 | | |

^a Angles in degrees. ^b Primes refer to atoms related by the mirrors to the unprimed designation.

is appropriate. The packing environment for each molecule is very nearly identical. These averages are also included in Tables III and IV.

Discussion

Molecular association in the form of dimers as shown has been postulated by Neunhoeffer and Maiwald for the related phosphate $\text{OP}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$ from cryoscopic measurements in benzene.¹⁵ In addition to the lack of any such behavior in the crystal structure re-



ported here, further evidence for the lack of association of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ ⁴ and $\text{OP}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ stems from the proton nmr absorptions of these compounds in deuteriochloroform which remain quite constant upon dilution. Furthermore, our molecular weight measurements on $\text{OP}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ obtained over a range of concentrations in benzene and chloroform revealed only monomeric behavior as shown in Table V. Because of the insufficient solubility of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ in benzene and chloroform, similar molecular weight measurements could not be carried out. However, it was found previously that $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ is monomeric in nitrobenzene by cryoscopic means.¹⁶ Thus these molecules are evidently monomeric under most conditions in spite of their high dipole moments (ca. 4 D).¹⁷

(15) O. Neunhoeffer and W. Maiwald, *Chem. Ber.*, **95**, 108 (1962).

(16) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

Table V. Molecular Weight Determinations of $\text{OP}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ ^{a,b}

| Solvent | No. of detn | Concn ranges, M | Found av mol wt |
|------------|-------------|--------------------------|-----------------|
| Benzene | 8 | 0.005-0.021 ^c | 181 ± 4 |
| Chloroform | 4 | 0.006-0.027 | 183 ± 2 |

^a Measurements were carried out at 25° on a Mechrolab Model 301A vapor pressure osmometer using benzil as a standard. ^b Calculated molecular weight is 178. ^c The upper limit represents near-saturation.

On the basis of P³¹ nmr experiments carried out earlier in our laboratories, it was indicated that the chemical shift data for the phosphite $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ was consistent with an O-P-O bond angle of 104°⁵ using the calculations of Parks for three-covalent phosphorus systems.¹⁸ At present, similar predictions of bond angles from P³¹ resonance data have not been extended to four-coordinate phosphorus compounds such as $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$. Because of the constrained nature of these molecules, however, it is probable that bond-angle changes within the cage will be small from $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ to $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$. This assumption gains support from the fact that the O-P-O bond angle increases by only 2.5° from P₄O₆ to P₄O₁₀.^{19,20} Thus the observed bond angle of 103.7° in $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ compares very favorably with the approximate angle of 104° calculated for $\text{P}(\text{OCH}_2)_3\text{CCH}_3$. Because the Parks calculation involves an exponential term, the O-P-O bond angle is very sensitive to the third significant figure of the electronegativity of the alkoxy groups. Inasmuch as this group electronegativity is not known and that of oxygen necessarily substituted,⁴ the above arguments are rendered somewhat tenuous.

The O=P and P-O bond distances in $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ are within experimental error of those in the only other trialkyl phosphates $\text{OP}(\text{OCH}_2)_2(\text{OCH}_3)$ and $\text{OP}(\text{OC}(\text{CH}_3)_2)_2(\text{OCH}_3)$ whose structures are known.²¹ If there are differences in π bonding present in these O=P and P-O links, it is not evident from their bond lengths. Because of the five-membered ring and an unconstrained OCH₃ group in the two monocyclic phosphates cited above, the O-P-O and P-O-C bond angles are different from those in $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ which consists of six-membered rings. Thus the O-P-O and P-O-C bond angles in the strained five-membered ring phosphates are about 99 and 112°, respectively, whereas in $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ some of the strain is relieved by increasing these angles to about 104 and 115°, respectively. If the O-P-O and P-O-C bond angles in $\text{OP}(\text{OCH}_2\text{C}_6\text{H}_5)_2(\text{OH})$ (about 104 and 120°, respectively²²) can be assumed to be representative of strainless angles of this type, some evidence of strain is present in $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ in the 115° POC angles. The average P-O bond lengths and OPO bond angles in $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$ are also very similar

(17) T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

(18) J. R. Parks, *J. Am. Chem. Soc.*, **79**, 757 (1957).

(19) G. C. Hampson and A. J. Stosick, *ibid.*, **60**, 1814 (1938).

(20) L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.*, **5**, 626 (1937).

(21) M. G. Newton, J. R. Cox, and J. A. Bertrand, *J. Am. Chem. Soc.*, **88**, 1503 (1966).

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

Table VI. Phosphoryl Oxygen Stretching Modes for Trialkyl Phosphates in Solution

| Compound | $\nu_{\text{O=P}}$, cm^{-1} | Ref |
|--|---------------------------------------|-----|
| OP(O- <i>n</i> -C ₄ H ₉) ₃ | 1260 | g |
| OP(OC ₂ H ₅) ₃ | 1265 | b |
| OP(OCH ₃) ₃ | 1281 | b |
| OP[OC(CH ₃) ₂] ₂ (OCH ₃) | 1290 | c |
| OP(OCH ₂) ₂ (OCH ₃) | 1300 | d |
| OP(OCH ₂) ₂ C(CH ₃) ₂ (OCH ₃) | 1311 | e |
| OP(OCH ₂) ₃ C(CH ₂) ₄ CH ₃ ^a | 1319 | g |
| OP(OCH ₂) ₂ CH | 1340 | f |

^a Although OP(OCH₂)₃CCH₃ is too insoluble for a solution measurement of the O=P frequency, it is expected to be nearly the same as for the more soluble OP(OCH₂)₃C(CH₂)₄CH₃. ^b F. S. Mortimer, *Spectrochim. Acta*, **9**, 270 (1957). ^c M. G. Newton, private communication. ^d F. Westheimer, private communication. ^e To be published. ^f D. B. Denney and S. L. Varga, *Tetrahedron Letters*, 4935 (1966).

to those found in the adamantane thiophosphate SP-(OCH)₃(CH₂)₃ (1.58 Å and 105°, respectively).²³

(23) P. Anderson and K. E. Hjortaa, *Acta Chem. Scand.*, **14**, 829 (1960).

From Table VI, it can be seen that the center of the band assigned to the O=P stretching mode ranges from 1260 to 1340 cm^{-1} in trialkyl phosphates. Only three O=P bond distances are known for such compounds: OP(OCH₂)₃CCH₃ (1.46 Å), OP(OCH₂)₂(OCH₃) (1.44 Å),²¹ and OP[OC(CH₃)₂]₂(OCH₃) (1.44 Å).²¹ Unfortunately, the uncertainties in these lengths and the O=P frequencies are on the order of the differences, making conclusions concerning a bond-order-bond-length correlation impossible. From a consideration of the gross structures of the phosphates in Table VI, however, it is apparent that there is a general increase in $\nu_{\text{O=P}}$ from open-chain (1260–1281 cm^{-1}) to monocyclic (1290–1311 cm^{-1}) to bicyclic (1319–1340 cm^{-1}) systems. That a decrease in the metal extraction properties of the phosphoryl oxygen parallels an increase in $\nu_{\text{O=P}}$ has been observed by Burdett and Burger.²⁴ From these results and the abnormally high $\nu_{\text{O=P}}$ value for OP(OCH₂)₃C(CH₂)₄CH₃ in Table VI, it is reasonable that this bicyclic phosphate was found to have no observable extraction ability.⁸ It is not clear at present what the causes of these trends are, and further studies are in progress in an effort to resolve this question.

(24) J. L. Burdett and L. L. Burger, *Can. J. Chem.*, **44**, 111 (1966).

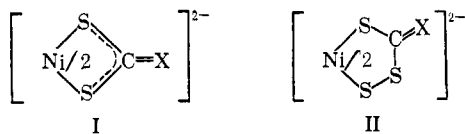
Sulfur Chelates. VIII.¹ Oxidative Addition of Sulfur to Dithioaryl Acid Complexes of Nickel(II) and Zinc(II)

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received December 27, 1967

Abstract: Sulfur-rich dithio aromatic acid complexes of nickel(II) and zinc(II) are described. The oxidative addition of sulfur to dithio aromatic acid nickel(II) complexes leads to the addition of one sulfur atom per chelate ring. The bis(perthio acid)nickel(II) species is achieved by metathesis starting with the perthio acid–zinc(II) complex. Evidence is presented that suggests the sulfur addition and abstraction reactions are metal ion influenced and that the perthiodithio mixed-ligand–nickel(II) complex contains both four- and five-membered chelate rings.

The oxidation of thiols to disulfides^{2,3} and the reductive abstraction of sulfur from disulfides by triphenylphosphine^{4,5} are well-known reactions in the chemistry of organic sulfur compounds. Recently⁶ we have described formally similar reactions involving anionic 1,1-dithiolate complexes of some group VIII metals. Certain of these complexes, I (X = S, NCN,



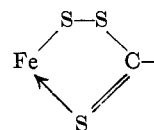
CH(NO₂), etc.), are oxidized chemically or with sulfur or polysulfides to sulfur-rich species which appear to be formulated as II. These complexes are reduced⁶ by triphenylphosphine to the original dithiolates.

In an earlier communication we demonstrated⁷ that the species originally formulated⁸ by Hieber and Brück as tetrakis(dithiobenzoato)- μ -dithio-dinickel(IV) is a ligand-oxidized nickel(II) species.^{8a} We have shown that this complex, III (R = H or CH₃, M = Ni(II)),

(7) J. P. Fackler, Jr. and D. Coucouvanis, *ibid.*, **89**, 1745 (1967).

(8) W. Hieber and R. Brück, *Z. Anorg. Allg. Chem.*, **269**, 13 (1952).

(8a) NOTE ADDED IN PROOF. D. Coucouvanis and S. Lippard, private communication, have shown conclusively using X-ray crystallography that Fe(S₂CC₆H₅)₂(S₃CC₆H₅) contains a



ring.

(1) Part VI: D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, **6**, 2047 (1967).

(2) F. H. McMillan and J. A. King, *J. Amer. Chem. Soc.*, **70**, 4143 (1948).

(3) M. Schmidt and W. Siebert, *Angew. Chem.*, **78**, 607 (1966).

(4) A. Schonberg and M. Z. Barakat, *J. Chem. Soc.*, 892 (1949).

(5) A. A. Watson, *ibid.*, 2100 (1964).

(6) D. Coucouvanis and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **89**, 1346 (1967).