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The Crystal and Molecular Structure of Bis(O,O'-diisopropylphosphorothionyl) Disulfide, $[(i\text{-}C_3H_7O)_2PS_2]_2$

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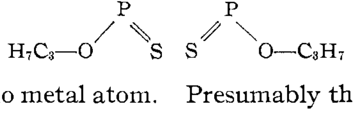
Received March 6, 1970

Bis(O,O'-diisopropylphosphorothionyl) disulfide, $[(i\text{-}C_3H_7O)_2PS_2]_2$, crystallizes in the triclinic space group $P\bar{1}$ (C_i^1) with unit cell parameters $a = 8.412 \pm 0.002$ Å, $b = 8.471 \pm 0.002$ Å, $c = 8.259 \pm 0.002$ Å, $\alpha = 110.79 \pm 0.02°$, $\beta = 94.86 \pm 0.02°$, $\gamma = 97.91 \pm 0.02°$. The observed and calculated densities are 1.30 ± 0.02 and 1.313 ± 0.002 g/cm^3 (for $Z = 1$ molecule/unit cell), respectively. The structure was refined by least-squares methods to a final conventional R index of 0.059 using three-dimensional X-ray diffraction counter data. The molecule possesses a crystallographic center of symmetry. Its backbone consists of a planar zigzag array of S=P—S—S—P=S linkages about a straight line passing more or less through the midpoint of each of the five bonds. About each tetrahedrally coordinated phosphorus are two OC_3H_7 groups oriented such that each $P(OC_3H_7)_2$ is centrosymmetrically related about the midpoint of the S—S bond. The methyl groups have staggered conformations with respect to the C—H bonds radiating from the vertex carbon atoms. Important parameters are as follows: S—S, 2.109 ± 0.004 Å; P—S, 2.072 ± 0.002 Å; P=S, 1.908 ± 0.003 Å; P—O, 1.561 ± 0.005 Å (average); P—S—S, $100.5 \pm 0.1°$; S=P—S, $104.8 \pm 0.1°$; O—P—O, $96.6 \pm 0.2°$. Correction of the phosphorus–sulfur and phosphorus–oxygen bond lengths for thermal effects, using the Busing–Levy model of sulfur and oxygen "riding" on phosphorus, results in increases ranging from 0.008 to 0.015 Å.

Introduction

Recently several metal O,O'-dialkylphosphorodithioates have been investigated by X-ray diffraction. Structures reported thus far include those of nickel,[1-4] zinc,[5,6] cadmium,[5] lead,[7] tellurium,[8] and potassium.[9] In all cases, except that of ionic potassium, the molecules consist of $(RO)_2PS_2$ ligands coordinated to the metal through the sulfur atoms. Owing to the widely differing coordination characteristics of the metal atoms, wide variations in the stereochemistry of the complexes result. Monomers, dimers, and polymers, for example, have been found. Moreover, the phosphorus–sulfur bonds within the phosphorodithioate ligands have been shown to be strongly influenced by the metal atom. This strong metal influence has been observed to have a marked effect on the properties of the materials as antioxidants and lubricating oil additives.[10]

In view of the conspicuous variability induced in the dialkylphosphorodithioates by the metal atom, it is of interest to examine the derivative



containing no metal atom. Presumably this compound commits the various phosphorus–sulfur bonds to adopt their extreme single- or double-bond characters. It should therefore serve as a useful reference.

Experimental Section

Preparation.—Bis(O,O'-diisopropylphosphorothionyl) disulfide, abbreviated $(dtp)_2$, was prepared as described elsewhere.[10c] Yellow prismatic crystals for use in the X-ray investigation were obtained by recrystallization of the compound from a warm ethanol–acetone mixture.

Crystal Data.—Bis(O,O'-diisopropylphosphorothionyl) disulfide, $[(i\text{-}C_3H_7O)_2PS_2]_2$, of formula weight 426.56, has the following characteristics: triclinic, space group $P\bar{1}$ (C_i^1); lattice parameters at 24° are $a = 8.412 \pm 0.002$ Å, $b = 8.471 \pm 0.002$ Å, $c = 8.259 \pm 0.002$ Å, $\alpha = 110.79 \pm 0.02°$, $\beta = 94.86 \pm 0.02°$, $\gamma = 97.91 \pm 0.02°$, $V = 539.3 \pm 0.6$ Å^3; $d_{\text{obsd}} = 1.30 \pm 0.02$ g/cm^3 (by flotation) and $d_{\text{calcd}} = 1.313 \pm 0.002$ g/cm^3 for $Z = 1$ formula unit/unit cell.

The assigned triclinic symmetry resulted from an examination of Weissenberg and precession X-ray photographs. Of the two possible space groups P1 and $P\bar{1}$, the centrosymmetric space group was initially indicated on the basis of intensity statistics,[11] from an analysis of the Patterson function utilizing the superposition technique, and later confirmed by the successful refinement of the derived structure. The lattice parameters were determined by a least-squares fit[12] to 111 independent pairs of high-angle $K\alpha$ reflections measured from zero-level Weissenberg zones taken with copper radiation [$\lambda(K\alpha_1)$ 1.54050 Å and $\lambda(K\alpha_2)$ 1.54434 Å] using crystals mounted in three different orientations; each film was calibrated with superimposed aluminum powder lines ($a_0 = 4.0330$ Å). The Nelson–Riley extrapolation function was employed in the refinement. Indicated errors in the cell parameters are 2σ. The observed lattice parameters correspond to the Niggli reduced cell. No symmetry higher than primitive triclinic was detected; the lack of higher symmetry

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was subsequently verified by the computer program TRACER II.[13]

Collection and Reduction of X-Ray Intensity Data.—Complete three-dimensional X-ray diffraction intensity data were taken at room temperature with zirconium-filtered molybdenum Kα radiation from a crystal of dimensions 0.12 × 0.17 × 0.17 mm. The crystal was mounted in a 0.3-mm Lindemann glass capillary with a^* (a 0.17-mm axis) coincident with the ϕ axis of the diffractometer. The half-widths of a number of narrow-source, open-counter 2θ scans[14] ranged from 0.03 to 0.06° θ, indicating that the crystal mosaicity was acceptably small. A General Electric quarter-circle Eulerian cradle mounted on a Siemens diffractometer equipped with a Siemens scintillation detector and a pulse height discriminator was used with the moving-crystal, moving-counter measurement technique (θ–2θ coupling) and a 3.5° takeoff angle. The receiving aperture size selected to minimize extraneous background was 5.5 mm wide by 5.5 mm high. The counter angle, 2θ, was scanned over 2° at a speed of 1°/min. Background counts of 24 sec were taken at each end of the 2θ scan. All scans were recorded on a chart recorder to provide visual evidence for the existence of observed reflections, proper peak shape, reflection centering in 2θ, and nonoverlap of adjacent reflections. A total of 2644 intensities in the range $2\theta \leq 55°$ were collected. Of these, 83 were symmetry related to others and were averaged; the deviation from the average for equivalent pairs did not exceed 6% for those reflections with $F_o > 3\sigma(F_o)$. Three standard reflections were measured periodically as a check on crystal decomposition and a total 3% decrease in intensities was observed.

The raw intensity of each reflection was corrected for background, crystal decomposition, Lorentz, and polarization effects. Transmission factors ranged from 0.91 to 0.93 based on a linear absorption coefficient of 5.84 cm^{-1}; no absorption corrections were therefore applied. Standard deviations were assigned to the intensities as described by Corfield, Doedens and Ibers,[15] using a value of 0.03 for p. The estimated standard deviation in each F_o was calculated by employing the method of finite differences.[16] A total of 1290 reflections were observed above the background level, of which 1073 had $F_o^2 \geq \sigma(F_o^2)$. Those with $F_o^2 < \sigma(F_o^2)$ were considered as unobserved and thus were omitted from the refinements.

Solution and Refinement of the Structure

The structure was solved using Patterson superposition and Fourier techniques.[17] Two successive superpositions of an unsharpened Patterson function revealed a direct image of the phosphorus–sulfur–oxygen framework with an indicated C_i symmetry. A series of three-dimensional electron density functions (F_o and $F_o - F_c$) and isotropic least-squares refinements in the space group $P\bar{1}$ led to the location of all remaining nonhydrogen atoms in the structure.

The structure was refined by using a full-matrix least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and w is the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral atoms tabulated by Hanson, *et al.*,[18] were used. Effects of anomalous scattering of S and P were included in the structure factor calculations,[19] using values for $\Delta f'$ and $\Delta f''$ given in ref 20. The best fully weighted isotropic refinement of all 11 atoms plus the scale factor resulted in $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.108$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.107$. A difference Fourier map calculated at this stage revealed anisotropic vibrational patterns of all 11 atoms which seemed physically reasonable. A subsequent refinement in which ellipsoidal thermal parameters were introduced for sulfur and phosphorus reduced R_1 and R_2 to 0.082 and 0.086, respectively; extension of anisotropic refinement to oxygen and carbon reduced R_1 and R_2 still further to 0.073 and 0.076, respectively.

Careful analysis of a new difference Fourier map revealed the location of all 14 independent hydrogen atoms, with the methyl groups oriented to adopt staggered conformations with respect to the C–H bonds radiating from the vertex carbon atoms. Inclusion of the positional and isotropic thermal parameters of these atoms in the refinement resulted in $R_1 = 0.058$ and $R_2 = 0.051$. The refined isotropic temperature values were in the range 1.1–7.4 Å^2. The C–H distances ranged from 0.85 to 1.11 Å and the C–C–H and H–C–H angles from 86 to 127°.[21–24] In keeping with the belief that constraints imposed upon the carbon–hydrogen bond lengths and methyl group geometries are to be preferred on physical grounds, idealized hydrogen coordinates were computed assuming an average C–H bond length of 0.98 Å and an H–C–H bond angle of 109° 28′. The methyl groups were rotated to give perfect staggered conformations with respect to the C–H bonds radiating from the vertex carbon atoms, in best agreement with the refined positions. These hydrogen atoms were included in the final cycles of refinement as fixed atoms with average isotropic temperature factors of 4.5 Å^2.

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(14) In the region examined, $2\theta < 15°$, the 2θ-scan and ω-scan techniques yield comparable results: T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

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(17) In addition to various local programs for the CDC 1604B computer, local modifications of the following programs were used in the solution and refinement of this structure: Guggenberger's FOUR Fourier program; Busing, Martin, and Levy's ORFLS crystallographic least-squares program; Busing and Levy's ORFFE function and error program; and Johnson's ORTEP thermal ellipsoid plotting program.

(18) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(19) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(20) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

(21) Although these wide variations showed no discernible trend with location of the atoms in the molecule, this distribution was believed to result from combined effects of anisotropic thermal motion of the carbon atoms and from random errors in the intensity data. The apparent shortening of the carbon–hydrogen bond relative to the true mean *internuclear* distance of 1.11 Å found in electron diffraction studies[22] is typical of X-ray analyses[23] and is associated with the concentration of the bonding electron density between the nuclei.[24]

(22) See, for example: (a) R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959); (b) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *ibid.*, **81**, 4765 (1959); (c) L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.*, **33**, 1254 (1960); (d) L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *ibid.*, **35**, 1211 (1961); (e) K. Kuchitsu and L. S. Bartell, *J. Phys. Soc. Jap., Suppl. B-II*, **17**, 23 (1962); (f) L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965); (g) L. S. Bartell, E. A. Roth, and C. D. Hollowell, *ibid.*, **42**, 2683 (1965); (h) L. S. Bartell and B. L Carroll, *ibid.*, **42**, 3076 (1965); (i) E. J. Jacob, H. B. Thompson, and L. S Bartell, *ibid.*, **47**, 3736 (1967); (j) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

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TABLE I

FINAL POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS FOR $[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Iso equiv[c] B, Å^2
S(1)	−0.06668 (25)	0.09768 (26)	0.05566 (24)	187 (4)	184 (4)	122 (4)	82 (3)	17 (3)	49 (3)	4.07
S(2)	−0.31482 (25)	0.28251 (25)	−0.08527 (27)	169 (4)	165 (4)	240 (5)	71 (3)	28 (3)	68 (4)	4.67
P(1)	−0.18715 (22)	0.10855 (22)	−0.16851 (23)	120 (3)	125 (3)	127 (4)	24 (3)	10 (3)	46 (3)	3.10
O(1)	−0.05855 (50)	0.12949 (52)	−0.28902 (53)	140 (8)	136 (9)	161 (9)	−7 (7)	30 (7)	53 (7)	3.71
O(2)	−0.27246 (49)	−0.07672 (51)	−0.28840 (54)	127 (8)	135 (9)	170 (9)	−2 (7)	40 (7)	32 (7)	3.77
C(1)	0.0567 (8)	0.2898 (8)	−0.2419 (9)	147 (14)	140 (14)	206 (16)	−16 (11)	18 (12)	70 (12)	4.2
C(2)	−0.4122 (9)	−0.1659 (9)	−0.2404 (9)	149 (14)	174 (15)	180 (16)	−13 (12)	45 (12)	31 (12)	4.5
C(3)	0.0104 (11)	0.3710 (11)	−0.3696 (13)	260 (20)	262 (21)	428 (28)	2 (16)	14 (19)	234 (20)	7.3
C(4)	0.2222 (9)	0.2402 (10)	−0.2552 (11)	170 (15)	214 (17)	297 (21)	9 (13)	42 (14)	111 (16)	5.5
C(5)	−0.5605 (9)	−0.1706 (11)	−0.3588 (12)	126 (14)	282 (21)	372 (25)	8 (14)	12 (15)	107 (18)	6.5
C(6)	−0.3788 (10)	−0.3408 (10)	−0.2610 (11)	210 (17)	182 (17)	350 (24)	−6 (14)	34 (16)	103 (16)	6.2

[a] All atoms are in the general symmetry position (2i). Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter. [b] The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β's and their estimated standard deviations have been multiplied by 10^4. [c] Calculated from the anisotropic thermal parameters by the equation $B \cong {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab\cos\gamma + 2\beta_{13}ac\cos\beta + 2\beta_{23}bc\cos\alpha)$: W. C. Hamilton. *Acta Crystallogr.*, **12,** 609 (1959).

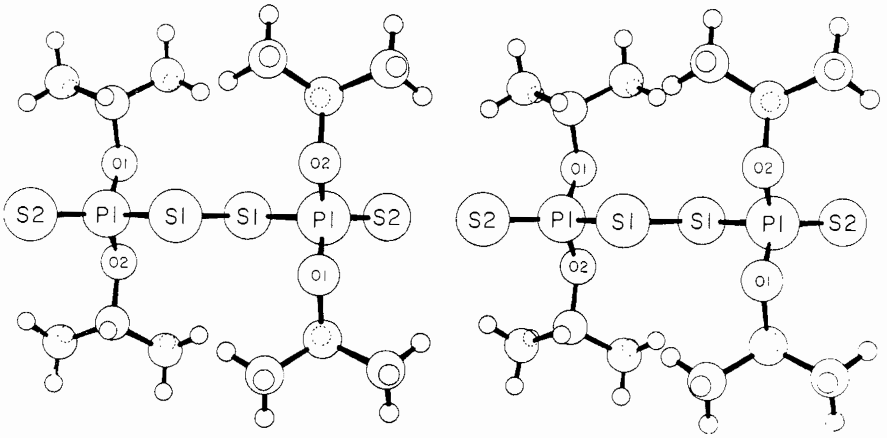

Figure 1.—A stereographic view of the $[(i\text{-}C_3H_7O)_2PS_2]_2$ molecule parallel to the P_2S_4 plane.

TABLE II

FINAL POSITIONAL PARAMETERS FOR HYDROGEN IN $[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Atom	x	y	z
H(1)	0.051	0.366	−0.122
H(2)	−0.424	−0.103	−0.118
H(3)	0.016	0.293	−0.489
H(4)	−0.100	0.393	−0.361
H(5)	0.085	0.479	−0.342
H(6)	0.226	0.164	−0.375
H(7)	0.305	0.344	−0.224
H(8)	0.243	0.181	−0.175
H(9)	−0.549	−0.234	−0.481
H(10)	−0.657	−0.228	−0.329
H(11)	−0.573	−0.053	−0.344
H(12)	−0.367	−0.404	−0.383
H(13)	−0.278	−0.329	−0.185
H(14)	−0.469	−0.404	−0.228

[a] Based on C–H = 0.98 Å.

TABLE III

FINAL ROOT-MEAN-SQUARE THERMAL AMPLITUDES OF VIBRATION (Å) IN $[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Atom	Min	Med	Max
S(1)	0.190 (3)	0.202 (3)	0.279 (3)
S(2)	0.193 (3)	0.256 (3)	0.274 (3)
P(1)	0.190 (3)	0.195 (3)	0.208 (3)
O(1)	0.184 (7)	0.216 (6)	0.246 (6)
O(2)	0.188 (7)	0.204 (6)	0.258 (6)
C(1)	0.181 (11)	0.246 (10)	0.254 (10)
C(2)	0.201 (11)	0.216 (10)	0.287 (10)
C(3)	0.210 (12)	0.298 (12)	0.379 (12)
C(4)	0.224 (11)	0.269 (10)	0.296 (10)
C(5)	0.207 (12)	0.301 (11)	0.338 (11)
C(6)	0.218 (11)	0.288 (11)	0.324 (11)

[a] An indication of the directions of these principal axes of vibration is given in Figure 3.

Convergence was reached with $R_1 = 0.059$ and $R_2 = 0.053$ for the 1073 observed reflections. Corresponding values for all 1290 reflections were $R_1 = 0.083$ and $R_2 = 0.067$. The final "error of fit" based on the 100 variables was 1.09. The relative correctness of the weighting scheme, as judged by the variation of mean $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) with $|F_o|$ and $(\sin\theta)/\lambda$, was satisfactory. A final difference map calculated on an absolute scale showed no peaks greater than 0.2 e$^-$/Å^3, consistent with good refinement. Comparison of the final values of $|F_o|$ and $|F_c|$ indicated that a correction for secondary extinction was not necessary.

The final positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. The hydrogen positions are listed in Table II. Table III gives the final root-mean-square

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS × 10) FOR BIS(O,O′-DIISOPROPYLPHOSPHOROTHIONYL) DISULFIDE, $[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

K	L	FO	FC
**** H = 0 ****			
0	1	419	411
0	2	426	-425
0	3	120	113
0	4	51	43
0	5	128	-118
0	6	85	-79
0	7	37*	-41
0	8	79	-88
0	9	90	-103
1	0	515	550
1	1	488	501
1	-1	30*	-31
1	2	127	122
1	-2	361	-363
1	3	69	62
1	4	45*	-20
1	-4	129	119
1	5	88	-93
1	-5	40*	50
1	-6	110	113
1	8	78	-73
1	-8	87	-87
1	9	87	-94
1	-9	62	-69
2	0	356	-352
2	1	104	-105
2	2	72	87
2	-2	47*	31
2	3	183	-179
2	-3	359	354
2	4	253	-254
2	-4	320	319
2	5	141	-141
2	-5	298	294
2	6	47*	-4
2	-6	239	244
2	7	63	64
2	-8	105	-108
3	0	57	-64
3	1	91	-82
3	-1	172	162
3	-2	252	252
3	3	118	-117
3	-3	145	154
3	4	252	-256
3	-4	349	353
3	5	226	-230
3	-5	288	288
3	6	81	-85
3	-6	36*	-28
3	-7	101	-102
3	8	54*	39
3	-10	49*	28
4	0	319	-311
4	-1	95	-96
4	2	169	171
4	-2	47*	28
4	-3	88	-89
4	4	75	-82
4	-4	142	144
4	5	72	-76
4	6	54	-52
4	-6	116	-116
4	-8	121	128
4	-9	101	109
4	-10	42*	44
5	0	387	-394
5	1	223	-224
5	-1	286	-285
5	2	51*	40
5	-2	54*	-70
5	3	42*	47
5	-3	52*	46
5	-7	88	88
5	-8	160	171
5	-9	90	94
6	0	136	-153
6	1	244	-253
6	-1	50*	40
6	2	92	-103
6	-2	66	74
6	4	43*	30
6	-6	77	-74
6	-8	88	94
6	-9	47*	40
7	1	59	-54
7	-1	151	164
7	-2	44*	24
7	3	39*	27
7	-3	120	-123
7	4	47*	47
7	-4	136	-133
7	-5	142	-148
7	-6	78	-82
8	0	48*	48
8	-1	54*	-4
8	-2	56	-55
8	-3	113	-101
8	-4	188	-182
8	-5	107	-108
8	-7	54*	44
9	-6	77	62
9	-8	63	-61
10	0	116*	52
10	-4	28*	-4
10	-5	42*	21
10	-6	79*	31
**** H = 1 ****			
0	0	321	311
0	1	250	-248
0	-1	607	591
0	2	219	-211
0	-2	346	339
0	3	58	68
0	-3	66	60
0	4	74	56
0	-4	36*	27
0	5	86	82
0	-5	61	-71
0	6	89	94
0	-6	65	-70
0	8	95	-95
0	-8	62	-40
0	9	47*	-38
0	-9	106	-103
0	-10	75	-68
1	0	379	385
1	1	698	745
1	-1	405	393
-1	1	671	-690
-1	-1	585	617
1	2	84	69
1	-2	686	705
-1	2	55	45
-1	-2	424	-416
1	3	157	-153
1	-3	45	50
-1	3	564	566
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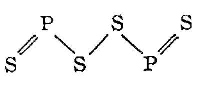
3	1	162	148
3	-1	162	-156
-3	1	303	-316
-3	-1	69	-64
3	2	143	153
3	-2	54	-52
-3	2	237	-238
-3	-2	93	106
3	3	105	97
3	-3	103	95
-3	3	171	-173
-3	-3	129	130
3	-5	61	-74
-3	5	93	82
3	-6	72	-65
-3	6	47*	20
-3	-6	111	107
3	-7	50*	-57
-3	-7	122	111
4	0	125	-137
-4	0	57	-78
4	-1	76	-87
-4	1	113	-114
-4	-1	62	-68
4	-2	103	133
-4	2	63	-60
-4	-2	42*	12
4	-3	198	201
-4	3	39*	42
-4	-3	80	100
4	-4	88	83
-4	4	114	108
-4	6	113	-113
4	-7	37*	-11
-4	7	92	-84
-4	-7	90	72
-5	0	139	151
-5	-1	116	109
5	2	62	-33
5	-2	210	218
-5	-2	102	102
5	-3	172	178
-5	3	134	150
-5	-3	134	137
-5	-4	60	65
-5	5	230	-228
-5	6	189	-193
-5	7	77	-81
5	-9	55*	18
-6	1	41*	-12
-6	-1	55	30
6	-2	82	78
-6	-2	93	96
-6	3	52	29
-6	-3	159	167
-6	4	77	-71
-6	-4	120	115
-6	5	150	-157
-6	6	83	-96
6	-8	46*	53
-7	1	74	95
-7	-1	77	-86
-7	2	114	110
-7	3	70	62
-7	-3	42*	37
7	-4	53	-29
7	-6	69	61
7	-8	46*	41
-8	0	99	88
-8	1	158	166
-8	2	164	144
-8	-2	46*	-58
-8	3	83	71
-8	-3	70	-43
-9	0	74	59
-9	1	74	78
-9	3	56	-45
-9	4	57	-40
-9	5	48*	15
-10	5	83	72
**** H = 6 ****			
0	0	41*	-41
0	1	44*	30
0	-1	59	49
0	3	52	-49
0	-3	205	-208
0	-4	248	-244
0	5	110	105
0	-5	83	-81
0	-6	59	37
0	-7	59	42
0	-9	46*	11
1	0	98	-104
-1	0	66	-60
1	-1	62	-55
-1	1	176	-176
-1	-1	115	118
1	2	27*	27
1	-2	105	-100
-1	2	146	-155
-1	-2	111	111
1	-3	234	-233
-1	3	159	-158
1	-4	154	-147
-1	-4	71	-73
1	5	105	95
-1	5	56	75
1	6	94	100
1	-6	85	85
1	-7	51*	50
1	-8	48*	-20
2	0	149	147
-2	0	262	-277
2	1	67	69
-2	1	307	-303
-2	-1	55	-38
2	2	64	-76
2	-2	130	-144
-2	2	186	-182
-2	-2	117	110
2	-4	66	61
-2	-5	93	94
-2	-6	75	66
2	-7	45*	-26
2	-8	64	-62
-2	-8	80	69
3	0	217	221
-3	0	150	-157
3	1	171	182
3	-1	58	-65
-3	1	99	-103
-3	-1	83	-81
3	-2	92	-87
-3	-2	63	63
3	-3	72	56
-3	3	116	95
3	-4	52	44
3	-5	60	-43
-3	5	44*	-37
3	-6	66	-75
-3	6	53*	-80
3	-7	51*	-67
-3	7	65	-68
3	-8	74	-75
4	0	44*	40
4	1	105	113
4	-1	85	-107
-4	1	93	108
4	2	90	83
4	-2	65	-57
-4	-2	116	116
4	3	66	53
4	-3	57	72
-4	3	42*	-39
-4	-3	169	164
4	-4	54*	2
-4	4	76	-78
-4	-4	103	101
-4	5	162	-156
-4	6	141	-147
-4	-6	55	-49
-4	7	82	-69
4	-8	69	-63
5	-1	50*	-36
-5	-2	40*	62
5	-3	101	102
-5	-3	140	146
5	-4	61	66
-5	4	101	-104
-5	-4	161	158
-5	5	150	-137
-5	-5	49*	53
5	-7	51*	-41
-6	1	43*	28
6	-2	80	84
-6	2	124	131
-6	-2	64	-79
6	-3	70	69
-6	3	111	103
6	-4	51*	64
-6	-4	47*	63
6	-6	50*	-48
-7	0	133	139
7	-1	52*	25
-7	1	141	151
-7	2	138	145
-7	3	58	68
-7	-3	64	-63
7	-5	64	-56
-8	0	98	106
-8	1	50*	56
-8	-1	60	66
8	-3	52*	-22
-8	6	65	54
-9	1	58	-42
-9	2	69	-60
-9	5	97	90
**** H = 7 ****			
0	0	73	-67
0	1	114	-121
0	2	105	-111
0	-2	123	121
0	-3	79	75
0	-5	63	-61
0	-6	54*	-9
0	-7	51*	36
1	0	76	100
-1	0	220	-228
1	1	76	-87
1	-1	107	121
-1	1	134	-126
-1	-1	172	-182
1	2	48*	-54
1	-2	55	-74
-1	2	72	-98
-1	-2	56	44
1	3	55	59
1	-3	127	-130
-1	3	53*	-30
-1	-3	110	105
1	-4	100	-103
1	-5	87	-97
-1	5	52*	35
1	-6	50*	-43
-2	0	133	-135
2	1	81	-79
2	-1	57	66
-2	1	38*	39
-2	-1	148	-150
2	-2	188	-196
-2	-2	54*	21
2	3	59	44
2	-3	148	-149
-2	-3	55	57
2	4	59	62
2	-4	49*	-39
2	5	59	52
-2	5	49*	-62
-2	6	80	-87
2	-8	45*	20
3	1	62*	26
-3	1	78	82
3	-2	40*	-51
-3	-2	113	117
3	3	43*	-31
-3	-3	119	132
-3	4	118	-111
-3	5	139	-141
-3	6	89	-105
3	-7	38*	33
3	-8	51*	-52
4	0	52	66
4	1	87	80
4	-1	63	49
-4	-1	39*	1
-4	3	98	-93
-4	-3	107	112
-4	4	108	-112
-4	-4	128	120
-4	5	80	-85
-4	-5	85	91
-4	6	68	-34
-4	-6	52*	33
-4	7	53*	23
4	-8	67	-74
5	0	38*	31
-5	0	69	77
5	1	55	56
-5	1	110	97
-5	-2	71	-74
-5	-4	51*	39
5	-5	60	47
-5	-5	62	56
5	-7	51*	-49
-6	0	140	162
-6	1	153	150
-6	-1	79	87
-6	2	110	104
-6	-2	56*	-18
6	-3	64	43
-6	-3	97	-66
6	-4	97	65
-6	-4	57	-39
6	-5	62	45
6	-6	45*	-21
-7	0	84	76
-7	1	52	34
-7	-1	119	102
7	-2	74*	35
-7	5	65	34
-8	0	42*	-35
-8	4	72	68
-8	5	101	103
-8	6	108	75
-9	3	76	57
-9	4	70	77
**** H = 8 ****			
0	0	191	-184
0	1	134	-143
0	-1	68	-61
0	3	48*	50
0	-4	63	54
1	0	93	-113
-1	0	82	-74
1	1	115	-128
-1	-1	70	-75
1	-2	76	77
-1	2	55	74
-1	-2	59	-65
1	3	50*	31
-1	5	61	-41
-1	6	64	-44
-2	1	57	52
-2	2	46*	-6
-2	-3	75	97
2	-4	75	-74
-2	4	96	-90
-2	-4	101	98
2	-5	104	-90
-2	5	90	-98
2	-6	58	-63
-3	0	58	70
3	1	51*	-16
3	-1	45*	1
-3	-1	53	-55
-3	2	68	-71
3	-3	59	-58
-3	3	77	-71
-3	-3	107	108
3	-4	78	-77
-3	4	88	-82
-3	-4	101	106
-3	5	78	-57
-3	-5	58	67
-3	6	44*	-4
-4	0	68	88
4	-1	60	55
-4	1	105	106
-4	-2	72	-53
5	0	50*	67
-5	0	142	154
-5	1	125	123
-5	-1	98	104
-6	0	57	65
-6	-1	109	105
-6	-2	53*	63
6	-4	46*	-7
-7	0	61	-50
-7	1	56	-47
-7	3	33*	25
-7	4	90	90
-7	5	97	97
-8	3	52*	74
-8	4	82	79
**** H = 9 ****			
0	0	61	-49
0	-1	73	-73
0	2	79	73
1	0	105	-110
-1	0	58*	20
1	-1	99	-84
1	2	42*	30
-1	3	61	-62
1	-4	54	37
-1	4	96	-89
2	0	67	-63
-2	2	50*	-50
-2	-3	40*	4
-2	4	46*	-55
-2	-5	96	91
-3	0	64	61
3	1	52*	-16
-3	-1	65	45
3	-2	83	50
3	-5	65	-50
3	-6	40*	-34
-4	0	148	140
4	-1	48*	8
-4	1	61	53
4	-5	40*	-45
-5	0	67	66
-5	-1	86	87
-6	1	64	-60
-6	-1	52*	-9
-6	3	77	75
-6	4	66	72
-7	3	80	80
**** H = 10 ****			
0	1	47*	47
-1	3	82	-78
1	-4	43*	-3
-3	0	47*	66
-3	-1	70	85
-3	-2	83	67
-4	-2	75	75

[a] Asterisks denote unobserved reflections.

amplitudes of vibration of the nonhydrogen atoms. Table IV lists the observed and calculated structure factors.

Description of the Structure

Molecules of $[(i\text{-}C_3H_7O)_2PS_2]_2$, illustrated in Figures 1–3, contain a planar zigzag array of linkages about a straight line passing more or less through the midpoint of each of the five bonds. Deviations of the six atoms from the best-weighted plane (see first equation of ref 25 and ref 26) do not exceed 0.002 (2) Å. About each tetrahedrally coordinated phosphorus atom are two OC_3H_7 groups, the two $P(OC_3H_7)_2$ groups in the molecule in turn being related to each other by an inversion operation located at the midpoint of the S–S bond. These isopropoxy groups are oriented such that a second plane is formed normal to the P_2S_4 plane.



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(25) The equations of the best planes, expressed in triclinic coordinates, are: $5.639x + 5.445y - 2.761z - 0.000 = 0$ for the P_2S_4 plane and $5.570x - 5.725y + 4.870z - 2.486 = 0$ for the $P(OC)_2$ plane.

(26) Weights were based on the variance–covariance matrix as obtained from the final cycle of least-squares refinement. The computed standard deviations include the standard deviations of the lattice parameters, which contribute significantly less than those of the atomic parameters.

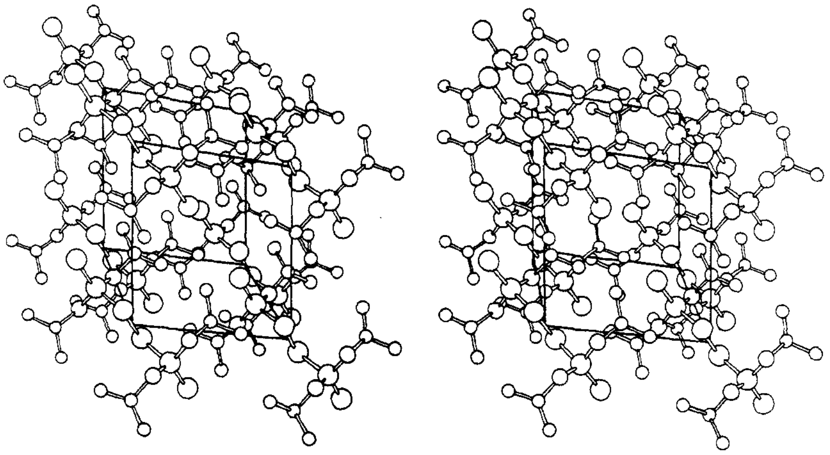


Figure 2.—A stereographic illustration of the molecular packing of $[(i\text{-}C_3H_7O)_2PS_2]_2$ in the unit cell. For clarity, the hydrogen atoms are not shown.

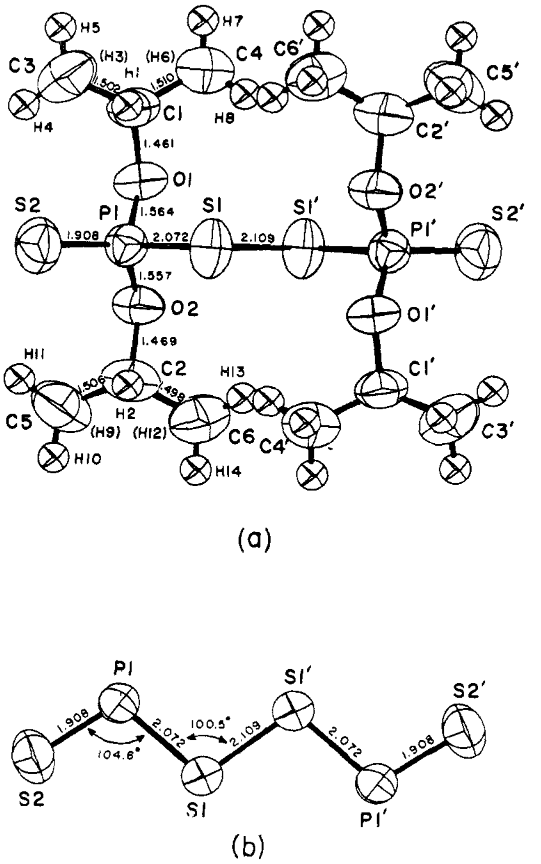
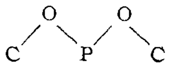


Figure 3.—Parallel projections of the $[(i\text{-}C_3H_7O)_2PS_2]_2$ molecule, showing the principal root-mean-square thermal displacements of the atoms. The ellipsoidal boundaries (except those of hydrogen) are drawn at the 72% probability level: (a) view parallel to the P_2S_4 plane; (b) view normal to the P_2S_4 plane.



Carbon exhibits the largest deviation, approaching 0.03 Å or 4σ, from the best-weighted plane (see second equation of ref 25 and ref 26).

Interatomic distances, angles, and standard deviations are given in Table V. Corrections of the P–S and P–O bond lengths for thermal motion may be estimated using the "riding" model of Busing and Levy.[27] In making these corrections it was convenient to divide the dimer into its monomeric halves, each half being assumed to librate somewhat independently of the other, constrained only through the S–S linkage. The centroid of each half was taken at phosphorus, the atom which is tetrahedrally coordinated and, significantly, also the atom with the lowest temperature factor (Table I). Corrected bond lengths of P(1)–S(1) = 2.081 (2), P(1)–S(2) = 1.923 (3), P(1)–O(1) = 1.572 (4), and P(1)–O(2) = 1.566 (4) Å were achieved. The standard deviations cited do not take into consideration uncertainties in the thermal parameters from which the corrections were made or the arbitrariness of the "riding" model itself. These corrections may be considered to represent upper limits.

TABLE V

INTERATOMIC DISTANCES AND ANGLES IN $[(i\text{-}C_3H_7O)_2PS_2]_2$[a]

Atoms	Dist, Å	Atoms	Angle, deg
S(1)–S(1′)	2.109 (4)	S(1′)–S(1)–P(1)	100.5 (1)
P(1)–S(1)	2.072 (2)	S(1)–P(1)–S(2)	104.8 (1)
P(1)–S(2)	1.908 (3)	S(1)–P(1)–O(1)	108.1 (2)
P(1)–O(1)	1.564 (4)	S(1)–P(1)–O(2)	108.2 (2)
P(1)–O(2)	1.557 (4)	S(2)–P(1)–O(1)	119.2 (2)
O(1)–C(1)	1.461 (7)	S(2)–P(1)–O(2)	119.4 (2)
O(2)–C(2)	1.469 (8)	O(1)–P(1)–O(2)	96.6 (2)
C(1)–C(3)	1.502 (10)	P(1)–O(1)–C(1)	121.0 (4)
C(1)–C(4)	1.510 (10)	P(1)–O(2)–C(2)	121.3 (4)
C(2)–C(5)	1.506 (10)	O(1)–C(1)–C(3)	106.9 (6)
C(2)–C(6)	1.498 (10)	O(1)–C(1)–C(4)	105.9 (5)
		O(2)–C(2)–C(5)	107.4 (6)
		O(2)–C(2)–C(6)	107.1 (6)
		C(3)–C(1)–C(4)	112.8 (6)
		C(5)–C(2)–C(6)	113.2 (6)

[a] The averages (plus associated root-mean-square deviations) of chemically equivalent bonds and angles are as follows: P–O, 1.561 (5) Å; O–C, 1.465 (6) Å; C–C, 1.504 (5) Å; S(1)–P–O, 108.2 (1)°; S(2)–P–O, 119.3 (1)°; P–O–C, 121.2 (2)°; O–C–C, 106.8 (6)°; C–C–C, 113.0 (3)°. The angle which each isopropyl group makes with its associated oxygen atom is as follows: O(1)–C(1)–i-C_3H_7(1), 124.0 (6)°; O(2)–C(2)–i-C_3H_7(2), 122.6 (6)°; the coordinates of i-C_3H_7(1) and i-C_3H_7(2) were taken as the midpoint of C(3) with C(4) and C(5) with C(6), respectively.

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

Comparison of the observed S–S bond length (2.109 (4) Å) and sulfur bond angle (100.5 (1)°) with those of other related compounds reveals no unusual bonding in (dtp)$_2$. According to Pauling's convention of summing covalent radii, the length of an S–S single bond is 2.08 Å.[28] From an extensive survey of sulfur-containing compounds, Abrahams found that the S–S bond varies in length from 1.89 to 2.39 Å.[29] By comparison, the length of the S–S bond in S$_8$, in which a small amount of double-bond character is believed to exist, is 2.037 (5) Å.[30] Therefore, it appears that the S–S bond in (dtp)$_2$ is essentially an unperturbed single bond. A survey of sulfur valency angles by Abrahams reveals a range of from 66 to 119°.[29] Of these, S–S–S bond angles are found to vary only from 103 to 108° with a mean value of 106°. The observed bond angle in S$_8$, for example, is 107.8°.[30] P–S–P angles in the phosphorus sulfides also fall into this range (102–109°).[29] Consequently, our observed S–S–P angle, though slightly smaller than the sulfur valency angle found in most sulfur-containing compounds, does not reveal any unusual bonding.

The two phosphorus–sulfur bonds are unequal in length. According to Pauling's scheme, the lengths of P–S single and double bonds are 2.14 and 1.94 Å, respectively.[28] By comparison, our observed (corrected) bond lengths were 2.081 (2) and 1.923 (3) Å, indicating the presence of multiple bonding in both cases.

The phosphorus–oxygen bond lengths in (dtp)$_2$ are similar to those found in previously determined metal phosphorodithioates.[1–6,8] If 1.76 and 1.44 Å are accepted as the single and double P–O bond lengths, respectively,[31] the average measured value 1.569 (5) Å (cor) in (dtp)$_2$ indicates the presence of some double-bond character in these bonds as well. This presence would be consistent with the vast majority of other compounds containing P–O– bonds. The bond order estimated from the Robinson equation[31]

$$n_{\text{P-O}} = 23.8/r_{\text{P-O}}^8 + 0.74$$

is 1.4. Such a value would not seem unreasonable if some π bonding due to delocalization of lone-pair electrons on oxygen into vacant 3d$_{x^2-y^2}$ and 3d$_{z^2}$ orbitals of phosphorus occurs.[31–38]

The C–H···S and C–H···O interactions are unexceptional. No distances less than 3.1 and 2.6 Å, respectively, were found, based on coordinates for the hydrogen atoms adjusted to give C–H bond lengths of 1.1 Å.

Acknowledgments.—This author is indebted to J. J. Dickert for the purified sample of this material and Mrs. J. C. Mahley for her experimental assistance. Helpful discussions with J. J. Dickert, C. N. Rowe, G. T. Kokotailo, and L. S. Bartell are gratefully acknowledged.

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CONTRIBUTION FROM THE FRANK J. SEILER RESEARCH LABORATORY, OFFICE OF THE AEROSPACE RESEARCH,
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The Crystal and Molecular Structure of 1,2′:1′,2-Di-μ-carbonyl-bis[1,2-dicarba-*closo*-dodecaborane(12)]

BY R. W. RUDOLPH,[1] J. L. PFLUG, C. M. BOCK, AND M. HODGSON

Received September 23, 1969

The dimeric carborane 1,2′:1′,2-di-μ-carbonyl-bis[1,2-dicarba-*closo*-dodecaborane(12)], $[o\text{-}B_{10}C_2H_{10}\cdot CO]_2$, crystallizes in the monoclinic space group P2$_1$/n, with two molecules per cell of dimensions a_0 = 9.528 (4) Å, b_0 = 13.704 (8) Å, c_0 = 7.078 (2) Å, and β = 95.64 (2)°, with Z = 2, ρ_{calcd} = 1.228 (2), and ρ_{obsd} = 1.23 ± 0.01 g/cm^3. The phases were determined by the symbolic addition method. Least-squares refinement with 1059 X-ray data resulted in a final unweighted residual of 7.1%. The molecules are located on crystallographic centers of symmetry which fall at the centers of the planar, six carbon atom ring. The carbonyl bond length is 1.217 (4) Å for the riding model. No corrections for thermal motion were found necessary among the skeletal bond lengths where the average bond distances are C–B = 1.730 (7) Å, B–B = 1.778 (8) Å, C–C = 1.645 (4) Å [polyhedral], and C–C = 1.517 (4) Å [exopolyhedral]. The average B–H length is 1.09 (5) Å.

Introduction

There is a pronounced tendency of the substituents attached to the carbon atoms in the *o*-carborane moiety to form exopolyhedral rings. No structural data have yet appeared for such species or for the related doubly connected bis *o*-carboranes. We wish to report the structure for one such carborane, $[o\text{-}B_{10}H_{10}C_2\cdot CO]_2$, 1,2′:1′,2-di-$\mu$-carbonyl-bis[1,2-dicarba-*closo*-dodecabo-

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