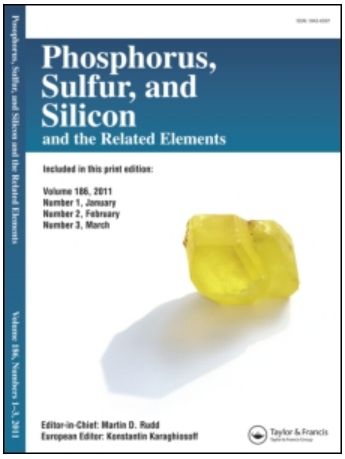

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CRYSTAL AND MOLECULAR STRUCTURE OF THE SPIRODIPHOSPHITE ESTER 3,9-DIMETHOXY-2,4,8,10-TETRAOXA-3,9-DIPHOSPHASPIRO[5.5]UNDECANE

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CRYSTAL AND MOLECULAR STRUCTURE OF THE SPIRODIPHOSPHITE ESTER 3,9-DIMETHOXY-2,4,8,10-TETRAOXA-3,9-DIPHOSPHASPIRO[5.5]UNDECANE

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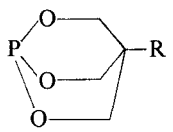
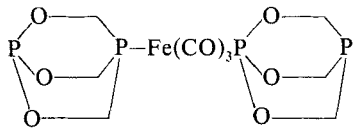
The crystal and molecular structure of the strainless phosphite ester $MeOP(OCH_2)_2C(CH_2O)_2POMe$ determined by x-ray means is reported. The methoxy groups are in axial positions on the chair-form-six-membered rings.

Striking changes in the sigma donor and pi acceptor character of phosphorus in phosphite triesters as a function of constraint have been attributed to conformational differences among the alkoxy groups and bond angle changes which occur preferentially at the oxygens rather than phosphorus.[1] An important premise in these arguments is that the structural parameters determined for the cage phosphite ester (**1**) (R = CH_2Br) render it essentially strainless.[2] The

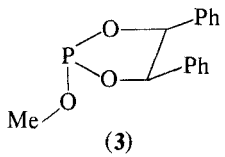


(**1**)

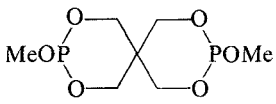


(**2**)

only other structural data for phosphite esters which have been reported are for a related cage compound (**2**)[3] and the strained five-membered ring structure (**3**).[4] It was important, therefore, to determine the



(**3**)



(**4**)

molecular structure of a strainless phosphite ester in order to evaluate our ideas on the origins of basicity changes in these systems more objectively. Although electron diffraction data on $P(OEt)_3$ and $P(OCHCH_2)_3$ have appeared,[5] the derived structural parameters are too crude for comparison with the results available from the x-ray diffraction experiments cited above.

Compound (**4**) is crystalline at room temperature and this is uncommon for phosphite triesters—especially those which are strain free. Spirodiphosphite (**4**) is also the P(III) parent compound of P(V) derivatives which function as fire retardants in polymers.[6] It is thus of interest to determine whether any structural properties of this system may be related to this application.

EXPERIMENTAL

A colorless crystal of (**4**) in the form of a thin hexagonal plate (~0.3 mm × 0.3 mm × 0.1 mm) obtained on sublimation at 76° and 0.01 torr, was mounted in a 0.3 mm Lindemann capillary. The capillary was sealed to prevent hydrolysis by atmospheric moisture. The crystal was found to be monoclinic with a = 10.87(4), b = 5.74(1), c = 18.76(7) Å and β = 99.7(6)° with four molecules of (**4**) per unit cell. A density of 1.47 g/cm³ was computed based on a cell volume of 1153.8 Å³. Systematic absences (hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$) indicated space group $C_{2/c}$ which was confirmed by subsequent solution and refinement of the structure.

Using an automated four-circle diffractometer, designed and built in the Ames Laboratory, equipped with scintillation counter and interfaced to a PDP-15 computer, data were collected at room temperature with graphite monochromated Mo K_α radiation (λ = 0.70954 Å) employing a procedure described previously.[7] Six octants were examined within a sphere of $2\theta < 50°$ yielding 3665 measured intensities. There was no significant crystal decomposition as judged by repeated measurements of three standard reflections. Corrections for Lorentz–polarization effects and averaging of equivalent data yielded 744 observed reflections ($F_o \geq 3\sigma(F_o)$). Lattice constants were obtained by a least squares refinement of the precise $\pm 2\theta$ ($|2\theta| > 25°$) measurements of 12 strong independent reflections.

The program MULTAN[8] was used to locate all of the non-hydrogen atoms. Isotropic refinement of these positions by full matrix least squares techniques[9] led to a conventional R factor of 0.123 and a weighted R factor of 0.133. Ring hydrogen positions were calculated and the hydrogen positions for the terminal methyl groups were obtained from an electron density difference map. Anisotropic refinement then gave a conventional

TABLE I
Calculated and observed structure factors for $MeOP(OCH_2)_2C(CH_2O)_2POMe$ (**4**)

K = 0

H	L	FO	FC
-12	4	11	10
-12	8	5	6
-12	10	6	7
-10	2	63	61
-10	4	10	9
-10	6	25	24
-10	8	30	30
-10	10	15	13
-10	12	23	22
-10	14	15	15
-10	16	25	25
-8	1	53	0
-8	2	171	160
-8	4	71	65
-8	6	67	61
-8	7	4	0
-8	10	52	51
-8	12	13	16
-8	14	25	23
-8	16	41	39
-8	18	26	27
-6	1	3	0
-6	2	17	19
-6	4	118	113
-6	6	4	7
-6	8	22	22
-6	10	26	26
-6	12	14	12
-6	14	33	32
-6	18	26	25
-4	2	40	43
-4	4	58	54
-4	8	26	24
-4	10	41	41
-4	12	14	15
-4	14	50	49
-4	16	5	6
-4	18	14	12
-4	20	5	7
-4	22	9	10
-2	2	87	92
-2	4	48	46
-2	6	37	39
-2	8	18	18
-2	10	67	69
-2	12	97	92
-2	14	74	71
-2	16	36	37
-2	20	17	16
-2	22	6	10
0	2	120	122
0	4	205	216
0	5	4	0
0	6	133	139
0	7	5	0
0	8	95	93
0	9	6	0
0	10	102	100
0	11	4	0
0	12	29	27
0	13	9	0
0	14	133	134
0	15	6	0
0	16	54	56
0	18	33	33
0	20	15	16
2	0	158	164
2	2	314	351
2	4	114	112
2	6	50	48
2	8	108	101
2	10	58	55
2	12	69	64
2	14	43	41
2	16	47	45
2	18	5	7
2	20	5	7
4	0	4	6
4	2	68	62
4	4	30	26
4	6	46	51
4	8	58	58
4	12	6	11
4	14	21	19
4	16	22	22
4	18	52	51
6	0	15	12
6	2	7	8
6	4	43	41
6	6	55	53
6	10	8	9
6	12	19	20
6	14	15	15
6	16	15	17
8	0	50	47
8	2	74	73
8	4	16	17
8	6	47	47
8	8	14	17
8	10	57	55
8	12	5	9
8	14	43	43
10	0	30	31
10	2	4	6
10	4	41	40
10	6	13	15
10	8	7	13
10	10	13	12
12	2	48	50

K = 1

H	L	FO	FC
-11	1	23	22
-11	2	5	9
-11	3	5	6
-11	4	27	25
-11	5	22	20
-11	6	5	6
-11	7	12	12
-11	9	10	11
-11	11	6	7
-9	1	66	62
-9	2	15	16
-9	3	61	57
-9	5	38	36
-9	7	6	6
-9	9	52	55
-9	10	12	14
-9	13	20	18
-9	14	9	10
-9	15	22	22
-9	17	21	19
-7	2	44	15
-7	3	111	104
-7	4	6	6
-7	5	22	18
-7	6	16	14
-7	7	45	46
-7	8	5	3
-7	9	29	27
-7	11	41	40
-7	12	20	19
-7	13	27	29
-7	14	11	12
-7	15	6	8
-7	17	32	30
-5	1	73	79
-5	2	82	82
-5	4	49	45
-5	5	26	27
-5	6	28	32
-5	7	18	21
-5	8	16	19
-5	10	4	7
-5	11	22	21
-5	12	31	29
-5	13	18	18
-5	14	35	35
-5	15	34	31
-5	16	37	37
-5	17	5	8
-5	18	4	5
-5	21	10	11
-3	1	110	111
-3	2	251	274
-3	3	96	99
-3	4	12	9
-3	5	45	47
-3	6	48	50
-3	7	13	15
-3	8	3	1
-3	9	27	28
-3	10	19	19
-3	11	50	46
-3	12	27	28
-3	13	20	20
-3	14	8	8
-3	15	36	35
-3	16	36	37
-3	17	13	14
-3	18	20	22
-3	19	14	14
-3	20	5	8
-1	1	129	142
-1	2	29	30
-1	3	177	190
-1	4	74	78
-1	5	62	63
-1	6	16	16
-1	7	195	202
-1	8	42	39
-1	9	42	50
-1	10	17	12
-1	11	32	31
-1	12	43	44
-1	13	93	97
-1	14	17	17
-1	15	31	31
-1	16	10	12
-1	17	32	30
-1	21	21	21
1	0	98	101
1	1	293	325
1	2	37	38
1	3	12	14
1	4	154	144
1	5	77	78
1	6	4	7
1	7	161	156
1	8	36	37
1	9	85	79
1	10	39	34
1	11	96	92
1	12	12	11
1	13	13	13
1	15	78	72
1	16	20	17
1	19	13	13
1	20	7	12
1	21	20	19
3	0	68	69
3	1	42	44
3	2	77	69
3	4	5	7
3	5	43	46
3	6	17	17
3	7	39	34
3	8	27	28
3	9	38	37
3	10	15	15
3	11	48	47
3	12	46	47
3	13	33	33
3	14	42	40
3	15	27	25
3	16	5	10
3	19	19	18
5	0	188	188
5	1	19	16
5	2	9	15
5	3	9	7
5	4	45	49
5	5	49	46
5	6	44	40
5	9	41	45
5	10	39	37
5	11	5	7
5	13	31	36
5	14	40	39
5	16	11	14
5	17	5	9
7	0	6	6
7	1	58	57
7	2	25	25
7	3	55	53
7	5	36	41
7	6	4	7
7	7	42	42
7	8	6	5
7	10	14	14
7	11	39	47
7	14	7	11
7	15	6	13
9	0	5	3
9	1	27	27
9	2	22	28
9	5	55	61
9	6	5	14
9	7	5	8
9	9	23	26
9	11	17	21
11	0	5	5
11	3	9	12
11	4	4	5
11	5	17	17
11	7	9	10

K = 2

H	L	FO	FC
-12	3	17	18
-12	4	19	19
-12	5	10	12
-12	7	9	9
-12	8	5	6
-10	2	15	18
-10	3	4	3
-10	4	15	18
-10	6	4	3
-10	7	5	8
-10	8	30	28
-10	10	5	7
-10	12	5	6
-10	15	6	5
-8	1	8	6
-8	2	10	8
-8	3	8	8
-8	4	10	15
-8	6	30	29
-8	8	22	27
-8	9	14	17
-8	10	51	48
-8	11	21	23
-8	12	5	5
-8	14	5	3
-8	15	7	7
-8	16	12	11
-6	1	63	54
-6	2	25	24
-6	3	44	38
-6	4	25	22
-6	5	31	31
-6	6	23	20
-6	7	46	44
-6	8	47	45
-6	9	5	8
-6	10	40	40
-6	12	30	28
-6	13	35	31
-6	14	32	31
-6	15	20	21
-6	17	4	5
-6	18	6	9
-6	19	5	5
-6	20	6	9
-4	1	181	195
-4	2	108	108
-4	3	62	59
-4	4	43	45
-4	5	87	90
-4	7	14	14
-4	8	64	64
-4	9	77	77
-4	10	27	29
-4	11	34	36
-4	12	28	27
-4	13	27	23
-4	14	15	15
-4	15	44	46
-4	16	34	35
-4	17	22	22
-4	18	9	10
-4	19	6	9
-2	1	33	33
-2	2	125	131
-2	3	64	68
-2	4	21	20
-2	5	39	39
-2	6	139	139
-2	7	28	24
-2	8	23	23
-2	9	24	27
-2	10	30	35
-2	12	24	25
-2	13	35	38
-2	16	28	29
-2	17	18	20
-2	20	21	21
0	0	21	23
0	1	39	38
0	2	5	1
0	3	53	49
0	4	35	36
0	5	11	16
0	6	126	128
0	7	112	113
0	8	119	120
0	9	80	80
0	10	33	31
0	11	17	19
0	12	13	12
0	13	19	19
0	14	38	37
0	16	20	20
0	17	15	14
0	18	6	10
0	19	7	7
0	20	19	18
2	0	33	36
2	1	86	75
2	3	40	42
2	4	68	68
2	5	35	33
2	6	5	4
2	8	85	79
2	9	25	23
2	10	21	18
2	11	51	49
2	12	45	43
2	13	7	9
2	14	20	15
2	15	11	12
2	16	11	12
2	18	26	24
4	0	79	85
4	1	19	15
4	2	82	81
4	3	89	87
4	4	36	38
4	5	60	59
4	6	81	79
4	7	72	66
4	8	16	16
4	9	55	54
4	10	14	14
4	11	7	9
4	12	37	38
4	13	56	56
4	14	25	24
4	15	14	15
4	16	15	14
4	17	15	14
6	0	71	70
6	1	68	64

TABLE I—*continued*

6	2	33	29	-5	6	25	27	3	5	135	124	-6	14	5	7	4	1	10	11
6	3	6	6	-5	7	87	87	3	6	90	81	-6	15	6	7	4	2	36	35
6	4	71	70	-5	8	75	75	3	7	46	47	-4	1	32	33	4	3	12	13
6	5	5	6	-5	9	68	69	3	8	25	24	-4	2	43	44	4	4	23	22
6	6	42	40	-5	10	5	4	3	9	37	35	-4	4	25	24	4	5	44	42
6	7	48	45	-5	11	30	27	3	10	12	11	-4	5	19	19	4	6	84	78
6	8	22	20	-5	12	7	8	3	11	16	16	-4	7	35	33	4	7	20	17
6	10	30	29	-5	14	21	21	3	12	33	33	-4	8	76	76	4	8	15	16
6	11	30	29	-5	15	22	20	3	13	15	17	-4	9	26	25	4	9	12	14
6	12	13	16	-5	16	6	9	3	15	13	15	-4	10	30	31	4	10	15	15
6	13	6	13	-5	18	9	10	3	16	12	15	-4	11	7	8	4	12	16	19
6	14	26	26	-3	1	41	40	5	0	56	52	-4	12	16	16	4	13	18	17
6	15	21	19	-3	2	59	58	5	1	10	11	-4	14	7	6	4	14	9	10
8	0	24	23	-3	3	12	14	5	2	17	18	-4	15	14	15	6	0	24	25
8	1	7	11	-3	5	63	64	5	3	66	63	-4	16	9	12	6	1	18	15
8	3	4	1	-3	6	43	43	5	5	46	47	-2	1	10	10	6	2	14	15
8	4	44	52	-3	7	12	12	5	6	68	65	-2	2	7	9	6	3	33	30
8	5	25	26	-3	8	56	57	5	7	89	88	-2	3	31	31	6	5	10	10
8	6	27	27	-3	9	100	106	5	8	31	36	-2	4	4	2	6	6	32	30
8	7	22	20	-3	10	46	48	5	10	30	30	-2	5	48	52	6	7	23	22
8	8	14	15	-3	11	26	27	5	11	5	10	-2	6	14	14	6	8	19	19
8	10	13	14	-3	12	30	32	5	13	30	29	-2	7	41	43	8	0	5	4
8	12	13	14	-3	13	22	21	5	14	22	24	-2	8	20	18	8	1	19	19
10	2	15	14	-3	15	20	19	5	16	5	6	-2	9	25	28	8	5	28	33
10	4	17	17	-3	16	19	21	7	0	17	19	-2	10	35	33	8	6	5	11
10	6	21	20	-3	19	13	15	7	3	38	37	-2	11	9	10	10	0	4	7
10	7	6	11	-1	1	7	12	7	6	19	20	-2	12	5	3	10	1	11	12
10	9	7	8	-1	2	9	7	7	7	20	21	-2	15	6	7				
12	0	5	9	-1	3	14	13	7	8	17	16	-2	16	7	9		K =	5	
12	1	4	5	-1	5	67	69	7	11	5	10	-2	17	7	10	H	L	FO	FC
				-1	6	9	2	7	12	4	10	0	0	8	11	-7	2	5	3
	K =	3		-1	7	22	22	7	13	5	10	0	1	10	10	-7	4	6	8
H	L	FO	FC	-1	8	10	9	9	3	5	9	0	2	11	8	-7	6	17	15
-11	2	5	7	-1	9	17	16	9	5	8	10	0	3	52	47	-7	10	27	27
-11	5	6	6	-1	10	23	23	9	8	10	11	0	4	14	15	-5	1	33	34
-11	7	4	3	-1	13	12	11	11	0	5	6	0	6	15	13	-5	3	6	7
-11	8	5	9	-1	14	20	20	11	1	7	9	0	7	79	81	-5	6	11	13
-9	2	16	15	-1	15	4	9	11	2	12	13	0	9	26	27	-5	7	5	7
-9	5	4	3	-1	16	7	8	11	3	16	19	0	11	24	23	-5	8	15	13
-9	9	11	8	-1	17	8	12					0	12	14	14	-3	1	28	31
-7	1	24	21	-1	19	17	16		K =	4		0	13	6	10	-3	2	13	13
-7	2	32	31	1	0	51	50	H	L	FO	FC	0	14	4	4	-3	3	31	32
-7	3	13	13	1	2	13	18	-10	1	7	10	0	15	5	7	-3	4	19	20
-7	4	18	13	1	3	50	46	-10	4	6	6	0	16	7	10	-3	6	17	19
-7	5	13	13	1	4	47	40	-10	5	8	13	0	17	11	13	-3	8	14	15
-7	6	26	24	1	5	5	10	-10	7	9	9	2	0	8	13	-3	9	5	6
-7	7	25	26	1	6	8	7	-8	3	12	11	2	1	27	30	-3	10	11	10
-7	8	5	8	1	7	48	46	-8	5	7	9	2	3	38	36	-3	11	4	4
-7	9	16	17	1	9	4	0	-8	9	26	28	2	4	55	50	-1	2	21	23
-7	11	15	14	1	10	24	23	-8	11	14	17	2	5	45	41	-1	3	9	10
-7	12	6	6	1	12	5	1	-8	13	6	7	2	6	21	21	-1	4	9	9
-7	14	4	7	1	13	28	24	-6	1	18	18	2	7	31	31	-1	6	64	64
-7	16	5	7	1	14	19	19	-6	3	8	7	2	8	12	11	-1	8	32	33
-7	17	5	4	1	15	4	3	-6	4	16	19	2	9	44	41	-1	10	22	20
-5	1	66	67	1	16	5	5	-6	5	13	16	2	10	7	9	-1	14	11	12
-5	2	26	29	1	17	17	17	-6	6	32	30	2	11	11	10	1	0	34	33
-5	3	10	12	3	1	52	51	-6	7	31	27	2	13	5	5	1	4	43	38
-5	4	60	62	3	2	65	59	-6	8	27	29	2	15	17	16	1	5	6	7
-5	5	33	33	3	4	43	43	-6	11	23	23	4	0	15	14	1	6	21	21

1	7	6	7				
1	8	65	59				
1	9	4	2				
1	14	12	14				
3	2	15	13				
3	3	6	3				
3	4	23	22				
3	5	8	11				
3	6	14	12				
3	7	6	8				
3	8	19	17				
3	10	4	6				
3	11	16	14				
3	12	10	11				
3	13	14	13				
5	0	5	7				
5	1	17	18				
5	2	12	15				
5	4	6	7				
5	5	7	7				
5	6	11	15				
5	7	4	3				
5	9	6	7				
7	0	13	16				
7	4	26	31				
	K =	6					
H	L	FO	FC				
-4	2	13	14				
-4	3	4	1				
-4	4	7	7				
-4	5	4	5				
-4	7	9	9				
-4	8	8	8				
-4	9	8	11				
-2	2	7	10				
-2	4	12	13				
-2	5	15	16				
-2	7	5	8				
-2	9	12	14				
-2	10	5	5				
0	0	14	16				
0	1	40	35				
0	2	7	8				
0	3	10	13				
0	7	27	28				
2	1	32	31				
2	4	5	7				
2	5	17	17				
2	6	8	9				
2	7	6	9				
4	0	10	12				
4	1	5	9				
4	2	14	11				
4	5	11	13				
4	6	16	14				

TABLE II
Final atomic and positional parameters

	x	y	z
P	0.5781(2)	0.7894(4)	0.1066(1)
O1	0.4691(4)	0.6085(9)	0.1177(2)
O2	0.6071(5)	0.9147(8)	0.1844(2)
O3	0.7000(4)	0.6220(10)	0.1152(2)
C1	0.4810(6)	0.473(1)	0.1832(4)
C2	0.6166(5)	0.778(1)	0.2500(3)
C3	0.5000	0.6250	0.5000
C4	0.7117(9)	0.468(2)	0.0566(4)
H1–C1	0.3995	0.3735	0.1821
H2–C1	0.5583	0.3606	0.1856
H1–C2	0.6955	0.6696	0.2542
H2–C2	0.6264	0.8911	0.2946
H1–C4	0.6451	0.3351	0.0537
H2–C4	0.6995	0.5624	0.0079
H3–C4	0.8038	0.4034	0.0635

R factor of 0.077 and a weighted R_w factor of 0.090. The calculated and observed structure factors, final atomic and positional parameters, final thermal parameters and intramolecular bond distances and angles appear in Tables I, II, III and IV, respectively.

DISCUSSION

The computer-drawn[10] structure of (**4**) stemming from the solution and refinement of the diffraction data is shown in Figure 1. Both methoxy groups are axial in the solid state of (**4**), as had been suggested earlier from solution nmr studies[11] and more recently from an analysis of dipole moment data of (**4**) and a monocyclic analog.[12]

From Table IV the average exocyclic OPO angle in (**4**) (101.1°) compares well with the endocyclic OPO angle of 101.8°. Similarly the exocyclic POC angle (117.8°) is close to the average endocyclic

TABLE IV
Intramolecular bond distances and angles

Distances (Å)		Angles (°)	
P–O1	1.616(5)	O1–P–O2	101.9(3)
P–O2	1.611(5)	O1–P–O3	102.1(3)
P–O3	1.624(5)	O2–P–O3	98.2(3)
O1–C1	1.443(8)	P–O1–C1	119.6(4)
O2–C2	1.448(7)	P–O2–C2	120.2(4)
O3–C4	1.431(10)	P–O3–C4	117.8(5)
C1–C2	1.514(7)	O1–C1–C3	111.9(5)
C3–C2	1.543(6)	O2–C2–C3	111.6(4)
		C1–C3–C2	109.1(4)

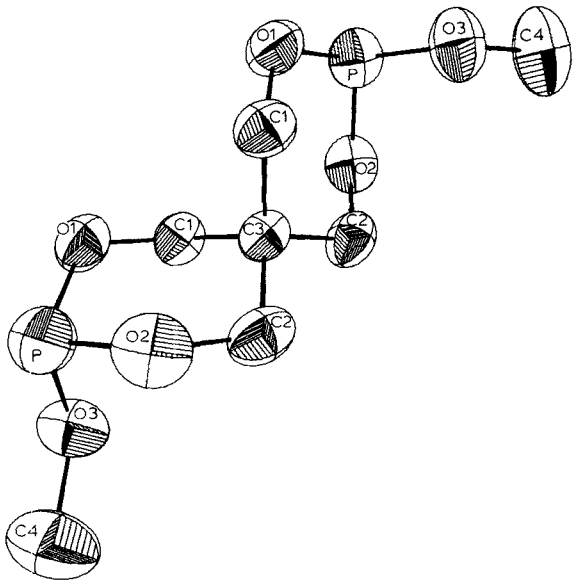


FIGURE 1 Computer drawing of the structure of $MeOP(OCH_2)_2C(CH_2O)_2POMe$ (**4**). The molecule lies on a two-fold crystallographic axis.

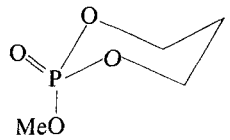
TABLE III
Final thermal parameters[a]

	β(1,1)	β(2,2)	β(3,3)	β(1,2)	β(1,3)	β(2,3)
P	0.0108(2)	0.0417(7)	0.00346(6)	0.0029(3)	0.00028(7)	0.0010(2)
O1	0.0092(4)	0.048(1)	0.0036(2)	0.0003(7)	−0.0004(2)	−0.0014(4)
O2	0.0129(4)	0.028(1)	0.0040(2)	−0.0018(7)	0.0013(2)	0.0003(4)
O3	0.0101(5)	0.051(2)	0.0036(2)	0.0046(8)	0.0002(2)	−0.0020(5)
C1	0.0096(6)	0.029(2)	0.0046(3)	−0.002(1)	0.0005(3)	−0.0025(6)
C2	0.0082(6)	0.032(2)	0.0035(2)	−0.0031(9)	0.0001(3)	−0.0007(6)
C3	0.0072(7)	0.024(2)	0.0034(3)	0.0	0.0003(3)	0.0
C4	0.0154(1)	0.078(5)	0.0042(2)	0.012(2)	0.0010(4)	−0.004(1)

[a] The β_{ij} are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. The isotropic temperature factors for all hydrogen atoms were set equal to 3.0 Å^2.

counterpart of 119.9°. The similarity in these angles and the PO bond lengths (1.63 Å avg) in (**4**) with those reported earlier for (**1**) where R = CH_2Br (OPO = 100.1°, POC = 117·5° and PO = 1.61 Å) strongly substantiates our earlier conclusion that the bicyclic cage phosphite is essentially strainless.[2]

Oxidation of (**1**) (where R = Me) leads to $OP(OCH_2)_3CMe$ (**5**) whose structure reveals only a decrease in the POC bond angle (115°) compared to acyclic phosphates (117–120°).[2] On the other hand oxidation of (**4**) to the diphosphate $MeO(O)P(OCH_2)_2C(CH_2O)_2P(O)OMe$ (**6**) can be expected to proceed without significant strain induction since the related compound (**7**) possesses



(**7**)

both angles and lengths[13] closely resembling those in acyclic phosphates. Thus, barring steric factors stemming from bulky phosphorus substituents, pentavalent phosphorus derivatives of (**4**) can reasonably be assumed to be quite strain free.

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