Effects of Axial *tert*-Butyl Substituents on Conformations and Geometries of Saturated Six-Membered Rings. Crystal and Molecular Structures of *trans*-2-Methoxy-2-oxo-5-*tert*-butyl- and *cis*-2,5-Di-*tert*-butyl-2-thio-1,3,2-dioxaphosphorinane

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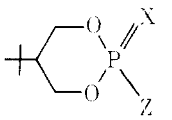
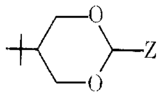
The title compounds crystallize in the orthorhombic system, the 2-methoxy compound (I) in the space group *Pnma*, and the 2-*tert*-butyl material (II) in space group *Pmcn*. Lattice parameters are: (I) a = 6.123 (4), b = 10.02 (1), c = 17.65 (1) Å, z = 4; (II) a = 10.077 (3), b = 10.662 (3), c = 12.703 (3) Å, z = 4. Compounds I and II both have chair-form ring conformations with the 5-*tert*-butyl group axial in both. For I the methoxy on phosphorus is axial and the phosphoryl oxygen is equatorial. The 2-*tert*-butyl is equatorial in II with the thiophosphoryl sulfur axial. In comparison to the structures of a large number of other phosphoranes, these rings systems, especially II, appear to be somewhat flattened about the C(5) end of the molecule. This apparently results from steric interactions involving the axial *tert*-butyl groups and the ring atoms C(4), C(6), O(1), and O(3) and hydrogens bonded thereto. Bond angle deformations within the 5-*tert*-butyl and at its point of attachment to the ring also attest to this fact. The phosphorus end of the ring associated with II is highly puckered. This property is shown to be a general one for 1,3,2-dioxaphosphorinanes with double-bonded O, S, or Se axial. For II the ring pucker is unusually large. Explanations based on nonbonded interactions of the 2-*tert*-butyl with ring oxygens O(1) and O(3) or across the ring with the axial 5-*tert*-butyl group are suggested.

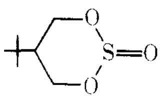
The 2-oxo- and 2-thio-1,3,2-dioxaphosphorinanes are readily substituted in a variety of ways both at phosphorus and on the ring carbons. As they are generally crystalline materials, they provide attractive systems for the determination of structural information on six-membered rings by X-ray crystallographic techniques. The present study presents unambiguous knowledge of the conformations of two such compounds, *trans*-2-methoxy-2-oxo-5-*tert*-butyl-1,3,2-dioxaphosphorinane (I) and *cis*-2,5-di-*tert*-butyl-2-thio-1,3,2-dioxaphosphorinane (II). A special structural feature of these compounds is the axial orientation of the 5-*tert*-butyl in both I and II in the solid phase, which provides an unusual opportunity to examine the effects on ring geometry of strain effects associated with so sterically bulky an axial substituent. Findings in the rings I and II are of wider interest as well, in relation to conformations of the corresponding 1,3-dioxanes (III)[1] and trimethylene sulfites (IV).[2]



I. X = O; Z = MeO
II. X = S; Z = *t*-Bu



III



IV

Experimental Section

The preparation of the phosphate I was reported earlier,[3] mp (*n*-hexane) 90–91 °C. Compound II was prepared from 2-*tert*-butyl-1,3-butanediol and *t*-BuP(S)Cl_2 in ether solution at 0–5 °C. The isomeric forms were separated by column chromatography on Florisil. Elution solvent was initially 3% ether in ligroin (60–90 °C). The fraction ether was gradually increased during chromatography. Compound II was crystallized from ligroin (60–90 °C), mp 96–97 °C (uncorrected).

Both substances crystallize in an orthorhombic space group with extinctions consistent with either *Pn*2_1*a* or *Pnma*. The centric space group has been shown to be correct. (I is in space group *Pnma* while II is in *Pmcn*; these are identical space groups with different axial orientations consistent with the conventions for reporting orthorhombic lattice dimensions.) Extinctions and crystal data are provided in Table I for each of the crystals.

Data were collected on a General Electric XRD-5 diffractometer equipped with a scintillation counter, pulse-height discriminator, and GE single-crystal orientor, using θ–2θ scan technique. Details of the experimental procedures for each crystal are given in Table II. Three standard reflections were monitored to check crystal deterioration. No deterioration was observed in either case. Both crystals were enclosed in Lindeman glass capillaries to prevent loss by sublimation.

Solution of the structures was accomplished by Patterson methods, by locating the phosphorus atoms and subsequently calculating phases from the phosphorus atom positions. All remaining nonhydrogen atomic positions were seen on these Fourier maps. Refinement was carried out by full-matrix least-squares procedures,[4] weighting according to counting statistics. Atomic scattering factors for the nonhydrogen atoms were taken from the International Tables for X-ray Crystallography; both real and imaginary terms were applied to phosphorus. Hydrogen scattering factors were those of Stewart, Davidson and Simpson.[5] Final R factors are reported in Table II. For crystal I a difference synthesis allowed location of some of the hydrogen atoms. The remaining hydrogen atom positions were calculated and included in the final structure factor calculation. All hydrogen atom positions were located from the difference maps for compound II and these were included in the refinement with fixed temperature factors.

Results

Bond distances and angles are given in Figures 1, 2, 3, and 4, and the conformations are shown in the ORTEP drawings of Figures 5 and 6. No intermolecular distances short enough to affect geometry were encountered.

Both molecules I and II lie on a crystallographic mirror plane. For compound I, atoms P(2), O(13), C(5), C(7), and C(10) are on the mirror plane in special positions $y = 1/4$ and $3/4$. The methoxy carbon C(11) of I is disordered, being found on either side of the mirror plane with an occupation factor of 0.5. The ring is a distorted chair with the *tert*-butyl and methoxy groups trans to each other in axial positions.

For compound II, atoms P(2), S(15), C(5), C(7), C(10), C(11), and C(14) lie on the mirror plane in special positions $x = 1/4$ and $3/4$. The ring is a distorted chair with the *tert*-butyl groups cis to each other. The *tert*-butyl group on the C(5) position is axial while that on the P(2) position is equatorial. In both I and II the *tert*-butyl groups are perfectly staggered

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Table I

5-*tert*-Butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane (registry no. 26344-06-9)

$C_8PO_4H_{17}$	$F(000) = 448$
fw 208.19	systematic absences: hkl, no conditions; $hk0$, $h \neq 2n$; $0kl$, $k + l \neq 2n$; $h0l$, no conditions; $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$
orthorhombic: space group *Pnma*	
$a = 6.123$ (4) Å	
$b = 10.02$ (1) Å	
$c = 17.65$ (1) Å	
vol of unit cell 1083 Å^3	
molecules/unit cell = 4	
$D_{exp} = 1.25$ g/cm^3	
$D_{calcd} = 1.277$ g/cm^3	

2,5-Di-*tert*-butyl-2-thio-1,3,2-dioxaphosphorinane (registry no. 67271-57-2)

$C_{11}PSO_2H_{23}$	$F(000) = 544$
fw 250.32	systematic absences: hkl, no conditions; $h0l$, $l \neq 2n$; $hk0$, $h + k \neq 2n$; $0kl$, no conditions; $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$
orthorhombic: space group *Pmcn*	
$a = 10.077$ (3) Å	
$b = 10.662$ (3) Å	
$c = 12.703$ (3) Å	
vol of unit cell 1364.8 Å^3	
molecules/unit cell = 4	
$D_{exp} = 1.210$ g/cm^3	
$D_{calcd} = 1.218$ g/cm^3	

Table II. Experimental Details

	I	II
crystal size	0.3 × 0.5 × 1.0 mm^3	0.16 × 0.26 × 0.58 mm^3
crystal mounted on	*a*	*a*
scan time	100 s	60 s
background count time	50 s/side	10 s/side
scan rate	2°/min	2°/min
takeoff angle	4°	4°
no. of reflections scanned	1008	818
obsd reflections ($I_{obsd} > 2\,\sigma(I)$)	585	763
μ (linear absorption coeff.)	2.41 cm^{-1}	3.33 cm^{-1}
final *R* factors: *R*	0.059	0.048
R_w	0.060	0.038

Radiation used in each case was Mo K(α) λ = 0.710 698 Å)
Functions minimized in least-squares refinement was $\sum w(|F_0| - 1/k|F_c|)^2$

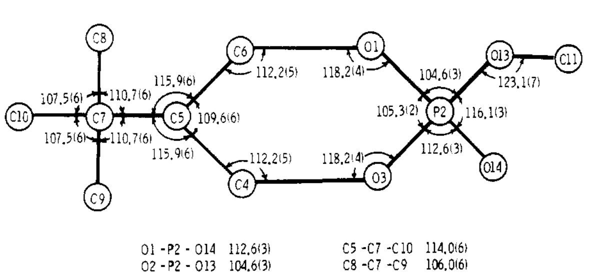


Figure 1. Bond angles for I.

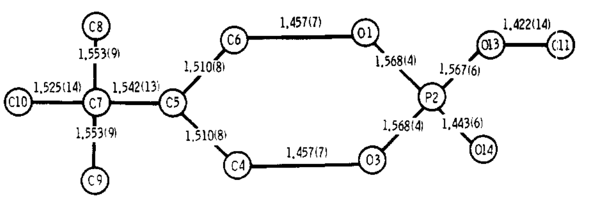


Figure 2. Bond distances for I (2-methoxy-2-oxo-5-*tert*-butyl-1,3,2-dioxaphosphorinane).

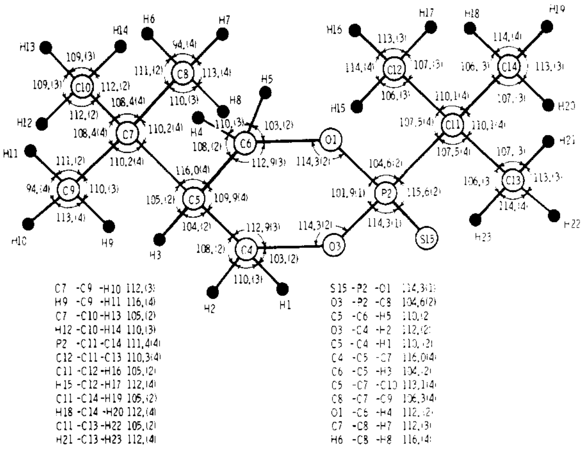


Figure 3. Bond angles for II.

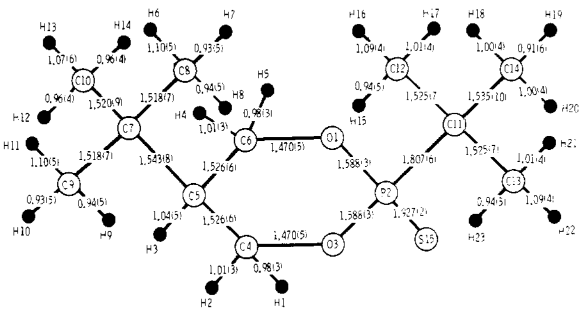


Figure 4. Bond distances for II (2,5-di-*tert*-butyl-2-thio-1,3,2-dioxaphosphorinane).

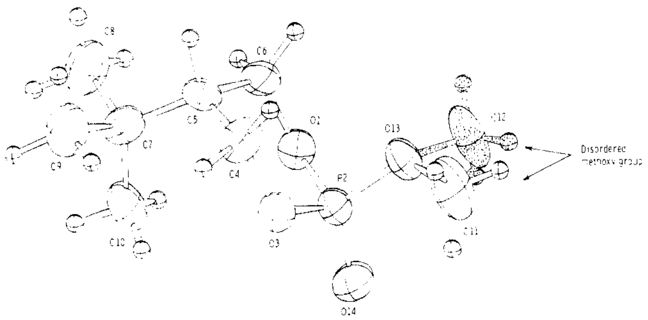


Figure 5. ORTEP drawing for I.

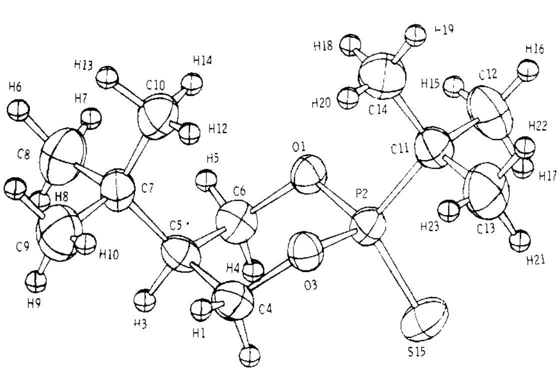
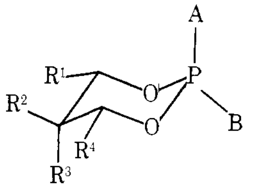
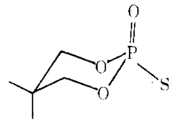
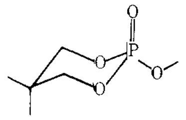


Figure 6. ORTEP drawing for II.

with respect to rotation about the C(5)–C(7) and P(2)–C(11) bonds. This symmetry also extends to the C–C bonds within the *tert*-butyl groups themselves such that, e.g., H(12) and H(14) in II are equivalent as are H(18) and H(20) and so forth. Bonding distances in I and II are not significantly different from those found for other 1,3,2 dioxaphosphorinanes.

Table III. X-ray Crystallographic Data for Various Substituted 1,3,2-Dioxaphosphorinanes



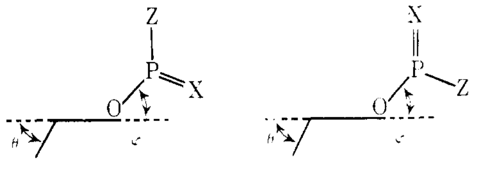
compd	R_1	R_2	R_3	R_4	A	B	∠P–O–C	∠φ	∠θ	ref
1	H	H	H	H	HO	=O	120, 121	40	54	*a*
2	H	H	H	H	PhO	=O	118, 118	37	53	*b*
3	H	CH_3	CH_3	H	Cl	=O	119, 123	35	52	*c*
4	H	CH_3	CH_3	H	Ph	=O	119, 120	33	51	*d*
5	H	CH_3	CH_3	H	PhNH	=O	118, 121	34	56	*e*
6	H	CH_3	CH_3	H		=O	120,121	31	55	*f*
7	H	CH_3	CH_3	H		=O		36		*g*
8	H	CH_3	CH_3	H	OCN	=O		34		*h*
9	H	CH_3	CH_3	H	PhO	=S	119, 119	37	54	*i*
10	H	CH_3	CH_3	H	CH_3O	=Se	116, 118	39	52	*j*
11	H	CH_3	CH_2Br	H	Br	=O	120, 121	37	53	*k*
12	CH_3	H	H	H	*t*-BuNH	=Se	118, 119	37	53	*l*
13	CH_3	H	H	CH_3	CH_3O	BH_3	119, 120	38	54	*m*
14	CH_3	H	H	CH_3	Ph_3C	=O	127, 128	3.7	53	*n*
15	H	*t*-Bu	H	H	CH_3	=O	120, 120	34	55	*o*
16	H	*t*-Bu	H	H	Ph	=S	117, 120	36	56	*p*
17	H	H	*t*-Bu	H	CH_3O	=O	118, 118	38	50	*q*
18	H	CH_3	CH_2Cl	H	=O		116, 116			*r*
19	H	CH_3	CH_3	H	=S	CH_3	116, 116	46	52	*s*
20	CH_3	H	H	H	=Se	*t*-BuNH	115, 118	44	56	*t*
21	H	H	*t*-Bu	H	=S	*t*-Bu	114, 114	50	46	*q*

[a] Reference 7. [b] Reference 6. [c] Reference 8. [d] Reference 9. [e] Reference 10. [f] Reference 11. [g] Reference 12. [h] Reference 13. [i] Reference 14. [k] Reference 15. [l] Reference 16. [m] Reference 17. [n] Reference 18. [o] Reference 19. [p] Reference 20. [q] This work. [r] Reference 21. [s] Reference 22. [t] Reference 23.

Discussion

That the 2-*tert*-butyl group of II has sufficient steric bulk to force the 5-*tert*-butyl group into the axial position is not surprising. This simply means that the repulsive interactions between the 2-*tert*-butyl methyls and the C(4), C(6) carbons and hydrogens are greater than the interactions between the C(5)-*tert*-butyl methyls and the O(1), O(3) oxygens. What would not have been predicted necessarily is the axial position for the 5-*tert*-butyl of I. Clearly the preferences of the MeO(axial) and P=O(equatorial) are so great as to determine which chair form is energetically favored. Although such preferences for RO and P=O have been noted before in crystals of 2-phenoxy-2-oxo-1,3,2-dioxaphosphorinane[6] (compound **2** of Table III) and in liquid phase ^1H NMR work with 2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane,[24] these systems were not energetically biased against such a conformation by substituents on ring carbons. In 1,3-dioxanes[1a,c] (III) and the trimethylene sulfite (IV),[2b,d] $\Delta G°_{25}$ for the process of 5-*t*-Bu(equatorial) → 5-*t*-Bu(axial) is unfavorable by 1.4 to 1.8 kcal/mol. The close similarity of the O(1)–C(6)–C(5)–C(4)–O(3) geometries in 1,3-dioxanes[25] and 1,3,2-dioxaphosphorinanes[26] indicates that the steric interactions for an axial 5-*tert*-butyl should be about the same in the two systems. Thus, neglecting effects of crystal packing forces, the sum of the energetic preferences of the MeO(axial) and phosphoryl oxygen(equatorial) is of the order 1.5 to 2.0 kcal/mol or greater.

The dihedral angle φ (see structures V and VI) between the planes O(1)–O(3)–C(4)–C(6) and O(1)–P(2)–O(3) in I is 37.9° and in II is 50.3°. Thus I, with P=O equatorial (V), is considerably more flattened about phosphorus than is II with P=S axial (VI). The greater pucker in the ring of II also shows itself in the angles C(4)–O(3)–P(2) and C(6)–O(1)–P(2) which are decreased to 114.3° from the value of 118.2° in I.



V VI

The effect on angle φ of inverting configuration about phosphorus seems to be very general and not merely a consequence of the presence of the 2-*tert*-butyl in II. Table III gives the dihedral angle φ and/or the ring angles C(4)–O(3)–P(2) and C(6)–O(1)–P(2) as determined by X-ray crystallography for a large variety of 1,3,2-dioxaphosphorinanes. For those of structure V, compounds 1–17 (excluding 14), φ ranges 31–40°. As we first pointed out[19] and as has been reemphasized recently[11] with the larger series of compounds now available, this variation primarily reflects changes in the steric size of Z. As Z becomes larger, the ring flattens to reduce the

Table IV. Selected Short Nonbonded Intramolecular Distances (Å) in I and II

compound I

C–C (3.5)[a]	C–O (3.3)	O–O (3.0)	P–C (3.6)
C(7)–C(6) 2.6	C(7)–O(3) 3.2	O(13)–O(1) 2.5	P(2)–C(11) 2.6
C(7)–C(4) 2.6	C(7)–O(1) 3.2	O(13)–O(3) 2.5	
C(9)–C(4) 3.1	C(10)–O(3) 3.1	O(13)–O(14) 2.6	
C(8)–C(6) 3.1	C(10)–O(1) 3.1	O(14)–O(3) 2.5	
C(10)–C(4) 3.2	C(4)–O(13) 3.1	O(14)–O(2) 2.5	
C(10)–C(6) 3.2	C(6)–O(13) 3.1		

compound II

C–C (3.5)	C–O (3.3)	H–O (2.7)	H–H (2.4)
C(7)–C(4) 2.6	C(10)–O(3) 3.2	H(12)–O(3) 2.7	H(1)–H(10) 2.2
C(7)–C(6) 2.6	C(10)–O(1) 3.2	H(14)–O(1) 2.7	H(5)–H(7) 2.2
C(9)–C(4) 3.0	C(7)–O(1) 3.3	H(20)–O(3) 2.7	H(1)–H(12) 2.8
C(10)–C(6) 3.0	C(7)–O(3) 3.3	H(18)–O(1) 2.7	H(5)–H(14) 2.8
C(10)–C(4) 3.0	C(11)–O(3) 2.7	H(23)–O(3) 2.7	H(12)–H(20) 2.7
C(10)–C(6) 3.0	C(11)–O(1) 2.7	H(15)–O(1) 2.7	H(14)–H(18) 2.7
C(10)–C(14) 3.7	C(14)–O(3) 3.1		H(3)–H(9) 2.4
	C(14)–O(1) 3.1		H(3)–H(8) 2.4

CH (3.0)		misc.	
C(4)–H(10) 2.9	C(10)–H(1) 3.2	S(15)–H(2) 3.1 (3.0)[a]	S(15)–C(4) 3.5 (3.5)
C(4)–H(7) 2.9	C(10)–H(5) 3.2	S(15)–H(4) 3.1 (3.0)	S(15)–C(12) 3.5 (3.5)
C(4)–H(12) 2.9	C(7)–H(3) 2.1	S(15)–H(16) 2.9 (3.0)	S(15)–C(13) 3.5 (3.5)
C(5)–H(14) 2.9	C(10)–H(20) 3.3	S(15)–H(22) 2.9 (3.0)	S(15)–C(11) 3.2 (3.5)
C(7)–H(1) 2.7	C(10)–H(18) 3.3	S(15)–C(6) 3.5 (3.5)	
C(7)–H(5) 2.7	C(14)–H(12) 3.3		
C(9)–H(1) 2.6	C(14)–H(14) 3.3		
C(8)–H(5) 2.6			

[a] Number in parentheses is van der Waals sum. van der Waal radii used are: C, 1.75; O, 1.5; P, 1.85; H, 1.2A. These agree with those given by Bondi.[29]

syn axial repulsions between Z and the C(4), C(6) axial hydrogens.

The highly distorted compound **14** particularly shows the effect of size of Z (−3.7°). By contrast compounds **19–21**, which have structure VI, exhibit values between 44 and 50°. Compound **18**, for which ϕ was not reported, has the ring angle reduced to 116° as expected for increased puckering about phosphorus. Particularly convincing are comparisons of compounds with identical or closely similar substituents on phosphorus, as for example **12** vs. **20** and **19** vs. **4**, **15**, and **16**.

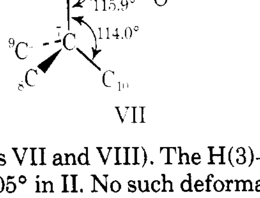
The simplest explanation of this effect seems to be based on the fact that regardless of the configuration at phosphorus, the bond angles about the P=X side of the phosphorus tetrahedron are increased well beyond 109°.[6–23] When Z is axial, this then has the effect of forcing the group Z close to the axial hydrogens at C(4) and C(6). To reduce the accompanying strain, the ring becomes flattened at phosphorus, increasing the Z···H(5), H(6) distances. Such flattening is not required with P=X axial. Inspection of intramolecular distances in Table IV shows that in compound II the S(15)–C(4), -C(6) distances are just at or slightly longer than van der Waal radii sums, while O(13)–C(4), -C(6) of I in which the ring has presumably been flattened to reduce that distance to 3.1 Å are slightly shorter (0.2 Å) than van der Waals sums.

Inspection of Table III shows that if one excludes the compounds I and II of this study (**17** and **21** in Table III), the angle θ covers a range of just 5°, 51–56°. Thus θ is remarkably independent of changes in φ at the other end of the molecule (φ = 3.7 to 46°). Especially compare **13** with **14** and **4, 5, 10, 11** with **19**.

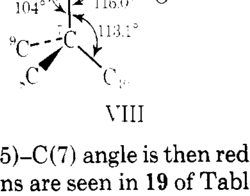
The axial 5-*tert*-butyl compounds of the present study, I and II (**17** and **21** of Table III), have low values of θ, 49.9° and 46.0°. This is evident when compared to the average θ for the other compounds of Table III, 54°, and especially to compounds **15** (θ = 55°) and **16** (θ = 56°) with 5-*tert*-butyl equatorial. The flattening which occurs at the C(5) end of rings I and II appears to come from repulsive steric interactions involving the axial *tert*-butyl group and the C(4), C(6), and associated hydrogen atoms as well as O(1) and O(3). In Table IV one finds that a number of the corresponding intramolecular distances are very near to or less than the sum of the van der Waals radii. Note, e.g., the C(8), C(9), and C(10) interactions with C(4) and/or C(6) and C(10) with O(1), O(3) in both I and II. Also note in II, H(10)–H(1), H(7)–H(5), H(1)–C(7), H(1)–C(9), H(5)–C(8), H(12)–O(3) and H(14)–O(1).

Since the locations of the hydrogens are less well defined than those of the carbons and oxygens, one may also evaluate the C···O and C···C intramolecular distances with the usually assumed radius of the methyl group (2.0 Å[27]). Again contacts well under van der Waals sums (3.5 Å for CH_3 plus oxygen) are encountered for C(10)–C(1), O(3) interactions, and C(10)–C(4), -C(6).

The strain in I and II engendered by the axial 5-*tert*-butyl is also relieved by an increase in the angles C(4)–C(5)–C(7) and C(6)–C(5)–C(7) to 115.9° in I and 116.0° in II (see structures VII and VIII). The H(3)–C(5)–C(7) angle is then reduced to 105° in II. No such deformations are seen in **19** of Table III. In addition, the angle C(5)–C(7)–C(10) is increased to 114.0° in I and to 113.1° in II.



VII



VIII

Another significant structural effect in these compounds is the 4° increase in angle φ of II compared to compound **19** of Table III for which the equatorial substituent on phosphorus (CH_3) is much smaller. Some evidence that ring pucker at phosphorus in II occurs in relief of steric interaction between the ring oxygens and C(14) comes from the bond angle P(2)–C(11)–C(14) of 111.4°. At the same time the angles P(2)–C(11)–C(12) and P(2)–C(11)–C(13) are 107.5°, as though the whole *tert*-butyl group had tipped at the C(11) slightly toward S(15). The angle O(1)– or O(3)–P(2)–C(11), 104.6°, is only slightly and hardly significantly increased over that of the methyl compound **19** of Table III (103.2°). Angle S(15)–P(2)–C(11) is decreased 1°. The C(11)–O(1), –O(3) interatomic distances are 3.1 or 0.2 Å below van der Waals sums. Furthermore, H(18)–O(1), H(18)–O(3), H(20)–O(1), and H(20)–O(3) distances are right at van der Waals sums. Use of the methyl radius estimate of 2.0 Å rather than the imprecisely determined hydrogen–oxygen distance puts H(18)–O(1) and H(20)–O(3) well under van der Waals distances. Slight ring puckering effects have been noted in certain cyclohexanes at the point of equatorial *tert*-butyl substitution.[28]

An alternative source of ring pucker at phosphorus in II could be the axial 5-*tert*-butyl if the two *tert*-butyl groups interact sterically in intermolecular fashion. The 4° decrease in θ in II compared with that for I makes this an attractive idea, especially since ring pucker at phosphorus has no demonstrable effect on θ (vida supra, Table III). In this view both ends of the molecule are repelled away from each other. From Table IV the *tert*-butyl-*tert*-butyl distances are C(10)–C(14) at 3.70 Å (van der Waals sum, 3.54 Å). Use of the 2.0 Å methyl radius concept,[27] however, puts the corresponding H–H contacts well under van der Waals sums (0.3 Å). Measured C···H and H···H distances are just above van der Waals sums, e.g., H(12)–H(20) and H(14)–H(18), 2.65 Å; C(10)–H(18) and C(10)–H(20), 3.30 Å. It should also be remembered that C–C rotations will bring the H···H contacts in solution closer than those in the crystal. If one considers also the measurement errors especially in H positions, it seems quite possible that the *tert*-butyl groups do repell each other. A final resolution of the question of the origin of the apparent concerted distortions of both ends of the ring of II awaits a crystallographic study of 2-*tert*-butyl-2-thio-1,3,2-dioxaphosphorinane itself.

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Registry No.—2-*tert*-Butyl-1,3-butanediol, 67271-58-3; *t*-BuP(S)Cl_2, 21187-18-8.

Supplementary Material Available: Listing of structure factor amplitudes and positional and thermal parameters for compounds I and II (6 pages). Ordering information is given on any current masthead page.

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