

12*H*-Dibenzo[*d,g*][1,3,2]dioxaphosphocins: Synthesis, Structures and "Through-Space" Spin-Spin Coupling in Their NMR Spectra

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A series of 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins has been prepared by the reactions of bisphenols with either ethyl phosphorodichloridate or phosphorus pentasulfide. The structures of a pair of *cis* and *trans* isomers in this series were elucidated by X-ray crystallography. Both isomers adopt the boat-chair conformation in the solid state with the bulky group at C-12 in the pseudo-equatorial position. Some flattening of the heterocyclic ring due to the pseudo-axial ethoxy group was observed in the *cis* isomer. A novel transannular cyclisation reaction was observed in the mass spectra of the *cis* isomers and this has allowed us to assign the configurations of all the isomers in the series. The pmr spectra of the compounds have been explained in terms of the rigid boat-chair conformation; however, as bulky groups were introduced at C-12, signs of mobility were observed for the *cis* isomers and an equilibrium was established with mobile boat forms. A stereo-specific long-range coupling between P and the proton at C-12 could be transmitted "through space" by the antiperiplanar lone-pair electrons on the ring oxygen atoms.

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Because of their potential use as antioxidants and stabilizers, the 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins are currently of considerable interest in the polymer and oil industries. A measure of this interest was revealed in a recent on-line search [2] of Chemical Abstracts when 258 structures and 101 references to the dibenzodioxaphosphocins were retrieved. However, whilst these materials have been widely reported in the literature [3], it has been only recently that any definitive preparations and spectra of the dioxaphosphocins [4] have appeared.

We have been assaying various classes of compounds for their ability to stabilize the dyes in coloured photographs against the actions of light and heat. The dibenzodioxaphosphocins were found to be useful for that purpose [5] and in this paper we wish to report the synthesis and structures of some of our compounds.

The dioxaphosphocins **2** were readily prepared from their phenolic precursors **1**, many of which are low cost commercially available materials [6], through the reaction

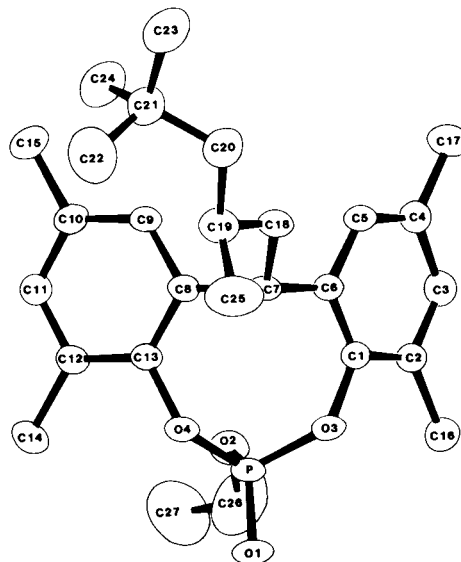
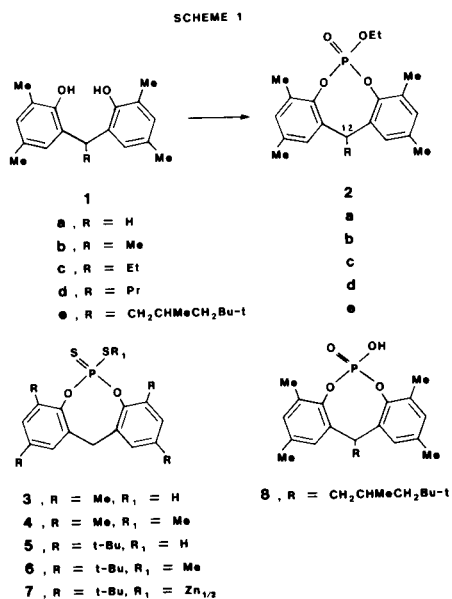


Figure 1. ORTEP plot of *Cis* **2e** drawn with 30% probability thermal ellipsoids.

of the phenols with ethyl phosphorodichloridate in the presence of catalytic quantities of 4-dimethylaminopyridine (Scheme 1).

Compounds **2b-e** can be formed in both *cis* and *trans* configurations (ethoxy group relative to R) and in each case the two isomeric compounds were separable by recrystallization. *Cis* and *trans* isomerism has been noted only once before [4a] for dibenzodioxaphosphocins and in that case it was possible neither to separate the isomers nor assign their configurations.

Analysis by X-rays of single crystals of the isomers of compound **2e** confirmed the *cis* and *trans* relationship between the two compounds (Figures 1 and 2). Bond distances and angles are given in Tables 1 and 2. Both isomers adopt the boat-chair conformation (Figures 3 and 4) in the solid state with the bulky groups at C7 (in this discussion the designations C7 and C-12 refer to the same carbon atom in Figures 1 and 2 and Scheme 1 respectively) residing in the sterically more favoured pseudo-equatorial position. This conformation is in accord with previous data gathered on similar heterocyclic [7] and carbocyclic [8] systems. Furthermore, whilst our work was in progress, the X-ray structure of a closely related dibenzodioxaphosphocin was published [9] in which the boat-chair conformation was also observed.

The heterocyclic and two fused benzo rings in each isomeric structure can be described by three least-squares planes (Table 3). The dihedral angles enclosed by these planes are similar, although the angles involving plane 3 are larger in the *cis* isomer. This latter observation is con-

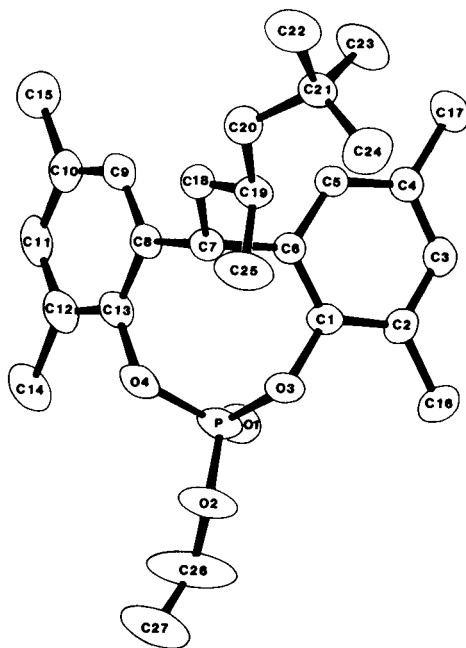


Figure 2. ORTEP plot of *Trans 2e* drawn with 30% probability thermal ellipsoids.

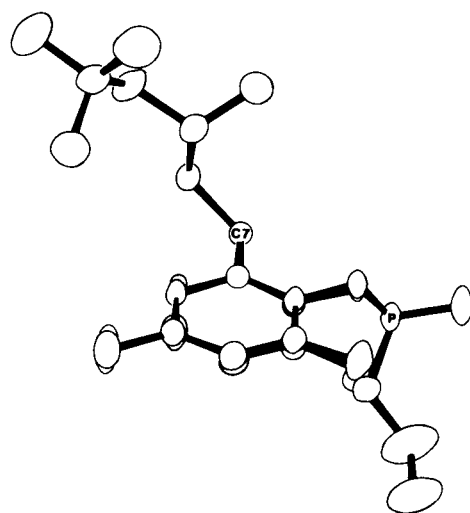


Figure 3. *Cis 2e*

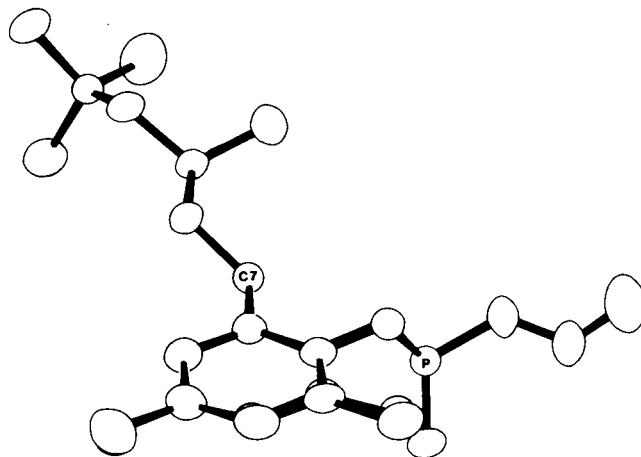
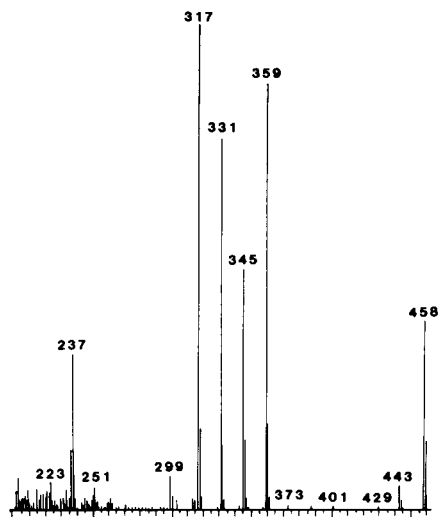
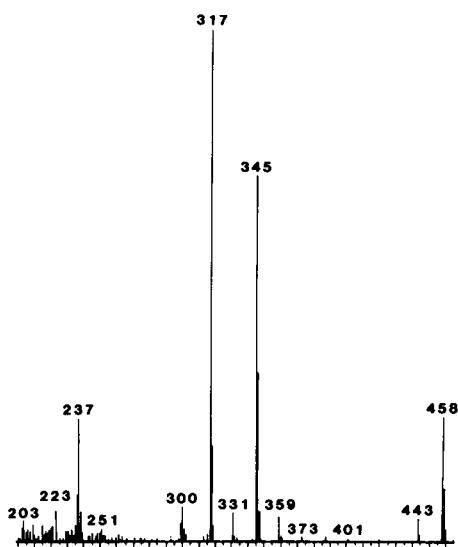


Figure 4. *Trans 2e*

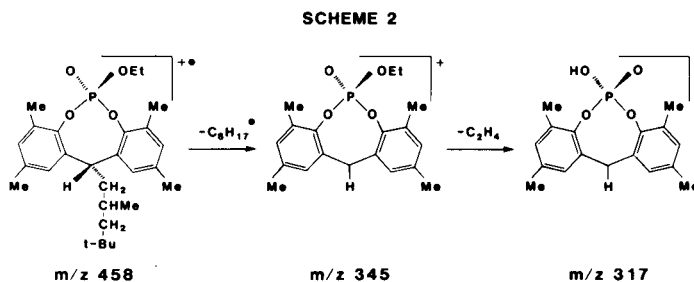
sistent with a flattening of the heterocyclic ring at the phosphorus end in the *cis* isomer. This effect has been observed before [10] in 6-membered phosphorus heterocycles and appears to be a reflection of the capacity of phosphorus for meliorating the sterically unfavourable position of bulky axial groups. In the case of the *cis* isomer, the bulky (relative to the phosphoryl oxygen) pseudo-axial ethoxy group causes a flattening of the heterocyclic ring. This flattening effect is also manifest in the exocyclic O2-P-O3 and O2-P-O4 bond angles (105.1° and 104.4° in the *cis* isomer and 98.6° and 100.2° , respectively, in the *trans* isomer) and in the O4-P-O3-C1 and O3-P-O4-C13 torsion angles (-78.3° and $+79.0^\circ$ in the *cis* isomer and -86.0° and $+86.2^\circ$, respectively, in the *trans* isomer). Furthermore, the phosphorus atom is 0.8 \AA out of the C1-O3-O4-C13 least-squares plane in the *cis* isomer and 0.86 \AA out of this plane in the *trans* isomer.

As expected, the geometry about phosphorus is approximately tetrahedral. The P-O (average $d = 1.566 \text{ \AA}$) and P=O (average $d = 1.445 \text{ \AA}$) bond distances are equivalent in the two isomers and near expected values (see, for example, details of the structure of 2-oxo-2-methyl-6-aza-6-phenyl-1,2,3-dioxaphosphacyan [11] where P-O, $d = 1.575 \text{ \AA}$ and P=O, $d = 1.461 \text{ \AA}$). As expected from VSEPR theory [12], the O-P=O bond angles are larger than the O-P-O angles. There are no unusual features about the remaining bond distances and angles.

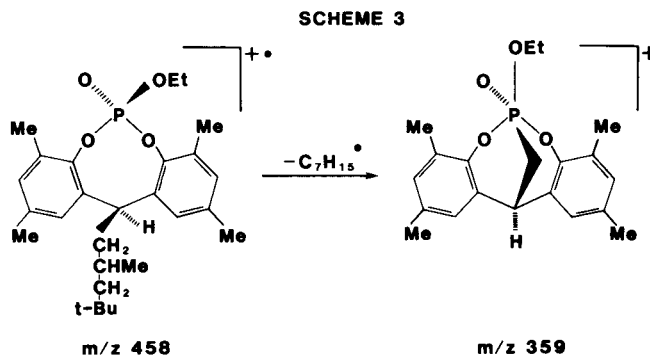
The mass spectra of the dibenzodioxaphosphocins **2b-e** are extremely interesting since they can be used to assign the configurations of pairs of isomers. This is illustrated in detail for the *cis* and *trans* isomers of **2e** where their stereochemistry had already been assigned unambiguously from the X-ray data. Both these compounds gave rise to

Figure 5. *Cis* **2e**Figure 6. *Trans* **2e**

electron impact mass spectra (Figures 5 and 6) exhibiting intense molecular ion peaks of m/z 458 and consistent with isomeric materials having the molecular formulas $C_{27}H_{39}O_4P$. Fragment peaks were consistent with the structural formula **2e**, for instance, both isomers showed a major loss of the C_8H_{17} side chain to give the stable fragment of m/z 345 followed by loss of ethylene to give the base peak due to the fragment of m/z 317 (Scheme 2). Also, both isomers exhibited weak fragmentations corresponding to losses of the following radicals: CH_3 (m/z 443), C_4H_9 (m/z 401), C_5H_{11} (m/z 387) and C_6H_{13} (m/z 373).



Whilst the two isomers exhibited the same ion peaks in their mass spectra, the relative intensities of these peaks were quite different. The most significant difference was that the *cis* isomer exhibited a greatly enhanced propensity to form a fragment of m/z 359 (corresponding to a loss of a C_7H_{15} radical from the side chain) in the mass spectrometer. This process was followed by the loss of ethylene to give an intense fragment peak of m/z 331. The enhanced loss of the C_7H_{15} radical in the *cis* isomer was surprising since, at first sight, this would not appear to be a particularly energetically favourable mode of fragmentation. However, these data may be rationalised in terms of a novel transannular reaction of the terminal methylene radical in the side chain of the *cis* isomer with the phosphorus atom (Scheme 3) giving the triheterocyclic fragment of m/z 359. The favourable stereochemistry of this latter species is confirmed by molecular models (Figure 7). In the *trans* isomer this transannular reaction is effectively blocked by the phosphoryl oxygen. This rationale has allowed us to assign the configurations of the other pairs of isomers **2b-d** in the series.



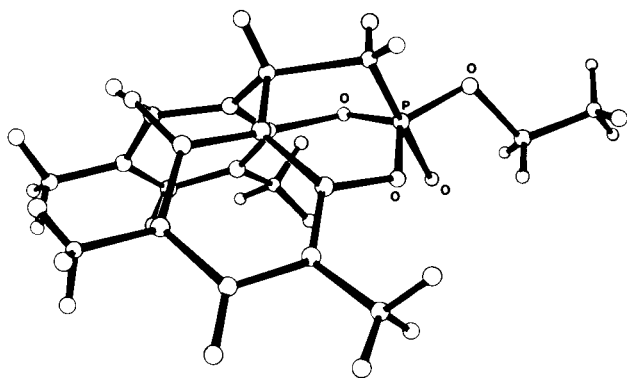


Figure 7. Molecular model of triheterocyclic fragment m/z 359.

Having assigned the configurations of compounds **2b-e** pure samples of these isomers were used as standards to calibrate the response of a high performance liquid chromatography machine. The ratios of the amounts of *cis* and *trans* isomers **2b-e** formed in the various reaction mixtures were thus determined. The ratio of *trans* to *cis* was found to be 2.3 to 1 on average. Presumably the *trans* isomer is favoured due to less steric hindrance in the approach of the bisphenols **1** to the acid chloride in the *trans* configuration. These quantitative results confirmed our observations made of thin layer chromatograms where the *trans* isomers always gave a more intense spot. Furthermore, the *trans* isomers have a larger R_f on silica tlc plates than the *cis* isomers. This latter test would appear to be diagnostic [13] for configuration in this particular series.

Odorisio *et al* [4] have previously reported the syntheses of some 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins, the structures of which are closely related to the ones given in this paper. By examination of molecular models they were able to suggest a rigid saddle-like conformation for their heterocycles. Our X-ray data, those of others [9] on a dibenzodioxaphosphocin and studies on structurally related heterocyclic systems [7] all support the rigid boat-chair [14] conformation (Figures 3 and 4) for the dibenzodioxaphosphocins.

Odorisio *et al* also noted a long-range coupling (between the phosphorus atom and the proton at C-12) in the pmr spectra of their compounds which was suggestive of the operation of a "through-space" [15] mechanism. The pmr spectra of some of our materials also show the presence of a long-range coupling between phosphorus and the C-12 proton (Figure 8) and we believe that we have now found evidence to support the "through-space" mechanism for this. The 400 MHz pmr spectra of the *cis* and *trans* isomers of compounds **2b-e** show that the coupling is highly stereospecific, since the small heteronuclear coupling (~ 2 Hz) is evident only in the spectra of the *trans* isomers. Since both isomers adopt similar rigid boat-chair conformations and since, therefore, the pathway between

phosphorus and the C-12 proton is the same in both isomers, it seems unlikely that the long-range coupling is through-bond. The observed long-range coupling in the spectra of only the *trans* isomers is more consistent with a "through-space" mechanism. In the *trans* configuration the two lone-pairs of electrons of the ring oxygen atoms on the same side of the heterocyclic ring as the C-12 proton are antiperiplanar to the phosphoryl oxygen (Figure 9) and are therefore in a position to interact with the P=O bond. If it is assumed that the lone-pairs of electrons on the oxygen atoms can be represented by atoms at these points and that these are then in tetrahedral positions relative to the atoms bonded to O3 and O4 (Figures 1 and 2), the torsion angles for the lone-pairs pointing in towards the heterocyclic ring can be calculated as 164° (O1-P-O3-lone-pair) and -165° (O1-P-O4-lone-pair). This arrangement could provide the "through-space" pathway for coupling between the phosphorus atom and the distant proton at C-12. The transmission of coupling through space *via* the lone-pair electrons of oxygen has been proposed before [15], although to our knowledge this is the first time such an observation has been made for phosphorus to hydrogen coupling.

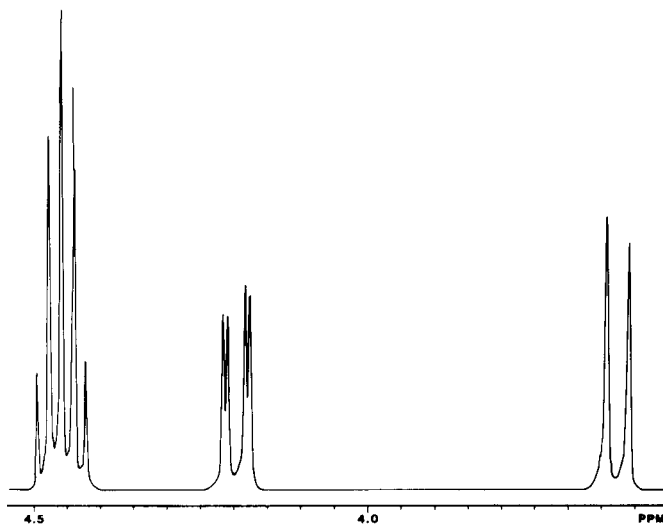


Figure 8. 400 MHz PMR spectrum of **2a** showing "through-space" coupling between P and low field methylene proton

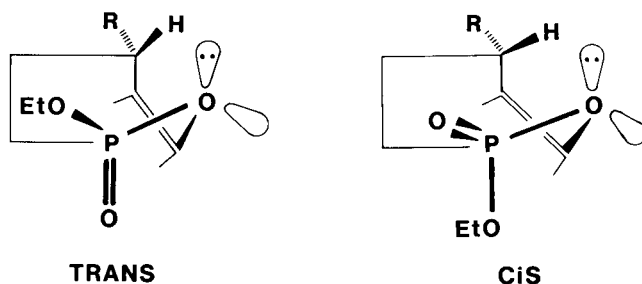


Figure 9

Another major difference between the pmr spectra of the *cis* and *trans* isomers **2b-e** is that the signal due to the proton at C-12 appears to be broadened for some of the *cis* isomers and that this broadening increases as the size of the group R increases. This is consistent with the presence

of some conformational mobility in those *cis* isomers which have large R groups. The origin of this conformational mobility in the *cis* isomers is twofold. Firstly, the rigid boat-chair conformation of the *cis* isomers is less stable than that of the *trans* since it requires the relatively

Table 1

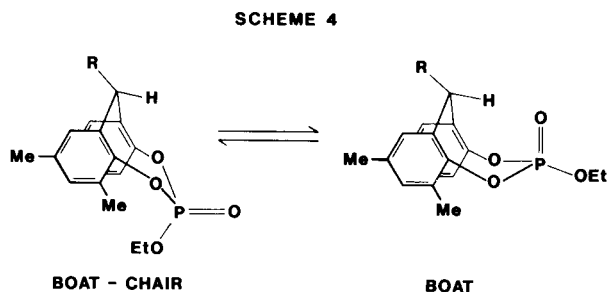
Table of Bond Distances (Å) for Compound **2e**

Table 1 (continued)

<i>trans</i> isomer			<i>cis</i> isomer		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
P	O1	1.450(2)	C8	C9	1.388(4)
P	O2	1.557(2)	C8	C13	1.388(4)
P	O3	1.570(2)	C9	C10	1.382(4)
P	O4	1.578(2)	C9	H9	0.97(3)
O2	C26	1.294(5)	C10	C11	1.384(5)
O3	C1	1.414(3)	C10	C15	1.510(6)
O4	C13	1.423(4)	C11	C12	1.378(5)
C1	C2	1.384(4)	C11	H11	0.92(3)
C1	C6	1.387(4)	C12	C13	1.381(4)
C2	C3	1.383(4)	C12	C14	1.511(5)
C2	C16	1.508(5)	C14	H141	0.91(4)
C3	C4	1.379(4)	C14	H142	0.99(4)
C3	H3	0.92(3)	C14	H143	0.95(4)
C4	C5	1.387(4)	C15	H151	0.91(5)
C4	C17	1.504(5)	C15	H152	0.98(5)
C5	C6	1.393(4)	C15	H153	0.88(6)
C5	H5	0.98(3)	C16	H161	0.96(4)
C6	C7	1.523(4)	C16	H162	1.01(4)
C7	C8	1.523(4)	C16	H163	0.98(5)
C7	C18	1.527(4)	C17	H171	0.89(5)
C7	H7	0.93(3)	C17	H172	0.81(6)
C17	H173	0.93(7)	C23	H231	1.03(5)
C18	C19	1.528(4)	C23	H232	0.93(5)
C18	H181	0.99(3)	C23	H233	0.96(8)
C18	H182	1.00(3)	C24	H241	1.00(6)
C19	C20	1.544(4)	C24	H242	0.90(7)
C19	C25	1.511(5)	C24	H243	0.83(8)
C19	H19	1.03(3)	C25	H251	0.93(6)
C20	C21	1.516(4)	C25	H252	0.95(6)
C20	H201	1.01(3)	C25	H253	0.93(5)
C20	H202	1.07(4)	C26	C27	1.291(6)
C21	C22	1.530(5)	C26	H261	0.95
C21	C23	1.512(5)	C26	C262	0.95
C21	C24	1.519(6)	C27	H271	0.95
C22	H221	1.02(5)	C27	H272	0.95
C22	H222	1.08(5)	C27	H273	0.95
C22	H223	0.97(5)			
			P	O1	1.440(2)
			P	O2	1.550(2)
			P	O3	1.575(2)
			P	O4	1.568(2)
			O2	C26	1.410(6)
			O3	C1	1.417(4)
			O4	C13	1.413(3)
			C1	C2	1.374(4)
			C1	C6	1.383(4)
			C2	C3	1.378(5)
			C2	C16	1.511(5)
			C3	C4	1.381(5)
			C3	H3	0.97(3)
			C4	C5	1.375(5)
			C4	C17	1.509(5)
			C5	C6	1.388(4)
			C5	H5	0.89(3)
			C6	C7	1.520(4)
			C7	C8	1.528(4)
			C7	C18	1.529(4)
			C7	H7	0.90(3)
			C8	C9	1.385(4)
			C18	H181	1.00(3)
			C18	H182	0.92(3)
			C19	C20	1.545(5)
			C19	C25	1.520(6)
			C19	H19	0.88(4)
			C20	C21	1.521(6)
			C20	H201	0.91(5)
			C20	H202	1.09(6)
			C21	C22	1.505(7)
			C21	C23	1.546(6)
			C21	C24	1.526(6)
			C22	H221	0.98(8)
			C22	H222	1.10(6)
			C22	H223	1.09(7)
			C23	H231	1.06(5)
			C8	C13	1.382(4)
			C9	C10	1.384(4)
			C9	H9	0.91(3)
			C10	C11	1.378(4)
			C10	C15	1.507(5)
			C11	C12	1.387(4)
			C11	H11	0.94(3)
			C12	C13	1.379(4)
			C12	C14	1.514(4)
			C14	H141	0.95
			C14	H142	0.95
			C14	H143	0.95
			C15	H151	0.82(6)
			C15	H152	0.92(5)
			C15	H153	0.96(6)
			C16	H161	0.96(5)
			C16	H162	0.97(5)
			C16	H163	1.06(5)
			C17	H171	0.95
			C17	H172	0.95
			C17	H173	0.95
			C18	C19	1.512(5)
			C23	H232	1.08(6)
			C23	H233	1.05(6)
			C24	H241	1.04(8)
			C24	H242	1.03(6)
			C24	H243	0.98(7)
			C25	H251	1.01(5)
			C25	H252	1.11(8)
			C25	H253	0.88(5)
			C26	C27	1.200(8)
			C26	H261	0.95
			C26	H262	0.95
			C27	H271	0.95
			C27	H272	0.95
			C27	H273	0.95

Numbers in parentheses are estimated standard deviations in the least significant digits.

bulky ethoxy group to adopt a pseudo-axial position. Secondly, increasing the size of R also tends to destabilize the rigid boat-chair conformation through non-bonded interactions between R and hydrogen atoms on the nearby phenyl rings. Both these factors result in a tendency for the rigid boat-chair conformation to exist in equilibrium with mobile boat forms (Scheme 4) when R is relatively large. The rigid boat-chair conformation is particularly stable for the *trans* isomers since the ethoxy group is in the pseudo-equatorial position and since boat forms would involve an unfavourable interaction between the relatively bulky ethoxy group and the proton at C-12.



The assignment of the rigid boat-chair conformation to the *trans* isomers **2b-e** and the proposal of a conformational equilibrium between boat-chair and mobile boat forms to the *cis* isomers (large R) are supported by some preliminary variable temperature studies on the *cis* and *trans* isomers of **2d**. The 400 MHz pmr spectra of the *cis* isomer exhibited a temperature dependence for the signal due to the proton in the 12-position of the heterocyclic ring. At 80° a sharp triplet was observed which broadened into a singlet between 40° and -30°. At -50° a sharp triplet was again observed. The chemical shift of this signal moved approximately 0.3 ppm upfield as the temperature was decreased. In contrast, the signal due to the proton in the 12-position of the *trans* isomer showed no variation either in chemical shift or appearance over this temperature range.

Interestingly, the 400 MHz pmr spectrum of the *trans* isomer of compound **2e** did not show the expected heteronuclear coupling. Instead a broadened triplet was observed. The heteronuclear long-range coupling was, however, observable when the spectrum was run at 100 MHz. This behaviour indicates the first signs of conformational mobility becoming apparent in the *trans* series of the compounds **2b-e**. The 400 MHz pmr spectrum of *cis* **2e** shows, as expected, a very broad "hump" for the 12-H signal, consistent with conformational mobility.

The thioacids **3** and **5** were prepared by reaction of the parent bisphenols with phosphorus pentasulfide. The acids were converted to their esters **4** and **6** by alkylation with methyl iodide and the zinc complex **7** was obtained from **5** and zinc acetate in methanol at room temperature.

Hydrolysis of the intermediate acid chloride, prepared from **1e** and phosphoryl chloride, gave the acid **8**.

In summary, a series of dibenzodioxaphosphocins has

Table 2

Table of Bond Angles (degrees) for Compound **2e**

<i>trans</i> isomer							
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	P	O2	118.8(1)	C4	C5	H5	120.(1)
O1	P	O3	115.7(1)	C6	C5	H5	118.(2)
O1	P	O4	114.7(1)	C1	C6	C5	116.6(3)
O2	P	O3	98.6(1)	C1	C6	C7	121.2(2)
O2	P	O4	100.2(1)	C5	C6	C7	122.2(3)
O3	P	O4	106.6(1)	C6	C7	C8	109.2(2)
P	O2	C26	127.2(3)	C6	C7	C18	113.6(2)
P	O3	C1	121.5(2)	C6	C7	H7	107.(2)
P	O4	C13	122.7(2)	C8	C7	C18	115.0(2)
O3	C1	C2	118.0(2)	C8	C7	H7	106.(2)
O3	C1	C6	118.4(2)	C18	C7	H7	105.(2)
C2	C1	C6	123.6(3)	C7	C8	C9	123.1(3)
C1	C2	C3	116.9(3)	C7	C8	C13	120.1(3)
C1	C2	C16	121.4(3)	C9	C8	C13	116.7(3)
C3	C2	C16	121.7(3)	C8	C9	C10	122.0(3)
C2	C3	C4	122.7(3)	C8	C9	H9	117.(2)
C2	C3	H3	119.(2)	C10	C9	H9	121.(2)
C4	C3	H3	119.(2)	C9	C10	C11	118.5(3)
C3	C4	C5	118.0(3)	C9	C10	C15	121.0(4)
C3	C4	C17	121.1(4)	C11	C10	C15	120.5(4)
C5	C4	C17	120.9(4)	C10	C11	C12	122.1(3)
C4	C5	C6	122.2(3)	C10	C11	H11	120.(2)
C12	C11	H11	118.(2)	H161	C16	H162	106.(3)
C11	C12	C13	117.2(3)	H161	C16	H163	113.(3)
C11	C12	C14	121.5(4)	H162	C16	H163	108.(4)
C13	C12	C14	121.3(4)	C4	C17	H171	114.(3)
O4	C13	C8	118.4(3)	C4	C17	H172	111.(4)
O4	C13	C12	117.9(3)	C4	C17	H173	107.(4)
C8	C13	C12	123.5(3)	H171	C17	H172	108.(5)
C12	C14	H141	110.(3)	H171	C17	H173	118.(5)
C12	C14	H142	110.(2)	H172	C17	H173	97.(5)
C12	C14	H143	112.(3)	C7	C18	C19	113.5(3)
H141	C14	H142	111.(3)	C7	C18	H181	109.(2)
H141	C14	H143	98.(4)	C7	C18	H182	111.(2)
H142	C14	H143	116.(4)	C19	C18	H181	108.(2)
C10	C15	H151	112.(3)	C19	C18	H182	107.(2)
C10	C15	H152	112.(3)	H181	C18	H182	108.(3)
C10	C15	H153	110.(4)	C18	C19	C20	110.7(3)
H151	C15	H152	105.(4)	C18	C19	C25	111.9(3)

Table 2 (continued)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
H151	C15	H153	107.(5)	C18	C19	H19	107.(2)
H152	C15	H153	111.(5)	C20	C19	C25	111.4(3)
C2	C16	H161	109.(2)	C20	C19	H19	102.(2)
C2	C16	H162	108.(2)	C25	C19	H19	114.(2)
C2	C16	H163	112.(3)	C19	C20	C21	117.7(3)
C19	C20	H201	106.(2)	C21	C24	H242	107.(4)
C19	C20	H202	109.(2)	C21	C24	H243	109.(6)
C21	C20	H201	109.(2)	H241	C24	H242	101.(5)
C21	C20	H202	105.(2)	H241	C24	H243	109.(6)
H201	C20	H202	110.(3)	H242	C24	H243	124.(7)
C20	C21	C22	108.2(3)	C19	C25	H251	118.(3)
C20	C21	C23	109.3(3)	C19	C25	H252	109.(4)
C20	C21	C24	111.7(4)	C19	C25	H253	111.(3)
C22	C21	C23	108.1(4)	H251	C25	H252	103.(5)
C22	C21	C24	106.6(4)	H251	C25	H253	102.(5)
C23	C21	C24	112.7(6)	H252	C25	H253	114.(5)
C21	C22	H221	108.(3)	O2	C26	C27	125.7(5)
C21	C22	H222	112.(3)	O2	C26	H261	100.0
C21	C22	H223	108.(3)	O2	C26	H262	110.5
H221	C22	H222	111.(4)	C27	C26	H261	102.2
H221	C22	H223	113.(4)	C27	C26	H262	107.6
H222	C22	H223	104.(4)	H261	C26	H262	109.5
C21	C23	H231	108.(2)	C26	C27	H271	113.0
C21	C23	H232	107.(3)	C26	C27	H272	110.4
C21	C23	H233	112.(5)	C26	C27	H273	104.9
H231	C23	H232	105.(4)	H271	C27	H272	109.5
H231	C23	H233	116.(6)	H271	C27	H273	109.5
H232	C23	H233	108.(6)	H272	C27	H273	109.5
C21	C24	H241	106.(3)				
<i>cis</i> isomer							
O1	P	O2	117.3(1)	C1	C6	C5	115.8(3)
O1	P	O3	110.8(1)	C1	C6	C7	121.7(3)
O1	P	O4	111.5(1)	C5	C6	C7	122.5(3)
O2	P	O3	105.1(1)	C6	C7	C8	108.3(2)
O2	P	O4	104.4(1)	C6	C7	C18	113.7(3)
O3	P	O4	107.1(1)	C6	C7	H7	105.(2)
P	O2	C26	123.2(4)	C8	C7	C18	113.4(3)
P	O3	C1	127.3(2)	C8	C7	H7	108.(2)
P	O4	C13	125.2(2)	C18	C7	H7	108.(2)
O3	C1	C2	116.7(3)	C7	C8	C9	121.7(3)
O3	C1	C6	119.1(3)	C7	C8	C13	121.3(3)
C2	C1	C6	124.1(3)	C9	C8	C13	117.0(3)
C1	C2	C3	117.1(3)	C8	C9	C10	122.1(3)

Table 2 (continued)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	C2	C16	121.4(3)	C8	C9	H9	127.(2)
C3	C2	C16	121.4(4)	C10	C9	H9	111.(2)
C2	C3	C4	122.0(4)	C9	C10	C11	118.3(3)
C2	C3	H3	119.(2)	C9	C10	C15	121.0(3)
C4	C3	H3	119.(2)	C11	C10	C15	120.7(3)
C3	C4	C5	118.1(3)	C10	C11	C12	121.9(3)
C3	C4	C17	121.0(3)	C10	C11	H11	120.(2)
C5	C4	C17	120.9(3)	C12	C11	H11	118.(2)
C4	C5	C6	122.9(3)	C11	C12	C13	117.3(3)
C4	C5	H5	119.(2)	C11	C12	C14	120.5(3)
C6	C5	H5	118.(2)	C13	C12	C14	122.1(3)
O4	C13	C8	119.4(3)	H171	C17	H172	109.5
O4	C13	C12	117.3(3)	H171	C17	H173	109.5
C8	C13	C12	123.3(3)	H172	C17	H173	109.5
C12	C14	H141	110.5	C7	C18	C19	115.6(3)
C12	C14	H142	109.2	C7	C18	H181	110.(2)
C12	C14	H143	108.7	C7	C18	H182	110.(2)
H141	C14	H142	109.5	C19	C18	H181	107.(2)
H141	C14	H143	109.5	C19	C18	H182	105.(2)
H142	C14	H143	109.5	H181	C18	H182	109.(3)
C10	C15	H151	120.(4)	C18	C19	C20	109.7(4)
C10	C15	H152	110.(3)	C18	C19	C25	111.3(4)
C10	C15	H153	115.(3)	C18	C19	H19	113.(2)
H151	C15	H152	98.(5)	C20	C19	C25	112.5(4)
H151	C15	H153	113.(5)	C20	C19	H19	104.(2)
H152	C15	H153	98.(4)	C25	C19	H19	106.(2)
C2	C16	H161	108.(3)	C19	C20	C21	117.7(4)
C2	C16	H162	108.(3)	C19	C20	H201	104.(3)
C2	C16	H163	109.(3)	C19	C20	H202	116.(3)
H161	C16	H162	119.(4)	C21	C20	H201	106.(3)
H161	C16	H163	91.(3)	C21	C20	H202	102.(3)
H162	C16	H163	119.(4)	H201	C20	H202	110.(4)
C4	C17	H171	109.1	C20	C21	C22	112.4(5)
C4	C17	H172	109.1	C20	C21	C23	106.8(4)
C4	C17	H173	110.3	C20	C21	C24	110.5(4)
C22	C21	C23	108.3(5)	C19	C25	H251	115.(3)
C22	C21	C24	109.5(5)	C19	C25	H252	109.(4)
C23	C21	C24	109.2(5)	C19	C25	H253	110.(3)
C21	C22	H221	98.(5)	H251	C25	H252	115.(5)
C21	C22	H222	112.(3)	H251	C25	H253	101.(4)
C21	C22	H223	111.(3)	H252	C25	H253	107.(5)
H221	C22	H222	111.(6)	O2	C26	C27	127.7(8)
H221	C22	H223	128.(6)	O2	C26	H261	106.3
H222	C22	H223	97.(5)	O2	C26	H262	102.5

Table 2 (continued)

<i>trans</i> isomer							
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C21	C23	H231	110.(3)	C27	C26	H261	108.0
C21	C23	H232	110.(3)	C27	C26	H262	101.8
C21	C23	H233	111.(3)	H261	C26	H262	109.5
H231	C23	H232	111.(4)	C26	C27	H271	114.1
H231	C23	H233	105.(4)	C26	C27	H272	104.0
H232	C23	H233	110.(5)	C26	C27	H273	110.2
C21	C24	H241	100.(4)	H271	C27	H272	109.5
C21	C24	H242	105.(3)	H271	C27	H273	109.5
C21	C24	H243	104.(4)	H272	C27	H273	109.5
H241	C24	H242	115.(6)				
H241	C24	H243	109.(5)				
H242	C24	H243	121.(5)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

been prepared and the structures of a pair of those compounds, **2e**, *cis* and *trans* isomers, have been determined by X-ray crystallography. Some flattening of the heterocyclic ring was observed in the *cis* isomer. The dibenzodioxaphosphocins adopt the boat-chair conformation in the solid state with the bulky group at C-12 in the pseudo-equatorial position. We have observed a novel transannular cyclisation reaction in the mass spectra of the *cis* isomers which has enabled us to make structural assignments for all the compounds in the series. The pmr spectra of the dibenzodioxaphosphocins show a stereospecific, long-range coupling which is probably a "through-space" phenomenon transmitted from phosphorus to hydrogen *via* the lone-pair electrons of oxygen. The pmr spectra also show evidence for a conformational equilibrium between rigid boat-chair and mobile boat forms in solution, especially for the *cis* isomers with bulky groups attached.

EXPERIMENTAL

All melting points (uncorrected) were taken on an Electrothermal capillary melting point apparatus. The pmr spectra were recorded on a JEOL JNM-GX400 FT nmr spectrometer operating at 400 MHz and are given in δ ppm relative to TMS in deuteriochloroform. Coupling constants (*J*) are given in Hz. Pmr spectra were also recorded for comparison on a JEOL JNM-FX100 FT nmr spectrometer at 100 MHz in deuteriochloroform but these spectra are not reported in detail here. Elemental analyses were performed by Dr. D. Lewis of our Molecular Spectroscopy Laboratory in Harrow, mainly on a CEC 240-XA autoanalyser. Mass spectra were obtained in the electron ionisation mode (70 eV) using either a VG Analytical ZAB-2F or a Finnigan MAT 4600 mass spectrometer. The ionisation source temperatures were 220° in the former and 140° in the latter. The tlc were performed on Merck silica gel plates, type 60 F-254 and hplc on a Hewlett Packard 1090A Liquid Chromatograph using a reverse phase 5 micron Hypersil ODS column and an eluant of methanol/sodium acetate buffer.

Table 3

Least-Squares Planes and Dihedral Angles
Between Planes for Compound **2e**

Plane No.	Atom	Distance from plane (Å)		
		<i>trans</i> isomer	<i>cis</i> isomer	
1	O3	-0.004	0.031	
	C1	-0.019	-0.015	
	C2	0.007	-0.020	
	C3	0.016	-0.004	
	C4	-0.012	0.007	
	C5	-0.006	0.021	
	C6	0.006	0.003	
	C7	0.011	-0.022	
	2	O4	-0.021	0.008
		C7	0.012	0.000
		C8	-0.009	0.001
		C9	-0.012	0.003
		C10	0.001	0.000
3	C11	-0.003	0.003	
	C12	0.008	0.001	
	C13	0.024	-0.015	
	P	0.000	0.000	
	O3	0.000	0.000	
	O4	0.000	0.000	
Plane No.	Plane No.	Dihedral Angle (degrees)		
		<i>trans</i> isomer	<i>cis</i> isomer	
1	2	108.6	107.3	
1	3	122.3	130.2	
2	3	124.7	127.1	

6-Ethoxy-2,4,8,10-tetramethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxide (**2a**).

2,2'-Methylenebis(4,6-dimethylphenol) (**1a**) (7.69 g, 0.03 mole), triethylamine (6.06 g, 0.06 mole) and 4-dimethylaminopyridine (0.5 g) were dissolved in dry toluene (400 ml), stirred and treated with a solution of ethyl phosphorodichloridate (5.1 g, 0.03 mole) in dry toluene (50 ml). The mixture was stirred overnight then washed with dilute hydrochloric acid, water and dried (magnesium sulfate). The solvent was removed under reduced pressure and the residue recrystallized twice from acetonitrile yielding 6.4 g (62%) of the product as a pure white solid, mp 204-205°; pmr: δ 1.50 (dt, 3H, OCH₂CH₃, *J* = 7, 1 Hz), 2.23 and 2.28 (two bs, 6H each, ArCH₃), 3.62 (d, 1H, 12-*H*, *J* = 13 Hz), 4.23 (dd, 1H, 12-*H*, *J* = 13, 3 Hz), 4.47 (dq, 2H, OCH₂, *J* = 7, 8 Hz), 6.80 and 6.93 (two s, 2H each, Ar*H*); ms: 346 (84), 317 (100), 303 (14), 300 (43), 237 (61), 223 (41), 200 (14).

Anal. Calcd. for C₁₇H₂₃O₄P: C, 65.9; H, 6.7; P, 8.9. Found: C, 66.2; H, 6.8; P, 8.4.

6-Ethoxy-2,4,8,10-tetramethyl-12-methyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxide (**2b**).

1,1-Bis(2-hydroxy-3,5-dimethylphenyl)ethane (**1b**) (27.0 g, 0.1 mole), triethylamine (20.2 g, 0.2 mole) and 4-dimethylaminopyridine (0.5 g) were

Table 4

Summary of Crystal Data, Data Collection and Refinement Parameters for **2e**

	<i>trans</i> isomer	<i>cis</i> isomer
Chemical Formula	C ₂₇ H ₃₉ PO ₄	C ₂₇ H ₃₉ PO ₄
Formula Weight	458.58	458.58
Space Group	P2 ₁ /n	P2 ₁ /a
Cell constants at 23(1) ^o a, Å	14.417(2)	21.731(5)
b, Å	13.259(2)	8.771(2)
c, Å	13.748(4)	14.377(3)
β, degrees	91.92(2)	104.34(2)
V, Å ³	2627(2)	2655(2)
Number of molecules/unit cell (Z)	4	4
Density (calculated), g cm ⁻³	1.160	1.147
Crystal dimensions, mm	0.33 × 0.36 × 0.38	0.36 × 0.38 × 0.38
Absorption coefficient (μ MoKα), cm ⁻¹	1.28	1.26
Scan Technique	ω - 2θ	ω - 2θ
Scan rate, degrees 2θ minute ⁻¹	2.2 to 20	2.2 to 20
2θ limit, degrees	46	46
hkl range	-15 to 15 0 to 14 0 to 15	-23 to 23 0 to 9 0 to 15
Number of unique data measured	3650	3687
Number of data used in refinement (I > σ(I))	2736	2758
Number of parameters	425	401
R = Σ F _o - k F _c /Σ F _o	0.050	0.057
R _w = (Σw(F _o - k F _c) ² /ΣwF _o ²) ^{1/2}	0.061	0.073
S = [(Σw(F _o - k F _c) ² /(n _o -n _p)] ^{1/2}	1.276	1.417
Weighting parameters		
(w ⁻¹ = σ ² (F _o) + (pF _o) ² + q)	p q	0.03 1.0
Scale factor, k	1.994(5)	1.925(5)
Maximum shift in final cycle (Δ/σ)	0.09	0.19
Residual electron density in final difference Fourier synthesis (e/Å ³)	-0.27 to 0.25	-0.33 to +0.38

dissolved in dry toluene (550 ml) and a solution of ethyl phosphorodichloridate (17.0 g, 0.1 mole) in dry toluene (50 ml) added dropwise with stirring. The mixture was stirred overnight then washed with dilute hydrochloric acid, water and dried (magnesium sulfate). The solution was evaporated to dryness under reduced pressure to yield a crude, crystalline mass. The product was recrystallized twice from acetonitrile yielding 4.2 g (12%) of the *trans* isomer as a pure white solid, mp 183-185°; pmr: 1.53 (dt, 3H, OCH₂CH₃, J = 7, 1 Hz), 1.67 (d, 3H, Ar₂CHCH₃, J = 7 Hz), 2.23 and 2.28 (two s, 6H each, ArCH₃), 4.51 (dq, 2H, OCH₂, J = 7, 8 Hz), 4.87 (dq, 1H, 12-*H*, J = 7, 2 Hz), 6.79 and 6.99 (two bs, 2H each, ArH); ms: 360 (56), 345 (19), 331 (26), 317 (100), 251 (21), 237 (42), 234 (18), 29 (22).

Anal. Calcd. for C₂₀H₂₅O₄P: C, 66.7; H, 7.0; P, 8.6. Found: C, 66.7; H, 7.0; P, 8.4.

A second crop of crystals was obtained from the acetonitrile mother liquors and this was purified by chromatography on a column of silica gel,

using as eluant a mixture of petroleum ether (bp 60-80°) and ethyl acetate in the proportions 75:25. Evaporation of the eluate under reduced pressure afforded the *cis* isomer 2.1 g (6%) as a pure white crystalline mass, mp 162-164°; pmr: δ 1.37 (dt, 3H, OCH₂CH₃, J = 7, 1 Hz), 1.69 (d, 3H, Ar₂CHCH₃, J = 7 Hz), 2.25 (bs, 12H, ArCH₃), 4.33 (dq, 2H, OCH₂, J = 7, 8 Hz), 4.67 (bq, 1H, 12-*H*, J = 7 Hz), 6.66 and 6.83 (two bs, 2H each, ArH); ms: 360 (100), 345 (21), 331 (97), 317 (83), 251 (55), 237 (80), 234 (54), 29 (58).

Anal. Calcd. for C₂₀H₂₅O₄P: C, 66.7; H, 7.0; P, 8.6. Found: C, 66.6; H, 7.0; P, 8.8.

6-Ethoxy-12-ethyl-2,4,8,10-tetramethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxide (**2e**).

1,1-Bis(2-hydroxy-3,5-dimethylphenyl)propane (**1c**) (20.0 g, 0.07 mole), triethylamine (14.1 g, 0.14 mole) and 4-dimethylaminopyridine (0.3 g) were dissolved in dry toluene (500 ml) and a solution of ethyl phosphoro-

Table 5

Positional Parameters and Equivalent Isotropic Thermal Parameters (esd) for Compound **2e**

<i>trans</i> isomer				
Atom	x	y	z	B(Å ²)
P	0.90840(6)	0.13771(8)	0.12854(6)	5.33(2)
O1	0.8164(2)	0.1194(2)	0.1642(2)	6.26(6)
O2	0.9930(2)	0.0850(2)	0.1803(2)	8.17(7)
O3	0.9248(1)	0.1016(2)	0.0218(1)	4.76(5)
O4	0.9411(1)	0.2512(2)	0.1345(1)	5.18(5)
C1	0.8576(2)	0.1175(2)	-0.0539(2)	4.04(6)
C2	0.8017(2)	0.0371(2)	-0.0820(2)	4.44(7)
C3	0.7377(2)	0.0540(2)	-0.1574(2)	4.67(7)
C4	0.7279(2)	0.1462(2)	-0.2030(2)	4.46(7)
C5	0.7873(2)	0.2235(2)	-0.1735(2)	4.22(6)
C6	0.8543(2)	0.2110(2)	-0.0991(2)	3.75(6)
C7	0.9193(2)	0.2960(2)	-0.0665(2)	4.15(6)
C8	0.8726(2)	0.3593(2)	0.0103(2)	4.28(6)
C9	0.8170(2)	0.4421(3)	-0.0123(2)	5.13(8)
C10	0.7737(2)	0.4969(3)	0.0586(3)	5.59(8)
C11	0.7877(2)	0.4687(3)	0.1549(3)	6.07(8)
C12	0.8418(2)	0.3870(3)	0.1816(2)	5.44(8)
C13	0.8820(2)	0.3333(3)	0.1079(2)	4.75(7)
C14	0.8557(3)	0.3563(4)	0.2870(3)	7.5(1)
C15	0.7124(3)	0.5858(3)	0.0322(4)	8.3(1)
C16	0.8099(2)	-0.0639(3)	-0.0321(3)	6.20(9)
C17	0.6543(3)	0.1630(3)	-0.2814(3)	6.9(1)
C18	0.9586(2)	0.3557(2)	-0.1507(2)	4.68(7)
C19	1.0143(2)	0.2912(2)	-0.2201(2)	4.62(7)
C20	1.0486(2)	0.3556(3)	-0.3052(2)	5.35(8)
C21	1.0415(2)	0.3105(3)	-0.4066(2)	4.92(7)
C22	1.0881(3)	0.3828(4)	-0.4765(3)	8.4(1)
C23	0.9404(3)	0.3011(4)	-0.4380(3)	9.1(1)
C24	1.0933(4)	0.2110(4)	-0.4120(3)	9.7(1)
C25	1.0937(3)	0.2373(4)	-0.1678(3)	8.5(1)
C26	0.9967(3)	0.0464(5)	0.2668(4)	16.1(2)
C27	1.0707(4)	0.0363(5)	0.3214(4)	13.3(2)
H3	0.701(2)	0.001(2)	-0.179(2)	4.5(6) [a]
H5	0.783(2)	0.290(2)	-0.206(2)	3.8(6) [a]
H7	0.970(2)	0.266(2)	-0.035(2)	3.7(5) [a]
H9	0.809(2)	0.460(2)	-0.081(2)	4.7(6) [a]
H11	0.762(2)	0.506(2)	0.203(2)	5.9(7) [a]
H141	0.826(2)	0.401(3)	0.326(3)	9(1) [a]
H142	0.923(2)	0.354(3)	0.304(3)	8.0(9) [a]
H143	0.821(3)	0.297(3)	0.302(3)	10(1) [a]
H151	0.710(3)	0.632(3)	0.081(3)	10(1) [a]
H152	0.648(3)	0.566(3)	0.019(3)	12(1) [a]

Table 5 (continued)

<i>trans</i> isomer				
Atom	x	y	z	B(Å ²)
H153	0.735(3)	0.618(4)	-0.019(4)	13(1) [a]
H161	0.874(2)	-0.085(3)	-0.030(3)	8.5(9) [a]
H162	0.792(3)	-0.054(3)	0.038(3)	9(1) [a]
H163	0.768(3)	-0.114(3)	-0.062(3)	11(1) [a]
H171	0.625(3)	0.107(3)	-0.300(3)	10(1) [a]
H172	0.616(3)	0.203(4)	-0.264(4)	14(2) [a]
H173	0.680(4)	0.203(4)	-0.329(4)	15(2) [a]
H181	1.000(2)	0.409(2)	-0.124(2)	5.4(7) [a]
H182	0.908(2)	0.389(2)	-0.190(2)	6.9(8) [a]
H19	0.968(2)	0.243(2)	-0.255(2)	5.8(7) [a]
H201	1.116(2)	0.372(2)	-0.289(2)	6.1(7) [a]
H202	1.008(3)	0.423(3)	-0.310(3)	10(1) [a]
H221	1.157(3)	0.386(3)	-0.457(3)	11(1) [a]
H222	1.078(3)	0.360(4)	-0.552(3)	12(1) [a]
H223	1.057(3)	0.448(3)	-0.473(3)	13(1) [a]
H231	0.911(3)	0.245(3)	-0.396(3)	9(1) [a]
H232	0.938(3)	0.276(3)	-0.501(3)	11(1) [a]
H233	0.909(5)	0.365(6)	-0.438(5)	22(3) [a]
H241	1.085(3)	0.188(3)	-0.481(3)	12(1) [a]
H242	1.058(4)	0.165(4)	-0.382(4)	16(2) [a]
H243	1.149(5)	0.221(5)	-0.399(5)	20(2) [a]
H251	1.079(3)	0.188(4)	-0.123(3)	12(1) [a]
H252	1.128(3)	0.285(4)	-0.129(4)	15(2) [a]
H253	1.129(3)	0.202(3)	-0.211(3)	11(1) [a]
H261	0.981	-0.022	0.252	16 [b]
H262	0.950	0.075	0.306	16 [b]
H271	1.061	-0.002	0.378	13 [b]
H272	1.119	0.006	0.286	13 [b]
H273	1.088	0.103	0.339	13 [b]
<i>cis</i> isomer				
P	0.73386(4)	0.0017(1)	0.26478(7)	3.94(2)
O1	0.7322(1)	0.1589(3)	0.2355(2)	5.85(7)
O2	0.7429(1)	-0.0309(3)	0.3733(2)	4.87(6)
O3	0.7897(1)	-0.0857(2)	0.2360(2)	4.11(5)
O4	0.6707(1)	-0.0832(2)	0.2151(2)	3.94(5)
C1	0.8184(2)	-0.2242(4)	0.2751(2)	3.74(7)
C2	0.8761(2)	-0.2133(4)	0.3409(3)	4.37(8)
C3	0.9057(2)	-0.3477(5)	0.3760(3)	5.1(1)
C4	0.8790(2)	-0.4883(4)	0.3474(3)	4.85(9)
C5	0.8214(2)	-0.4917(4)	0.2808(3)	4.45(8)
C6	0.7889(2)	-0.3607(4)	0.2426(2)	3.65(7)
C7	0.7243(2)	-0.3654(4)	0.1712(2)	3.67(7)
C8	0.6731(2)	-0.3577(4)	0.2272(2)	3.37(7)
C9	0.6493(2)	-0.4881(4)	0.2599(2)	3.75(7)

Table 5 (continued)

Atom	x	y	z	B(Å ²)
C10	0.6030(2)	-0.4824(4)	0.3109(2)	4.13(8)
C11	0.5801(2)	-0.3418(4)	0.3287(3)	4.42(8)
C12	0.6023(2)	-0.2076(4)	0.2977(2)	4.00 (8)
C13	0.6490(2)	-0.2197(4)	0.2484(2)	3.47(7)
C14	0.5734(2)	-0.0557(4)	0.3135(3)	5.8(1)
C15	0.5770(2)	-0.6263(5)	0.3439(3)	6.4(1)
C16	0.9072(2)	-0.0606(5)	0.3697(3)	6.2(1)
C17	0.9129(2)	-0.6339(5)	0.3856(4)	7.7(1)
C18	0.7161(2)	-0.5000(4)	0.1016(2)	4.33(8)
C19	0.6549(2)	-0.5021(5)	0.0238(3)	5.22(9)
C20	0.6462(2)	-0.6596(5)	-0.0258(3)	6.4(1)
C21	0.5828(2)	-0.7400(5)	-0.0361(3)	5.7(1)
C22	0.5281(3)	-0.6503(8)	-0.0957(4)	9.8(2)
C23	0.5871(3)	-0.8931(6)	-0.0874(4)	9.6(2)
C24	0.5710(3)	-0.7717(7)	0.0624(4)	8.3(1)
C25	0.6526(3)	-0.3720(6)	-0.0468(4)	8.5(2)
C26	0.7601(4)	0.0821(9)	0.4447(4)	15.0(3)
C27	0.7359(4)	0.1086(9)	0.5094(4)	14.6(3)
H3	0.948(1)	-0.344(4)	0.419(2)	4.7(8) [a]
H5	0.805(1)	-0.581(3)	0.258(2)	2.9(6) [a]
H7	0.722(1)	-0.279(3)	0.136(2)	3.7(7) [a]
H9	0.661(1)	-0.586(3)	0.253(2)	3.4(6) [a]
H11	0.551(1)	-0.334(4)	0.367(2)	4.5(8) [a]
H141	0.542	-0.069	0.349	6 [b]
H142	0.606	0.010	0.348	6 [b]
H143	0.554	-0.012	0.253	6 [b]
H151	0.593(2)	-0.709(6)	0.336(4)	12(2) [a]
H152	0.537(2)	-0.645(5)	0.306(3)	9(1) [a]
H153	0.566(2)	-0.619(6)	-0.405(4)	11(2) [a]
H161	0.951(2)	-0.078(5)	0.402(3)	9(1) [a]
H162	0.880(2)	-0.003(5)	0.402(3)	8(1) [a]
H163	0.921(2)	-0.011(5)	0.310(3)	10(1) [a]
H171	0.952	-0.609	0.430	8 [b]
H172	0.887	-0.692	0.417	8 [b]
H173	0.922	-0.692	0.335	8 [b]
H181	0.752(2)	-0.501(4)	0.069(2)	5.2(8) [a]
H182	0.716(1)	-0.590(4)	0.134(2)	4.1(7) [a]
H19	0.621(2)	-0.492(4)	0.047(2)	5.4(8) [a]
H201	0.649(2)	-0.640(5)	-0.087(3)	8(1) [a]
H202	0.680(3)	-0.747(7)	0.007(4)	12(2) [a]
H221	0.494(3)	-0.714(8)	-0.084(5)	17(2) [a]
H222	0.525(3)	-0.534(7)	-0.068(4)	13(2) [a]
H223	0.537(3)	-0.617(7)	-0.164(4)	14(2) [a]
H231	0.545(2)	-0.956(6)	-0.094(3)	10(1) [a]
H232	0.628(3)	-0.957(6)	-0.048(4)	12(2) [a]

Table 5 (continued)

Atom	x	y	z	B(Å ²)
H233	0.590(2)	-0.874(6)	-0.158(4)	12(2) [a]
H241	0.612(3)	-0.834(8)	0.093(5)	17(2) [a]
H242	0.568(3)	-0.666(6)	0.092(4)	12(2) [a]
H243	0.534(3)	-0.841(6)	0.048(4)	13(2) [a]
H251	0.612(2)	-0.363(5)	-0.099(3)	8(1) [a]
H252	0.696(3)	-0.375(9)	-0.074(5)	18(3) [a]
H253	0.653(2)	-0.284(5)	-0.017(3)	8(1) [a]
H261	0.763	0.175	0.412	14 [b]
H262	0.802	0.051	0.478	14 [b]
H271	0.757	0.186	0.552	13 [b]
H272	0.694	0.142	0.478	13 [b]
H273	0.733	0.018	0.544	13 [b]

[a] Atoms were refined isotropically. [b] Atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^{*2}\beta(1,1) + b^{*2}\beta(2,2) + c^{*2}\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

dichloridate (11.9 g, 0.07 mole) in dry toluene (30 ml) added dropwise with stirring. The mixture was stirred overnight then washed with dilute hydrochloric acid, water and dried (magnesium sulfate). Ethyl acetate (800 ml) was added to the reaction mixture and slow evaporation of the solvent under reduced pressure induced crystal formation. The crude, crystalline mass was filtered off and recrystallized twice from acetonitrile to afford the *cis* isomer 3.1 g (12%) as a pure white solid, mp 220-222°; pmr: δ 0.89 (t, 3H, Ar₂CHCH₂CH₃, J = 7 Hz), 1.33 (dt, 3H, OCH₂CH₃, J = 7, 1 Hz), 2.22 (q, 2H, Ar₂CHCH₂CH₃, J = 7 Hz), 2.24 and 2.25 (two s, 6H each, ArCH₃), 4.25-4.40 (m, 3H, OCH₂, 12-*H*), 6.91 and 6.82 (two bs, 2H each, ArH); ms: 374 (37), 359 (4), 345 (63), 331 (19), 317 (100), 299 (14), 237 (14), 85 (14.5), 71 (20), 57 (33.5), 43 (18).

Anal. Calcd. for C₂₁H₂₇O₄P: C, 67.4; H, 7.3; P, 8.3. Found: C, 67.1; H, 7.3; P, 8.0.

After the acetonitrile mother liquors had been allowed to stand for some time a crystalline deposit of the *trans* isomer was obtained 4.5 g (17%), mp 184-186°; pmr: δ 0.95 (t, 3H, Ar₂CHCH₂CH₃, J = 7 Hz), 1.54 (dt, 3H, OCH₂CH₃, J = 7, 1 Hz), 2.0-2.4 (m, 14H, ArCH₃, Ar₂CHCH₂CH₃), 4.48-4.58 (m, 3H, 12-*H*, OCH₂), 6.79 and 6.93 (two bs, 2H each, ArH); ms: 374 (21), 345 (38.5), 317 (100), 237 (12).

Anal. Calcd. for C₂₁H₂₇O₄P: C, 67.4; H, 7.3; P, 8.3. Found: C, 67.6; H, 7.4; P, 8.1.

6-Ethoxy-2,4,8,10-tetramethyl-12-propyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxide (**2d**).

1,1-Bis(2-hydroxy-3,5-dimethylphenyl)butane (**1d**) (23.9 g, 0.08 mole), triethylamine (16.2 g, 0.16 mole) and 4-dimethylaminopyridine (0.4 g) were dissolved in dry toluene (500 ml). A solution of ethyl phosphorodichloridate (13.7 g, 0.08 mole) in dry toluene (40 ml) was added dropwise with stirring. The mixture was stirred at room temperature overnight. Ethyl acetate (900 ml) was added to the reaction mixture which was then washed with dilute hydrochloric acid, water and dried (magnesium sulfate). Slow evaporation of the solvent under reduced pressure afforded a crop of crystals of the crude *cis* isomer. These were recrystallized from acetonitrile to yield a pure sample of the *cis* isomer 4.1 g (13%), mp 220-222°; pmr: δ 0.92 (t, 3H, Ar₂CH(CH₂)₂CH₃, J = 7 Hz), 1.27 (m, 2H, Ar₂CHCH₂CH₂CH₃), 1.33 (dt, 3H, OCH₂CH₃, J = 7, 1 Hz), 2.17 (m, 2H, Ar₂CHCH₂CH₂CH₃), 2.24 and 2.26 (two s, 6H each, ArCH₃), 4.32 (dt, 2H, OCH₂, J = 7, 8 Hz), 4.42 (bt, 1H, 12-*H*), 6.68 and 6.92 (two bs, 2H each,

ArH); ms: 388 (51.5), 359 (38), 345 (57), 331 (49), 317 (100), 299 (10.5), 237 (29).

Anal. Calcd. for $C_{22}H_{31}O_4P$: C, 67.7; H, 8.0; P, 7.9. Found: C, 67.8; H, 7.6; P, 8.0.

On standing, the toluene mother liquor yielded another crop of crystals which were filtered off and recrystallized from acetonitrile to afford the *trans* isomer 6.9 g (22%), mp 121-123°; pmr: δ 0.95 (t, 3H, $Ar_2CH(CH_2)_2CH_3$, $J = 7$ Hz), 1.34 (m, 2H, $Ar_2CHCH_2CH_2CH_3$), 1.53 (dt, 3H, OCH_2CH_3 , $J = 7$, 1 Hz), 2.13 (m, 2H, $Ar_2CHCH_2CH_2CH_3$), 2.23 and 2.28 (two s, 6H each, $ArCH_3$), 4.51 (m, 2H, OCH_2CH_3 , $J = 7$, 8 Hz), 4.67 (dt, 1H, 12-*H*, $J = 8$, 2 Hz), 6.78 and 6.94 (two bs, 2H each, *ArH*); ms: 388 (26.5), 359 (2), 345 (52), 331 (2), 317 (100), 299 (2), 237 (11).

Anal. Calcd. for $C_{22}H_{31}O_4P$: C, 67.7; H, 8.0; P, 7.9. Found: C, 68.1; H, 7.6; P, 8.2.

6-Ethoxy-2,4,8,10-tetramethyl-12-(2,4,4-trimethylpentyl)-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxide (2e).

1,1-Bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (1e) (29.44 g, 0.08 mole) was dissolved in dry toluene (750 ml) with triethylamine (16.2 g, 0.16 mole) and 4-dimethylaminopyridine (0.4 g). A solution of ethyl phosphorodichloridate (13.7 g, 0.08 mole) in dry toluene (50 ml) was added dropwise with stirring. The mixture was stirred overnight. Precipitated triethylamine hydrochloride was filtered off and the filtrate washed with dilute hydrochloric acid, water and dried (magnesium sulfate). The solvent was removed under reduced pressure and the residue crystallized from diethyl ether. The first crop of crystals obtained was recrystallized from acetonitrile to yield the pure *cis* isomer 9.2 g (25%), mp 155-157°; pmr: δ 0.83 (s, 9H, *t*-Bu), 0.91 (d, 3H, $CHCH_3$, $J = 7$ Hz), 1.10 (m, 1H, *CH* of R), 1.20-1.40 (m, 5H, OCH_2CH_3 , CH_2 of R), 1.87 (m, 1H, *CH* of R), 1.88 (m, 1H, *CH* of R), 2.20-2.30 (m, 13H, $ArCH_3$, *CH* of R), 4.31 (bm, 2H, OCH_2), 4.59 (bs, 1H, 12-*H*), 6.82 (s, 2H, *ArH*), 6.92 and 6.94 (two s, 1H each, *ArH*); ms: 458 (34.5), 443 (7.5), 359 (91), 345 (44), 331 (75), 317 (100), 237 (22.5), 57 (13.5), 41 (11).

Anal. Calcd. for $C_{27}H_{39}O_4P$: C, 70.7; H, 8.6; P, 6.8. Found: C, 70.7; H, 8.8; P, 6.4.

Evaporation of the ethereal mother liquor gave rise to a second crop of crystals which was filtered off and recrystallized from acetonitrile to yield the pure *trans* isomer 10.9 g (30%), mp 132-134°; pmr: δ 0.85 (s, 9H, *t*-Bu), 0.95 (d, 3H, $CHCH_3$, $J = 6$ Hz), 1.13 (m, 1H, *CH* of R), 1.35 (m, 1H, *CH* of R), 1.42 (m, 1H, *CH* of R), 1.54 (dt, 3H, OCH_2CH_3 , $J = 7$, 1 Hz), 1.86 (m, 1H, *CH* of R), 2.15-2.40 (m, 13H, *CH* of R, $ArCH_3$), 4.51 (m, 2H, OCH_2), 4.78 (bt, 1H, 12-*H*), 6.78 and 6.95 (two s, 2H each, *ArH*); ms: 458 (39), 443 (7), 359 (7.5), 345 (91.5), 331 (5), 317 (100), 237 (14.5), 57 (5), 41 (3).

Anal. Calcd. for $C_{27}H_{39}O_4P$: C, 70.7; H, 8.6; P, 6.8. Found: C, 70.7; H, 8.7; P, 6.5.

6-Mercapto-2,4,8,10-tetramethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfide, Partial Triethylamine Salt (3).

2,2'-Methylenebis(4,6-dimethylphenol) (1a) (10.24 g, 0.04 mole) was added with stirring to a slurry of phosphorus pentasulfide (4.4 g, 0.02 mole) in toluene (150 ml) at 80°. Twelve drops of triethylamine were added and the mixture heated overnight. Not all the phosphorus pentasulfide had been consumed so the mixture was heated to reflux and a further twelve drops of triethylamine added. The reaction mixture was held at reflux for 30 minutes, decanted off from a resinous material and evaporated to dryness under reduced pressure. The residue was recrystallized from ethyl acetate to yield 4.2 g (27%) of the heterocycle containing 0.43 mole (by nmr) of the triethylamine salt, mp 168-170°; pmr: δ 1.43 (t, 4.6H, CH_3 of triethylamine, $J = 7$ Hz), 3.30 (dq, 3H, CH_2 of triethylamine, $J = 7$, 5 Hz), 2.23 and 2.24 (two s, 3H each, $ArCH_3$), 2.31 (s, 6H, $ArCH_3$), 2.5-3.0 (bs, 0.6H, *SH*), 3.84-3.92 (bd, 2H, 12-*H*), 6.83 and 6.93 (two s, 2H each, *ArH*), 9.89 (bs, 0.4H, *NH*); ms: 350 (19), 335 (4), 317 (100), 300 (7), 283 (21), 253 (68), 237 (26), 223 (13).

Anal. Calcd. for $C_{19}H_{25}N_0.43O_2PS_2$: C, 59.7; H, 6.5; N, 1.5; P, 7.9; S, 16.3. Found: C, 59.5; H, 6.6; N, 1.2; P, 7.7; S, 16.4.

2,4,8,10-Tetramethyl-6-methylmercapto-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfide (4).

6-Mercapto-2,4,8,10-tetramethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-sulfide triethylamine salt (3) (1.1 g, 0.0028 mole) was dissolved in tetrahydrofuran (200 ml) containing anhydrous potassium carbonate (8.6 g) and iodomethane (10 ml). The mixture was heated to reflux for 15 minutes, filtered and the solvent removed under reduced pressure to yield a crude brown material. The product was obtained as a pure white solid by slurrying the crude material in warm heptane to yield 0.8 g (78%), mp 152-153°; pmr: δ 2.25 and 2.26 (two s, 6H each, $ArCH_3$), 2.68 (d, 3H, SCH_3 , $J = 18.5$ Hz), 3.57 (d, 1H, 12-*H*, $J = 13$ Hz), 4.16 (dd, 1H, 12-*H*, $J = 13$, 4 Hz), 6.85 and 6.96 (two s, 2H each, *ArH*); ms: 364 (11), 349 (2), 331 (14), 317 (100), 283 (15), 253 (43), 237 (27), 223 (9).

Anal. Calcd. for $C_{18}H_{21}O_2PS_2$: C, 59.3; H, 5.8; P, 8.5; S, 17.6. Found: C, 59.2; H, 5.9; P, 8.4; S, 18.0.

2,4,8,10-Tetra-*t*-butyl-6-mercapto-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfide (5).

2,2'-Methylenebis(4,6-di-*t*-butylphenol) (21.3 g, 0.05 mole) was added with stirring to a slurry of phosphorus pentasulfide (5.6 g, 0.25 mole) in toluene (175 ml). The mixture was heated at 85° for 3 hours and then five drops of triethylamine were added whereupon immediate consumption of the phosphorus pentasulfide was noted. The mixture was heated at 85° for a further 20 minutes, the solvent removed under reduced pressure and the white residue recrystallized twice from ethyl acetate yielding 11.2 g (43%), mp 211-212°; pmr: δ 1.32 and 1.48 (two s, 18H each, *t*-Bu), 2.5-3.5 (bs, ~1H, *SH*), 3.98 (s, 2H, 12-*H*), 7.21-7.34 (m, 4H, *ArH*); ms: 518 (13), 503 (2), 501 (4), 485 (100), 469 (23), 451 (10), 57 (50).

Anal. Calcd. for $C_{25}H_{43}O_2PS_2$: C, 67.1; H, 8.4; P, 6.0; S, 12.4. Found: C, 67.2; H, 8.6; P, 5.8; S, 12.4.

2,4,8,10-Tetra-*t*-butyl-6-methylmercapto-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfide (6).

2,4,8,10-Tetra-*t*-butyl-6-mercapto-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-sulfide (5) (5.2 g, 0.01 mole) was dissolved in tetrahydrofuran (250 ml) with iodomethane (3 ml) and anhydrous sodium carbonate (10 g). The mixture was heated to reflux on a steam bath for 25 minutes, filtered and evaporated to dryness under reduced pressure. The residue was recrystallized from heptane yielding 3.8 g (71%), mp 166-168°; pmr: δ 1.31 and 1.45 (two s, 18H each, *t*-Bu), 2.65 (d, 3H, SCH_3 , $J = 19$ Hz), 3.97 (d, 1H, 12-*H*, $J = 14$ Hz), 4.18 (bd, 1H, 12-*H*, $J = 14$ Hz), 7.17-7.33 (m, 4H, *ArH*); ms: 532 (12), 499 (29), 485 (100), 469 (17), 451 (13), 427 (5), 57 (84).

Anal. Calcd. for $C_{30}H_{45}O_2PS_2$: C, 67.6; H, 8.5; P, 5.8; S, 12.0. Found: C, 67.6; H, 8.8; P, 6.3; S, 12.1.

Bis[2,4,8,10-tetra-*t*-butyl-6-mercapto-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfidato(1-)-*S,S'*] Zinc(2+) (7).

2,4,8,10-Tetra-*t*-butyl-6-mercapto-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-sulfide (5) (5.2 g, 0.01 mole) and zinc acetate (1.1 g, 0.005 mole) were dissolved together in methanol (600 ml) at room temperature with stirring. After 30 minutes a white precipitate formed and this was filtered off and dried under vacuum to yield 4.7 g (43%), mp (crystals soften at 175°) 304-306°; pmr: δ 1.31 and 1.48 (two s, 18H each, *t*-Bu), 4.02 (bs, 2H, 12-*H*), 7.10-7.40 (m, 4H, *ArH*); ms: 1066/1068/1070 (3), 875/877/879 (1), 485 (42), 469 (76), 57 (100); (ammonia DCI) 1099/1101/1103 (MH⁺).

Anal. Calcd. for $C_{58}H_{88}O_4P_2S_4Zn$: C, 63.1; H, 8.0; P, 5.6; S, 11.6. Found: C, 63.4; H, 8.0; P, 5.7; S, 11.9.

6-Hydroxy-2,4,8,10-tetramethyl-12-(2,4,4-trimethylpentyl)-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxide (8).

1,1-Bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (1e) (36.8 g, 0.1 mole) was dissolved in a mixture of dry toluene (650 ml) and tetrahydrofuran (90 ml) with triethylamine (20.3 g, 0.2 mole) and 4-dimethylaminopyridine (5.0 g). The mixture was cooled to 10° and a solution of phosphoryl chloride (13.4 g, 0.1 mole) in dry toluene (100 ml) added with stirring. The reaction mixture was allowed to warm to room temperature and an additional 4 g of phosphoryl chloride added. Stirring was con-

tinued for 12 hours. The mixture was extracted several times with dilute hydrochloric acid, washed well with water and dried (magnesium sulfate). The solvent was removed under reduced pressure to furnish an oil which crystallized after 2 weeks. The product was obtained as a highly crystalline colourless solid by recrystallizations from acetonitrile yielding 12.9 g (30%), mp 213-215°C; pmr: δ 0.84 (s, 9H, *t*-Bu), 0.96 (d, 3H, CH₃ of R, J = 6 Hz), 1.12 (dd, 1H, CH of R, J = 6, 8 Hz), 1.33 (m, 1H, CH of R), 1.40 (m, 1H, CH of R), 1.84 (m, 1H, CH of R), 2.1-2.5 (m, 13H, CH of R, ArCH₃), 4.75 (bs, 1H, 12-H), 6.79 and 6.95 (two s, 2H each, ArH), 11.6 (bs, 1H, POH); ms: 430 (10), 331 (16), 317 (100), 237 (9), 57 (7).

Anal. Calcd. for C₂₅H₃₅O₄P: C, 69.7; H, 8.2; P, 7.2. Found: C, 69.9; H, 8.2; P, 7.2.

X-Ray Structural Determination of *cis* and *trans* 2e.

Samples of the *cis* and *trans* isomers of compound 2e were grown from acetonitrile. Chunky samples were cut to size and glued onto thin glass rods for data collection on an Enraf-Nonius CAD4 diffractometer with graphite monochromated MoK α radiation. The setting angles for 25 accurately centred reflections were used to refine the unit cell parameters given in Table 4 with a summary of data collection and refinement parameters.

Each reflection was scanned from $2\theta(\text{MoK}\alpha_1) - \Delta^\circ$ to $2\theta(\text{MoK}\alpha_2) + \Delta^\circ$ where $\Delta = 0.70$ for the *trans* isomer and 0.75 for the *cis* isomer. The scan width was extended 25% at each end to measure background. Three standard reflections were remeasured every hour to check crystal and electronic stability. A significant change was noted for the *cis* isomer and this data set was corrected (average correction factor = 1.032 on I).

Both structures were solved by direct methods using MULTAN 11/82 [16]. E-maps calculated with the best phase sets gave correct structures. Subsequent difference electron-density maps gave most hydrogen atom positions. The remaining hydrogens were input at calculated positions.

Refinement was by full matrix least-squares. Anisotropic thermal parameters were applied to all nonhydrogen atoms. A few hydrogen atoms (denoted by [b] in the table of positional parameters, Table 5) did not refine well and were included at calculated positions riding on the parent carbon atoms. Isotropic thermal parameters for these atoms were fixed at the isotropic equivalent of the parent carbon atoms. Scattering factors and anomalous dispersion corrections for all atoms were from Ref 17. Tables of anisotropic thermal parameters and structure factors are available as supplementary material from the authors.

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