

Synthesis of Substituted Dibenzophospholes. Part 3. Synthesis of 4,6-Diaryldibenzophospholes from *m*-Quaterphenyls †

By Sir John Cornforth,* Damon D. Ridley, Andrew F. Sierakowski, Daniel Uguen, and Timothy W. Wallace (with an Appendix by Peter B. Hitchcock), School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Some observations on T. Cohen's method for coupling 2-iodonitrobenzenes to 2,2'-dinitrobiphenyls are reported. A general method for making 2',2''-di-iodo-*m*-quaterphenyls from the 2',2''-diamines, reported in Part 2, features decomposition of the bis-diazonium iodomercurates to dibenziodolium iodomercurates and pyrolysis of the latter. The procedure can be used to prepare other aryl iodides. 2',2''-Di-iodo-*m*-quaterphenyls, on successive treatment with butyl-lithium, phosphorus trichloride, water, and hydrogen peroxide, yield 4,6-diaryl-5-hydroxydibenzophosphole 5-oxides, three of which were prepared. The structures of two derivatives of these, 2,8-dichloro-3,7-di-(2-hydroxyethoxy)-5-methoxy-4,6-diphenyldibenzophosphole 5-oxide and 5-hydroxy-3,7-dimethoxy-4,6-di-(4-methoxy-3,5-di-*t*-butylphenyl)dibenzophosphole 5-oxide, have been determined by X-ray crystallography and are reported in the Appendix.

In Part 2 of this series¹ we reported a general synthesis of 2',2''-diamino-*m*-quaterphenyls (1) in five steps from 1,3-dinitrobenzene. The operations necessary to convert these intermediates into 4,6-diaryldibenzophosphole derivatives (2) are now described.

A limitation on the synthesis had been the occurrence of unsymmetrical coupling in the Ullmann reaction of 3-iodo-2-nitrobiphenyls that contain additional iodine in the other phenyl ring, *e.g.* compound (3a). This limitation could be largely removed by using Cohen's coupling procedure;^{2,3} copper(I) trifluoromethanesulphonate(triflate) in acetone-acetonitrile containing ammonia. With this reagent the di-iodide (3a) gave the di-iodoquaterphenyl (4a) in 54% yield. No unsymmetrical coupling product was found, but a 25% yield of the mono-iodide (3b) (which could be recycled) was also isolated. Some exploration of the procedure was made. The iodide (3c) could be coupled to yield the quaterphenyl (4b) in *ca.* 60% yield, not only by copper(I) triflate, but also by copper(I) iodide. Replacement of the cuprous salt by a mixture of copper powder and cupric sulphate was ineffective with compound (3c), but with 2-iodonitrobenzene this mixture gave an 83% yield of 2,2'-dinitrobiphenyl. Again, an 82% yield of 2,2'-dinitrobiphenyl was obtained by stirring 2-iodonitrobenzene with copper powder, acetone, acetonitrile, and ammonia in the presence of air.

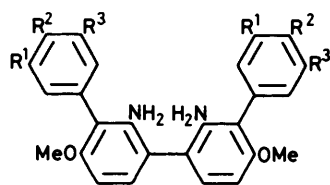
Much effort was expended on the smooth conversion of 2',2''-diamino-*m*-quaterphenyls into the corresponding di-iodides (5) or dibromides. It was not difficult to obtain moderate yields (*ca.* 40%) of di-iodides by tetrazotization followed by the addition of potassium iodide, but no experimental conditions tried would give good yields. The preparation of 2,2'-di-iodobiphenyls from the diamines has always been found difficult to achieve in good yields.⁴⁻⁶ Partly, this is because dibenziodolium iodides [as (6)] accompany the di-iodides; and although thermal conversion of the former into the latter is possible,⁷ the yields, in our experience, depend markedly on the purity of the material pyrolysed. We turned,

† No reprints available.

at last, to an isolated study half a century old: Nesmeyanov⁸ observed that phenyldiazonium iodomercurates [PhN_2HgI_3 or $(\text{PhN}_2)_2\text{HgI}_4$] decomposed on standing to yield iodobenzene, biphenyl, and diphenyliodonium salts (*e.g.* $\text{Ph}_2\text{I}^+\text{HgI}_3^-$).

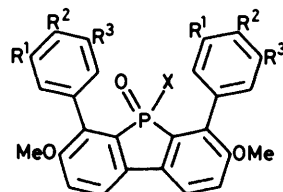
Precipitation of bis-diazonium salts from the diamines (1a—c) with potassium iodomercurate gave insoluble complexes which, on resuspension in water, lost two equivalents of nitrogen at room temperature overnight. The product obtained from compound (1a), believed to be the dibenziodolium pentaiododimercurate (6a) from the stoichiometry, was converted, by stirring it with sodium iodide in acetone, into the yellow, highly crystalline bis-dibenziodolium tetraiodomercurate (6b). When this was heated at 180 °C, preferably, but not essentially, in the presence of potassium iodide and a little free iodine, it yielded the di-iodo-compound (5a) in 70—76% overall yield from the diamine. The di-iodo-compound (5b) was prepared similarly; with the more heavily substituted diamine (1c), dimethylformamide was found to be a good medium for tetrazotization and the final pyrolysis, at 160 °C, avoided the partial dealkylation that occurred at higher temperatures [the di-iodides (5d) and (5e) were obtained along with (5c) in such experiments].

A few other amines were examined, for general interest. 2,2'-Diaminobiphenyl gave a disappointing 50% yield of di-iodide and 2,6-diaminobiphenyl a yield of 45%. However, neither conversion was optimized; and the diazonium iodomercurate from 2-aminobiphenyl gave an 82% yield of 2-iodobiphenyl directly when it was stirred with water, with a further 5% by pyrolysis of the small amounts of iodonium iodomercurates formed as by-product. A modified procedure gave a 91% yield. This is a much better result than was obtained by the usual procedure.⁹ The iodomercurate method appears to be worth a trial in any case of difficulty with the normal procedure of treating the diazonium salt directly with iodide ion. By-products noted in the preparation of the 2',2''-di-iodo-*m*-quaterphenyls included the cinolines (7a,b), the carbazoles (8a,b), and the mono-

All $R^n = H$ unless stated otherwise

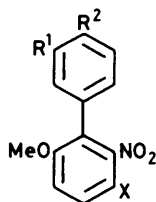
(1a)

b; $R^2 = OMe$
 c; $R^1 = R^3 = Bu^t$, $R^2 = OMe$



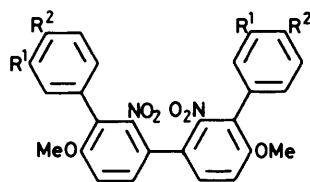
(2)

a; $X = OH$
 b; $R^2 = OMe$, $X = OH$
 c; $R^1 = R^3 = Bu^t$, $R^2 = OMe$,
 $X = OH$
 d; $X = OMe$
 e; $R^2 = X = OMe$
 f; $R^1 = R^3 = Bu^t$,
 $R^2 = X = OMe$
 g; $X = Bu^n$
 h; $R^1 = R^3 = Bu^t$, $R^2 = OMe$,
 $X = Bu^n$



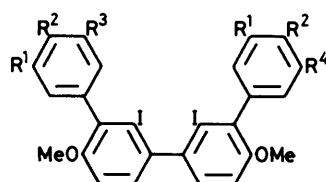
(3)

a; $R^1 = X = I$, $R^2 = OMe$
 b; $R^1 = I$, $R^2 = OMe$, $X = H$
 c; $X = I$



(4b)

a; $R^1 = I$, $R^2 = OMe$



(5a)

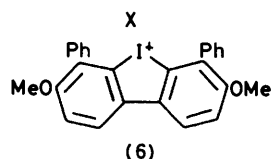
b; $R^2 = OMe$
 c; $R^1 = R^3 = R^4 = Bu^t$,
 $R^2 = OMe$
 d; $R^1 = R^3 = Bu^t$, $R^2 = OMe$
 e; $R^1 = Bu^t$, $R^2 = OMe$

iodides [isolated only in the phenyl series, (9)]. The latter were formed to a greater extent if a source of hydrogen (*e.g.* water) was present during pyrolysis of the dibenziodolium salts.

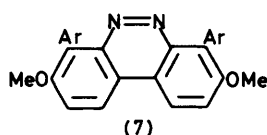
Exchange, with butyl-lithium, of iodine for lithium in the di-iodides (5a—c) proceeded readily. In view of the smooth formation of bis-biphenylphosphinates from 2-lithiobiphenyls and alkyl dichlorophosphates (see Part 2, preceding paper), it might have been thought that a similar reaction would provide the dibenzophosphole 5-oxides (2) from 2',2''-dilithio-*m*-quaterphenyls. We had already had contrary indications (Part 1) with 2,2'-dilithiobiphenyls and in fact we have never been success-

ful with this type of ring-closure using pentavalent phosphorus derivatives. Presumably, there is an intramolecular constraint preventing attainment of the transition state for cyclization. No such limitation applied to trivalent phosphorus derivatives and the first successful experiments were done with dichloromorpholinophosphine, $O(CH_2CH_2)_2NPhCl_2$. It was soon found that replacement of one chlorine in phosphorus trichloride by a less reactive group is not necessary for making dibenzophospholes of type (2), and that phosphorus trichloride can be used more conveniently and without the formation of triarylphosphines, which would be expected with less hindered aryl-lithiums. The

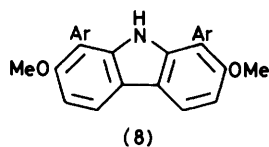
expected product of cyclization is a 5-chlorodibenzo-phosphole, but this was never isolated. The reaction mixtures were treated with water and then with hydrogen peroxide in acetone; this produced directly the phosphinic acids (2a–c) which were sometimes conveniently isolated in the form of their methyl esters (2d–f). The yields in this conversion of di-iodides (5) into dibenzophosphole 5-oxides (2) are generally *ca.* 70%. A by-product sometimes encountered is the 5-butyldibenzophosphole 5-oxide (2g,h); this is thought to arise *via* formation of butyldichlorophosphine from phosphorus trichloride and the small excess of butyl-lithium used in the halogen-metal exchange.



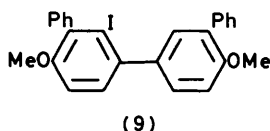
(6)
a; X = [Hg₂I₅]⁻
b; X = $\frac{1}{2}$ [HgI₄]²⁻



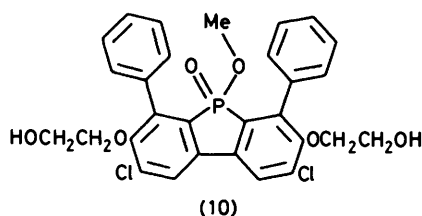
(7)
a; Ar = Ph
b; Ar =



(8)
a; Ar = Ph
b; Ar =



(9)



(10)

Two derivatives of 4,6-diaryl-3,7-dialkoxydibenzophosphole 5-oxides were examined by X-ray crystallography and the results are reported in the Appendix. One derivative (10), was made from the phosphinic ester (2d) by procedures to be described later (Part 4, following paper). The other was the phosphinic acid (2c); the crystals examined had separated from an acetone-diethyl ether mixture and, as can be seen, a molecule of diethyl ether was selected for occupation of the cleft formed by the 4- and 6-aryl substituents and for hydrogen-bonding with the phosphinic acid hydrogen. The X-ray structures confirmed expectations

not only of the general geometry of the molecules, but also of the limited, but potentially useful, mobility of the flanking aryl groups. The preference, in the derivative (10), for the methyl ester to occupy the space between the two phenyl rings seems to be exercised also in solutions of the esters (2d–f) since the n.m.r. signals of their ester methyl hydrogens show a marked shift upfield relative to both the non-arylated analogue (3,5,7-trimethoxydibenzophosphole 5-oxide) and the non-cyclized methyl bis-(2-biphenyl)phosphinates.¹ A similar effect can be seen in the 5-butylderivatives (2g,h).

EXPERIMENTAL

General.—See the directions in the preceding paper.¹

3,3''-Di-iodo-4,4'',4''',6'-tetramethoxy-2',2''-dinitro-m-quaterphenyl (4a).—Copper(I) trifluoromethanesulphonate was prepared as described^{2,3} from the copper(II) salt [7.2 g; (CF₃SO₃)₂Cu, 5.5 H₂O] in acetone (145 ml) and acetonitrile (7.5 ml). To the stirred mixture at room temperature was added a solution of 3,3'-di-iodo-4',6'-dimethoxy-2-nitrobiphenyl¹ (5.9 g) in dimethyl sulphoxide (DMSO) (35 ml) under nitrogen. After a few minutes aqueous ammonia (8 ml; *d* 0.88) was added; the mixture became green. After 2.5 h more copper(I) trifluoromethanesulphonate in acetone-acetonitrile was added (one sixth of the previous quantity). Next day the mixture was poured into 0.5M sulphuric acid and extracted with chloroform; the extract was separated after filtration. The washed (water) and dried extract was evaporated; the residue, with acetone-ethanol, gave a cream solid which was recrystallized from chloroform-ethanol to give the quaterphenyl (4a) (2.4 g; 54%; 2 crops), m.p. 300–302 °C, identical with the material prepared¹ by Ullmann synthesis (t.l.c., n.m.r., i.r.). The mother liquors in chloroform-hexane (1:1) were passed through an alumina column (15 × 2.5 cm). The first fraction eluted yielded 3-iodo-4,6'-dimethoxy-2-nitrobiphenyl (1.12 g, 25%) as a yellow crystalline solid, identical with authentic material¹ (m.p., t.l.c.).

4',6'-Dimethoxy-2',2''-dinitro-m-quaterphenyl (4b).—3-Iodo-6-methoxy-2-nitrobiphenyl was stirred with an equal weight of copper(I) iodide in an acetone-acetonitrile mixture (5:1; 16 ml/g biphenyl) in an atmosphere of dry ammonia for 24 h. The mixture was worked up essentially as in the previous experiment and yielded, on trituration with methanol, a 62% yield of the quaterphenyl (4b) m.p. 256–258 °C, identified by comparison with an authentic specimen.¹ A larger scale experiment, conducted for 40 h at 40 °C, gave a 49% yield. The major by-product (*ca.* 25% yield) was 2-methoxy-6-nitrobiphenyl, also identified by comparison with authentic material.¹

2,2'-Dinitrobiphenyl.—(a) To copper(II) sulphate (5 g; pentahydrate) and copper powder (1.3 g) in acetone (100 ml) and acetonitrile (10 ml) was added first 2-iodonitrobenzene (2.5 g) and then aqueous ammonia (10 ml; *d* 0.88). The mixture (deep green) was stirred under nitrogen overnight. The reaction mixture was poured into brine and extracted with methylene dichloride. The extract, after filtration through alumina, was evaporated and the residue was recrystallized from ethanol to give 2,2'-dinitrobiphenyl (1.02 g, 83%), m.p. and mixed m.p. 124 °C.

(b) 2-Iodonitrobenzene (5 g), copper powder (5 g), acetone (50 ml), acetonitrile (10 ml), and aqueous ammonia (10 ml, *d* 0.88) were stirred together overnight in air. Isolated as

above, the 2,2'-dinitrobiphenyl (2.01 g; 82%) formed pale yellow needles from ethanol, m.p. 124 °C alone or mixed with authentic material.

2',2''-Di-iodo-4'',6'-dimethoxy-m-quaterphenyl (5a).—The diamine ¹(1a) (14.26 g) was boiled with 5M hydrochloric acid (360 ml). To the cooled (0–5 °C), stirred suspension was added sodium nitrite (6.34 g) in water (45 ml) dropwise over 45 min. After a further 1 h, ice-water (500 ml), and then urea (1.35 g) in water (4.5 ml) were added. After 1 h more, a solution of mercury(II) iodide (36 g) and potassium iodide (26.3 g) in water (90 ml) were added with vigorous stirring. The brown precipitate was collected, washed briefly with water, resuspended in water (900 ml), and stirred overnight, during which nitrogen was evolved. The solid was collected, stirred with acetone (1.3 l), and treated with a solution of sodium iodide (45 g) in acetone (125 ml) and water (10 ml). After 2.5 h the suspension was diluted to 5 l with water and stirred until filterable (2 h), when the brown solid was collected, washed (water), thoroughly dried *in vacuo*, ground with dry sodium iodide (55 g), and heated at 205 ± 5 °C for 5 h. The black solid product after cooling was extracted with hot chloroform (4 × 200 ml). The filtered extract was concentrated and put through alumina (20 × 8 cm). The di-iodide was in the first fractions; later fractions also contained some of the benzo[*c*]cinoline (7a). Fractions were monitored by t.l.c. (methanol–dichloromethane, 1:19) and the eluates containing di-iodide were evaporated, and the residue was triturated with ethanol. This gave the *di-iodide* (5a) as a white solid (15.19 g; a further 0.43 g on repeating the chromatography; total 70%). A sample crystallized from chloroform–ethanol as small needles, m.p. 261 °C (Found: C, 50.5; H, 3.3; I, 40.9. C₂₆H₂₀I₂O₂ requires C, 50.5; H, 3.3; I, 41.0%); *m/e* 618 (*M*⁺, 30%), 491 (*M*⁺ – I, 100) and 245.5 (30); δ 3.70 (6 H, s, 2 × OMe), 6.97 (2 H, d, *J* 8.5 Hz, 5',5''-H), 7.20 (2 H, d, *J* 8.5 Hz, 4',6''-H), and 7.25–7.45 (10 H, m); *v*_{max} 1 585, 1 275, 1 030, and 705 cm⁻¹.

In another preparation the iodo-mercurate, after evolution of nitrogen, was stirred for 3 h with a more concentrated solution of sodium iodide in acetone [sodium iodide (120 g) in acetone (800 ml) in a run starting from diamine (31.4 g)]. The mixture was then filtered. A sample of the brown solid (54 g) was recrystallized from dichloromethane–acetone to yield *bis*-[3,7-dimethoxy-4,6-diphenyldibenziodolium] *tetra-iodomercurate* (6b) as yellow-orange prisms, m.p. 149–150 °C (decomp.; sample resolidified, changed crystal form at 220–235 °C and melted again at 264–268 °C) (Found: C, 37.4; H, 2.7; Hg, 11.8, I, 45.2. C₅₂H₄₀HgI₆O₄ requires C, 37.0; H, 2.4; Hg, 11.9; I, 45.0%). This product and material obtained by precipitating the acetone mother liquor with water were pyrolysed separately at 175–180 °C for 24 h, giving a total yield of 37.3 g (76% on diamine) of di-iodide.

In these conditions the formation of moniodide (9a) was minimal, but larger amounts were formed if (i) the iodo-mercurate or sodium iodide were not dried thoroughly before pyrolysis, (ii) the pyrolysis was conducted under reduced pressure, or (iii) the pyrolysis was conducted in boiling dimethylformamide (DMF). 2'-Iodo-4'',6'-dimethoxy-m-quaterphenyl (9a) was first obtained from an experiment in which the diamine (1a) was tetrazotized and added to a cold mixture of aqueous potassium iodide and dichloromethane. The product was chromatographed on alumina and the first eluates (diethyl ether–hexane, 1:9) gave (9a) in 12% yield as colourless cubes (from dichloro-

methane–diethyl ether), m.p. 206–208 °C (Found: C, 63.2; H, 4.5; I, 25.4. C₂₆H₂₁IO₂ requires C, 63.4; H, 4.3; I, 25.8%); *m/e* 492 (*M*⁺, 100%); δ 3.66 (s) and 3.80 (s) (6 H, 2 × OMe), and 6.90–7.70 (15 H, m). The di-iodide (5a) (42% yield) was eluted with diethyl ether–hexane (1:4). A small amount of a product believed to be 2,7-dimethoxy-1,8-diphenyl-9H-carbazole (8a) was also found; m.p. 210–211 °C; δ 3.83 (6 H, s, 2 × OMe), 6.95 (2 H, d, *J* 8.5 Hz, 3-, 6-H), 7.45br (11 H, s, 2 × Ph + NH), and 7.90 (2 H, d, *J* 8.5 Hz, 4-, 5-H).

3,8-Dimethoxy-4,7-diphenylbenzo[*c*]cinoline (7a).—Compound (7a) was first noticed in a preparation ¹ of the diamine (1a) by reduction of the corresponding dinitro-compound with hydrazine and Raney nickel. The reaction mixture had been filtered hot without attempt to avoid aerial oxidation and the filtrate had become yellow. From the mother liquors of the diamine crystallization, by preparative t.l.c. (ethyl acetate–hexane, 1:1), the *cinoline* (7a) was isolated in 3% yield as orange prisms (from acetone–ethanol or diethyl ether), m.p. 215–217 °C (Found: C, 79.5; H, 5.1; N, 7.1. C₂₆H₂₀N₂O₂ requires C, 79.6; H, 5.1; N, 7.1%); *m/e* 392 (*M*⁺, 3%), 391 (50), 390 (100), and 360 (8); δ 3.95 (6 H, s, OMe), 7.5 (10 H, m), 7.73 (2 H, d, *J* 9.5 Hz, 2-, 9-H), and 8.62 (2 H, d, *J* 9.5 Hz, 1-, 10-H); *v*_{max} 1 280, 1 255, 1 145, 1 085, 800, and 700 cm⁻¹. The compound formed a purple complex with mineral acid and could be identified, on t.l.c., by spraying the plate with 10% methanolic sulphuric acid. It was consistently a minor by-product in preparations of the di-iodide (5a) (above), and on occasion was isolated and identified.

2',2''-Di-iodo-4,4'',4''',6'-tetramethoxy-m-quaterphenyl (5b).—The diamine (1b) (0.836 g) was tetrazotized in 5M hydrochloric acid as described for (1a), the excess of nitrous acid destroyed by urea, and the diazonium iodo-mercurate precipitated by the addition of mercuric iodide (1.83 g) in potassium iodide (1.34 g) and water (4.6 ml). The precipitate was collected, resuspended in water, and allowed to decompose overnight; the resulting solid was stirred with sodium iodide (2.3 g) in acetone (25 ml) for 45 min. After dilution to 600 ml with water the solid was collected and dried, finally in high vacuum. The solid (1.55 g) was ground with sodium iodide (3 g) and heated at 225 °C (bath) for 0.5 h. The residue was extracted with boiling chloroform (200 ml, 50 ml), the extracts filtered, concentrated and put through alumina (elution with warm chloroform). Evaporation of the eluate gave the *di-iodide* (5b) as a white solid (860 mg, 69%) which crystallized from chloroform–acetone as small needles, m.p. 284–286 °C (subl.) (Found: C, 49.3; H, 3.5; I, 37.2. C₂₈H₂₄I₂O₄ requires C, 49.6; H, 3.6; I, 37.4%); *m/e* 678 (*M*⁺, 25%) and 551 (*M*⁺ – I, 100); δ 3.77 (6 H, s, 2 × OMe), 3.87 (6 H, s, 2 × OMe), and 6.87–7.35 (12 H, m).

2',2''-Di-iodo-4,4'',4''',6'-tetramethoxy-3,5,3''',5'''-tetra-*t*-butyl-m-quaterphenyl (5c).—The diamine ¹(1c) (6.4 g) was dissolved in warm DMF (80 ml) and the solution was cooled before addition of 7M hydrochloric acid (15 ml). The suspension, stirred at 0–5 °C, was treated dropwise over 0.5 h with sodium nitrite (2 g) in water (4 ml). The red suspension was stirred for a further 2 h after addition of DMF (10 ml) and water (5 ml); when more water (5 ml) was then added a clear red solution was obtained. Urea (2.3 g) in water (3 ml) was added and stirring was continued, still at 0–5 °C, for 2.5 h. A cold solution of mercury(II) iodide (8.6 g) and potassium iodide (6.24 g) in water (10 ml) was added. The thick red–brown paste was diluted

sixfold with water and after 20 min the solid was collected, resuspended in water (900 ml), and stirred overnight. The brown solid was collected and stirred with acetone (120 ml) and sodium iodide (12 g). After 1.5 h the mixture was slowly diluted with water to 1 l and the precipitate collected. It was dried *in vacuo* (yield, 10.0 g), mixed thoroughly with powdered sodium iodide (20 g), and heated at 160 °C (bath) for 24 h. Work-up as for (5b) afforded the *di-iodide* (5c) as a cream solid; recrystallization from chloroform-ethanol gave needles (5.98 g, 71%), m.p. 257 °C (Found; C, 58.6; H, 6.4; I, 28.5. $C_{44}H_{56}I_2O_4$ requires C, 58.5; H, 6.3; I, 28.1%); *m/e* 902 (M^+ , 14%) and 775 ($M^+ - I$, 100); δ 1.47 (36 H, s), 3.73 (s) and 3.74 (s) (12 H, 4% OMe), 7.01 (2 H, d, *J* 8.5 Hz, 5'-,5''-H), and 7.10 (s) overlapping 7.18 (d, *J* 8.5 Hz) (total 6 H).

In another experiment the temperature of the final pyrolysis, after 20 h at 160 °C, was raised to 200 °C for 2 h. Extraction as before gave a mixture of three products which were separated by preparative t.l.c. (ethyl acetate-hexane, 1:9; then dichloromethane-hexane, 1:3). The most mobile band yielded the di-iodide (5c) above. The intermediate band yielded a white solid which crystallized from dichloromethane-ethanol as small prisms of 2',2''-*di-iodo-4,4'',4''',6'-tetramethoxy-3,3''',5-tri-*t*-butyl-*m*-quaterphenyl* (5d), m.p. 213.5—215 °C (Found: C, 56.8; H, 5.7; I, 29.9. $C_{40}H_{48}I_2O_4$ requires C, 56.8; H, 5.7; I, 30.0%); *m/e* 846 (M^+ , 18%) and 719 ($M^+ - I$, 100); δ 1.40 (s, minor) and 1.47 (s, major) (total 27 H, 3 × Bu^t), 3.73 (9 H, s, 3 × OMe), 3.84 (3 H, s, OMe), and 6.87—7.32 (9 H, m). The slowest running band yielded, on elution and recrystallization from chloroform-acetone, 2',2''-*di-iodo-4,4'',4''',6'-tetramethoxy-3,3''',di-*t*-butyl-*m*-quaterphenyl* (5e) as a white, microcrystalline powder, m.p. 263—264 °C (Found: C, 54.6; H, 5.0; I, 32.1. $C_{36}H_{40}I_2O_4$ requires C, 54.7; H, 5.1; I, 32.1%); *m/e* 790 (M^+ , 16%), and 663 ($M^+ - I$, 100); δ 1.43 (18 H, s), 3.75 (s) and 3.89 (s) (12 H, 4 × OMe), and 6.8—7.3 (10 H, m). The di-iodides (5c), (5d), and (5e) were obtained in the approximate ratio 2:1:2.

3,8-Dimethoxy-4,7-di-(4-methoxy-3,5-di-*t*-butylphenyl)-benzo[c]cinnoline (7b).—The diamine (1c) (350 mg), in acetic acid (5 ml) and 1M sulphuric acid (1 ml), was treated slowly at 0—5 °C with sodium nitrite (85 mg) in water (0.5 ml). The cold mixture was stirred for 45 min at 0—5 °C and poured onto a stirred mixture of chloroform (5 ml), sodium iodide (400 mg), iodine (250 mg), and water (10 ml). After 1 h the chloroform layer was washed (10% aqueous NaHSO₃, 2M Na₂CO₃, water), dried, and evaporated. Trituration of the residue with methanol yielded the crude *cinnoline* (7b) (158 mg; small further amounts by chromatography of mother liquors) which was recrystallized twice from acetone to give yellow needles, m.p. 318—320 °C (Found: C, 78.3; H, 8.4; N, 4.1. $C_{44}H_{56}N_2O_4$ requires C, 78.1; H, 8.3; N, 4.1%); *m/e* 676 (M^+ , 15%), 661 (15), and 619 (100); δ 1.47 (36 H, s), 3.75 (6 H, s), 3.93 (6 H, s), 7.48 (4 H, s), 7.62 (2 H, d, *J* 9 Hz, 2-, 9-H), and 8.48 (2 H, d, *J* 9 Hz, 1-, 10-H).

2,7-Dimethoxy-1,8-di-(4-methoxy-3,5-di-*t*-butylphenyl)carbazole (8b).—A solution of the diamine (1c) (40 mg) in acetonitrile (4 ml) and 1,2-dimethoxyethane (4 ml) was treated at 0—5 °C with isoamyl nitrite (0.2 ml). After 2 h the mixture, at room temperature, was stirred with copper(I) iodide (100 mg) and iodine (2 mg) overnight. Water and chloroform were added; the chloroform layer was washed (10% aqueous NaHSO₃, water), dried, and evaporated. Examination by t.l.c. indicated the presence of the *cinnoline*

(7b) and one other major, less polar product. Preparative t.l.c. (chloroform-hexane 1:3; 4 × developed) separated these; from the more mobile band the *carbazole* (8b) was extracted. It crystallized from dichloromethane-ethanol as pale yellow laths (14 mg, 36%); recrystallization gave prismatic colourless needles, m.p. 335—336 °C (Found: C, 80.0; H, 6.7; N, 2.1. $C_{44}H_{57}NO_4$ requires C, 79.7; H, 8.5; N, 2.1%); *m/e* 663 (M^+ , 100%); δ 1.33 (36 H, s), 3.70 (6 H, s), 3.87 (6 H, s), 6.93 (2 H, d, *J* 8.5 Hz, 3-, 6-H), 7.34 (4 H, s), and 7.89 (d, *J* 8.5 Hz, overlapping bs; total 3 H, 4-, 5-, 9-H); ν_{max} 3 460m (very sharp; N-H) and complex peak around 1 600 cm⁻¹.

2,2'-*Di-iodobiphenyl*.—To a stirred solution of 2,2'-diaminobiphenyl (1 g) in hydrochloric acid (5 ml, *d* 1.16) and ice (10 g) at 0 °C was slowly added sodium nitrite (0.825 g). The mixture was stirred at 0 °C for 30 min, then urea (0.2 g) was added and stirring continued for 15 min, when a test for nitrite was negative. The solution was added to a cold solution of mercury(II) iodide (4.94 g) and potassium iodide (3.62 g) in water (200 ml). The mixture was shaken for 15 min, and the solid was collected and stirred in water (200 ml). Nitrogen (270 ml) was evolved overnight. The black-brown powder was dried under reduced pressure over phosphoric oxide and then weighed 5.95 g. A sample (4.7 g) of this was heated with dried potassium iodide (4.7 g) at 200 °C for 3 h. The residue was exhaustively extracted with warm diethyl ether and the concentrated diethyl ether extract was put through a short alumina column to yield 2,2'-*di-iodobiphenyl* (0.88 g, 50%) as prisms from hexane, m.p. 106—107 °C (lit.,⁷ 106—108 °C).

2,6-*Di-iodobiphenyl*.—To a stirred solution of 2,6-diaminobiphenyl (0.5 g, prepared by reduction of the dinitro compound with Raney nickel and hydrazine) in 5M hydrochloric acid (10 ml) at 0 °C was added sodium nitrite (0.413 g) over 5 min. The red-black mixture was stirred for 1 h, then urea (0.5 g) was added and stirring continued for 1 h more. The solution was added to an ice-cold solution of mercury(II) iodide (2.47 g) and potassium iodide (1.81 g) in water (200 ml). The mixture was shaken for 15 min, then filtered; the residue was dried at room temperature, under continuous pumping, for 3 days. The brown powder (2.48 g) was heated with dried potassium iodide (3 g) at 200 °C for 3 h. The product was isolated by chloroform extraction and passage in hexane through alumina. Recrystallization from hexane then gave needles (0.56 g, 45%), m.p. 79—80 °C (lit.,¹⁰ m.p. 80—81 °C).

2-*Iodobiphenyl*.—(a) A mixture of 2-acetamidobiphenyl (1 g) and hydrochloric acid (10 ml, *d* 1.16) was boiled under reflux for 1 h, diluted with water (10 ml), and stirred at 0 °C during the addition of sodium nitrite (0.36 g) during 10 min. After 1 h urea (0.5 g) was added and stirring was continued until a nitrite test was negative (0.5 h). To the rapidly stirred solution was then added a solution of mercury(II) iodide (2.15 g) and potassium iodide (1.58 g) in water (5 ml). After 0.5 h the pale yellow precipitate was collected and dried for 2 days with continuous evacuation. The powder (3.39 g), mixed with oven-dried potassium iodide (3.4 g), was heated at 190 °C for 2 h. Water (50 ml) and diethyl ether (100 ml) were added and the mixture was boiled under reflux for 1 h; the diethyl ether layer was washed (10% aqueous NaHSO₃, water) dried, and put through a short alumina column. Evaporation left an oil (1.212 g) that was analysed by g.l.c. (OV 17, 30 ml/min N₂, 225 °C) and shown to be a mixture of biphenyl (1.1%; retention time 1.4 min) and 2-iodobiphenyl (98.9%; retention time 3.5

min). This is an overall yield of 91% from 2-acetamidobiphenyl.

(b) 2-Acetamidobiphenyl (4.22 g) was converted into the diazonium iodomercurate as above. This was suspended in water (100 ml) and stirred for 18 h (480 ml gas collected) at 20 °C. Light petroleum was added and the mixture was filtered; the brown solid was washed with hot, light petroleum. The residue from evaporation of the solvent was passed in diethyl ether through a short alumina column to yield, on evaporation, almost pure 2-iodobiphenyl (4.59 g, 82%; 1.5% biphenyl and 98.5% 2-iodobiphenyl by g.l.c.). The brown solid (8.2 g) was dissolved in acetone (100 ml) containing sodium iodide (0.5 g). This solution was slowly added to a rapidly stirred solution of sodium iodide (20 g) in water (100 ml). The black precipitate [0.61 g; m.p. 150–152 °C (decomp.)] was heated for 1 h at 200 °C and yielded further 2-iodobiphenyl (0.31 g, total 87%).

3,5,7-Trimethoxy-4,6-diphenyldibenzophosphole 5-Oxide (2d).—A solution of the di-iodide (5a) (6.18 g) in tetrahydrofuran (THF) (200 ml), made by heating the mixture to ca. 60 °C, was cooled to –78 °C under nitrogen. Butyllithium (15 ml; 1.46M in hexane) was added with cooling; after 3.5 h at –78 °C phosphorus trichloride (2 ml, freshly distilled in a stream of nitrogen) was added (transient red colour). After 2.5 h more, still at –78 °C, water (5 ml) was added dropwise, and the nitrogen cover and cooling were discontinued. Next day the clear yellow solution was evaporated and the residue was extracted with dichloromethane (3 × 50 ml) after addition of water. The orange extract was evaporated and the residue, suspended in acetone (150 ml) at ca. 40 °C, was treated dropwise during 10 min with hydrogen peroxide (25 ml of 30%) then boiled gently (reflux) for 4 h, with the addition of more hydrogen peroxide (10 ml) after 1 h. Water (250 ml) was added when the phosphinic acid (2a) crystallized. It was collected, washed (water, dichloromethane), and methylated with an excess of ethereal diazomethane. The product on evaporation crystallized from methanol to give three crops of the pure *phosphinic ester* (2d) (2.875 g, 65%; a further 5% by chromatography of mother liquors). The analytical specimen, very pale yellow prisms, had m.p. 232–233 °C (Found: C, 73.3; H, 5.3; P, 7.0. C₂₇H₂₃O₄P requires C, 73.3; H, 5.2; P, 7.0%); *m/e* 442 (M⁺, 100%), 427 (4), 395 (10), 379 (7), and 213.5 (27); δ 2.63 (3 H, d, J 11.5 Hz, POME), 3.75 (6 H, s, ArOMe), 7.07 (2 H, d, J 8.5 Hz, 2-, 8-H), and 7.61 (2 H, dd, J 4, 8.5 Hz, 1-, 9-H); δ (³¹P) 97.738 upfield from trimethyl phosphite; *v*_{max} 1 580, 1 500, 1 285, 1 265, 1 230, 1 180, 1 155, 1 075, 1 050, 1 035, 890, 835, 815, 780, 745, 700, and 670 cm⁻¹; *λ*_{max} (ε_{max}) 253.5 (33 400), 296 (25 400), 306.5 (23 500), and 374 nm (2 470).

In another experiment the peroxide oxidation was effected in alkaline solution and without addition of acetone, when the phosphinic acid separated as a solid sodium salt, which was removed. The filtrate was concentrated and extracted with chloroform; the evaporated extract when boiled with acetone gave a residue of the di-iodide (5a) and a soluble fraction which was separated by preparative t.l.c. The major component was *5-butyl-3,7-dimethoxy-4,6-diphenyldibenzophosphole 5-oxide* (2g), m.p. 254–255 °C (after crystallization from dichloromethane-diethyl ether) (Found: C, 76.8; H, 6.2. C₃₀H₂₉O₃P requires C, 76.9; H, 6.2%); δ 0.40–1.00 (9 H, m, Bu), 3.73 (6 H, s, 2 × OMe), 7.03br (2 H, d, J 8.7 Hz, 2-, 8-H), 7.40 (10 H, m, 2 × Ph), and 7.57 (2 H, dd, J 8.7, 3.0 Hz, 9-H); *v*_{max} 1 240 (P=O), 808, and 700 cm⁻¹.

5-Hydroxy-3,7-dimethoxy-4,6-diphenyldibenzophosphole 5-Oxide (2a).—This phosphinic acid could be isolated directly from the reaction mixture above, but was first prepared from its methyl ester (2d) by demethylation with a 5% solution of lithium iodide in DMF at 110 °C for 20 h, or by a chloroform solution of iodotrimethylsilane¹¹ at room temperature for 14 h. The *phosphinic acid* (2a) crystallized from ethanol as needles, m.p. 304–305 °C (decomp.) (Found: C, 72.8; H, 5.0; P, 7.4. C₂₆H₂₁O₄P requires C, 72.9; H, 5.0; P, 7.2%); *m/e* 428 (M⁺, 100%), other peaks at 413, 395, 380, and 379; *v*_{max} 1 420, 1 270, 1 235, 810, 775, 745, 700, and 665 cm⁻¹; *λ*_{max} (ε_{max}) 249 (34 100), 294.5 (26 400), 305 (23 300), and 358 nm (1 370).

5-Hydroxy-3,7-dimethoxy-4,6-bis(4-methoxyphenyl)dibenzophosphole 5-Oxide (2b).—The di-iodide (5b) (415 mg) in THF (70 ml) was treated with butyl-lithium (1 ml of 1.46M in hexane) and then with phosphorus trichloride (0.3 ml) as described for compound (5a). The mixture, on regaining room temperature, was treated with water (2 ml), 2M sodium hydroxide (5 ml), and hydrogen peroxide (8 ml of 30%) and stirred overnight; then it was poured into water, acidified (2M hydrochloric acid), and extracted with chloroform. Evaporation of the dried extract left a residue that was triturated and washed with diethyl ether, leaving the *phosphinic acid* (222 mg, 74%). Crystallization from chloroform-ethanol yielded fine needles, m.p. 315–317 °C (decomp.) (Found: C, 68.8; H, 5.2. C₂₈H₂₅O₆P requires C, 68.9; H, 5.2%); *m/e* 488 (M⁺, 100%).

The methyl ester, *3,5,7-trimethoxy-4,6-bis(4-methoxyphenyl)dibenzophosphole 5-oxide* (2e), was made by suspending the acid in dichloromethane, adding an excess of ethereal diazomethane, and stirring the mixture overnight. The product from evaporation crystallized from chloroform-diethyl ether as cream-coloured needles, m.p. 216.5–217.5 °C (Found: C, 69.0; H, 5.4; P, 6.3. C₂₉H₂₇O₆P requires C, 69.3; H, 5.4; P, 6.2%); *m/e* 502 (M⁺, 100%) and 487 (M⁺ – Me, 5); δ 2.76 (3 H, d, J 11 Hz, P – OMe), 3.75 (s) and 3.77 (s) (12 H, 4 × OMe), 6.80–7.22 (6 H, m), and 7.33–7.72 (6 H, m).

3,5,7-Trimethoxy-4,6-bis(4-methoxy-3,5-di-*t*-butylphenyl)dibenzophosphole 5-Oxide (2f).—A solution of the di-iodide (5c) (5 g) in THF (50 ml) was stirred under nitrogen at –78 °C during the addition of butyl-lithium (8 ml of 1.47M in hexane). After 1.5 h, phosphorus trichloride (1.4 ml) was added and, after 15 min, the cold bath was removed. After a further 1 h water (100 ml) and ethyl acetate were added; the organic layer was washed (water), dried, and evaporated. The residue in warm acetone (300 ml) was treated with an excess of hydrogen peroxide (30%; 2 × 25 ml) and boiled under reflux for 3 h. Next day most of the acetone was removed at low pressure, water (100 ml) and 2M hydrochloric acid (50 ml) were added and the mixture was extracted with ethyl acetate. The extract was washed (10% aqueous NaHSO₃, water) dried, and evaporated. The yellow residue was stirred with chloroform (100 ml) and treated with ethereal diazomethane. This seemed to give incomplete methylation: the solvent was removed and the residue was treated overnight with lithium carbonate (1 g) and methyl iodide (1 ml) in DMF (10 ml). The mixture was acidified (2M hydrochloric acid) and extracted with ethyl acetate which was washed (water), dried, and evaporated. The residue in chloroform (5 ml) was applied to an alumina column (25 × 2.5 cm) prepared in chloroform-hexane (1 : 1). Elution with this mixture yielded, after a small fore-run, the *phosphinic ester* (2f); elution of which was completed

with chloroform. Recrystallization from dichloromethane-ethanol gave clusters of needles (2.2 g), m.p. 293–295 °C (Found: C, 74.6; H, 8.1; P, 4.4. $C_{45}H_{59}O_6P$ requires C, 74.4; H, 8.2; P, 4.3%; m/e 726.5 (M^+ , 100%); δ 1.42 (36 H, s), 2.48 (3 H, d, J 11 Hz, P-OMe), 3.63 (6 H, s, $2 \times$ OMe), 3.76 (6 H, s, $2 \times$ OMe), 7.05 (2 H, d, J 8.5 Hz, 2-, 8-H), and 7.50 (s) overlapping 7.58 (dd, J 8.5, 4 Hz) (total 6 H). Further elution of the column yielded 5-butyl-3,7-dimethoxy-4,6-bis-(4-methoxy-3,5-di-*t*-butylphenyl)dibenzophosphole 5-oxide (2h), purified with difficulty by preparative t.l.c. (ethyl acetate-hexane, 3:7; then dichloromethane $3 \times$ developed) and obtained as fine needles from acetone, m.p. 304–306 °C (Found: C, 76.8; H, 8.6. $C_{48}H_{65}O_5P$ requires C, 76.6; H, 8.7%; m/e 752.5 (M^+ , 100%); δ 0.22–0.80 (9 H, m, Bu), 1.42 (36 H, s), 3.65 (6 H, s), 3.80 (6 H, s), 7.13 (2 H, d, J 8.5 Hz), and 7.50–7.75 (6 H, m).

5-Hydroxy-3,7-dimethoxy-4,6-bis-(4-methoxy-3,5-di-*t*-butylphenyl)dibenzophosphole 5-Oxide (2c).—A solution of the above ester (2f) (145 mg) in dry chloroform (5 ml) containing iodotrimethylsilane (200 mg) was stirred at room temperature for 3 h, poured into methanol (10 ml), and evaporated. More methanol (15 ml) was added and the solution was boiled before being evaporated. The residue in ethyl acetate was washed (10% aqueous $NaHSO_3$, water), dried, and evaporated to yield the phosphinic acid as a pale yellow solid. Recrystallization from acetone-ether gave elongated prisms, m.p. 265–267 °C. These were solvated (see Appendix) and were dried before analysis for 12 h at 115 °C/0.1 mmHg (Found: C, 73.8; H, 8.0. $C_{44}H_{57}O_6P$ requires C, 74.1; H, 8.1%; m/e 712.5 (M^+ , 100%); δ 1.44 (3 H, s), 3.0br (3 H, s, PO_2H and H_2O); exchanged with D_2O), 3.69 (s) and 3.76 (s) (12 H), 7.11 (2 H, d, J 8.5 Hz), 7.50 (4 H, s), and 7.62 (2 H, dd, J 8.5, 4 Hz); ν_{max} 3 560 (OH) and 1 245 cm^{-1} (P=O).

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APPENDIX

Structure of Two 4,6-Diaryldibenzophospholes by X-Ray Diffraction

Molecule A, $C_{29}H_{25}Cl_2O_6P$ (10).—The molecular conformation and atom numbering scheme* are shown in

Figure 1 (a) and (b), and bond lengths, angles, and torsion angles are listed in Table 1. The geometry of the dibenzophosphole nucleus is essentially the same as that seen in 5-hydroxy-5*H*-dibenzophosphole 5-oxide.¹ The bond lengths in the benzo-rings do not differ significantly from those of benzene (1.395 Å), and the two P-C bonds are equal [P-C(1), 1.82(1); P-C(2), 1.81(2) Å] compared with the values of 1.781(5) and 1.779(7) Å for P-C(Ph) bonds in 1-diphenylphosphoryl-1*H*-trifluoromethyldiphenylphosphinate.² The two P-O bonds are significantly different at 1.49(1) Å for the double bond (oxo) and 1.57(1) Å for the single bond (methoxy), in good agreement with equivalent bonds in (\pm)-*O*-methyl- α -phenylphosphinylpropionic acid³ [1.479(1) and 1.577(2) Å, respectively] and in (–)-*O*-methylphenylphosphinylacetic acid⁴ [1.487(1) and 1.575(3) Å].

The deviations from co-planarity of the atoms of the three fused rings and their substituents (Table 2) suggest that the dibenzophosphole nucleus is slightly bowed about the line joining the P atom to the mid point of the C(6)–C(20) bond; the displacement is greater for those atoms near the top of the molecule as viewed in Figure 1. Thus, the P atom is 0.08 Å above the plane with C(2) and C(16) slightly (0.06 Å) behind the plane. This effect is most obvious from the positions of the *para*-carbon atoms of the substituent phenyl rings which are –0.36 for C(10) and –0.68 Å for C(24) behind the mean plane of the dibenzophosphole nucleus. This effect is also seen by considering the benzo-rings separately, when it appears that each is planar to within 0.01 Å and the P atom is co-planar with each. The angle between these two planes is 5°.

It is quite possible that the molecule 5-hydroxy-5*H*-dibenzophosphole 5-oxide has the same bowing since the P atom is stated to be 0.06 Å out of the mean plane of the fused ring system, but the lack of substituents on the benzo-rings may have made this less obvious. A similar dihedral angle of 3° is seen in the nickel(II) complex of 5-methyl-5*H*-dibenzophosphole and in other related co-ordinated dibenzophosphole ligands.⁵

It can be seen from Figure 1 that the pendant phenyl groups are slightly bent towards the P atom; this bending occurs at the C(7) and C(21) positions. Thus, the angle between the lines C(2)–C(7) and C(16)–C(21) is 45° whilst the angle between the lines C(7) \cdots C(10) and C(21) \cdots C(24) is only 38°. No obvious reason for this effect comes to mind. The phenyl groups themselves are planar and their normals both make angles of 113° with the mean plane of the dibenzophosphole nucleus. This appears to be a consequence of minimizing short contacts of the *ortho*-positions C(8) to the C(13) methylene group and the O(4) methoxy-group; and correspondingly from C(26) to the C(27) methylene group and the O(1) oxo-group.

The only unusually short intermolecular contact is that between O(1) and O(3), related by \bar{x} , $-\frac{1}{2} + y$, $-\frac{1}{2} - z$, which, at 2.79 Å, is indicative of hydrogen bonding.

* The atom numbering scheme used in the Appendix is not that of the IUPAC systematic name.

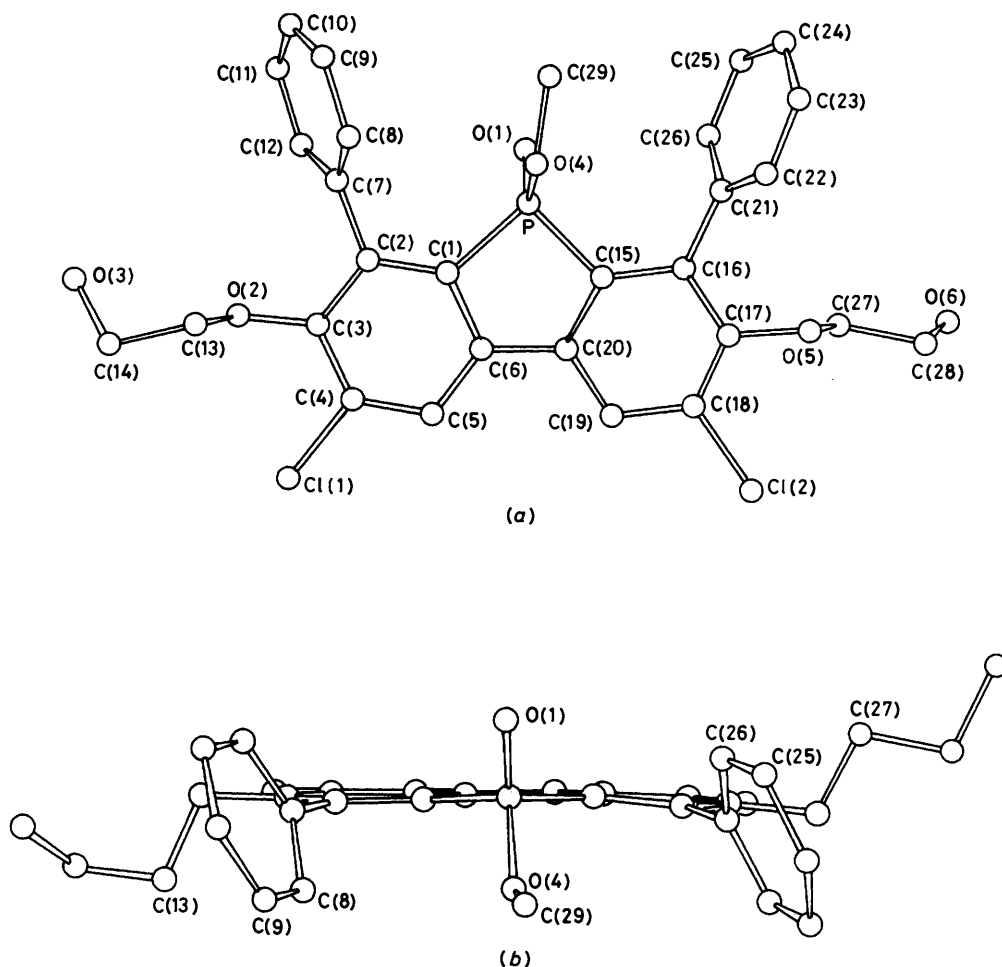


FIGURE 1 View of molecule A, $C_{29}H_{25}Cl_3O_6P$, (a) perpendicular to and (b) parallel to, the mean plane of the fused ring system

Molecule B, $C_{44}H_{57}O_6P \cdot C_4H_{10}O$ (2c) (*Diethyl Ether Solvate*).—The molecular conformation and atom numbering are shown in Figure 2, and bond lengths, bond angles, and torsion angles are listed in Table 3. The dibenzophosphole nucleus is similar to that in molecule A with bond lengths not significantly different at 1.808(4) and 1.816(4) Å for P–C and 1.465(3) and 1.568(4) Å respectively for the P–O double and single bonds. The three fused rings again show some bowing with the angle between the mean planes of the C(1) to C(6) ring and the C(13) to C(18) ring equal to 3°. However in this case the deviations of the pendant phenyl rings are on opposite sides of the overall mean plane of the fused ring system [Table 4 and Figure 2(b)].

The pendant phenyl rings are themselves both distorted. As seen from Table 4 the central C atoms of the two t-butyl groups are pushed slightly to one side of the phenyl ring whilst the O atom of the methoxy-group and the ring C atom to which it is attached are slightly out of the plane on the other side. Thus both phenyl rings are curved about the C(7) ··· C(10) and C(19) ··· C(22) lines. However, the C(7)–C(12) ring has its convex side

pointing towards the centre of the molecule whilst the C(19)–C(22) ring has its concave side facing the centre. Other rotational isomers might conceivably exist, related by 180° rotations about the C(2)–C(7) and C(14)–C(19) bonds. In both phenyl rings the conformations about the C(ring)–C(t-butyl) bonds and the C(ring)–O bonds are the same and result in three bonds [those to C(28), C(33), C(30) in one ring and to C(36), C(42), C(40) in the other] pointing out from the convex side of each ring with each making a torsion angle at the exocyclic ring bond of close to 90°. The distortion of these rings also involves a decrease in the internal ring angle to average 116.3(3)° at the t-butyl substituted positions, an increase in the two ring bonds from these two positions to the OMe substituted position [average 1.404(8) Å], and also an increase in the bonds to the three *ortho*-substituents with average values of 1.542(8) for C(ring)–C(t-butyl) and 1.401(2) Å for C(ring)–O(Me). This last value may be compared with the average of 1.368(5) Å for the non-affected bonds C(3)–O(2) and C(15)–O(3). These distortions of the pendant phenyl groups are due to the steric crowding as can be seen from the occurrence

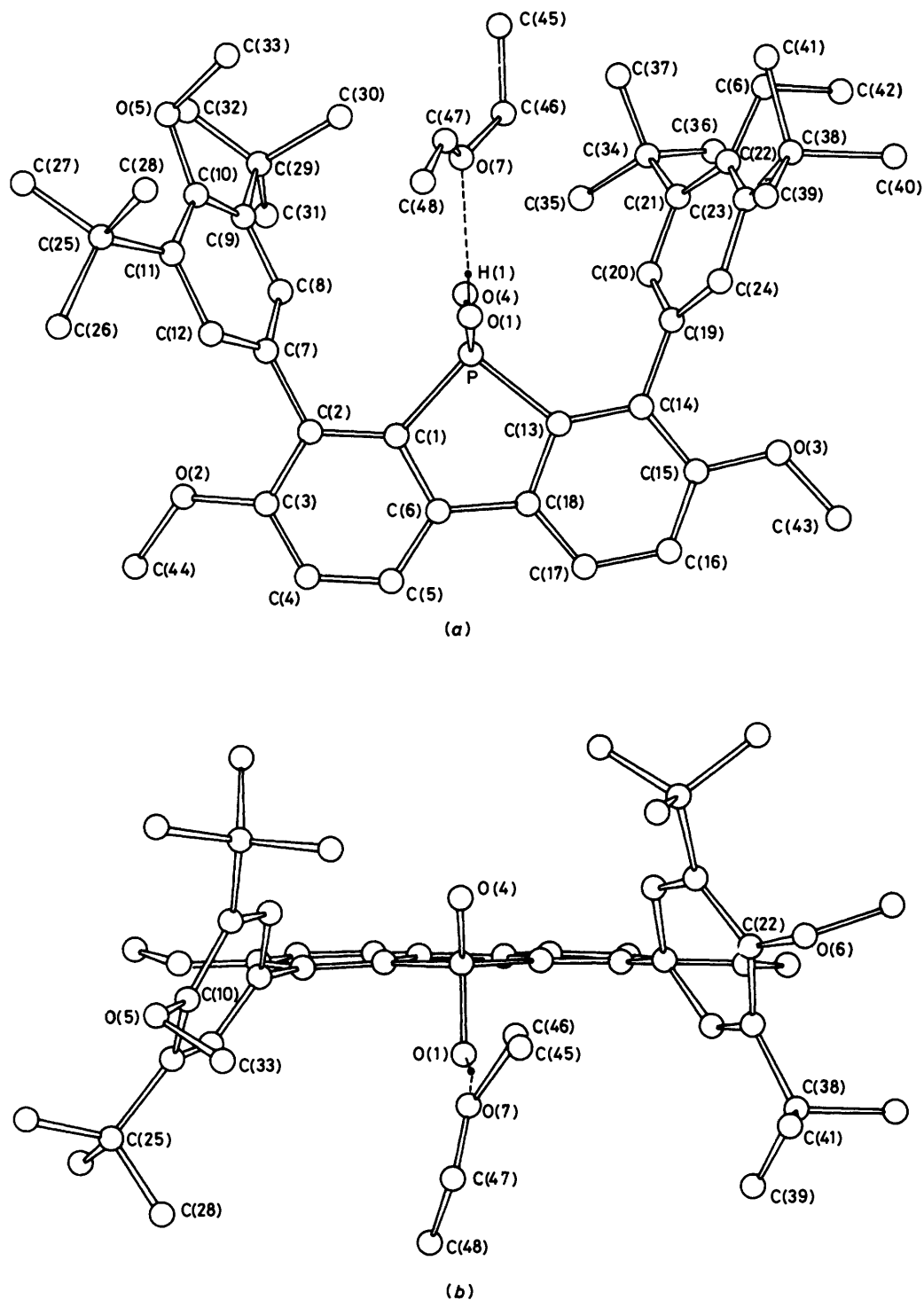


FIGURE 2 Views of molecule B and diethyl ether solvate, $C_{44}H_{86}O_6 \cdot P \cdot C_4H_{10}O$, (a) perpendicular to, and (b) parallel to, the mean plane of the fused ring system

of equivalent effects in the two related molecules 4-methyl-2,6-di-*t*-butylphenol⁶ and *N*-benzyl-*N*-methyl-2,4,6-tri-*t*-butylbenzamide.⁷

Because of the non-planarity of the pendant phenyl rings it is difficult to define an angle between them. However a few possible lines are defined in Table 4 and by reference to this and to Figure 2 (*a*) it seems that whilst the angle between C(2)–C(7) and C(14)–C(19) is 48° the ring C(7) to C(12) then bends slightly (4°) towards the centre of the molecule. Further evidence of this bending is that atom C(2) is 0.14 Å out of the plane of the C(7)–C(12) ring. The inherent distortion of the ring then bends the C(10)–O(5) bond a further 6° towards the centre of the molecule. The other ring does not look as if it is bent at C(19), but the line C(19)–C(22) makes an angle of 4° with C(14)–C(19) because the sterically induced bending of the ring pushes C(22) away from the centre of the molecule and also does the same for O(6).

The molecule of diethyl ether solvate lies almost in the plane of the PO₂ group and with the O(7) atom almost

directly above the O(1) position [Figure 2(*b*)]. The O(1) ··· O(7) distance of 2.61 and H(1) ··· O(7) distance of 1.95 Å are indicative of a hydrogen bond. The orientation of the pendant phenyl rings seems to be dictated by the need to optimize the contacts with the ether molecule, causing the C(25) and C(38) *t*-butyl groups to be pushed slightly apart such that the angles between the planes of the phenyl rings and the fused ring system are 63° for ring C(7)–C(12) and 70° for ring C(19)–C(24). The atoms C(45) and C(46) of the ether molecule which lie near the centre of the host molecule seem to be held much more rigidly than C(47) and C(48) as evidenced by their lower thermal vibration parameters.

Apart from the hydrogen bond from the host molecule to the diethyl ether solvate there are no intermolecular contacts significantly shorter than the sum of the relevant Van der Waals radii. It seems probable therefore that the major details of the conformation are decided by the intramolecular steric constraints of the host-diethyl ether complex with minimal effects from crystal packing forces.

TABLE 1

Intramolecular distances and angles with estimated standard deviations in parentheses and selected torsion angles for molecule A

(a) Bonds (Å)

P–O(1)	1.49(1)	C(7)–C(8)	1.37(2)
P–O(4)	1.57(1)	C(7)–C(12)	1.40(2)
P–C(1)	1.82(1)	C(8)–C(9)	1.35(3)
P–C(15)	1.82(2)	C(9)–C(10)	1.36(3)
Cl(1)–C(4)	1.75(1)	C(10)–C(11)	1.38(2)
Cl(2)–C(18)	1.76(2)	C(11)–C(12)	1.39(3)
O(2)–C(3)	1.35(1)	C(13)–C(14)	1.51(2)
O(2)–C(13)	1.44(2)	C(15)–C(16)	1.39(2)
O(3)–C(14)	1.41(2)	C(15)–C(20)	1.38(2)
O(4)–C(29)	1.49(2)	C(16)–C(17)	1.40(2)
O(5)–C(17)	1.38(1)	C(16)–C(21)	1.49(2)
O(5)–C(27)	1.45(2)	C(17)–C(18)	1.37(2)
O(6)–C(28)	1.53(3)	C(18)–C(19)	1.38(2)
C(1)–C(2)	1.39(2)	C(19)–C(20)	1.40(2)
C(1)–C(6)	1.42(2)	C(21)–C(22)	1.40(2)
C(2)–C(3)	1.41(2)	C(21)–C(26)	1.38(2)
C(2)–C(7)	1.46(2)	C(22)–C(23)	1.37(2)
C(3)–C(4)	1.42(2)	C(23)–C(24)	1.37(3)
C(4)–C(5)	1.37(2)	C(24)–C(25)	1.38(2)
C(5)–C(6)	1.38(2)	C(25)–C(26)	1.39(2)
C(6)–C(20)	1.46(2)	C(27)–C(28)	1.50(3)

(b) Angles (°)

O(4)–P–O(1)	115.1(6)	C(4)–C(3)–C(2)	117.8(11)
C(1)–P–O(1)	115.0(5)	C(3)–C(4)–Cl(1)	116.3(8)
C(1)–P–O(4)	107.8(5)	C(5)–C(4)–Cl(1)	119.6(12)
C(15)–P–O(1)	117.6(6)	C(5)–C(4)–C(3)	124.0(12)
C(15)–P–O(4)	105.3(5)	C(6)–C(5)–C(4)	118.6(14)
C(15)–P–C(1)	93.4(6)	C(5)–C(6)–C(1)	118.4(11)
C(13)–O(2)–C(3)	113.6(9)	C(20)–C(6)–C(1)	114.7(11)
C(29)–O(4)–P	122.2(10)	C(20)–C(6)–C(5)	126.9(14)
C(27)–O(5)–C(17)	111.2(9)	C(8)–C(7)–C(2)	122.3(13)
C(2)–C(1)–P	128.8(12)	C(12)–C(7)–C(2)	121.2(11)
C(6)–C(1)–P	107.6(8)	C(12)–C(7)–C(8)	116.5(15)
C(6)–C(1)–C(2)	123.5(11)	C(9)–C(8)–C(7)	123.2(15)
C(3)–C(2)–C(1)	117.6(14)	C(10)–C(9)–C(8)	120.4(15)
C(7)–C(2)–C(1)	120.4(11)	C(11)–C(10)–C(9)	119.6(23)
C(7)–C(2)–C(3)	122.0(11)	C(12)–C(11)–C(10)	119.3(19)
C(2)–C(3)–O(2)	121.4(14)	C(11)–C(12)–C(7)	120.8(13)
C(4)–C(3)–O(2)	120.7(11)	C(14)–C(13)–O(2)	108.1(10)

TABLE 1 (continued)

(b) Angles (°)

C(13)-C(14)-O(3)	110.6(14)	C(15)-C(20)-C(6)	115.0(13)
C(16)-C(15)-P	128.0(11)	C(19)-C(20)-C(6)	124.8(12)
C(20)-C(15)-P	109.0(8)	C(19)-C(20)-C(15)	119.9(10)
C(20)-C(15)-C(16)	122.8(14)	C(22)-C(21)-C(16)	119.4(14)
C(17)-C(16)-C(15)	116.8(12)	C(26)-C(21)-C(16)	121.1(10)
C(21)-C(16)-C(15)	122.0(14)	C(26)-C(21)-C(22)	119.2(13)
C(21)-C(16)-C(17)	121.0(10)	C(23)-C(22)-C(21)	120.0(15)
C(16)-C(17)-O(5)	119.4(12)	C(24)-C(23)-C(22)	120.8(13)
C(18)-C(17)-O(5)	120.5(14)	C(25)-C(24)-C(23)	119.9(16)
C(18)-C(17)-C(16)	120.0(11)	C(26)-C(25)-C(24)	120.3(19)
C(17)-C(18)-Cl(2)	118.2(9)	C(25)-C(26)-C(21)	119.8(12)
C(19)-C(18)-Cl(2)	118.1(12)	C(28)-C(27)-O(5)	106.9(14)
C(19)-C(18)-C(17)	123.6(14)	C(27)-C(28)-O(6)	104.5(19)
C(20)-C(19)-C(18)	116.8(12)		

(c) Torsion angles (°)

O(1)-P-O(4)-C(29)	-6(1)	C(1)-C(6)-C(20)-C(19)	174(1)
C(13)-O(2)-C(3)-C(2)	-93(1)	C(5)-C(6)-C(20)-C(15)	-178(1)
C(13)-O(2)-C(3)-C(4)	88(1)	C(5)-C(6)-C(20)-C(19)	-5(2)
C(3)-O(2)-C(13)-C(14)	-159(1)	C(2)-C(7)-C(8)-C(9)	175(1)
C(27)-O(5)-C(17)-C(16)	-93(2)	C(12)-C(7)-C(8)-C(9)	-1(2)
C(27)-O(5)-C(17)-C(18)	89(2)	C(2)-C(7)-C(12)-C(11)	-175(1)
C(17)-O(5)-C(27)-C(28)	-163(1)	C(8)-C(7)-C(12)-C(11)	1(2)
C(6)-C(1)-C(2)-C(3)	0(2)	C(7)-C(8)-C(9)-C(10)	0(3)
C(6)-C(1)-C(2)-C(7)	176(1)	C(8)-C(9)-C(10)-C(11)	3(3)
C(2)-C(1)-C(6)-C(5)	0(2)	C(9)-C(10)-C(11)-C(12)	-3(3)
C(2)-C(1)-C(6)-C(20)	180(1)	C(10)-C(11)-C(12)-C(7)	2(3)
C(1)-C(2)-C(3)-O(2)	-176(1)	O(2)-C(13)-C(14)-O(3)	-67(2)
C(1)-C(2)-C(3)-C(4)	1(2)	C(20)-C(15)-C(16)-C(17)	3(2)
C(7)-C(2)-C(3)-O(2)	5(2)	C(20)-C(15)-C(16)-C(21)	-173(1)
C(7)-C(2)-C(3)-C(4)	-176(1)	C(16)-C(15)-C(20)-C(6)	172(1)
C(1)-C(2)-C(7)-C(8)	-65(2)	C(16)-C(15)-C(20)-C(19)	0(2)
C(1)-C(2)-C(7)-C(12)	111(2)	C(15)-C(16)-C(17)-O(5)	-178(1)
C(3)-C(2)-C(7)-C(8)	112(2)	C(15)-C(16)-C(17)-C(18)	-1(2)
C(3)-C(2)-C(7)-C(12)	-70(2)	C(21)-C(16)-C(17)-O(5)	-2(2)
O(2)-C(3)-C(4)-Cl(1)	-3(2)	C(21)-C(16)-C(17)-C(18)	174(1)
O(2)-C(3)-C(4)-C(5)	178(1)	C(15)-C(16)-C(21)-C(22)	113(2)
C(2)-C(3)-C(4)-Cl(1)	178(1)	C(15)-C(16)-C(21)-C(26)	-61(2)
C(2)-C(3)-C(4)-C(5)	0(2)	C(17)-C(16)-C(21)-C(22)	-62(2)
Cl(1)-C(4)-C(5)-C(6)	-178(1)	C(17)-C(16)-C(21)-C(26)	122(2)
C(3)-C(4)-C(5)-C(6)	0(2)	O(5)-C(17)-C(18)-Cl(2)	0(2)
C(4)-C(5)-C(6)-C(1)	1(2)	O(5)-C(17)-C(18)-C(19)	177(1)
C(4)-C(5)-C(6)-C(20)	-177(1)	C(16)-C(17)-C(18)-Cl(2)	-177(1)
C(1)-C(6)-C(20)-C(15)	1(2)	C(16)-C(17)-C(18)-C(19)	0(2)
C(22)-C(21)-C(26)-C(25)	1(2)	Cl(2)-C(18)-C(19)-C(20)	179(1)
C(21)-C(22)-C(23)-C(24)	0(3)	C(17)-C(18)-C(19)-C(20)	2(2)
C(22)-C(23)-C(24)-C(25)	0(3)	C(18)-C(19)-C(20)-C(6)	-173(1)
C(23)-C(24)-C(25)-C(26)	0(3)	C(18)-C(19)-C(20)-C(15)	0(2)
C(24)-C(25)-C(26)-C(21)	0(2)	C(16)-C(21)-C(22)-C(23)	-174(1)
O(5)-C(27)-C(28)-O(6)	-169(1)	C(26)-C(21)-C(22)-C(23)	0(2)
		C(16)-C(21)-C(26)-C(25)	175(1)

TABLE 2

Least squares mean planes and lines for molecule A. Deviations (Å) of atoms from various mean planes. Atoms marked + were not included in the calculation of the plane

(a) C(1), -0.02; C(2), -0.07; C(3), -0.05; C(4), 0.00; C(5), 0.02; C(6), 0.03; C(15), 0.06; C(16), -0.05; C(17), -0.08; C(18), -0.04; C(19), 0.03; C(20), 0.09; P, 0.08; Cl(1)⁺, -0.03; Cl(2)⁺, -0.14; O(2)⁺, -0.04; O(5)⁺, -0.21; C(7)⁺, -0.19; C(10)⁺, -0.36; C(21)⁺, -0.22; C(24)⁺, -0.68

(b) C(7), -0.01; C(8), 0.01; C(9), 0.01; C(10), -0.02; C(11), 0.02; C(12), 0.00; C(2)⁺, -0.12

(c) C(21), 0.00; C(22), 0.00; C(23), 0.00; C(24), 0.00; C(25), 0.00; C(26), 0.00; C(16)⁺, 0.11

(d) C(1), 0.00; C(2), -0.01; C(3), 0.00; C(4), 0.01; C(5), -0.01; C(6), 0.00; P⁺, 0.09; Cl(1)⁺, -0.03; O(2)⁺, 0.05; C(7)⁺, -0.08; C(10)⁺, -0.17

(e) C(15), 0.01; C(16), -0.01; C(17), 0.00; C(18), 0.01; C(19), -0.01; C(20), 0.00; P⁺, -0.05; Cl(2)⁺, -0.03; O(5)⁺, -0.04; C(21)⁺, -0.14; C(24)⁺, -0.53

Angles (°) between normals to planes; (a)-(b), 113; (a)-(c), 113; (b)-(c), 33; (d)-(e), 5; (b)-(d), 112; (c)-(e), 117

If the following lines are defined by two atoms each as (f) C(2)-C(7), (g) C(7)-C(10), (h) C(16)-C(21), (i) C(21)-C(24), then the angles (°) between these lines are: (f)-(g), 4; (h)-(i), 5; (g)-(i), 38; (f)-(h), 45

TABLE 3

Intramolecular distances and angles with estimated standard deviations in parentheses and selected torsion angles in molecule B

(a) Bonds (Å)

P—O(1)	1.568(4)	C(14)—C(15)	1.409(6)
P—O(4)	1.465(3)	C(14)—C(19)	1.493(6)
P—C(1)	1.808(4)	C(15)—C(16)	1.389(6)
P—C(13)	1.816(4)	C(16)—C(17)	1.391(7)
O(2)—C(3)	1.363(5)	C(17)—C(18)	1.383(6)
O(2)—C(44)	1.443(7)	C(19)—C(20)	1.393(6)
O(3)—C(15)	1.373(6)	C(19)—C(24)	1.376(7)
O(3)—C(43)	1.423(6)	C(20)—C(21)	1.398(6)
O(5)—C(10)	1.399(6)	C(21)—C(22)	1.394(7)
O(5)—C(33)	1.441(10)	C(21)—C(34)	1.541(7)
O(6)—C(22)	1.402(6)	C(22)—C(23)	1.401(7)
O(6)—C(42)	1.456(7)	C(23)—C(24)	1.398(7)
C(1)—C(2)	1.391(6)	C(23)—C(38)	1.549(8)
C(1)—C(6)	1.417(5)	C(25)—C(26)	1.532(9)
C(2)—C(3)	1.401(6)	C(25)—C(27)	1.540(9)
C(2)—C(7)	1.480(5)	C(25)—C(28)	1.539(9)
C(3)—C(4)	1.382(6)	C(29)—C(30)	1.498(12)
C(4)—C(5)	1.384(7)	C(29)—C(31)	1.517(10)
C(5)—C(6)	1.376(6)	C(29)—C(32)	1.503(10)
C(6)—C(18)	1.491(6)	C(34)—C(35)	1.504(11)
C(7)—C(8)	1.391(6)	C(34)—C(36)	1.478(12)
C(7)—C(12)	1.381(6)	C(34)—C(37)	1.499(11)
C(8)—C(9)	1.398(6)	C(38)—C(39)	1.537(11)
C(9)—C(10)	1.415(6)	C(38)—C(40)	1.524(9)
C(9)—C(29)	1.529(6)	C(38)—C(41)	1.511(10)
C(10)—C(11)	1.407(6)	C(45)—C(46)	1.355(15)
C(11)—C(12)	1.392(6)	C(46)—O(7)	1.471(12)
C(11)—C(25)	1.547(6)	O(7)—C(47)	1.308(16)
C(13)—C(14)	1.382(6)	C(47)—C(48)	1.294(21)
C(13)—C(18)	1.404(6)		

(b) Angles (°)

O(4)—P—O(1)	116.1(2)	C(29)—C(9)—C(10)	126.0(4)
C(1)—P—O(1)	105.6(2)	C(9)—C(10)—O(5)	117.6(4)
C(1)—P—O(4)	116.6(2)	C(11)—C(10)—O(5)	119.5(4)
C(13)—P—O(1)	105.3(2)	C(11)—C(10)—C(9)	122.9(4)
C(13)—P—O(4)	116.8(2)	C(12)—C(11)—C(10)	116.6(4)
C(13)—P—C(1)	93.4(2)	C(25)—C(11)—C(10)	124.0(4)
C(44)—O(2)—C(3)	118.6(4)	C(25)—C(11)—C(12)	119.4(4)
C(43)—O(3)—C(15)	118.1(4)	C(11)—C(12)—C(7)	122.8(4)
C(33)—O(5)—C(10)	114.7(4)	C(14)—C(13)—P	128.3(3)
C(42)—O(6)—C(22)	113.7(4)	C(18)—C(13)—P	109.2(3)
C(2)—C(1)—P	129.1(3)	C(18)—C(13)—C(14)	122.5(4)
C(6)—C(1)—P	109.3(3)	C(15)—C(14)—C(13)	116.8(4)
C(6)—C(1)—C(2)	121.6(4)	C(19)—C(14)—C(13)	122.0(3)
C(3)—C(2)—C(1)	117.2(4)	C(19)—C(14)—C(15)	121.2(4)
C(7)—C(2)—C(1)	121.4(4)	C(14)—C(15)—O(3)	115.9(4)
C(7)—C(2)—C(3)	121.4(4)	C(16)—C(15)—O(3)	122.8(4)
C(2)—C(3)—O(2)	115.9(4)	C(16)—C(15)—C(14)	121.3(4)
C(4)—C(3)—O(2)	123.0(4)	C(17)—C(16)—C(15)	120.4(4)
C(4)—C(3)—C(2)	121.1(4)	C(18)—C(17)—C(16)	119.4(4)
C(5)—C(4)—C(3)	121.2(4)	C(13)—C(18)—C(6)	114.4(3)
C(6)—C(5)—C(4)	119.3(4)	C(17)—C(18)—C(6)	126.2(4)
C(5)—C(6)—C(1)	119.5(4)	C(17)—C(18)—C(13)	119.4(4)
C(18)—C(6)—C(1)	113.6(4)	C(20)—C(19)—C(14)	117.8(4)
C(18)—C(6)—C(5)	126.9(4)	C(24)—C(19)—C(14)	123.6(4)
C(8)—C(7)—C(2)	120.2(4)	C(24)—C(19)—C(20)	118.6(4)
C(12)—C(7)—C(2)	121.5(4)	C(21)—C(20)—C(19)	122.1(4)
C(12)—C(7)—C(8)	118.4(4)	C(22)—C(21)—C(20)	116.4(4)
C(9)—C(8)—C(7)	122.7(4)	C(34)—C(21)—C(20)	118.4(4)
C(10)—C(9)—C(8)	115.8(4)	C(34)—C(21)—C(22)	125.1(4)
C(29)—C(9)—C(8)	118.2(4)	C(21)—C(22)—O(6)	117.9(4)
C(23)—C(22)—O(6)	118.6(5)	C(32)—C(29)—C(31)	104.3(6)
C(23)—C(22)—C(21)	123.4(4)	C(35)—C(34)—C(21)	112.8(4)
C(24)—C(23)—C(22)	116.2(5)	C(36)—C(34)—C(21)	112.2(6)
C(38)—C(23)—C(22)	124.7(4)	C(36)—C(34)—C(35)	109.5(7)
C(38)—C(23)—C(24)	119.0(4)	C(37)—C(34)—C(21)	112.1(6)
C(23)—C(24)—C(19)	122.5(4)	C(37)—C(34)—C(35)	102.1(8)
C(26)—C(25)—C(11)	110.2(4)	C(37)—C(34)—C(36)	107.7(8)
C(27)—C(25)—C(11)	112.4(4)	C(39)—C(38)—C(23)	109.9(6)
C(27)—C(25)—C(26)	104.9(5)	C(40)—C(38)—C(23)	111.9(5)
C(28)—C(25)—C(11)	110.2(4)	C(40)—C(38)—C(39)	109.7(7)
C(28)—C(25)—C(26)	107.8(5)	C(41)—C(38)—C(23)	113.1(6)
C(28)—C(25)—C(27)	111.2(5)	C(41)—C(38)—C(39)	105.6(6)

TABLE 3 (continued)

(b) Angles (°) (continued)

C(30)-C(29)-C(9)	110.6(6)	C(41)-C(38)-C(40)	106.4(7)
C(31)-C(29)-C(9)	109.2(4)	O(7)-C(46)-C(45)	118.9(9)
C(31)-C(29)-C(30)	109.9(6)	C(47)-O(7)-C(46)	134.4(11)
C(32)-C(29)-C(9)	113.3(5)	C(48)-C(47)-O(7)	130.3(17)
C(32)-C(29)-C(30)	109.4(6)		

(c) Torsion angles (°)

O(1)-P-C(1)-C(2)	71.2(5)	C(2)-C(7)-C(12)-C(11)	175.8(4)
O(1)-P-C(1)-C(6)	-109.8(3)	C(8)-C(7)-C(12)-C(11)	-4.7(7)
O(4)-P-C(1)-C(2)	-59.5(5)	C(7)-C(8)-C(9)-C(10)	3.5(7)
O(4)-P-C(1)-C(6)	119.6(3)	C(7)-C(8)-C(9)-C(29)	-176.4(4)
C(13)-P-C(1)-C(2)	178.1(4)	C(8)-C(9)-C(10)-O(5)	171.4(4)
C(13)-P-C(1)-C(6)	-2.9(3)	C(8)-C(9)-C(10)-C(11)	-10.3(6)
O(1)-P-C(13)-C(14)	-70.6(4)	C(29)-C(9)-C(10)-O(5)	-8.7(7)
O(1)-P-C(13)-C(18)	108.9(3)	C(29)-C(9)-C(10)-C(11)	169.5(4)
O(4)-P-C(13)-C(14)	59.9(5)	C(8)-C(9)-C(29)-C(30)	-89.0(6)
O(4)-P-C(13)-C(18)	-120.6(3)	C(8)-C(9)-C(29)-C(31)	32.1(6)
C(1)-P-C(13)-C(14)	-177.8(4)	C(8)-C(9)-C(29)-C(32)	147.8(5)
C(1)-P-C(13)-C(18)	1.7(3)	C(10)-C(9)-C(29)-C(30)	91.1(6)
C(44)-O(2)-C(3)-C(2)	172.9(4)	C(10)-C(9)-C(29)-C(31)	-147.8(5)
C(44)-O(2)-C(3)-C(4)	-5.8(7)	C(10)-C(9)-C(29)-C(32)	-32.1(7)
C(43)-O(3)-C(15)-C(14)	178.4(4)	O(5)-C(10)-C(11)-C(12)	-172.2(4)
C(43)-O(3)-C(15)-C(16)	-2.6(6)	O(5)-C(10)-C(11)-C(25)	8.7(7)
C(33)-O(5)-C(10)-C(9)	-87.9(5)	C(9)-C(10)-C(11)-C(12)	9.5(7)
C(33)-O(5)-C(10)-C(11)	93.8(6)	C(9)-C(10)-C(11)-C(25)	-169.6(4)
C(42)-O(6)-C(22)-C(21)	-94.9(6)	C(10)-C(11)-C(12)-C(7)	-1.7(7)
C(42)-O(6)-C(22)-C(23)	88.9(6)	C(25)-C(11)-C(12)-C(7)	177.5(4)
P-C(1)-C(2)-C(3)	177.6(3)	C(10)-C(11)-C(25)-C(26)	156.5(5)
P-C(1)-C(2)-C(7)	-1.9(7)	C(10)-C(11)-C(25)-C(27)	40.0(7)
C(6)-C(1)-C(2)-C(3)	-1.4(7)	C(10)-C(11)-C(25)-C(28)	-84.6(6)
C(6)-C(1)-C(2)-C(7)	179.1(4)	C(12)-C(11)-C(25)-C(26)	-22.5(6)
P-C(1)-C(6)-C(5)	-178.3(3)	C(12)-C(11)-C(25)-C(27)	-139.1(5)
P-C(1)-C(6)-C(18)	3.3(5)	C(12)-C(11)-C(25)-C(28)	96.3(5)
C(2)-C(1)-C(6)-C(5)	0.8(7)	P-C(13)-C(14)-C(15)	177.6(3)
C(2)-C(1)-C(6)-C(18)	-177.6(4)	P-C(13)-C(14)-C(19)	-4.7(7)
C(1)-C(2)-C(3)-O(2)	-177.7(4)	C(18)-C(13)-C(14)-C(15)	-1.8(7)
C(1)-C(2)-C(3)-C(4)	1.0(7)	C(18)-C(13)-C(14)-C(19)	175.9(4)
C(7)-C(2)-C(3)-O(2)	1.8(6)	P-C(13)-C(18)-C(6)	-0.1(5)
C(7)-C(2)-C(3)-C(4)	-179.5(4)	P-C(13)-C(18)-C(17)	179.8(3)
C(1)-C(2)-C(7)-C(8)	61.4(6)	C(14)-C(13)-C(18)-C(6)	179.4(4)
C(1)-C(2)-C(7)-C(12)	-119.0(5)	C(14)-C(13)-C(18)-C(17)	-0.7(7)
C(3)-C(2)-C(7)-C(8)	-118.0(5)	C(13)-C(14)-C(15)-O(3)	-178.2(4)
C(3)-C(2)-C(7)-C(12)	61.5(6)	C(13)-C(14)-C(15)-C(16)	2.8(6)
O(2)-C(3)-C(4)-C(5)	178.5(4)	C(19)-C(14)-C(15)-O(3)	4.1(6)
C(2)-C(3)-C(4)-C(5)	-0.1(7)	C(19)-C(14)-C(15)-C(16)	-174.9(4)
C(3)-C(4)-C(5)-C(6)	-0.4(7)	C(13)-C(14)-C(19)-C(20)	-64.1(6)
C(4)-C(5)-C(6)-C(1)	0.1(7)	C(13)-C(14)-C(19)-C(24)	113.1(5)
C(4)-C(5)-C(6)-C(18)	178.3(4)	C(15)-C(14)-C(19)-C(20)	113.5(5)
C(1)-C(6)-C(18)-C(13)	-2.1(6)	C(15)-C(14)-C(19)-C(24)	-69.4(6)
C(1)-C(6)-C(18)-C(17)	178.0(4)	O(3)-C(15)-C(16)-C(17)	179.7(4)
C(5)-C(6)-C(18)-C(13)	179.6(4)	C(14)-C(15)-C(16)-C(17)	-1.4(7)
C(5)-C(6)-C(18)-C(17)	-0.3(8)	C(15)-C(16)-C(17)-C(18)	-1.2(7)
C(2)-C(7)-C(8)-C(9)	-176.7(4)	C(16)-C(17)-C(18)-C(6)	-177.9(4)
C(12)-C(7)-C(8)-C(9)	3.7(7)	C(16)-C(17)-C(18)-C(13)	2.2(7)
C(14)-C(19)-C(20)-C(21)	-177.7(4)	C(22)-C(21)-C(34)-C(37)	-48.6(8)
C(24)-C(19)-C(20)-C(21)	5.0(7)	O(6)-C(22)-C(23)-C(24)	-173.3(4)
C(14)-C(19)-C(24)-C(23)	-179.9(4)	O(6)-C(22)-C(23)-C(38)	10.1(7)
C(20)-C(19)-C(24)-C(23)	-2.7(7)	C(21)-C(22)-C(23)-C(24)	10.7(7)
C(19)-C(20)-C(21)-C(22)	0.5(7)	C(21)-C(22)-C(23)-C(38)	-165.9(5)
C(19)-C(20)-C(21)-C(34)	-177.1(4)	C(22)-C(23)-C(24)-C(19)	-4.7(7)
C(20)-C(21)-C(22)-O(6)	175.4(4)	C(38)-C(23)-C(24)-C(19)	172.0(4)
C(20)-C(21)-C(22)-C(23)	-8.6(7)	C(22)-C(23)-C(38)-C(39)	152.1(6)
C(34)-C(21)-C(22)-O(6)	-7.2(7)	C(22)-C(23)-C(38)-C(40)	-85.8(7)
C(34)-C(21)-C(22)-C(23)	168.8(4)	C(22)-C(23)-C(38)-C(41)	34.3(8)
C(20)-C(21)-C(34)-C(35)	14.2(7)	C(24)-C(23)-C(38)-C(39)	-24.4(7)
C(20)-C(21)-C(34)-C(36)	-110.0(7)	C(24)-C(23)-C(38)-C(40)	97.8(6)
C(20)-C(21)-C(34)-C(37)	128.7(6)	C(24)-C(23)-C(38)-C(41)	-142.1(6)
C(22)-C(21)-C(34)-C(35)	-163.2(5)	C(45)-C(46)-O(7)-C(47)	-33.1(19)
C(22)-C(21)-C(34)-C(36)	72.6(8)	C(46)-O(7)-C(47)-C(48)	-177.9(15)

TABLE 4

Least squares mean planes and lines for molecule B. Deviations (\AA) of atoms from various mean planes. Atoms marked + were not included in the calculation of the plane.

- (a) C(1), 0.00; C(2), 0.04; C(3), 0.03; C(4), 0.00; C(5), -0.03; C(6), -0.03; C(13), -0.04; C(14), -0.02; C(15), 0.05; C(16), 0.04; C(17), -0.01; C(18), -0.02; P⁺, -0.07; C(7)⁺, 0.09; C(19)⁺, -0.13
- (b) C(7), 0.04; C(8), -0.01; C(9), -0.04; C(10), 0.06; C(11), -0.03; C(12), -0.02; C(2)⁺, 0.14; C(25)⁺, -0.16; C(29)⁺, -0.18; O(5)⁺, 0.22
- (c) C(19), -0.04; C(20), 0.03; C(21), 0.02; C(22), -0.06; C(23), 0.04; C(24), 0.00; C(14)⁺, -0.08; C(34)⁺, 0.16; C(38)⁺, 0.27; O(6)⁺, -0.16
- (d) C(1), -0.01; C(2), 0.01; C(3), 0.00; C(4), 0.00; C(5), 0.00; C(6), 0.00; P⁺, -0.06; C(7)⁺, 0.02; C(18)⁺, 0.04; O(2)⁺, -0.04
- (e) C(13), 0.00; C(14), -0.02; C(15), 0.01; C(16), 0.00; C(17), -0.01; C(18), 0.01; P⁺, 0.03; C(19)⁺, -0.12; C(6)⁺, 0.05; O(3)⁺, 0.03
- Angles ($^\circ$) between normals to planes; (a)-(b), 63; (a)-(c), 70; (a)-(d), 2; (a)-(e), 2; (b)-(c), 115; (b)-(d), 62; (b)-(e), 64; (c)-(d), 71; (c)-(e), 68; (d)-(e), 3
- If the following lines are defined by two atoms each as (f) C(2)-C(7), (g) C(7)-C(10), (h) C(10)-O(5), (i) C(14)-C(19), (j) C(19)-C(22), (k) C(22)-O(6), then the angles ($^\circ$) between these lines are, (f)-(i), 48; (g)-(j), 45; (h)-(k), 44; (g)-(f), 4; (h)-(g), 6; (f)-(h), 11; (i)-(j), 4; (j)-(k), 4; (i)-(k), 7

TABLE 5

Final atomic co-ordinates ($\text{\AA} \times 10^4$) with estimated standard deviations in parentheses for molecule A

	<i>x</i>	<i>y</i>	<i>z</i>
P	2 570(2)	5 748(3)	773(2)
Cl(1)	-1 949(2)	7 415(3)	-856(2)
Cl(2)	1 410(3)	4 088(3)	3 854(2)
O(1)	2 747(6)	5 112(6)	95(5)
O(2)	-677(6)	7 863(7)	-1 761(6)
O(3)	-1 311(7)	9 358(7)	-3 236(7)
O(4)	3 435(6)	6 533(6)	1 338(6)
O(5)	3 460(6)	3 800(7)	4 025(6)
O(6)	3 970(10)	1 214(12)	4 600(10)
C(1)	1 302(8)	6 347(9)	200(8)
C(2)	862(9)	6 970(9)	-611(9)
C(3)	-172(9)	7 292(9)	-950(8)
C(4)	-681(9)	6 972(9)	-431(9)
C(5)	-231(9)	6 373(9)	380(9)
C(6)	777(9)	6 038(8)	709(8)
C(7)	1 475(9)	7 301(9)	-1 062(9)
C(8)	2 339(11)	7 882(11)	-564(10)
C(9)	2 957(11)	8 138(13)	-936(13)
C(10)	2 744(14)	7 818(13)	-1 851(17)
C(11)	1 858(15)	7 266(12)	-2 417(13)
C(12)	1 232(11)	6 998(10)	-2 019(11)
C(13)	-584(11)	8 880(12)	-1 531(11)
C(14)	-1 458(10)	9 399(10)	-2 406(11)
C(15)	2 380(9)	5 172(9)	1 719(8)
C(16)	3 107(9)	4 655(9)	2 546(9)
C(17)	2 770(9)	4 307(9)	3 187(9)
C(18)	1 777(10)	4 504(9)	2 999(9)
C(19)	1 059(8)	5 046(9)	2 196(9)
C(20)	1 380(9)	5 379(9)	1 540(8)
C(21)	4 213(9)	4 526(10)	2 782(9)
C(22)	5 027(10)	4 963(11)	3 638(9)
C(23)	6 040(11)	4 913(15)	3 823(11)
C(24)	6 272(10)	4 437(14)	3 184(14)
C(25)	5 480(12)	4 005(12)	2 339(13)
C(26)	4 445(10)	4 052(10)	2 134(10)
C(27)	3 368(13)	2 767(15)	3 839(13)
C(28)	3 910(21)	2 276(14)	4 838(19)
C(29)	4 424(11)	6 564(14)	1 293(14)

TABLE 6

Final atomic co-ordinates ($\text{\AA} \times 10^4$) with estimated standard deviations in parentheses in molecule B

	<i>x</i>	<i>y</i>	<i>z</i>
P	292.1(8)	3 956.8(7)	8 831.2(5)
O(1)	379(3)	3 972(2)	8 143(1)
O(2)	-3 245(2)	5 101(2)	8 525(2)
O(3)	3 707(2)	5 271(2)	9 778(2)
O(4)	275(2)	3 070(2)	9 110(1)
O(5)	-2 794(3)	1 443(2)	7 245(2)
O(6)	4 050(3)	1 421(2)	9 007(2)
C(1)	-692(3)	4 700(3)	8 865(2)
C(2)	-1 672(3)	4 578(3)	8 629(2)
C(3)	-2 287(3)	5 254(3)	8 743(2)
C(4)	-1 931(4)	6 014(3)	9 069(2)
C(5)	-955(3)	6 135(3)	9 295(2)
C(6)	-328(3)	5 482(3)	9 196(2)
C(7)	-2 047(3)	3 765(3)	8 276(2)
C(8)	-1 896(3)	2 926(3)	8 552(2)
C(9)	-2 192(3)	2 132(3)	8 234(2)
C(10)	-2 610(3)	2 225(3)	7 598(2)
C(11)	-2 866(3)	3 060(3)	7 316(2)
C(12)	-2 558(3)	3 815(3)	7 671(2)
C(13)	1 196(3)	4 737(3)	9 230(2)
C(14)	2 183(3)	4 642(3)	9 367(2)
C(15)	2 728(3)	5 369(3)	9 662(2)
C(16)	2 288(3)	6 126(3)	9 832(2)
C(17)	1 292(3)	6 193(3)	9 701(2)
C(18)	741(3)	5 504(3)	9 390(2)
C(19)	2 656(3)	3 798(3)	9 232(2)
C(20)	2 495(3)	3 025(3)	9 543(2)
C(21)	2 932(3)	2 210(3)	9 464(2)
C(22)	3 545(3)	2 211(3)	9 061(2)
C(23)	3 638(3)	2 938(3)	8 682(2)
C(24)	3 205(3)	3 737(3)	8 801(2)
C(25)	-3 472(4)	3 175(4)	6 651(2)
C(26)	-3 965(5)	4 092(5)	6 577(3)
C(27)	-4 299(5)	2 493(5)	6 490(3)
C(28)	-2 821(5)	3 125(5)	6 189(3)
C(29)	-2 041(4)	1 253(3)	8 594(2)
C(30)	-1 073(7)	868(5)	8 597(5)
C(31)	-2 131(7)	1 425(4)	9 248(3)
C(32)	-2 801(7)	566(5)	8 353(4)
C(33)	-2 005(6)	1 136(4)	6 998(3)
C(34)	2 673(4)	1 380(3)	9 804(2)
C(35)	1 794(6)	1 519(4)	10 055(5)
C(36)	3 480(7)	1 086(10)	10 305(7)
C(37)	2 383(11)	602(6)	9 378(5)
C(38)	4 130(4)	2 897(4)	8 132(3)
C(39)	3 693(8)	3 607(7)	7 650(4)
C(40)	5 212(5)	3 037(7)	8 336(4)
C(41)	3 986(8)	2 012(6)	7 796(4)
C(42)	5 012(5)	1 398(5)	9 402(4)
C(43)	4 289(4)	5 996(4)	10 062(3)
C(44)	-3 920(4)	5 720(4)	8 688(3)
C(45)	1 095(8)	1 052(6)	7 622(5)
C(46)	997(9)	1 867(7)	7 868(5)
O(7)	535(5)	2 591(4)	7 459(3)
C(47)	505(16)	2 811(11)	6 887(6)
C(48)	96(12)	3 482(9)	6 564(6)

EXPERIMENTAL

Compound A.—*Crystal Data:* $C_{28}H_{25}Cl_2O_6P$, $M = 571.45$, monoclinic, $a = 14.716(2)$, $b = 13.839(3)$, $c = 15.502(3)$ \AA , $\beta = 120.01$ (1°), $U = 2 733.9$ \AA^3 , $Z = 4$, $D_c = 1.39$ g cm^{-3} , $F(000) = 1 184$, Mo- K_α radiation, $\lambda = 0.710 69$ \AA , $\mu = 3.4$ cm^{-1} . Space group $P2_1/c$ from systematic absences of $0k0$ for k odd, and $h0l$ for l odd.

A crystal, *ca.* $0.3 \times 0.2 \times 0.2$ mm was used for data collection on a Hilger and Watts Y290 four circle diffractometer. Accurate cell parameters were calculated from the setting angles of 12 reflections. The intensities of $h\bar{k} \pm l$ reflections with $2 < \theta < 22^\circ$ were measured by an $\omega/2\theta$ step scan with stationary background counts at each end of the scan

and using Mo- K_{α} radiation with a graphite crystal monochromator. The intensities of three standard reflections were monitored every 100 reflections and showed no significant changes. Data were corrected for Lorentz and polarisation effects, but not for absorption and, after averaging any equivalent reflections, 1 789 reflections with $I > 3\sigma(I)$ were used in the structure refinement.

The positions of all non-H atoms were derived by routine direct methods and refined by full matrix least squares with anisotropic temperature factors to R_F 0.098. At this point three suspect reflections (-111 , -112 , -113), which had anomalously high differences between $|F_{\text{obs}}|$ and $|F_{\text{calc}}|$, were removed from the data set. Continued refinement converged at R_F 0.095 and a difference map showed some, but not all, of the H-atom positions. All the methylene and phenyl H atoms were included at fixed idealized positions (C-H 1.08 Å) and were given a common isotropic temperature factor of $U = 0.08 \text{ \AA}^2$, and the least squares refinement finally converged at R_F 0.087, R_{wF} 0.104, where $w = 4.6/[\sigma^2(F) + 0.0007 F^2]$ and the maximum shift/error was 0.06. A final difference map was everywhere $< 0.5e \text{ \AA}^{-3}$.

Final atom parameters are listed in Table 5, and H atom positions, temperature factors and a structure factor listing are available in Supplementary Publication No. SUP 23337 (30 pages).*

Compound B.—Crystal Data: $C_{44}H_{57}O_6P \cdot C_4H_{10}O$, M 787.0, monoclinic, $a = 14.303(2)$, $b = 14.942(2)$, $c = 22.311(4) \text{ \AA}$, $\beta = 103.22(2)^\circ$, $U = 4\ 641.8 \text{ \AA}^3$, $Z = 4$, $D_c = 1.12 \text{ g cm}^{-3}$, $F(000) = 1\ 704$, Mo- K_{α} radiation, $\lambda = 0.710\ 69 \text{ \AA}$, $\mu = 1.1 \text{ cm}^{-1}$. Space group $P2_1/c$ from systematic absences of $0k0$ for k odd and $h0l$ for l odd.

The data crystal was a translucent block, ca. $0.3 \times 0.3 \times 0.3 \text{ mm}$, which was sealed in a Lindemann glass capillary to prevent loss of solvent from the crystal. Details of the data measurements and processing are as for the first compound. The standard reflections showed no significant changes during the data collection. After averaging of any equivalent data, 5 271 non-zero reflections remained of which 3 895 with $I > 3\sigma(I)$ were used in the structure refinement.

The positions of most of the non-H atoms of the molecule were derived by routine direct methods using the SHELX programme, and the remainder were located on a difference map. Refinement of atom positions and anisotropic temperature factors was carried out by full-matrix least-squares, the parameters being divided into two large blocks containing roughly the same number of atoms each and refined in alternate cycles. A difference map then revealed some more peaks consistent with the presence of a molecule of diethyl ether solvent. These atoms were included in the refinement with anisotropic temperature factors which rapidly became

very large for the two atoms C(47) and C(48). Removal of these two atoms followed by a further difference map did not suggest disorder between two recognisable sites and it was felt best to leave these two atoms as single sites and as such they were returned to the least squares. At R 0.085 an angle weighted difference map revealed the positions of all the phenyl H atoms, the H atom attached to O(1), and several of the methyl H atoms. The positions of the non-methyl H atoms were taken from the map and held fixed with a common U_{iso} value of 0.08 \AA^2 . The methyl H atoms were placed at calculated positions (C-H, 1.08 Å) with a common U_{iso} value which refined to 0.20 \AA^2 , and the methyl groups refined as rigid bodies. Because of programme limitations on the total number of atoms, half the methyl groups were first treated to four cycles of refinement. The H atoms from these methyl groups were then omitted whilst the other half of the methyl groups were refined for four cycles. At the end of this procedure the methyl H atoms were held fixed whilst the non-H atoms were refined in alternate cycles as before. Again, because of programme limitations the H atoms attached to atoms C(42), C(43), and C(44) had to be omitted from this final refinement. At convergence R_F 0.065 and R_{wF} 0.099, where $w = 1.9/[\sigma^2(F) + 0.0027 F^2]$ and the maximum shift/error was 0.1. A final difference map had peaks of up to $0.4 e \text{ \AA}^{-3}$ near the solvent atoms and smaller peaks near some of the omitted H atoms but was elsewhere featureless.

In both structure analyses scattering factors for neutral atoms and dispersion corrections were taken from ref. 8. The programme system used was SHELX by G. M. Sheldrick as set up on the IBM 360/195 at the Rutherford Laboratory. Final atom co-ordinates are listed in Table 6, and H atom parameters, temperature factors and a structure factor listing have been deposited in the Supplementary Publication.

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