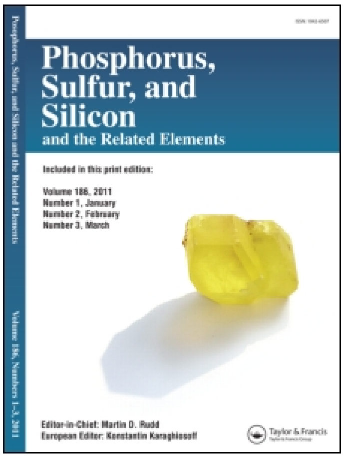

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THE CONFORMATION OF MEDIUM-SIZED HETEROCYCLES: SYNTHESIS AND SOLID-STATE CONFORMATION OF A 6-ARYLTHIO-SUBSTITUTED DIBENZO-[*d,f*][1,3,2]DIOXAPHOSPHEPIN

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THE CONFORMATION OF MEDIUM-SIZED HETEROCYCLES: SYNTHESIS AND SOLID-STATE CONFORMATION OF A 6-ARYLTHIO-SUBSTITUTED DIBENZO-[*d,f*][1,3,2]DIOXAPHOSPHEPIN

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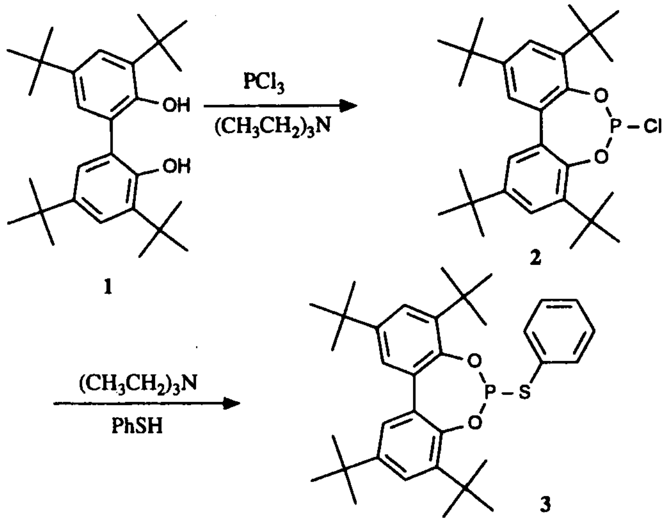
Although the conformational analysis of both carbocyclic and small-membered heterocyclic compounds has played a key role in the development of mechanistic and synthetic chemistry, the stereochemistry of medium-sized organophosphorus heterocycles has received little attention until very recently.[1] Sterically congested bisphosphite ligands that incorporate a seven-membered dibenzo[*d,f*][1,3,2]dioxaphosphepin ring have been claimed as superior ligands for transition-metal-catalyzed reactions.[2] Quite recently, the highly regioselective formylation of α-olefins by the rhodium(I) complexes of these bisphosphite ligands was communicated by Buchwald and Cuny.[3] The observation of unprecedented eight-bond P—P J coupling in the $^{31}P\{^1H\}$ NMR spectra of these bisphosphite ligands had been attributed to the proximity of the phosphorus atoms due to intramolecular steric interactions.[4] Recent studies have shown that sterically hindered medium-sized phosphorus heterocycles may adopt an unusual diequatorial placement in pentaoxyphosphoranes. Rapid advances have been made by Holmes and co-workers on establishing the factors that influence ring orientation and conformation in pentaoxyphosphoranes which incorporate these ring systems.[5–11] Our efforts to further elaborate the factors that dictate the conformation of the seven-membered dibenzo[*d,f*][1,3,2]dioxaphosphepin ring are reported herein.

RESULTS AND DISCUSSION

The formation of dioxaphosphepins by the reaction of dibenzo[*d,f*][1,3,2]dioxasilepins with arylphosphonous dichlorides was reported by Zuckerman.[12] The reaction of biphenyl-2,2′-diol with phosphorus(III) chloride was described by



Verizhnikov and Kirpichnikov.[13] We reported the analogous reaction of 3,3′,5,5′-tetra-*tert*-alkyl-1,1′-biphenyl-2,2′-diols with phosphonous dichlorides to prepare the sterically hindered dibenzo[*d*,*f*][1,3,2]dioxaphosphepins, for which non-planar ring structures were suggested.[14]

The phosphorochloridite **2** was prepared *in situ*, as previously reported, by the reaction of the bisphenol **1** with phosphorus(III) chloride in the presence of triethylamine as an acid acceptor.[15] The reaction of **2** with benzenethiol in the presence of triethylamine gave the thiophosphite **3** as colorless crystals (69% recrystallized yield). Interestingly, in the $^{31}P\{^1H\}$ NMR spectrum of **3**, the phosphorus resonance was observed downfield of the phosphorochloridite **2** (δ 173.3)[4] at δ 212.0. Downfield shifts of this magnitude have been observed in thiophosphites prepared from catachol.[16]

Upon growing suitable crystals, an X-ray crystal structure was obtained (Figure 1, Tables I–III). In the solid state, the seven-membered ring in **3** assumes a nonplanar twist conformation (Figure 2). The C(1)-C(6)-C(7)-C(12) torsion angle about the single bond joining the two phenyl rings is −49.9°. Quite recently, Holmes *et al.* reported the crystal structure of the analogous thiophosphite **4** without *tert*-butyl substitution, albeit with methyl substitution on the 6-arylthio group.[5] The corresponding torsion angle in **4**, which is 39.6°, is significantly smaller than found in **3**. These observations suggest that the aryl substitution has a pronounced effect on the nonplanarity of the ring, presumably because of steric interactions within the ring. This contention is supported by recently published crystallographic studies on related phosphites, in which the corresponding torsion angles for the *tert*-butyl-substituted (51.7°)[4] and unsubstituted (41.4°)[17] dibenzo[*d*,*f*][1,3,2]dioxaphosphepins showed similar trends. Further support for a steric argument is provided by semi-empirical MO geometry calculations on model compounds.[4]

Given the posit that pyramidal geometry about phosphorus is achieved when the sum of the requisite bond angles is 270°, the phosphorus atom in **3** (299.6°) is midway between pyramidal and tetrahedral geometry. An identical geometry at phosphorus is found in **4** (298.4°). The endocyclic O(1)—P—O(2) bond angles in

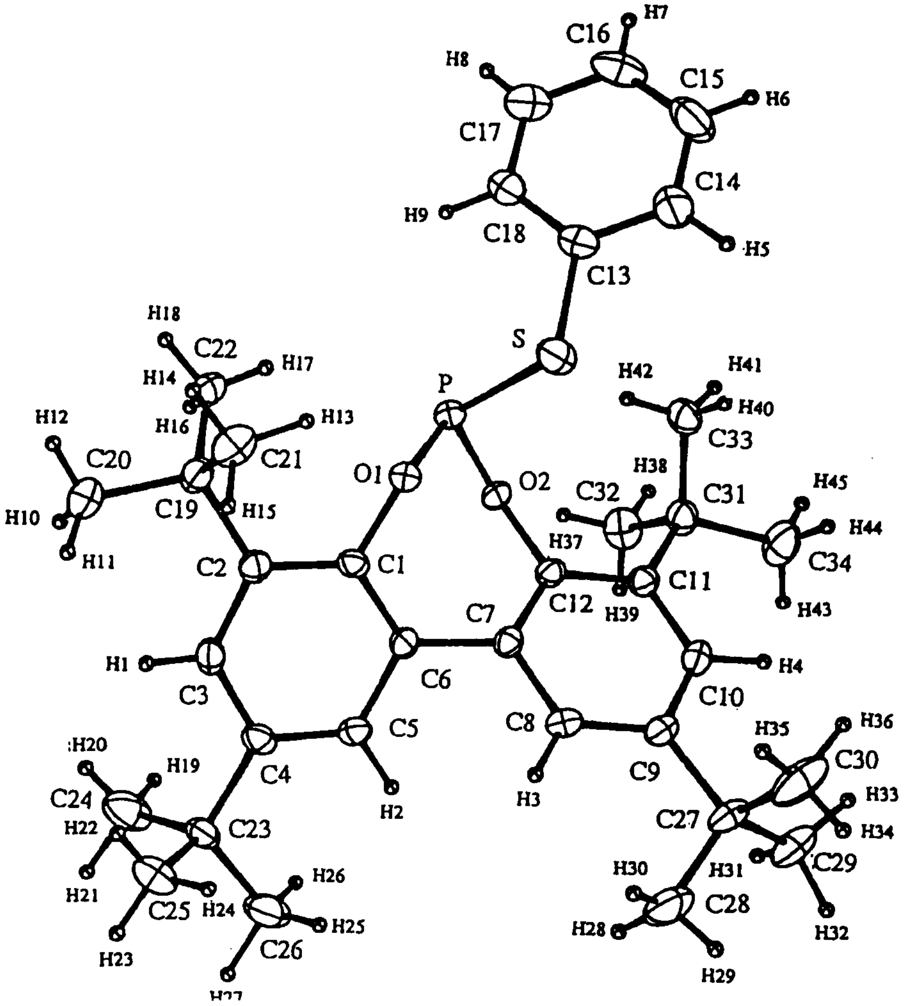


FIGURE 1 ORTEP view of 3 showing the crystallographic numbering scheme (arbitrary).

TABLE I

Selected torsion angles [°] for 3.

P-O(2)-C(12)-C(7)	64.89 (0.27)	P-O(1)-C(1)-C(6)	72.52 (0.25)
O(1)-P-O(2)-C(12)	-42.72 (0.19)	O(2)-P-O(1)-C(1)	-46.56 (0.18)
O(2)-C(12)-C(7)-C(6)	5.83 (0.35)	O(1)-C(1)-C(6)-C(7)	-1.75 (0.35)
C(1)-C(6)-C(7)-C(12)	-49.92 (0.36)	C(13)-S-P-O(1)	-150.65 (0.11)
C(13)-S-P-O(2)	107.05 (0.11)	P-S-C(13)-C(14)	-147.39 (0.22)
P-S-C(13)-C(18)	37.81 (0.25)		

TABLE II

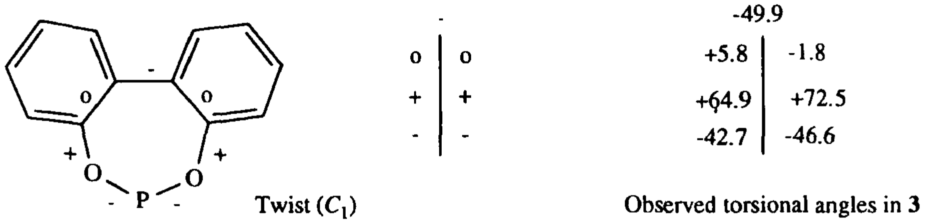
Selected bond distances [Å] for **3**

S-P	2.1247 (6)	S-C(13)	1.779 (2)
P-O(1)	1.650 (1)	P-O(2)	1.628 (1)
O(1)-C(1)	1.401 (2)	O(2)-C(12)	1.412 (2)
C(1)-C(6)	1.380 (2)	C(7)-C(12)	1.381 (2)
C(6)-C(7)	1.493 (2)		

TABLE III

Selected bond angles [°] for **3**

C(13)-S-P	102.59 (6)	S-P-O(1)	88.87 (5)
S-P-O(2)	108.68 (5)	O(1)-P-O(2)	102.02 (6)
O(1)-C(1)-C(6)	117.4 (1)	O(2)-C(12)-C(7)	118.2 (1)

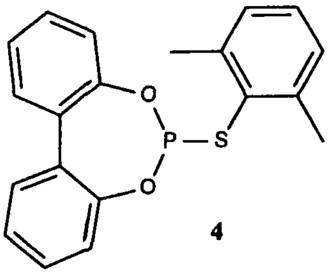


a. J. B. Hendrickson *J. Am. Chem. Soc.* **86**, 4854 (1964)

FIGURE 2 Twist conformation of the dibenzo[*d,f*][1,3,2]dioxaphosphepin ring specified by the signs of the torsional angles following the formalism of Hendrickson.[a]

3 (102.0°) and **4** (100.0°) are similar in magnitude. The P—O(1)—C(1) (121.7°) and P—O(2)—C(12) (125.1°) bond angles in **3** are comparable to those found in **4** (118.5° and 124.1°), as well as the corresponding O—$C_{Aromatic}$—$C_{Aromatic}$ bond angles in both compounds. The P—O(1), P—O(2), and P—S bond distances (1.65 Å, 1.63 Å, and 2.13 Å, respectively) found in **3** are on the same order of magnitude as found in **4** (1.64 Å, 1.63 Å, and 2.11 Å, respectively).[5]

These observations suggest that the *tert*-butyl substitution manifests itself by increasing the degree of twist within the seven-membered ring, which is reflected primarily by the difference found in the torsion angle about the single bond joining



4

the two phenyl rings in **3** and **4**. An examination of Dreiding molecular models would suggest that the *tert*-butyl substitution adjacent to the oxygen atoms are largely responsible for increasing the ring twist in the dibenzo[*d*,*f*][1,3,2]dioxaphosphepins ring.

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. The ^{1}H and ^{31}P NMR spectra were taken on a Varian Model Unity-500 at 499.84 MHz and 202.33 MHz, respectively. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. The abbreviations used for NMR peak multiplicity are: s = singlet, d = doublet, t = triplet, m = multiplet. Merck pre-coated (0.25 mm) silica gel 60 F-254 plates were used for TLC.

Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry, inert atmosphere of nitrogen.

2,4,8,10-tetra-tert-butyl-6-phenylthio-dibenzo[d,f][1,3,2]dioxaphosphepin, (**3**). To a solution of 0.69 g (5 mmol) of phosphorus(III) chloride in 10 mL of toluene was added dropwise at 10°C a solution of 2.05 g (5 mmol) of **1** and 1.01 g (10 mmol) of triethylamine in 20 mL of toluene. After the addition was complete, the reaction mixture was stirred at room temperature for 24 hours. To the resultant reaction mixture at 10°C was added dropwise a solution of 0.55 g (5 mmol) of benzenthiol and 0.51 g (5 mmol) of triethylamine in 10 mL of toluene. After the addition was complete, the reaction mixture was stirred at room temperature for 24 hours. The precipitate of triethylamine hydrochloride was removed by filtration and the solvent was removed *in vacuo*. The residue was recrystallized twice from a mixture of 50 mL of acetonitrile and 7 mL of toluene to give 1.88 g (69% yield) of a white crystalline solid, mp 170–172°C. ^{31}P{^{1}H} NMR (202.33 MHz)($CDCl_3$) δ 212.0; ^{1}H NMR (499.84 MHz)($CDCl_3$) δ 1.37 (s, $(CH_3)_3C$, 18H), 1.50 (s, $(CH_3)_3C$, 18H), 7.16 (d, 2H), 7.25–7.35 (complex m, 3H), 7.46 (d, 2H), 7.52 (complex m, 2H). Anal. Calcd for $C_{34}H_{45}O_2PS$: C, 74.4; H, 8.3; S, 5.8. Found: C, 74.6; H, 8.3; S, 6.0.

Suitable crystals for X-ray analysis (colorless plates) were grown from acetonitrile:toluene. Crystal data: $C_{34}H_{45}O_2PS$; formula weight ($g \cdot mol^{-1}$) = 548.77; crystal size (mm) 0.30 × 0.30 × 0.25; crystal system is monoclinic; number of reflections used for unit cell determination (2Θ range) is 35°–44°; cell parameters a = 12.574 (5) Å, b = 13.927 (9) Å, c = 18.220 (3) Å, β = 103.76 (2) deg, V = 3099.2 (22) Å^3; space group = $P2_1/n$; d_{calc} = 1.176 g/cm^3; $F_{(000)}$ = 4736 (electrons); μ(MoKα) = 1.176 cm^{-1}; Z = 4; data collection: temperature = 99(2) K; Enraf-Nonius CAD4 diffractometer; MoKα (λ = 0.71073 Å) radiation; Zr foil (factor 17.69) attenuators; take-off angle = 4.2°; detector aperture = 4.0 × 4.0 mm; scan type ω-2Θ, 2Θ max = 50°; number of reflections measured 5438; s = 2.46 for 3668 observed structure factors ($F > 3\sigma$) and 523 variables; R indices (observed) R = 0.045, R_W = 0.062.

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