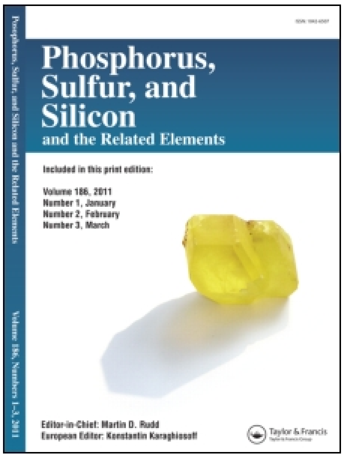

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CONFORMATION OF EIGHT-MEMBERED DIOXATHIASILOCIN HETEROCYCLES IN SOLUTION

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CONFORMATION OF EIGHT-MEMBERED DIOXATHIASILOCIN HETEROCYCLES IN SOLUTION

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The dibenzo[d, g][1,3,6,2]dioxathiasilocin derivatives **3a–f** were prepared by the reaction of the thiobisphenols **1a–b** with the corresponding dichlorosilanes **2a–e** using triethylamine as an acid acceptor. The free energy of activation for ring inversion of the 2,4,8,10-tetra-*tert*-butyl-substituted **3a** was determined by variable temperature ^{1}H NMR to be 13.9 kcal/mol. The ^{1}H NMR spectral data of **3a** requires that the ring conformer possess a σ plane of symmetry passing through the silicon and bridging sulfur atoms. In the variable temperature ^{1}H NMR spectra of the 2,4,8,10-tetramethyl-substituted **3b** no evidence was observed for the slowing of ring inversion at −55°C, suggesting that the energy of activation for ring inversion is less than 10.9 kcal/mol. The ^{1}H NMR spectral data of **3e–f** indicates the presence of equilibrating conformational isomers. The results of this study supports the suggestion that steric factors are a major contributor to the barrier of ring inversion for the dibenzo-[d, g][1,3,6,2]dioxathiasilocin ring system.

Recently, we reported the synthesis and conformational analysis of the eight-membered 12H-dibenzo[d, g][1,3,2]dioxasilocin ring system.[1] The conformational analysis and factors which effect the free energy of activation (ΔG^*) for ring inversion of these systems has received renewed importance in light of recent work. In particular, Denney *et al.* have provided the first example of the inhibition of intramolecular ligand reorganization (pseudorotation) on the NMR time scale of a monocyclic pentaoxyphosphorane prepared from the analogous dibenzo[d, g][1,3,2]dioxaphosphocin ring system, which was attributed to the steric effects of the large *tert*-butyl substituents on the heterocyclic ring.[2] Quite recently, Abdou and co-workers have reported the inhibition of pseudorotation of phosphoranes incorporating the dibenzo[d, g][1,3,6,2]dioxathiaphosphocin ring system and have questioned whether factors other than steric may contribute to the observed slowing of pseudorotation.[3,4] Due to the high ΔG^* for ring inversion of the dibenzo[d, g][1,3,2]dioxaphosphocin ring, variable-temperature (VT) ^{1}H NMR studies in our laboratory have been unsuccessful in providing insight into the factors determining the barrier to ring inversion in these systems.[5]

Although the synthesis of the dibenzo[d, g][1,3,6,2]dioxathiasilocin ring system (Figure 1) has been reported, no information is available concerning the conformation of the ring.[6] We report in this paper a VT ^{1}H NMR study of the

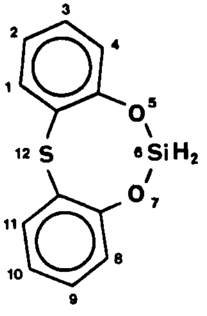


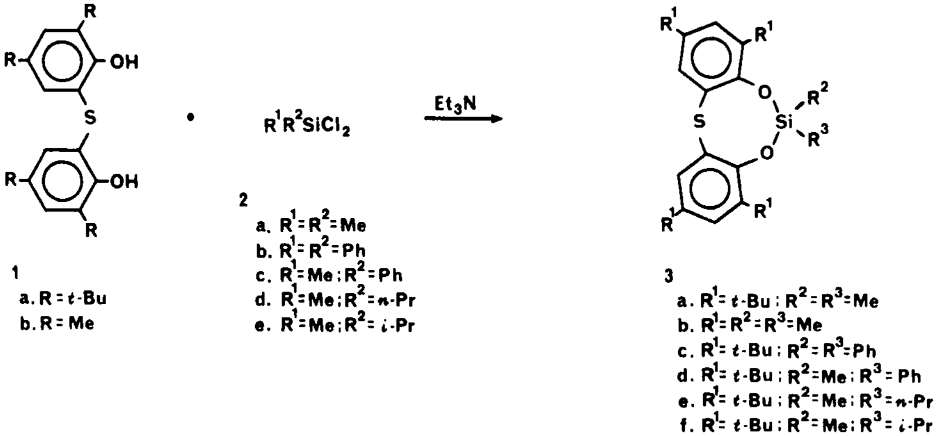
FIGURE 1

dioxathiasilocin ring system which provides information concerning the factors contributing to the ΔG^* for ring inversion.

RESULTS AND DISCUSSION

Following the methodology previously reported,[6] the dioxathiasilocin **3a** was prepared by the reaction of the dichlorosilane **2a** with the thiobisphenol **1a**[6] at room termperature using triethylamine as an acid acceptor (60% recrystallized). Similarly, **3b–f** were prepared by the reaction of **1a–b** with the corresponding chlorosilanes **2a–e**, although elevated temperatures were required for the more hindered silanes **2b–e**.

In the ^1H NMR spectrum (80 MHz) of **3a** at 23°C, a broad-singlet resonance was observed at δ 0.77 which was assigned to the protons of two equivalent methyl groups bonded to silicon. The VT ^1H NMR spectra showed that the broad singlet sharpened at 55°C (Figure 2). The spectrum of **3a** showed below 2.5 ± 1.5°C, the coalesence temperature, the presence of two nonequivalent methyl groups with resonances at $\delta 0.56$ and $\delta 0.83$, respectively. The activation energy (ΔG^*) required to render them equivalent is 13.9 ± 0.1 kcal/mol.[7] The



SCHEME I

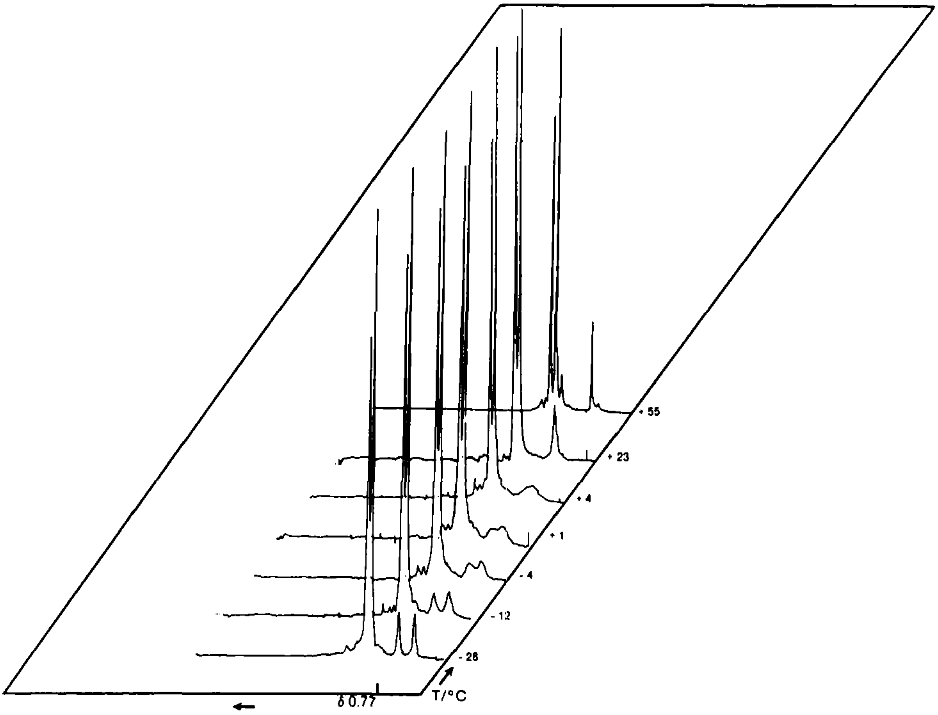


FIGURE 2 VT ^{1}H NMR spectrum of **3a** in $CDCl_3$

VT ^{1}H NMR spectrum of **3a** showed below the coalescence temperature the presence of two equivalent pairs of *tert*-butyl groups. Similarly, two equivalent pairs of *meta* aromatic protons were observed as two doublets below the coalescence temperature. The dynamic NMR data can be reasonably explained if the ring inversion of **3a** requires an activation energy of 13.9 kcal/mol.

The ^{1}H NMR data of **3a** requires that below the coalescence temperature the ring conformer must possess a σ plane of symmetry passing through the silicon and the sulfur atom such as in structures **4** or **5**, which were suggested by the examination of molecular models. This must be the case in order to explain both the observation of two nonequivalent methyl groups bonded to silicon and the observation of two equivalent pairs of *tert*-butyl groups along with two pairs of equivalent aromatic protons below the coalescence temperature. The presence of twisted conformers (to minimize steric interactions) that rapidly pass through structures possessing the required symmetry plane either as an intermediate or transition state below the coalescence temperature cannot be excluded.

The ^{1}H NMR spectrum of **3a** above the coalescence temperature is, of course, consistent with rapid ring inversion of conformers such as **4** or **5**. Rapid ring inversion would remove the nonequivalence of the methyl group protons bonded to silicon.

In the ^{1}H NMR spectrum (80 MHz) of the hexamethyl derivative **3b** at 23°C, a sharp singlet resonance was observed at δ0.57 which was assigned to the protons of two equivalent methyl groups bonded to silicon. No change was observed in

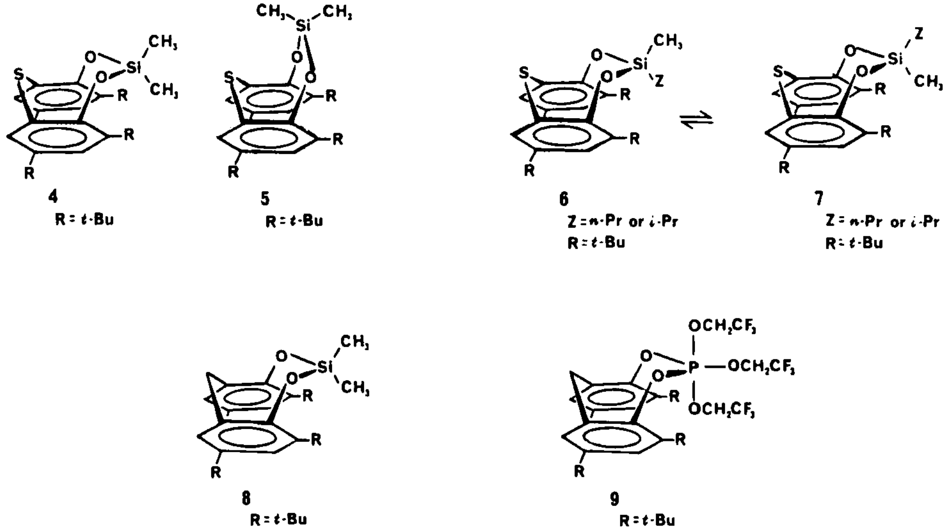


FIGURE 3

the ^{1}H NMR spectrum of **3b** upon cooling to −55°C. If the reasonable assumption is made that the degree of nonequivalence ($\Delta\delta$) of the methyl groups of **3b** would be similar to that of **3a** below its coalescence temperature, the energy of activation for ring inversion of **3b** must be less than 10.9 kcal/mol.

In the ^{1}H NMR spectra (200 MHz) of both **3e** and **3f** at 21°C, a broad singlet resonance was observed for the protons of the methyl group bonded directly to silicon. Similarly the triplet and doublet resonances of the methyl-group protons on the propylsubstituents of **3e** and **3f**, respectively, were broadened. At 60°C, sharp resonances were observed for both the methyl-group protons bonded either to silicon or to the propyl substituents of both **3e** and **3f**. These observations can be explained by the interconversion of conformational isomers such as **6** and **7** illustrated. The appearance of the ^{1}H NMR spectra of both **3e** and **3f** at 21°C indicates that the methyl groups bonded to silicon are near their coalescence temperature.

The results obtained indicate that the steric effects of the large *tert*-butyl substituents are a significant contributor to the observed barrier for ring inversion in the dibenzo[d, g][1,3,6,2]-dioxathiasilocin ring system. This of course is not the first time that steric effects have been shown to increase the ΔG^* for ring inversion in large-membered heterocycles. Previous studies have shown that factors which effect the ΔG^* for ring inversion of large-membered heterocycles include the steric effects of substituents, the annulation of benzene rings, and the conformational preference of a non-bonding pair of electrons on a heteroatom.[8] Quin[9] has recently shown, for example, that fused benzo groups can contribute significantly to the barrier for ring inversion in the phosphonin ring system.

Interestingly, the barrier for ring inversion of **8** was previously measured to be 13.9 kcal/mol.[1] This observation suggests that the substitution of the C-12 methylene group in **8** by sulfur has no significant effect on ΔG^* for ring inversion. A similar observation was made by Ollis and co-workers in the eight-membered

7,12-dihydro-5H-dibenzo[c, f]thiocin ring system where the substitution of the bridging methylene carbon by sulfur led to a small increase in ΔG^* (1.5 kcal/mole) for the interconversion of the boat-chair to twist-boat conformation.[10] The results of this study are also supportive of the suggestion by Denney that steric factors are operative in the slowing of pseudorotation in phosphoranes such as 9,[2] although at present, a detailed knowledge of the factors which determine the apical-equatorial preference of a eight-membered ring in a phosphorane structure is not available.[11]

EXPERIMENTAL

All melting points were determined in open-capillary tubes with a Thomas-Hoover melting point apparatus. IR spectra (1% solution in Perkin–Elmer sodium chloride cells) were recorded on a Perkin–Elmer model 1300 spectophotometer. All ^{1}H NMR spectra were obtained on either a Varian model CFT-20 or XL-200 spectrometer. VT ^{1}H NMR spectra were obtained on a Varian model FT-80 spectrometer equipped with a 5 mm variable-temperature broad-band probe. ^{13}C NMR spectra were obtained on a Varian model XL-200 spectrometer using a 55° flip angle, a 0.8-s repetition rate with no pulse delay, and with full proton decoupling. All ^{1}H and ^{13}C NMR are reported relative to tetramethylsilane, where a positive sign is downfield from the standard. All solvents were dried prior to use. Reagents were purchased from commercial laboratory supply houses. Reactions were carried out in flame-dried apparatus under an atmosphere of nitrogen. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation.

2,2′-Thiobis(4,6-dimethylphenol)

To a mixture of 122.17 g (1 mol) of 2,4-dimethylphenol, 1.0 g (7.5 mmol) of anhydrous zinc chloride, and 250 mL of petroleum ether at 0 to −5°C was added dropwise 55.5 g (0.5 mol) of sulfur dichloride. The resultant dark-colored reaction mixture was stirred overnight at rt. The petroleum ether was decanted from the precipitated solid. The solid was dissolved in a hot mixture of 1L of hexane and 100 mL of toluene and the hot solution was decanted from the insoluble black tar. The solution was concentrated *in vacuo* and the resultant precipitated solid was collected by filtration to give 79.5 g (58%) of a light yellow solid. The product was recrystallized twice from toluene to give a white solid: mp 94–95°C; IR(CH_2Cl_2) 3595, 3460 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, CH_3, 6 H) 2.31 (s, CH_3, 6 H), 6.39 (s, OH, 2 H), 6.95 (d, ArH, 2 H), 7.11 (s, ArH, 2 H). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.0; H, 6.6. Found: C, 69.8; H, 6.7.

2,4,8,10-Tetra-tert-butyl-6,6-dimethyl-dibenzo[d, g][1,3,6,2]-dioxathiasilocin, (**3a**)

To a solution of 6.45 g (50 mmol) of **2a** in 50 mL of toluene maintained at 5 to 10°C with an ice bath was added dropwise a solution of 22.15 g (50 mmol) of **1a** and 10.12 g (100 mmol) of triethylamine in 100 mL of toluene. The reaction mixture was stirred overnight at room temperature and then the resultant reaction mixture was diluted with diethyl ether. The precipitate of triethylamine hydrochloride was removed by filtration and the solvent was removed *in vacuo*. The residue was recrystallized from 2-butanone to give 15.01 g (60%) of fine white needles: mp 251–253°C; ^{1}H NMR ($CDCl_3$) (23°C) δ 0.77 (broad s, $Si(CH_3)_2$, 6 H), 1.33 (s, $C(CH_3)_3$, 18 H), 1.40 (s, $C(CH_3)_3$, 18 H), 7.36 (d, 2 H), 7.65 (d, 2 H); ^{1}H NMR ($CDCl_3$) (−20°C) δ 0.56 (s, $SiCH_3$, 3 H), 0.83 (s, $SiCH_3$, 3 H), 1.33 (s, 18 H), 1.40 (s, 18 H), 7.39 (d, 2 H), 7.63 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 3.3 (broad s), 29.3 (s), 31.3 (s), 32.9 (s), 35.3 (s), 123.3 (s), 126.1 (s), 131.3 (s), 139.3 (s), 143.7 (s), 153.3 (s), Anal. Calcd for $C_{30}H_{46}O_2SSi$: C, 72.2; H, 9.3; S, 6.4. Found: C, 72.2; H. 9.3; S, 6.4.

2,4,6,6,8,10-Hexamethyl-dibenzo[d, g][1,3,6,2]dioxathiasilocin, (**3b**)

Following the method used to prepare **3a**, compound **3b** was prepared using 6.45 g (50 mmol) of **2a**, 13.75 g (50 mmol) of **1b**, and 10.12 g (100 mmol) of triethylamine. The crude product was recrystallized from 2-butanone to give 2.90 g (18%) of a white solid: mp 111.5–112.5°C; ^{1}H NMR (CDCl$_3$) δ 0.57 (s, Si(CH$_3$)$_3$, 6 H), 2.25 (s, 6 H), 2.27 (s, 6 H), 6.99 (s, 2 H), 7.37 (s, 2 H); ^{13}C NMR (CHCl$_3$): δ −1.1 (s), 16.1 (s), 19.7 (s), 123.7 (s), 128.9 (s), 131.3 (s), 132.9 (s), 134.1 (s), 152.5 (s). Anal. Calcd for $C_{19}H_{22}O_2SSi$: C, 65.4; H, 6.7. Found: C, 65.3; H, 6.6.

2,4,8,10-Tetra-tert-butyl-6,6-diphenyl-dibenzo[d, g][1,3,6,2]dioxathiasilocin, **(3c)**

Following the method used to prepare **3a**, compound **3c** was prepared using 12.66 g (50 mmol) of **2b**, 22.14 g (50 mmol) of **1a**, and 10.12 g (100 mmol) of triethylamine. The reaction mixture was heated at 90 to 100°C for 54 h. The crude product was recrystallized from 2-butanone to give 13.49 g (43%) of a white solid: mp 202–203°C; ^{1}H NMR (CDCl$_3$) δ 1.35 (s, C(CH$_3$)$_3$, 18 H), 1.41 (s, C(CH$_3$)$_3$, 18 H), 7.39 (complex m, 6 H), 7.49 (d, 2 H), 7.61 (d, 2 H), 7.75 (m, 4 H). Anal. Calcd for $C_{40}H_{50}O_2SSi$: C, 77.1; H 8.1. Found: C, 76.9; H, 8.2.

2,4,8,10-Tetra-tert-butyl-6-methyl-6-phenyl-dibenzo[d, g][1,3,6,2]-dioxathiasilocin, **(3d)**

Following the method used to prepare **3a**, compound **3d** was prepared using 9.56 g (50 mmol) of **2c**, 22.14 g (50 mmol) of **1a**, and 10.12 g (100 mmol) of triethylamine. The reaction mixture was heated at 97°C for 24 h. The crude product was recrystallized from acetonitrile to give 23.23 g (83%) of a white solid: mp 162.5–165°C; ^{1}H NMR (CDCl$_3$) δ 0.77 (s, SiCH$_3$, 3 H), 1.37 (s, C(CH$_3$)$_3$, 18 H), 1.53 (s, C(CH$_3$)$_3$, 18 H), 7.41 (complex m, 3 H), 7.43 (d, 2 H), 7.61 (d, 2 H), 7.73 (m, 2 H). Anal. Calcd for $C_{35}H_{48}O_2SSi$: C, 75.0; H 8.6. Found: C, 75.1; H, 8.6.

2,4,8,10-Tetra-tert-butyl-6-methyl-6-n-propyl-dibenzo[d, g]-[1,3,6,2]dioxathiasilocin, **(3e)**

Following the method used to prepare **3a**, compound **3e** was prepared using 7.86 g (50 mmol) of **2d**, 22.14 g (50 mmol) of **1a**, and 10.12 g (100 mmol) of triethylamine. The reaction mixture was heated at 91°C for 14 h. The crude product was recrystallized from acetonitrile to give 12.14 g (46%) of a white solid: mp 162–166°C; ^{1}H NMR (CDCl$_3$) (60°C) δ 0.61 (s, SiCH$_3$, 3 H), 1.09 (t, 3 H), 1.33 (s, C(CH$_3$)$_3$, 18 H), 1.41 (s, C(CH$_3$)$_3$, 18 H), 1.67 (complex m, 4 H), 7.37 (d, 2 H), 7.63 (d, 2 H). Anal. Calcd for $C_{32}H_{50}O_2SSi$: C, 73.0; H 9.6. Found: C, 73.1; H, 9.4.

2,4,8,10-Tetra-tert-butyl-6-methyl-6-(2-propyl)-dibenzo[d, g][1,3,6,2]dioxathiasilocin, **(3f)**

Following the method used to prepare **3a**, compound **3f** was prepared using 7.86 g (50 mmol) of **2e**, 22.14 g (50 mmol) of **1a**, and 10.12 g (100 mmol) of triethylamine. The reaction mixture was heated at 82°C for 72 h. The crude product was recrystallized from 2-butanone to give 11.85 g (45%) of a white solid: mp 190–191.5°C; ^{1}H NMR (CDCl$_3$) (60°C) δ 0.45 (s, SiCH$_3$, 3 H), 1.13 (d, 3 H), 1.33 (s, C(CH$_3$)$_3$, 18 H), 1.41 (s, C(CH$_3$)$_3$, 18 H), 7.37 (d, 2 H), 7.63 (d, 2 H)[12]. Anal. Calcd for $C_{32}H_{50}O_2SSi$: C, 73.0; H 9.6. Found: C, 72.8; H, 9.6.

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REFERENCES AND NOTES

1. S. D. Pastor, J. D. Spivack, R. K. Rodebaugh, and D. Bini, *J. Org. Chem.*, **49,** 1297 (1984).
2. W. M. Abdou, D. B. Denney, D. Z. Denney, and S. D. Pastor, *Phosphorus Sulfur,* **22,** 99, (1985).
3. W. M. Abdou, and M. R. Mahran, *Phosphorus Sulfur,* **26,** 119 (1986).
4. W. M. Abdou, M. R. H. Mahran, T. S. Hafez, and M. M. Sidky, *Phosphorus Sulfur,* **27,** 345 (1986).
5. (a) P. A. Odorisio, S. D. Pastor, J. D. Spivack, L. P. Steinhuebel, and R. K. Rodebaugh,

Phosphorus Sulfur, **15,** 9 (1983). (b) P. A. Odorisio, S. D. Pastor, J. D. Spivack, D. Bini, and R. K. Rodebaugh, *Phosphorus Sulfur,* **19,** 285 (1984).

6. S. D. Pastor, J. D. Spivack, and L. P. Steinhuebel, *J. Heterocycl. Chem.*, **21,** 1285 (1984).
7. C. Peccinni-Leopardi, O. Fabre, and J. Reisse, *Org. Magn. Reson.*, **8,** 233 (1976).
8. For a discussion, see: F. A. Anet, and R. Anet in *Dynamic Nuclear Magnetic Resonance Spectroscopy*; L. M. Jackman, F. A. Cotton, Eds.; Academic Press: New York, 1975, pp. 592–613 and references therein.
9. L. D. Quin, E. D. Middlemas, N. S. Rao, R. W. Miller, and A. T. McPhail, *J. Am. Chem. Soc.*, **104,** 1893 (1982).
10. (a) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. Perkin I,* 913 (1976). (b) For a general discussion and definition of boat-chair and twist-boat conformations, see: J. A. Moore and F. A. L. Anet in *Comprehensive Heterocyclic Chemistry Vol 7,* A. R. Katritzky, C. W. Rees, Eds.; Pergamon Press: Oxford, 1984, pp. 653–707.
11. The transannular interaction of sulfur with phosphorus suggested by Abdou and coworkers has been observed by Akiba *et al.* in either the boat-boat or twist-boat conformation of 5H-dibenzo[c, f][1,5]thiaphosphocins, see: K. Akiba, K. Okada, and K. Ohkata, *Tetrahedron Lett.*, **27,** 5221 (1986).
12. The methine multiplet was not specifically observed, and may have either been obscured by the *tert*-butyl resonances or lost due to coalescence.