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MEDIUM-SIZED ORGANOGERMANIUM HETEROCYCLES CONTAINING A TRANSANNULAR SULFUR ATOM: FIRST SYNTHESIS AND CHARACTERIZATION OF A STERICALLY HINDERED EIGHT-MEMBERED 1 2H-DIBENZO[*d, g*] [13,6,2]DIOXATHIAGERMOCIN

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MEDIUM-SIZED ORGANOGERMANIUM HETEROCYCLES CONTAINING A TRANSANNULAR SULFUR ATOM: FIRST SYNTHESIS AND CHARACTERIZATION OF A STERICALLY HINDERED EIGHT-MEMBERED 12H-DIBENZO[*d,g*] [13,6,2]DIOXATHIAGERMOCIN

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The synthesis and characterization of a sterically hindered eight-membered 12H-dibenzo[*d,g*][1,3,6,2]dioxathiagermocin is described. The $\Delta G^{\ddagger}_{273}$ for ring inversion ($12.8 \text{ kcal.mol}^{-1}$) was determined by variable temperature ^1H NMR spectroscopy.

Keywords: 12H-dibenzo[*d,g*][1,3,6,2]dioxathiagermocin; Ring inversion; free energy of; Conformation; Variable temperature ^1H NMR spectra.

Although the conformational analysis of both carbocyclic and small-membered heterocyclic compounds has been extensively developed, the conformational analysis of medium-sized heterocycles has not until very recently received much attention.¹ Investigations directed towards developing an understanding of the conformational preferences exhibited by dioxametalloins containing phosphorus has been stimulated in part by recent studies. In particular, 12H-dibenzo[*d,g*][1,3,2]dioxaphosphocin derivatives have been shown to provide unique coordination geometries when employed as ligands for transition-metal-catalyzed hydroformylation reactions.²⁻⁴ The

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equatorial axial aptitude of 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins incorporated in pentaoxyphosphoranes has important ramifications on literature proposals describing activated states for cyclic adenosine monophosphites where trigonal bipyramidal geometries about phosphorus are invoked.⁵ Certain sterically congested molecules incorporating medium-sized organophosphorus heterocycles exhibit unique spectral properties.^{6,7} Several reviews on the conformational analysis of 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins have appeared.^{8,9} Studies on the conformation of the corresponding 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin ring system have been reported,¹⁰ including a very recent crystallographic study.^{11,12} Quite interestingly, Holmes *et al.*¹² observed that in certain 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiasilocins hypervalent bonding of the transannular sulfur to silicon occurred.

Nothing was known about the corresponding ring system with germanium, until our recent report on the synthesis, characterization, and crystallographic analysis of a substituted 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin ring system.¹³ The first synthesis and characterization of a sterically hindered 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiaagermocin is reported herein.

RESULTS AND DISCUSSION

The thiobisphenol **1** was prepared as previously described.¹⁴ Similar to the methodology used to prepare the 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin derivatives,¹³ the sterically hindered 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiaagermocin **3** was prepared as a white crystalline solid by the reaction of **1** with dimethylgermanium (IV) chloride (**2**) using triethylamine as an acid acceptor.

In the ¹H NMR spectrum (benzene-*d*₆) of **3** at 26 °C, a broad singlet was observed at δ 0.86, which was assigned to the methyl group protons bonded to germanium. At 60 °C the resonance at δ 0.86 sharpened to a distinct singlet. In the ¹H NMR spectrum of **3**, two singlets were observed at δ 1.21 and δ 1.44 whose peak areas integrated to 18 protons each, which were assigned to the protons of two equivalent pairs of *tert*-butyl substituents. Two doublets were observed at δ 7.44 and δ 7.82 whose peak areas integrated to two protons each, which were assigned to the protons of two

equivalent pairs of aromatic protons. The mass spectrum observed was identical to the calculated spectrum for a mixture of germanium and sulfur isotopes.

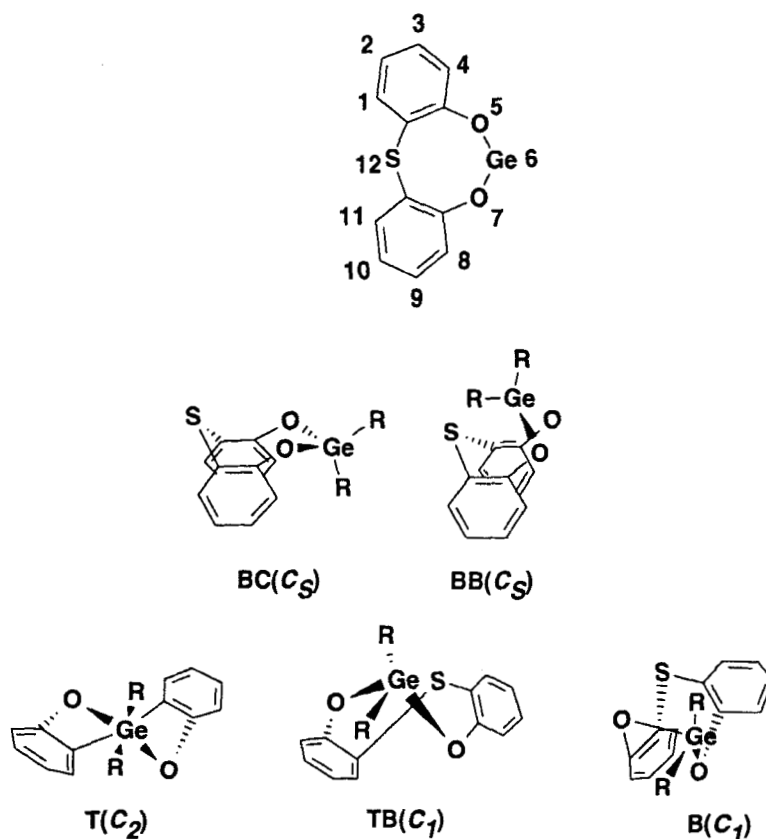


FIGURE 1 The *Chem. Abstr.* numbering system and conformations of the 12 *H*-dibenzo[*d,g*][1,3,2]dioxathiagermocin ring system. The TB structure represents only one member of a family of flexible TB forms

In the ^1H NMR spectrum (CD_2Cl_2) of **3** below 0°C , the coalescence temperature (T_c), two singlets were observed at δ 0.85 and δ 1.14 whose peak areas integrated to three protons each that were assigned to the protons of two anisochronous methyl groups bonded to germanium. In the ^1H NMR spectrum below the T_c , two equivalent pairs of *tert*-butyl substituents as well as two equivalent pairs of aromatic protons were observed.

The free energy of activation (ΔG^\ddagger) required to render the anisochronous methyl groups equivalent is $12.8 \text{ kcal.mol}^{-1}$. The process rendering the methyl group protons equivalent can reasonably be assigned to inversion of the eight-membered 12*H*dibenzo[*d,g*][1,3,6,2] dioxathiagermocin ring. The ΔG^\ddagger for ring inversion of **3** ($\Delta G^\ddagger_{273} = 12.8 \text{ kcal.mol}^{-1}$) compares with the slightly higher barriers measured for the similarly substituted 12*H*-dibenzo[*d,g*][1,3,2] dioxagermocin **4** ($\Delta G^\ddagger_{299} = 13.3 \text{ kcal.mol}^{-1}$), 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin **5** ($\Delta G^\ddagger_{279} = 13.9 \text{ kcal.mol}^{-1}$), and 12*H*-dibenzo[*d,g*][1,3,6,2] dioxathiasilocin **6** ($\Delta G^\ddagger_{276} = 13.9 \text{ kcal.mol}^{-1}$).^{10,13}

Given the observation of Holmes and co-workers on the ability of sulfur to participate in transannular hypervalent bonding to silicon in certain 12*H*dibenzo[*d,g*][1,3,6,2]dioxathiasilocins,¹² a comparison of the conformation of **3** to that of the previously prepared 12*H*-dibenzo[*d,g*][1,3,2] dioxagermocin **4** is of considerable interest. The commonly accepted nomenclature to describe the conformation of eight-membered rings is used herein; namely the boat-chair (C_s symmetry), boat-boat (C_s symmetry), twist-boat (C_1 symmetry), and Twist (C_2 symmetry), which are abbreviated BC, BB, TB, and T, respectively.^{15–17} Arshinova has noted that the boat conformer (C_1 symmetry; abbreviated B) should also be considered as it is commonly found in the solid state (Figure 1).⁸ The B conformation represents a highly distorted TB geometry about halfway between the symmetric C_2 T and BB geometry.¹⁵ The B conformation is characterized by a $C_{\text{Aromatic}}\text{-O-P-O}$ torsion angle of 0° .^{8a}

The VT ^1H NMR spectral data of **3** requires that below the coalescence temperature the ring conformer possess a σ plane of symmetry passing through the germanium and S(12)-sulfur atom. This must be the case in order to explain both the observation of anisochronous methyl groups bonded to germanium along with the observation of two equivalent pairs of *tert*-butyl groups and two equivalent pairs of aromatic protons. The presence of twisted conformations that rapidly pass through the required symmetry plane cannot be rigorously excluded. Either a BC or BB conformation is consistent with the VT ^1H NMR spectra. Although calculations suggest the BB conformation to be considerably higher in energy than the BC conformation in 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocins,¹⁸ 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins,¹⁹ and the corresponding carbocycle,^{15,20} stabilization of the BB conformation by hypervalent bonding of sulfur to germanium as observed in certain

12*H*-dibenzo[*d,g*][1,3,6,2]dioxathia- phosphocins²¹ and 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiasilocins,¹² as for example in **7** and **8**, cannot be excluded. Indeed, these prior calculations were performed on eight-membered rings without transannular donor atoms and do not provide insight to the present case. The BB conformation is observed in the 6,6-dimethyl-substituted 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin **5** in the solid state.¹¹ Caution must be observed, however, in comparing solid-state and solution conformations. Lattice energy and the resultant crystal-packing effects in the solid state can render the solid-state geometry of flexible conformations different from that in solution.¹⁵ Unfortunately, suitable crystals of **3** could not be grown for crystallographic analysis.

A comparison between the solution ¹H NMR spectrum (CD₂Cl₂) of **3** below the T_c with that of structurally known analogs suggests that the conformation of **3** is indeed a BB with transannular bonding of sulfur to germanium (see Table I). Strong anisotropic shielding is observed for the methyl groups bonded to either silicon or germanium when the ring adopts a BC conformation (compare **4** and **9**).^{12d, 13} In the case of a BC conformation, one of the methyl groups bonded to silicon or germanium is significantly shielded (¹H chemical shifts near zero). The tacit assumption that the solid state ring conformation is also found in solution has generally been shown to be true in the case of certain related pentacoordinate phosphorus compounds.²² In the case of TB conformations (dependent upon the degree of distortion or twist from the symmetrical BB), the anisotropic shielding of the methyl groups is reduced (compare **5** and **10**).^{10a,12d,11,23} In the case of derivative **5**, the conformation in solution is reported because crystal packing forces render the solid state and solution conformations different.²³ In BB conformation found for **6**, for which donor..acceptor bonding of sulfur to silicon has been found, the nonequivalence of the two methyl groups bonded to silicon is significantly reduced and the ¹H chemical shifts of both methyl groups are downfield.^{10b, 12a} The observed ¹H chemical shifts of the methyl groups bonded to germanium in **3** suggest that a BB conformation is obtained in solution with transannular bonding of sulfur to germanium. This is consistent with the donor and acceptor properties of sulfur and germanium, respectively.²⁴

In summary, the first synthesis and characterization of the 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiagermocin ring system is described as well as the determination of the corresponding ΔG[‡] for ring inversion. The NMR spectral data suggests that a BB conformation is obtained in solution

with transannular bonding of sulfur to germanium. The data experimental data available for the 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiagermocin ring system is limited, however, and further studies are warranted.

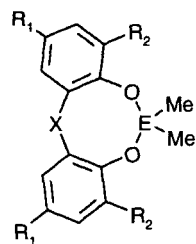
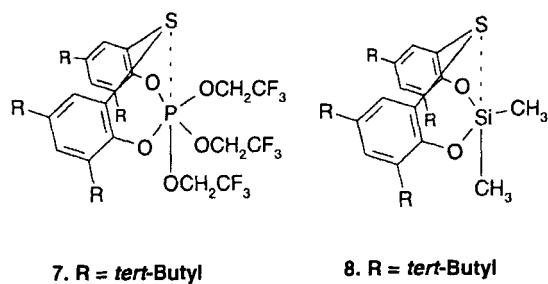
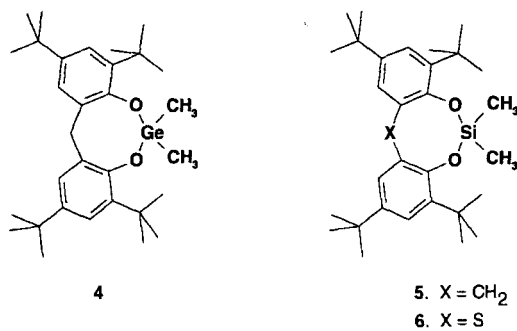
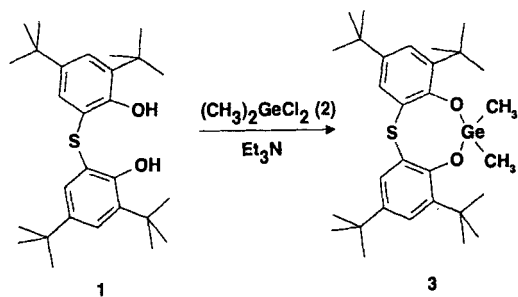
TABLE I Comparison of the anisotropic shielding of the 6,6-dimethyl substituents in the ^1H NMR of 3 and structurally related compounds with the ring conformation

<i>Cmpd.</i>	<i>R</i> ₁	<i>R</i> ₂	<i>X</i>	<i>E</i>	$^1\text{H NMR}^a$ (<i>E</i> -CH ₃) δ	<i>X...E</i> <i>I</i> <i>nteraction</i>	<i>Ring</i> <i>Conform.</i> ^b	<i>Ref.</i>
9	Me	Me	SO ₂	Si	0.02, 0.58	poor donor & weak acceptor	BC	12d
10	Me	But	SO ₂	Si	0.11, 0.65	poor donor & weak acceptor	TB	12d
5	But	But	CH ₂	Si	0.18, 0.57	non-donor & weak acceptor	TB ^c	23
6	But	But	S	Si	0.56, 0.83 ^d	strong donor & weak acceptor	BB	12a
4	But	But	CH ₂	Ge	-0.03, 1.01	non-donor & strong acceptor	BC	13
3	But	But	S	Ge	0.85, 1.14	strong donor & strong acceptor	BB	This work

a. ^1H NMR spectra in CD₂Cl₂ below T_c. b. Solid-state ring conformation by x-ray crystallography. c. Solution conformation. d. CDCl₃ solvent

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Fisher-Johns melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR (499.86 and 75.46 MHz, respectively) spectra were taken on a Varian Model Unity-500 spectrometer. All ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Significant ^1H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; br, broad), atom assignments, coupling constant in Hertz, and number of protons. Merck precoated (0.25 mm) silica gel 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. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

2,2'-Thiobis[4,6-bis(1, 1-dimethylethylphenol)] (1). The procedure of Pastor *et al.*¹⁴ was followed using 12.93 g (62.5 mmol) of 2,4-di-*tert*-butylphenol, 3.22 g (31.3 mmol) of sulfur dichloride, and 0.064 grams of anhydrous zinc(II) chloride in 45 mL of petroleum ether. The crude product was recrystallized three times from acetonitrile to give 6.83 g (51 %) of a white solid, mp 99–102 °C (lit¹⁴ 98–101 °C). ¹H NMR (CDCl₃) δ 1.23 (s, 18 H), 1.43 (s, 18 H), 6.47 (s, OH, 2 H), 7.17 (d, 2 H), 7.28 (d, 2H); ¹H NMR (C₆D₆) δ 1.13 (s, 18 H), 1.49 (s, 18 H), 6.44 (s, OH, 2 H), 7.33 (d, 2 H), 7.37 (d, 2H).

6,6-Dimethyl-2,4,8, 10-tetrakis (1,1-dimethylethyl)-12H-dibenzo[d,g][1,3,6,2] dioxathiasilocin (3). To a solution of 1.00 g (5.76 mmol) of 2 in 5 mL of toluene at room temperature was added dropwise over a 15 minute period a solution of 2.55 g (5.76 mmol) of 1 and 1.20 g (12 mmol) of triethylamine in 10 mL of toluene. The reaction mixture was stirred overnight at room temperature and the resultant precipitate of triethylamine hydrochloride removed by filtration. The volatiles were removed *in vacuo* and the residue recrystallized four times from a mixture of acetonitrile and toluene to give 0.80 g (25 %) of a white crystalline solid, mp 275 – 278 °C. ¹H NMR (CDCl₃)(50 °C) δ 1.04 (br s, 6 H), 1.30 (s, 18 H), 1.39 (s, 18 H), 7.30 (d, 2 H), 7.53 (d, 2H); ¹H NMR (C₆D₆)(60 °C) δ 0.86 (br s, 6 H), 1.21 (s, 18 H), 1.44 (s, 18 H), 7.44 (d, 2 H), 7.82 (d, 2H); ¹³C{¹H} NMR (CD₂Cl₂)(27 °C) δ 29.97 (s), 31.56 (s), 34.54 (s), 35.69 (s), 122.68 (s), 126.22 (s), 130.63 (s), 139.33 (s), 142.94 (s), 155.41 (s). The methyl group carbons bonded to Ge were not specifically observed presumably due to coalescence phenomena. MS *m/z* 540, 541, 542, 543, 544, 545, 546, 547 (M⁺) observed in the ratio calculated for the naturally abundant isotopic mixture of ³²S, ³³S, ³⁴S, ⁷⁰Ge, ⁷²Ge, ⁷³Ge, ⁷⁴Ge, and ⁷⁶Ge. Anal. Calcd for C₃₀H₄₆O₂SGe: C, 66.31; H, 8.53. Found: C, 66.64; H, 8.86.

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