The Synthesis and Conformation of Sterically Congested Seven-membered Rings Containing Tetracoordinate Germanium(IV): Determination of the ΔG^* For Ring Inversion[1]

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Introduction

Recently, a significant amount of research has focused on the synthesis and conformational analysis of hetero-substituted medium-sized rings.[2] In particular, studies on the spectral characteristics[3,4] and ligand properties[5] of molecules containing the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring system have been reported, as well as the apical−equatorial aptitude of the seven-membered ring where the phosphorus atom is pentacoordinate.[6] A crystallographic study reported the effect of aryl substitution upon the conformation of the seven-membered ring.[7] The synthesis of the corresponding dibenzo[*d*,*f*][1,3,2]dioxasilepin ring system has been reported,[8−10] and Holmes et al. prepared anionic five-coordinate silicates containing a dioxasilepin ring.[11] Except for the pioneering studies of Zuckerman[8c,12] and Heinrich,[13] nothing is known about the corresponding dibenzo[*d*,*f*][1,3,2]dioxagermepin ring system (Figure 1). We report herein the synthesis and characterization of sterically congested mono and spirocyclic dibenzo[*d*,*f*][1,3,2]dioxagermepin derivatives, as well as the first determination of the free energy of activation (ΔG^*) for the dioxagermepin ring system.

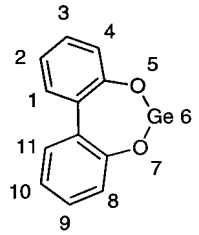

Figure 1. *Chemical Abstracts* numbering system for the dibenzo[*d*,*f*]-[1,3,2]dioxagermepin ring system.

Experimental Section

All melting points were determined in open capillary tubes with a Thomas−Hoover melting point apparatus and are uncorrected. ^{1}H NMR (300.08 and 499.84 MHz) spectra were obtained on a Varian Model Gemini-300 or Unity-500 spectrometer, respectively. ^{13}C NMR (125.6998 MHz) spectra were taken on a Varian Model Unity-500 spectrometer and are proton decoupled. All ^{1}H and ^{13}C chemical shift values are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Merck silica gel 60 (200−400 mesh) was used for column chromatography. 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 a flame-dried apparatus under a dry inert atmosphere of nitrogen. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, New Jersey.

2,4,8,10-Tetra-*tert*-butyl-6,6-dimethyl-dibenzo[*d*,*f*][1,3,2]-dioxagermepin (3a). To a stirred solution of **2a** (1.00 g, 5.80 mmol) in 9 mL of toluene was added dropwise over 10 min a solution of **1** (1.03 g, 2.50 mmol) and triethylamine (0.51 g, 5.0 mmol) in 10 mL of toluene. The reaction mixture was heated at 83 °C for 16 h and then after cooling to room temperature, the precipitate of triethylamine hydrochloride was removed by filtration. The volatiles were removed in vacuo, and the residue was recrystallized from acetonitrile to give 1.11 g (87%) of a white solid, mp 185−187 °C. ^{1}H NMR ($CDCl_3$): δ 0.75 (s, 6 H), 1.33 (s, 18 H), 1.43 (s, 18 H), 7.02 (d, ^4J = 2.4 Hz, 2 H), 7.32 (d, ^4J = 2.4 Hz, 2 H). Anal. Calcd for $C_{30}H_{46}O_2Ge$: C, 70.47; H, 9.07. Found: C, 70.62; H, 9.02.

2,4,8,10-Tetra-*tert*-butyl-6,6-diphenyl-dibenzo[*d*,*f*][1,3,2]-dioxagermepin (3b). The procedure for the preparation of compound **3a** was repeated using **2b** (1.00 g, 3.1 mmol), **1** (1.03 g, 2.50 mmol), and triethylamine (0.51 g, 5.0 mmol) in 19 mL of toluene (83 °C, 24 h). The residue was recrystallized from a mixture of toluene (10 mL) and acetonitrile (30 mL) to give 1.21 g (76%) of a white solid, mp 221−222 °C. ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 18 H), 1.36 (s, 18 H), 7.17 (d, 2 H), 7.26 (d, 2 H), 7.37 (m, 4 H), 7.49 (tt, 2 H), 7.59 (dd, 4 H). ^{13}C{^{1}H} NMR ($CDCl_3$; 125.6998 MHz): δ 30.68, 31.55, 34.35, 35.06, 123.32, 128.10, 128.23, 130.10, 131.27, 132.81, 134.68, 139.07, 143.29, 151.71. Anal. Calcd for $C_{40}H_{50}O_2Ge$: C, 75.61; H, 7.93. Found: C, 76.03; H, 7.92.

3,3′,5,5′-Tetrakis(1,1,3,3-tetramethylbutyl)-2,2′-dihydroxy-1,1′-biphenyl (4). To a stirred mixture of 2,4-bis(1,1,3,3-tetramethylbutyl)phenol (29.5 g, 0.1 mole) and potassium hydroxide (44.0 g, 0.8 mol) in 250 mL of distilled water at 85−90 °C was added dropwise over 1 h a 30% aqueous solution of hydrogen peroxide (30 mL, 0.27 mol).

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The reaction mixture was stirred at 85 °C for 1 h. The reaction mixture was cooled to room temperature, and then the aqueous phase was decanted. The organic phase was washed with water by decantation, and then the viscous organic phase was poured into a beaker of dilute hydrochloric acid. After standing overnight, the aqueous phase was decanted and the organic phase was diluted with diethyl ether. The ether solution was washed sequentially with dilute aqueous hydrochloric acid, water, saturated sodium bicarbonate, and water. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The product was purified by trituration with acetonitrile to give 13.3 g (42%) of a white solid, mp 141−142 °C. Proton assignments made by DNOE experiments. ^{1}H NMR ($CDCl_3$; 27 °C): δ 0.72 (s, 36 H), 1.31 (s, $C(CH_3)_2$, 12 H), 1.43 (s, 3,3′-$C(CH_3)_A$, 6 H), 1.44 (s, 3,3′-$C(CH_3)_B$, 6 H), 1.68 (s, 4 H), 1.85 (d, $^2J_{HCH}$ = 14.4 Hz, 2 H), 1.98 (d, $^2J_{HCH}$ = 14.4 Hz, 2 H), 4.96 (s, OH, 1 H), 6.93 (d, 2 H), 7.32 (d, 2 H). Anal. Calcd for $C_{44}H_{74}O_2$: C, 83.22; H, 11.75. Found: C, 82.97; H, 11.36.

2,4,8,10-Tetrakis(1,1,3,3-tetramethylbutyl)-6,6-dimethyl-dibenzo-[*d,f*][1,3,2]dioxa-germepin (5). The procedure for the preparation of compound **3a** was repeated using **2a** (1.25 g, 7.20 mmol), **4** (1.05 g, 1.7 mmol), and triethylamine (0.58 g, 5.70 mmol) in 26.3 mL of toluene (70 °C, 72 h). The residue was recrystallized from acetonitrile (30 mL) to give 0.52 g (43%) of a white solid, mp 183−185 °C. ^{1}H NMR (C_6D_6; 60 °C): δ 0.45 (s, 6 H), 0.86 (s, 18 H), 0.88 (s, 18 H), 1.40 (s, 12 H), 1.59 (s, 12 H), 1.78 (s, 4 H), 2.13 (s, 4 H), 7.21 (d, 2 H), 7.49 (d, 2 H). Anal. Calcd for $C_{46}H_{78}O_2Ge$: C, 75.10; H, 10.69. Found: C, 75.20; H, 10.34.

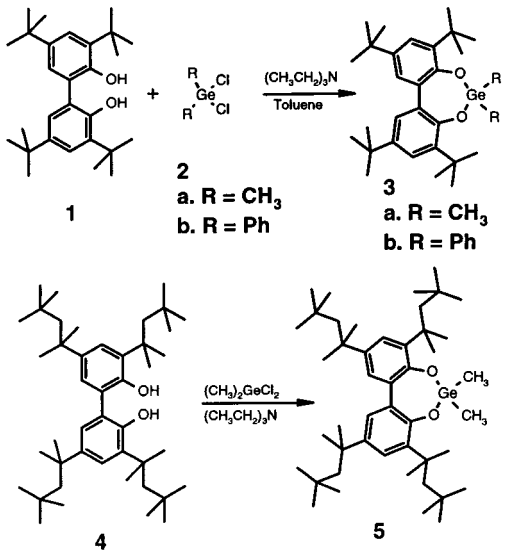
6-[(2,4,8,10-Tetra-*tert*-butyl-6-ethyl-dibenzo[*d,f*][1,3,2]-dioxagermepin-6-yl)oxy]- 2,4,8,10-Tetra-*tert*-butyl-6-ethyl-dibenzo-[*d,f*][1,3,2]dioxagermepin (6). The procedure for the preparation of compound **3a** was repeated using ethylgermanium(IV) trichloride (1.00 g, 4.80 mmol), **1** (3.28 g, 8.00 mmol), and triethylamine (1.46 g, 14.40 mmol) in 20 mL of toluene (74 °C, 21 h). The residue was recrystallized from a mixture of acetonitrile (40 mL) and toluene (7 mL) to give 1.89 g (46%) of a white solid, mp 236−238 °C. ^{1}H NMR ($C_2D_2Cl_4$; 110 °C): δ 0.96 (t, 6 H), 1.18 (q, 4 H), 1.31 (s, $C(CH_3)_3$, 36 H), 1.41 (s, $C(CH_3)_3$, 36 H), 6.95 (d, 4 H), 7.29 (d, ArH, 4 H). MS: The desired molecular ions ($M^{+\bullet}$) were observed in the ratio calculated for the naturally abundant isotope mixture of ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}-Ge. Anal. Calcd for $C_{60}H_{90}O_5Ge_2$: C, 69.52; H, 8.75. Found: C, 71.44; H, 8.70.

Bis(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenylen-2,2′-dioxy)germanium-(IV) (7). The procedure for the preparation of compound **3a** was repeated using germanium(IV) chloride (1.50 g, 7.0 mmol), **1** (5.80 g, 14.0 mmol), and triethylamine (2.90 g, 29.0 mmol) in 37 mL of toluene (60 °C, 2 h). The residue was recrystallized from a mixture of acetonitrile (20 mL) and toluene (3 mL) to give 3.92 g (62%) of a white crystalline solid, mp > 250 °C. Proton assignments were made by NOE experiments. ^{1}H NMR ($CDCl_3$; 27 °C): δ 1.26 (s, 4,8-$C(CH_3)_3$, 36 H), 1.35 (s, 2,10-$C(CH_3)_3$, 36 H), 7.10 (d, 1,11-ArH, 4 H), 7.38 (d, 3,9-ArH, 4 H) [for atom numbering, see Figure 1; assignments for $^1/_2$ of the S_2 symmetric molecule]. Anal. Calcd for $C_{56}H_{80}O_4Ge$: C, 75.59; H, 9.06. Found: C, 76.39; H, 8.96.

Results and Discussion

The reaction of the tetra-*tert*-butyl substituted biphenyldiol **1**[10] with dimethylgermanium(IV) dichloride, **2a**, using triethylamine as an acid acceptor gave the dibenzo[*d,f*][1,3,2]-dioxagermepin **3a** as a white crystalline solid (87% recrystallized) (Figure 1; Structures 1−5). The diphenyl derivative **3b** was prepared in an analogous reaction of **1** with **2b**.

In the ^{1}H NMR spectrum of **3a** at probe temperature (27 °C), a singlet was observed at δ 0.75, which was assigned to the protons of two equivalent methyl groups bonded to germanium. The protons of two equivalent pairs of *tert*-butyl substituents (singlets at δ 1.33 and 1.43, respectively) and aromatic protons (doublets at δ 7.02 and 7.32, respectively) were observed in the ^{1}H NMR spectrum. These observations are consistent either with a slow or noninverting staggered ring conformation with



C_2 symmetry that renders the methyl group protons isochronous or a ring that is rapidly inverting (atropisomerization about the C−C bond connecting the two aryl rings) on the NMR time scale.[14]

In an analogous manner, the diphenyl derivative **3b** was prepared by the reaction of **1** with **2b**. In the ^{1}H NMR spectrum of **3b**, a doublet of doublets, a triplet of triplets, and a doublet of doublets were observed at δ 7.37, 7.49, and 7.59, respectively, which were assigned to the aromatic protons that are meta, para, and ortho to germanium in the 6,6-diphenyl substituents. The aromatic protons of the two phenyl substituents bonded to germanium are expected to be isochronous if the dioxagermepin is either rapidly or slowly inverting on the NMR time scale.[15] However, the observation of only one signal for the two aromatic protons ortho to germanium in the phenyl substituent is only consistent with a dioxagermepin ring rapidly inverting on the NMR time scale. This must be the case because slow (or non) ring inversion on the NMR time scale would render the ortho aromatic protons anisochronous due to the presence of a stereoaxis about the single bond connecting the aryl groups in the dioxagermepin ring. In the ^{13}C{^{1}H} NMR spectrum of **3b**, all of the carbon atoms expected to be isochronous in a rapidly inverting dioxagermepin ring were found to be isochronous.

The conformation of the dibenzo[*d,f*][1,3,2]dioxagermepin ring was further delineated utilizing a diastereotopic proton probe. The substituted dioxagermepin **5** with diastereotopic methylene and methyl group protons was synthesized for a VT ^{1}H NMR study. The prerequisite bisphenol **4** was prepared by the oxidative coupling of 2,4-bis(1,1,3,3-tetramethylbutyl)phenol with hydrogen peroxide under basic conditions. In the ^{1}H NMR spectrum ($C_2D_2Cl_4$) of **4** at 27 °C, two doublets were observed at δ 1.85 and 1.98 that were assigned to two equivalent pairs of anisochronous methylene protons bonded to the C-2 carbon atom of the two 1,1,3,3-tetramethylbutyl substituents ortho to the oxygen atoms. The protons of the adjacent gem-dimethyl groups were also observed to be anisochronous. These observations are consistent with slow rotation about the stereoaxis (C−C bond connecting the two aryl groups) on the NMR time scale.[16]

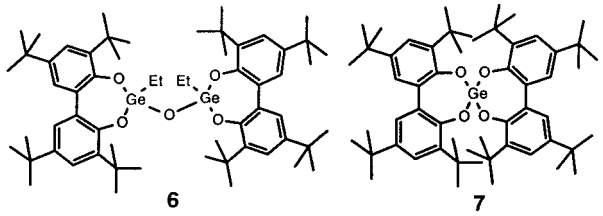
In the ^{1}H NMR spectrum ($C_2D_2Cl_4$) of **4** above 80 °C, the coalescence temperature (T_C), the two doublets observed at δ

(14) The examination of a Drieding molecular model suggests that the alternate explanation of a planar ring conformation is highly unlikely.
(15) For a discussion on topicity and anisochrony in NMR, see Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 465−508.

1.85 and 1.98 collapsed into a broad singlet, which sharpened upon raising the temperature to 110 °C. The free energy of activation for the process required to render these diastereotopic protons equivalent is $\Delta G^*_{353} = 17.2$ kcal mol^{-1}.[17,18] This process can reasonably be assigned to rotation about the C−C single bond connecting the two aryl groups in **4**. Simple ortho-substituted biphenyls are reported to have activation energies ranging between 17 and 20 kcal mol^{-1}.[19] Small increases in the ΔG^* for rotational processes in hydroxyaryl molecules due to hydrogen bonding has been reported.[20]

The 1,1,3,3-tetramethylbutyl-substituted dioxagermepin **5** was prepared by the reaction of **4** with **2a** as a white crystalline solid (43% recrystallized). Interestingly, in the ^{1}H NMR spectrum ($CDCl_3$) of **5** at probe temperature (27 °C), the signals for the gem-dimethyl and methylene protons of both pairs of 1,1,3,3-tetramethylbutyl substituents were observed to be broad. In the ^{1}H NMR spectrum (C_6D_6) of **5** at 60 °C, these signals sharpened considerably. In the VT ^{1}H NMR spectra (CD_2Cl_2) below 15 °C, the T_C, two doublets were observed at δ 1.60 and 1.75 (upfield and downfield arms of an AB quartet, respectively; $J_{AB} = 14.6$ Hz), which were assigned to the anisochronous methylene protons of one pair of equivalent 1,1,3,3-tetramethylbutyl substituents (interconverted by a C_2 symmetry operation below T_C). The free energy of activation for the process required to render these diastereotopic protons equivalent is $\Delta G^*_{288} = 13.8$ kcal.mol^{-1}. The process that interconverts these protons can be reasonably assigned to be ring inversion (atropisomerism about the sp^2−sp^2 single bond connecting the two aryl rings) of the dioxagermepin ring. As expected, in the VT ^{1}H NMR spectrum (CD_2Cl_2) of **5** at −40 °C, the methylene and gem-dimethyl group protons of both pairs of equivalent 1,1,3,3-tetramethylbutyl substituents were observed to be diastereotopic.

In an attempt to prepare a hydroxyaryl-substituted dioxagermocin by the reaction of 2 mol of **2a** with ethylgermanium(IV) trichloride, the digermoxane **6** was obtained as a white crystalline solid (46% recrystallized; see Structure 6). The formation of the digermoxane **6** is suggested to be the result of the reaction of the intermediate 6-chloro-substituted dioxagermepin with adventitious water.[21] In the VT ^{1}H NMR spectrum ($C_2D_2Cl_4$) of **6** at 27 °C, four broad singlets were observed at δ 1.26, 1.37, 1.47, and 1.56 which were assigned to the protons of four nonequivalent *tert*-butyl substituents.[22] Upon heating, the *tert*-butyl signals underwent coalescence. In the ^{1}H NMR spectrum of **6** at 110 °C, two sharp singlets were observed, which were assigned to the protons of two isochronous pairs of *tert*-butyl substituents.



6 **7**

A reasonable explanation for these observations is that below the T_C, ring inversion of the seven-membered rings is slow on the NMR time scale, which leads to observable diastereoisomerism because of the presence of two independent stereoaxes (sp^2−sp^2 C−C single bond connecting the two aryl rings). Below the T_C, two atropisomers would be expected to be observable with relative absolute configurations of (*R**, *R**) and (*R**, *S**), which refers throughout this paper to the relative configurations the two stereoaxes.[15,16] The observation of two pairs of equivalent *tert*-butyl substituents at 110 °C is consistent with rapid ring inversion of the dibenzo[*d,f*][1,3,2]dioxagermepin rings. Conformational averaging, because of rapid ring inversion and rotation of exocyclic bonds at 120 °C, leads to an overall C_{2v} symmetry for **3**, which renders the corresponding pairs of *tert*-butyl protons in each ring homotopic.[23]

The spirocyclic derivative **7** was prepared by the reaction of germanium(IV) tetrachloride with 2 mol of the bisphenol **1** (see Structure 7). In the ^{1}H NMR spectrum of **7**, two singlets at δ 1.26 and 1.35 were observed, which were assigned to the protons of two pairs of equivalent *tert*-butyl substituents. This observation is consistent with rapid ring inversion leading to an overall T_d averaged symmetry.[24]

No evidence was found for the formation of the corresponding pentacoordinate germanium(IV) species resulting from coordination of the chloride counterion of the triethylammonium cation during the preparation of the dibenzo[*d,f*][1,3,2]dioxagermepin derivatives of this study, which has been observed for certain spirocyclic catecholate derivatives.[25] A reasonable explanation for this observation is the steric inhibition of coordination of chloride to germanium as a result of the *tert*-alkyl substitution and the lower electron acceptor properties of germanium in derivatives **3a,b** and **5** because of the alkyl or aryl substitution at germanium. A similar steric effect, leading to reduced coordination at germanium, was observed by Holmes[25] in spirocyclic catecolate derivatives of germanium due to *tert*-butyl substitution.

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(16) (a) For the observation of atropisomers in a bisphenol, see Pastor, S. D.; Hyun, J. L.; Odorisio, P. A.; Rodebaugh *J. Am. Chem. Soc.* **1988**, *110*, 6547, and references therein. (b) Pastor, S. D.; Richardson, C. F.; Ali NabiRahni, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *90*, 95.

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(18) For a discussion of errors associated with the calculation of rate and ΔG^* from coalescence data, see (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436. (b) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; p 504.

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(21) A MS of the starting ethylgermanium(IV) trichloride suggested the hydrolysis to the corresponding 1,1,3,3-tetrachloro-1,3-dimethyldigermoxane prior to use.

(22) In the VT ^{1}H NMR spectrum ($C_2D_2Cl_4$) of **6** at 27 °C, the aromatic protons were observed as broad multiplets between δ 6.9−7.3. A broad triplet and a broad multiplet were observed at δ 0.91 and 1.08, which were assigned to the protons of the ethyl substituent.

(23) For a discussion of averaged symmetry, residual stereoisomers, and the NMR of conformationally mobile systems, see Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 54−58.

(24) The alternate explanation for the observation of two *tert*-butyl proton signals is that inversion on the NMR time scale is slow and requires the formation of only one diastereoisomer. Although less likely, this explanation cannot be totally ruled out.

(25) (a) Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 4129. (b) For related work, see Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 281.