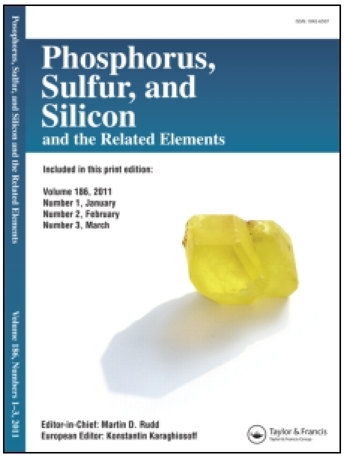


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE CONFORMATION OF STERICALLY CONGESTED EIGHT-MEMBERED RINGS CONTAINING GERMANIUM: FIRST X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF THE BOAT CONFORMATION

Nancy Khoury[a]; Stephen D. Pastor[a]; David Rahni[a]; Christine F. Richardson[a]; Nadya A. Syed[a]; Sai P. Shum[a]; A. Chandrasekaran[b]
[a] Pace University, Pleasantville, New York [b] University of Massachusetts, Amherst, Massachusetts

To cite this Article Khoury, Nancy , Pastor, Stephen D. , Rahni, David , Richardson, Christine F. , Syed, Nadya A. , Shum, Sai P. and Chandrasekaran, A.(2004) 'THE CONFORMATION OF STERICALLY CONGESTED EIGHT-MEMBERED RINGS CONTAINING GERMANIUM: FIRST X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF THE BOAT CONFORMATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 3, 483 — 497

To link to this Article: DOI: 10.1080/10426500490262676

URL: http://dx.doi.org/10.1080/10426500490262676

Phosphorus, Sulfur, and Silicon, 179:483–497, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490262676

THE CONFORMATION OF STERICALLY CONGESTED EIGHT-MEMBERED RINGS CONTAINING GERMANIUM: FIRST X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF THE BOAT CONFORMATION

Nancy Khoury,[a] *Stephen D. Pastor,*[a] *David Rahni,*[a]
Christine F. Richardson,[a] *Nadya A. Syed,*[a] *Sai P. Shum,*[a]
and A. Chandrasekaran[b]
Pace University, Pleasantville, New York;[a] *and*
University of Massachusetts, Amherst, Massachusetts[b]

(Received August 10, 2003; accepted August 16, 2003)

Keywords: 12-*H*-dibenzo[*d*,*g*][1,3,2] dioxagermocin; conformational analysis; eight-membered rings; germanium; solution- and solid-state conformation

Recently, a significant amount of research has focused on the synthesis, conformational analysis, and elucidation of transannular intramolecular bonding in certain heterosubstituted medium-sized rings,[1] stimulated in part by recent studies on the eight-membered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring.[2–6] Quite recently, we reported the first synthesis and characterization of a substituted 12*H*-dibenzo[*d*,*g*][1,3,2]dioxagermocin,[7] 12*H*-dibenzo[*d*,*g*][1,3,6,2]dioxathiagermocin,[8,9] and 12*H*-dibenzo[*d*,*g*][1,3,6,2]-dioxaselenagermocin,[10] for which solution and crystallographic evidence was found for transannular bonding of sulfur and selenium, respectively, to germanium.

In describing the conformation of the 12*H*-dibenzo[*d*, *g*][1,3,2]dioxagermocin ring system, the commonly accepted nomenclature for the conformers of eight-membered rings is used herein; namely the boat-chair (C_S symmetry), boat-boat (C_S symmetry), twist-boat (C_1 symmetry), boat (C_1 symmetry), and twist (C_2 symmetry), which are abbreviated BC, BB, TB, B, and T respectively (see Figure 1).[11] The

---

This work was supported in part by the Pace University Kenan Research Fund.

Presented in part at the 217th ACS National Meeting, Anaheim, CA; March 21–25, 1999; Abstract CHED 296a.

Address correspondence to Sai P. Shum, Ciba Specialty Chemicals Corporation, 540 White Plains Road, PO Box 2005, Tarrytown, New York 10591-9005. E-mail: sai.shum@cibasc.com

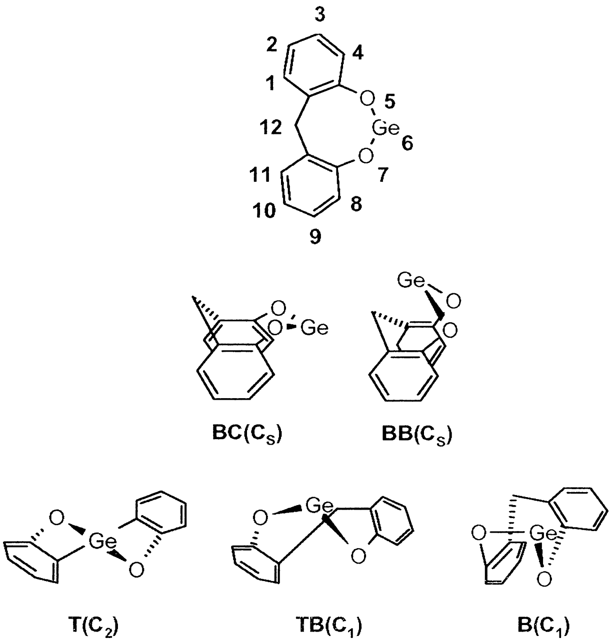
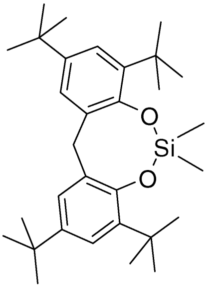


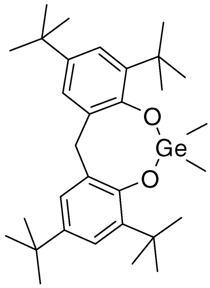
FIGURE 1 The *Chemical Abstracts* numbering system and conformations of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxagermocin ring system. The TB conformation illustrated is one member of the family of flexible TB forms.

B conformation represents a highly distorted TB geometry halfway between the C_2 symmetric T and BB geometry.[11c] In eight-membered 12*H*-dibenzo[*d*, *g*][1,3,2]dioxametallocins rings, the BC conformation is generally expected to be lowest in energy.[1] In a recent study on the corresponding substituted 12*H*-dibenzo[*d*, *g*][1,3,2]dioxasilocin ring system that did not contain heteroatoms capable of transannular bonding to silicon, the conformational preferences of a particular alkyl-substituted ring can be understood by the use of steric arguements.[12] The 6,6-dimethyl-substituted 12*H*-dibenzo[*d*, *g*][1,3,2]dioxasilocin **1** exists predominately as a TB conformation in solution rather than the generally preferred BC conformer. This observation can be understood in terms of ground-state destabilization of the BC conformation of **1** due to steric interaction of the pseudoaxial methyl substituents on silicon with the adjacent *tert*-butyl groups, which is attenuated in the TB conformer.[12] In contrast, spectroscopic and crystallographic evidence supported a BC conformation for the corresponding 6,6-dimethyl-substituted 12*H*-dibenzo[*d*, *g*][1,3,2]dioxagermocin **2**.[7] The observation of a BC conformation for **2** is consistent with longer

Ge—O and Ge—C bond lengths compared to the shorter Si—O and Si—C bonds in **1**, which is expected to reduce the steric interactions of the methyl groups bonded to germanium with the adjacent *tert*-butyl substituents in the BC conformation. Except for the study on **1**, nothing is known about the conformational preferences on alkyl-substituted 12*H*-dibenzo[*d*, *g*][1,3,2]dioxagermocin rings. This paper reports both the conformational preferences of unsubstituted-alkyl and phenyl substituents on 12*H*-dibenzo[*d*, *g*][1,3,2]dioxagermocin rings as well as the first crystallographic characterization of the boat conformation in this ring system.



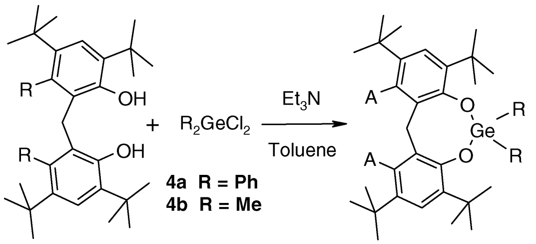
1



2

RESULTS AND DISCUSSION

If the previous explanation for the observation of a BC conformation for the germocin **2** rather than the TB conformation observed for the silocin **1** is due to the longer Ge—O and Ge—C bond lengths is correct (vide ante), increasing the steric requirements at germanium should cause the eight-membered 12*H*-dibenzo[*d*, *g*][1,3,2]germocin ring to adopt a TB conformation. The diphenyl-substituted germocin **5a** was obtained as a white solid (73% recrystallized) by the reaction of **3a** with **4a** using triethylamine as an acid acceptor.



3a R = H
3b R = Me

5a R = Ph; A = H
5b R = Me; A = Me
5c R = Ph; A = Me

In the ^{1}H NMR spectrum of **5a** at probe temperature (27°C), the signal for the C(12)-methylene protons (bridging methylene carbon) is a very broad singlet near coalescence. In the ^{1}H NMR ($C_2D_2Cl_4$) spectrum of **5a** at 110°C, a sharp singlet is observed at δ 4.15 that was assigned to the C(12)-methylene protons. Two singlets are observed at δ 1.17 and δ 1.33, which were assigned to the protons of two equivalent pairs of *tert*-butyl substituents. Similarly, two doublets are observed at δ 7.06 and δ 7.40 that were assigned to two equivalent pairs of aromatic protons. The observed NMR spectrum is consistent with a conformation undergoing rapid ring inversion that possess a σ plane of symmetry that passes through the germanium atom and the C(12) methylene proton. The presence of twisted non-planar conformers that rapidly pass through conformations possessing the required symmetry plane as either a transition state or intermediate cannot be excluded.

The magnitude of the geminal $^2J_{HCH}$ coupling constant for the C(12)-geminal protons in 12*H*-dibenzo[*d*, *g*][1,3,2]dioxametallocins is dependent on the orientation of the C(12)—H bond relative to the π orbitals of the two aromatic rings.[13] The hyperconjugative contribution to the magnitude of the geminal coupling reaches a minimum when the C(12)—H bonds are perpendicular to the π orbitals of the aromatic rings, as approached in the BC and BB conformation.[14] The observation of a geminal coupling constant of −12 to −13 Hz in 12*H*-dibenzo[*d*, *g*][1,3,2]dioxametallocins is indicative of a BC (or BB) conformation, whereas TB and B conformations were associated with coupling constants ranging from −14 to −19 Hz.[7,12,13a] Furthermore, the degree of nonequivalence of both the C(12) methylene protons and geminal dimethyl-substituent protons bonded to the heteroatom have been used a indicators of the conformation present in solution.[12] Given the caveat that rapidly equilibrating populations of conformations may be present in solution, these indicators must be used with caution.

Rapid ring inversion results in an averaging of the proton coupling constants of the various conformations present and prevents obtaining stereochemical information of the predominate conformer present.[15] This stereochemical averaging was mitigated by measuring the appropriate coupling constants and NOEs below the coalescence temperature (T_C) for ring inversion. In the ^{1}H NMR (CD_2Cl_2) (−60°C) spectrum of **5a** below the coalescence temperature (T_C), the methylene protons displayed significant nonequivalence. The anisochronous methylene protons are observed as two doublets at δ 3.51 and δ 4.58 with geminal coupling $^2J_{HCH} = -14$ Hz.[16,*] The magnitude of the observed geminal

---

[*] The two-bond geminal coupling constant is presumed to be negative.

coupling constant of the C(12) methylene protons is consistent with **5a** adopting a TB conformation in solution. The observation of a TB conformation for **5a** in solution is consistent with the increased steric demand of the two phenyl substituents bonded to germanium relative to the dimethyl-substituted **2** for which a BC conformation was previously observed.

Quite recently, Meier et al. described the synthesis of 1,11-substituted 12*H*-dibenzo[*d*, *g*][1,3,2]dioxathiocins in which the steric interaction of these substituents precluded the BC or BB conformation.[17] NMR spectroscopic and solid-state crystallographic studies of these 1,11-substituted 12*H*-dibenzo[*d*, *g*][1,3,2]dioxathiocins indicated that a B conformation was obtained in both solution and the solid state. 1,11-Dimethyl-substitution in a 12*H*-dibenzo[*d*, *g*][1,3,2]dioxametallocin forces the ring system into a B conformation in order to avoid steric interactions between the two methyl substituents in either the BC or BB conformation. An analogous strategy was employed to prepare a model of a 12*H*-dibenzo[*d*, *g*][1,3,2]dioxagermocin that adopts a B conformation. The 1,11-substituted derivative **5b** was prepared by the reaction of **3b** with the bisphenol **4b** in the presence of triethylamine as a hydrogen chloride acceptor. In the ^{1}H NMR (CD_2Cl_2) spectrum of **5b** below -10°C, the T_C, the methylene protons are observed as two doublets at δ 3.70 and δ 3.77 with geminal coupling $^2J_{HCH} = -16.5$ Hz. The magnitude of both the observed $^2J_{HCH}$ geminal coupling constant and the corresponding difference in chemical shifts[12] ($\Delta\delta = 0.07$ ppm) is consistent with a B conformation (or highly twisted TB) in solution. The observed magnitude of the $^2J_{HCH}$ geminal coupling constant for the model compound **5b** strongly supports the suggestion that **5a** adopts a TB conformation ($^2J_{HCH} = -14.0$ Hz) and **2** a BC conformation ($^2J_{HCH} = -13.2$ Hz) in solution. The degree of nonequivalence of the protons of the two methyl substituents bonded to germanium provides another stereochemical probe supporting a BC conformation of **2** (see Table I).[12] Additional evidence for the **5b** adopting a B conformation is the observation of four singlets in the ^{1}H NMR spectrum below the coalescence temperature at δ 1.25, δ 1.32, δ 1.34, and δ 1.38 that were assigned to the anisochronous protons of four nonequivalent *tert*-butyl substituents. Consistent with this observation, the protons of the C(1)- and C(11)-methyl substituents are observed to be nonequivalent (two singlets at δ 3.70 and δ 3.77).

The high degree of nonequivalence of the C(12)-methylene protons in the ^{1}H NMR spectrum of **5a** was unexpected (compare the to **5b** which adopts a B conformation).[12] However, the effect of geminal diphenyl substitution at Ge on this stereochemical indicator is unknown. The

TABLE I Comparison of the Anisotropic Shielding of the 6,6-Dimethyl Substituents and the C(12) Methylene Protons with the Ring Conformation in Related 12*H*-dibenzo[*d*, *g*][1,3,2]germocin Rings

			Δδ	
Compd	Conformation	$^2J_{HCH}$	$C(12)H_2$	$GeMe_2$
2[7]	BC	−13.2	0.92	1.04[a]
5a	TB	−14.0	1.07	—[b]
5b	B	−16.6	0.07	0.24[b]
5c	B	−16.4	0.27	—[c]
7a	BC	—	—	1.21[d]

[a] Obtained at −90°C in CD_2Cl_2.
[b] Obtained at −60°C in CD_2Cl_2.
[c] Obtained at −21.5°C in CD_2Cl_2.
[d] Obtained at 27°C in $CDCl_3$.

anisotropic ring current of the phenyl substituents bonded to Ge may increase the degree of nonequivalence C(12)-methylene protons in the TB conformation. To investigate this contention, the diphenyl-substituted **5c** was synthesized, which necessarily adopts the **B** conformation due to the 1,11-dimethyl substitution, vide ante.

The diphenyl-substituted **5c** was prepared as a crystalline white solid in 77% yield (recrystallized) by the reaction of **3b** with **4a** using triethylamine as an hydrogen chloride acceptor. In the ^{1}H NMR spectrum of **5c** at probe temperature (27°C), the signal for the 12*H*-methylene protons (bridging methylene carbon) is a broad singlet at δ 3.85. In the ^{1}H NMR spectrum of **5c**, two singlets are observed at δ 1.26 and δ 1.39, which were assigned to the protons of two equivalent pairs of *tert*-butyl substituents. A singlet is observed at δ 2.24 that was assigned to the protons of an equivalent pair of methyl substituents. The observed NMR spectrum is consistent with a conformation undergoing rapid ring inversion that possess a σ plane of symmetry (or twisted conformation that rapidly passes through the σ plane of symmetry) that passes through the germanium atom and C(12) methylene proton.

In the ^{1}H NMR (CD_2Cl_2)(499.8505 MHz) spectrum of **5c** below −10°C, the T_C, the C(12)-methylene protons are anisochronous. The C(12)-methylene protons are observed as two doublets at δ 3.71 and δ 3.98 with geminal coupling $^2J_{HCH} = -16.4$ Hz. The magnitude of the observed geminal coupling constant of the C(12) methylene protons is consistent with **5c** adopting a B conformation in solution. The magnitude of nonequivalence of the C(12) methylene protons of **5c** below the T_C is larger than that observed for **5b** in which Ge is bonded to two methyl substituents. This observation that the degree of nonequivalence of the C(12)-methylene protons is also dependent on

TABLE II Selected Bond Lenghts, Bond Angles, and Torsion Angles for **5c**

Bond lengths		Torsion angles	
Ge—O(1)	1.78	O(2)—Ge—O(1)—C(1)	−9.8
Ge—O(2)	1.78	O(1)—Ge—O(2)—C(13)	−91.1
Ge—C(14)	1.93	C(14)—Ge—O(1)—C(1)	−134.8
Ge—C(20)	1.92	C(20)—Ge—O(2)—C(13)	152.3
		Bond angles	
O(2)—Ge—O(1)	107.5	C(20)—Ge—C(14)	115.4
O(2)—Ge—C(14)	117.3	O(1)—Ge—C(14)	103.9
O(2)Ge—C(20)	101.8	O(1)—Ge—C(20)	110.9

the substituent on Ge warns that this stereochemical indicator[12] must be used with caution.

Crystals suitable for x-ray crystallographic analysis of **5c** were grown in a mixture of toluene and acetonitrile. In the solid-state x-ray crystal structure of **5c**, a B conformation is observed (Figures 2 and 3, Tables II and III). Characteristic for a B conformation, the O(2)—Ge—O(1)—C(1) torsion angle is near 0°, whereas the O(1)—Ge—O(2)—C(13) torsion angle is near 90–100° (−9.80° and −91.10° respectively). The O(2)—Ge—O(1)—C(1) atoms lie in a plane. The B conformation can be described as a highly distorted TB conformation lying halfway between a symmetric C_2 twist conformation and a BB conformation.[11c] The O(2)—Ge—O(1), C(20)—Ge—O(2), and C(14)—Ge—O(2) bond angles are 107.53°, 101.76°, and 117.30°, respectively, which is consistent with tetrahedral geometry at Ge ($\sum$ bond angles = 326.6°). The Ge—O bond lengths in **5c** are equal [Ge—O(1) and Ge—O(2) = 1.78 Å]. The Ge—C$_{sp}^{2}$(14) and Ge—C$_{sp}^{2}$ (2) bond lengths are 1.93 Å and 1.92 Å, respectively, and are in the range previously observed for a Ge—C single bond.[7,10,*]

To investigate the pseudoequatorial-pseudoaxial preference of a C(12) alkyl substituent(see Figure 4),[**] the substituted germocin **7**

---

[*] Tables of Interatomic Distances and Configurations in Molecules and Ions, The Chemical Society: Special Publication 11, 1958 and suppliment; Special Publication No. 18, 1965.

[**] In the BC conformation, substituents on germanium and the C(12)-methylene carbon atom of the germocin ring will be referred to as psuedoequatorial and pseudoaxial analogous to the nomenclature of cyclohexane. For clarity in the TB family of conformations, substituents on germanium and the C(12)-methylene carbon atom of the germocin ring will be referred to as either endo (pointing toward the inside of the boat-like concave ring system) or exocyclic (pointing to the outside of the ring). The endocyclic substituents would correspond to a pseudoaxial position, whereas an exocyclic substituent would correspond to a pseudoequatorial position.

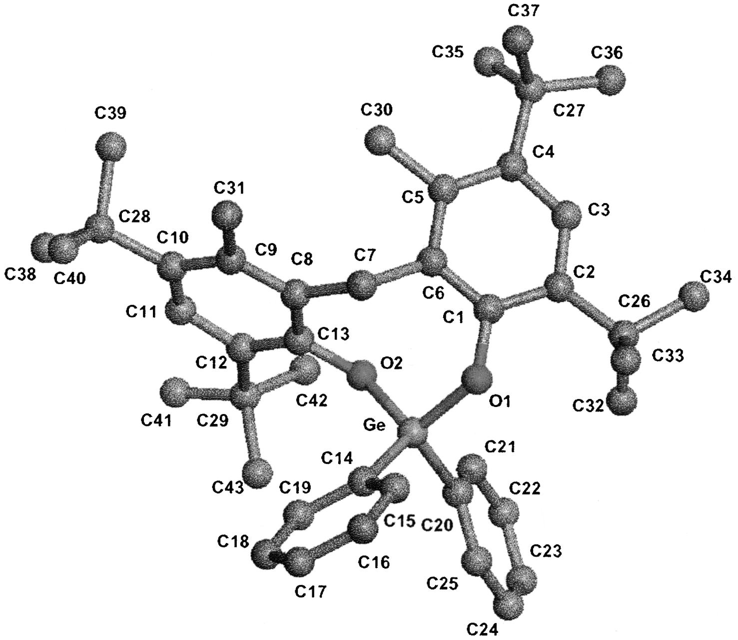


FIGURE 2 Molecular structure of **5c** showing the crystallographic numbering scheme.

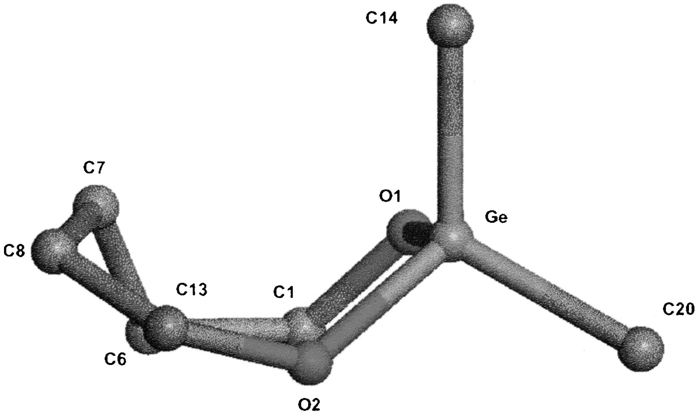


FIGURE 3 View of the atoms comprising the eight-membered ring of **5c** illustrating the boat conformation.

TABLE III Atomic Coordinates of **5c**

Atom	*x*	*y*	*z*	*U*
Ge	2841.9	1043.1	1393.6	39.5
O(1)	3465.4	526.1	833.3	44(3)
O(2)	2111.7	1919.1	871.3	40.2
C(1)	3233.9	724(13)	88.3	39.8
C(2)	2988.9	46.3	−426.5	46.4
C(3)	2748.6	296.7	−1165.3	53.5
C(4)	2768.3	1135.5	−1415.6	49(5)
C(5)	3093.6	1790.6	−875.2	43.4
C(6)	3330.6	1578.4	−118	38.5
C(7)	3864.9	2236.4	487(10)	38.9
C(8)	3245.1	2977.6	652.2	36.2
C(9)	3542.4	3851.1	642.5	39.7
C(10)	2921.5	4512.2	765.9	41.4
C(11)	2044.6	4267.1	908.7	42.2
C(12)	1747.0	3417.2	963.3	38.4
C(13)	2381.4	2774.6	840.3	36.1
C(14)	3952.2	1323(13)	2297(11)	44.4
C(15)	4880.3	8873(16)	2479.7	58.8
C(16)	5649.5	1025.7	3158.6	71.3
C(17)	5504.4	1602.8	3653.6	68.6
C(18)	4605(2)	2050(18)	3476.3	69.3
C(19)	3824.7	1906(16)	2806(12)	59.8
C(20)	1785.1	313.8	1513(11)	42.9
C(21)	793.8	314.4	999(14)	64.1
C(22)	44(18)	204.7	1094.3	73.8
C(23)	261(2)	726.8	1701.4	73.4
C(24)	1230	738.9	2216.9	76.5
C(25)	1988.4	220.6	2120.6	58(6)
C(26)	3064.5	915.1	−201.3	58.2
C(27)	2514.2	1295.9	−2260.1	64.4
C(28)	3150.5	5494.3	732.2	56.1
C(29)	764.1	3215.4	1137.3	47.2
C(30)	3260.9	2719.1	−1052.6	57.2
C(31)	4538.6	4042.9	506.8	53.6
C(32)	2353(2)	−1151.1	223.2	74.5
C(33)	4181(2)	−1109.1	298(2)	93.9
C(34)	2789(4)	−1515.3	−880.3	121.3
C(35)	1616(2)	1933(2)	−2579.5	80(8)
C(36)	2173(3)	451(2)	−2707.5	99(11)
C(37)	3481(2)	1609(3)	−2407(15)	94.6
C(38)	2341(3)	6054.9	903(2)	88
C(39)	3096(2)	5737.4	−60.5	80.7
C(40)	4190(2)	5759(18)	1314.7	85.5
C(41)	202.1	4045.5	1219.6	64.8
C(42)	12.8	2695.9	499.1	61.4
C(43)	1022.2	2710.6	1869.5	64.5

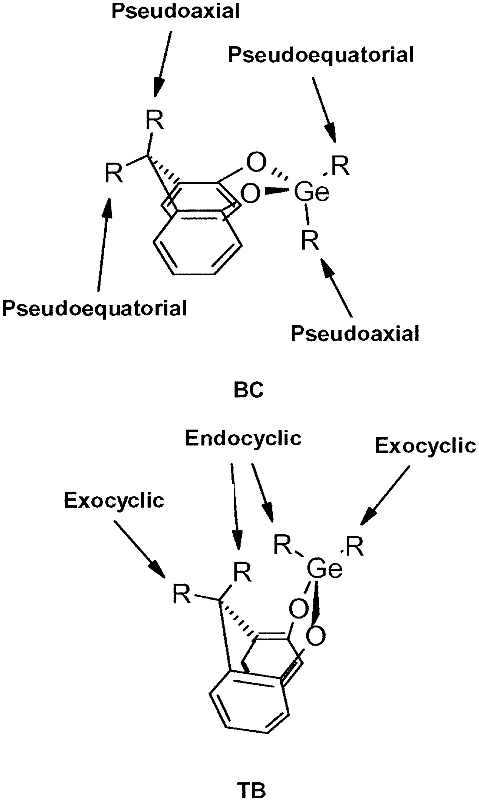


FIGURE 4 Pseudoaxial and pseudoequatorial positions in the BC conformation, and endocyclic and exocyclic positions in the family of TB conformations.

was prepared by the reaction of **4b** with the 2,2′-ethylidenebisphenol **6**. In the ^{1}H NMR spectrum ($CDCl_3$) of **7** at 27°C, two singlets are observed at δ −0.17 and δ 1.04 that were assigned to the protons of two nonequivalent methyl groups bonded to germanium. The observation of anisochronous methyl group protons suggests that the ring system is conformationally biased on the NMR time scale at probe temperature (27°C). The degree of nonequivalence of the anisochronous methyl group protons ($\Delta\delta = 1.21$ ppm) is consistent with a BC conformation (see Table I).[12] We have previously employed NOE studies to probe the solution conformation of eight-membered rings containing silicon.[12] An NOE study of **7** in solution showed the absence of a NOE enhancement between the C(12) methine proton and the protons

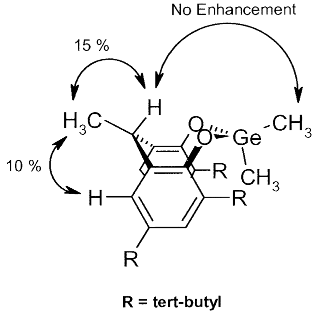
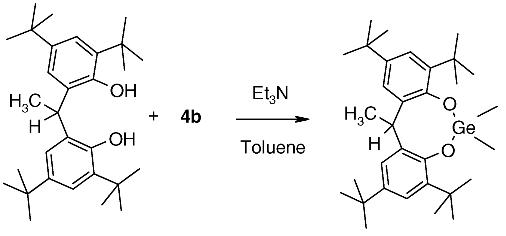


FIGURE 5 NOE enhancements observed upon irradiation of the C(12) methyl substituent in **7**.

of either of the methyl groups bonded to silicon (see Figure 5). A NOE enhancement was observed between the methyl group protons bonded to the C(12) methine carbon atom and the C(2) and C(10) *tert*-butyl substituent protons (10%). This observation supports the suggestion that **7** adopts a BC conformation in which the C(12) methyl substituent is pseudoequatorial.



6 **7**

CONCLUSIONS

The conformational analysis of the 12*H*-dibenzo[*d*, *g*][1,3,2]germocin ring suggests that the ring conformations observed can be interpreted based upon the steric interactions of the ring substituents, albeit subtle electronic effects cannot be excluded. As previously observed in the corresponding phosphorus and silicon heterocycles, the results of this study suggest that the exocyclic (or pseudoequatorial) preference for an alkyl or phenyl substituent bonded either to germanium or the C(12) carbon is larger than the difference in energy between a BC and TB in the 12*H*-dibenzo[*d*, *g*][1,3,2]germocin ring system.[12]

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (499.84) spectra were taken on a Varian Model Unity-500 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddq, doublet of doublets of quartets; br, broad), atom assignments, coupling constant in Hertz, and number of protons. 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 flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, New Jersey.

X-Ray Studies: The x-ray crystallographic studies were performed using an Nonius Kappa CCD difractometer and graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Data were collected at $23 \pm 2^\circ$C for $\theta_{\mathrm{MoK}\alpha} \leq 25^\circ$. All data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2 and computations were performed on a 600 MHz Pentium III computer using SHELXS-86 for solution[18] and SHELXL-97 for refinement.[19] All of the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (for C30 and C31) on the bonded atoms. The figures were generated using ORTEP-III for Windows program.[20]

2,2′-$CH_2(4,6\text{-di-}^tBuC_6H_4O)_2GePh_2$ (5a)

To a solution of **4a** (1.00 g, 3.1 mmol) in 9 mL of toluene was added dropwise over 10 min a solution of **3a** (1.06 g, 2.5 mmol) and triethylamine (0.51 g, 5 mmol) in 10 mL of toluene. After the addition was complete, the reaction mixture was heated to 70°C for 24 h. The resultant precipitate of triethylamine hydrochloride was removed by filtration. The volatiles were removed sin vacuo and the residue was recrystallized from a mixture of toluene (10 mL) and acetonitrile (20 mL) to give 1.18 g (73%) of a white solid, m.p. 220–221°C: ^{1}H NMR ($C_2D_2Cl_4$; 110°C) δ 1.17 (s, 18 H), 1.33 (s, 18 H), 4.15 (br s, 2 H), 7.06 (d, 2 H), 7.25 (m, 4 H), 7.34–7.42 (overlapping m, 6 H), 7.40 (d, 2 H). Anal. Calcd for $C_{41}H_{52}O_2Ge$: C, 75.83; H, 8.07. Found: C, 75.74; H, 8.06.

2,2′-CH_2(4,6-di-^{t}Bu-3-Me–$C_6H_4OH)_2$ (3b)

To a stirred mixture of 4,6-di-*tert*-butyl-3-methylphenol (110.17 g; 0.5 mmol) and paraformaldehyde (7.9 g at 95% assay; 0.25 mmol) in 125 mL heptane at 6°C was added a catalytic amount of concentrated sulfuric acid (0.37 g; 3.57 mmol). The reaction mixture was stirred at 5–6°C for 30 min and then the mixture was stirred at ambient temperature for 48 h. The reaction mixture was heated at reflux temperature and water was removed using a Dean-Stark trap (5 mL). The reaction mixture was allowed to set overnight at room temperature and the resultant solid was collected by filtration. The filter cake was washed sequentially with cold heptane (300 mL), distilled water (200 mL), and methyl alcohol (200 mL). The solid was dissolved in a mixture of heptane (300 mL) and toluene (200 mL) at reflux temperature to which activated charcoal (2.0 g) was added. The mixture was filtered hot and the solid that precipitated upon cooling was collected by filtration to give 47.88 g (42%) of a white solid, m.p. 213– 215°C (lit[21] 215.3–216.3°C). ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 18 H), 1.46 (s, 18 H), 2.55 (s, 6 H), 4.11 (s, 2 H), 5.21 (s, 2 H), 7.30 (2 H); MS m/z 452 (molecular ion). Anal. Calcd for $C_{31}H_{48}O_2$: C, 82.25; H, 10.69. Found: C, 82.24; H, 10.63.

2,2′-CH_2(4,6-di-^{t}Bu-3-Me–C_6H_4O)$GeMe_2$ (5b)

The procedure used to prepare compound **5a** was followed using **4b** (5.00 g, 28.8 mmol), **3b** (6.52 g, 14.4 mmol), and triethylamine (5.83 g, 57.6 mmol) in 130 mL of toluene (65–70°C for 15 h). The residue was recrystallized from a mixture of acetonitrile (200 mL) and toluene (30 mL) to give 5.79 g (72.6%) of colorless needles, m.p. 223–224.5°C. ^{1}H NMR ($CDCl_3$) δ 0.79 (br s, 6 H), 1.36 (s, 18 H), 1.41 (s, 18 H), 2.36 (s, 6 H), 3.83 (s, 2 H), 7.22 (2 H); MS m/z 550 (molecular ion) The desired molecular ions ($M^{+\cdot}$) 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 $C_{33}H_{52}GeO_2$: C, 71.63; H, 9.47. Found: C, 71.59; H, 9.26.

2,2′-CH_2(4,6-di-^{t}Bu-3-Me$C_6H_3O)_2GePh_2$ (5c)

The procedure used to prepare compound **5a** was followed using **4a** (5.00 g, 17 mmol), **3b** (4.53 g, 10 mmol), and triethylamine (3.44 g, 34 mmol) in 90 mL of toluene (80°C for 13 h). The volatiles were removed in vacuo and the residue was recrystallized from a mixture of toluene (17 mL) and acetonitrile (20 mL) to give 5.19 g (77%) of a white solid, m.p. 221–222°C: ^{1}H NMR ($CDCl_3$)(300.0802 MHz) δ 1.26 (s, 18 H); 1.39 (s, 18 H), 2.24 (s, 6 H), 3.85 (br s, 2 H), 7.21 (s, 2 H), 7.35 (m, 4 H), 7.45 (m, 2 H), 7.59 (m, 4 H). Anal. Calcd for $C_{43}H_{56}O_2Ge$: C, 76.23; H, 8.33. Found: C, 76.31; H, 8.28.

Crystallographic Data: Suitable crystals for x-ray analysis were grown from a 1:1 mixture by volume of toluene and acetonitrile. Crystal data: $C_{43}H_{56}GeO_2$; formula weight (g.mol) = 677.47; crystal size (mm) 0.75 × 0.75 × 0.75; crystal system is monoclinic; cell parameters: a = 13.8578 (2) Å, b = 15.4352 (2) Å, c = 19.1738 Å (3); $\alpha = 90.00°$; $\beta = 110.2107$ (6)°$\gamma = 90.00°$; V = 3848.72 (9) Å^3; space group = P2(1)/n; $d_{calc} = 1.169$ Mg.m^{-3}; Z = 4; R indices: R = 0.0421, $R_w = 0.0867$.

2,2′-$CHCH_3$(4,6-di-^{t}BuC_6H_4O)$_2$GeMe$_2$ (7a)

To a stirred solution of **4b** (1.04 g, 5.8 mmol) in 10 mL of toluene was added dropwise over 35 min a solution of **6** (2.00 g, 4.6 mmol) and triethylamine (1.17 g, 11.6 mmol) in 25 mL of toluene. The reaction mixture was heated at 70°C for 21 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 (20 mL) to give 1.95 g (79%) of a white solid, m.p. 180–181°C: ^{1}H NMR (C_6D_6, 27°C) δ −0.25 (s, 3 H), 0.75, (s, 3 H), 1.39 (s, 18 H); 1.46 (s, 18 H), 1.58 (d, $^3J_{HCCH} = 7.5$ Hz, 3 H), 5.53 (q, $^3J_{HCCH} = 7.5$ Hz, 1 H), 7.34 (d, $^4J_{HCCH} = 2.7$, Hz, 2 H), 7.75 (d,$^4J_{HCCH} = 2.7$, 2 H); ^{1}H NMR ($CDCl_3$, 27°C) δ −0.17 (s, 3 H), 1.04, (s, 3 H), 1.32 (s, 18 H); 1.37 (s, 18 H), 1.55 (d, 3 H), 5.09 (q, 1 H), 7.11 (d, 2 H), 7.45 (d, 2 H); Carbon assignments by DNOE, APT, and HMQC experiments. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 27°C) δ −1.44 (s, GeCH_3), 0.83 (s, GeCH_3), 23.04, CH$\underline{C}H_3$), 29.66 (s, $\underline{C}HCH_3$), 30.61 (s, C($\underline{C}H_3$)$_3$), 31.64 (s, C($\underline{C}H_3$)$_3$), 34.46 (s, $\underline{C}(CH_3)_3$), 35.23 (s, $\underline{C}(CH_3)_3$), 121.02 (s), 121.71 (s), 138.08 (s), 138.53 (s), 143.31 (s), 151.89 (s). Anal. Calcd for $C_{32}H_{50}O_2Ge$: C, 71.26; H, 9.34. Found: C, 71.28; H, 9.37.

REFERENCES

[1] L. D. Quin, in *Conformational Analysis of Medium-Sized Heterocycles*, edited by R. S. Glass (VCH: Weinheim, 1988), pp. 181–216.

[2] R. R. Holmes, T. K. Prakasha, and S. D. Pastor, in *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, edited by L. D. Quin, J. G. Verkade (VCH: New York, 1994), pp. 27–39.

[3] a) G. J. H. Buisman, P. C. J. Kamer, and P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry*, **4,** 1625 (1993). b) P. W. N. M. van Leeuwen, G. J. H. Buisman, A. van Rooy,

and P. C. J. Kamer, *Recl. Trav. Chim. Pays-Bas,* **113,** 61 (1994); c) T. Jongsma et al., *J. Molecular Cat.*, **83,** 17 (1993); d) A. van Rooy et al., *Organometallics*, **14,** 34 (1995); e) G. J. H. Buisman et al., *Tetrahedron: Asymmetry*, **6,** 719 (1995); f) A. van Rooy et al., *J. Organometal. Chem.*, **494,** C15 (1995).

[4] a) R. R. Holmes and J. A. Dieters, *Inorg. Chem.*, **33,** 3235 (1994); b) R. R. Holmes, *Acc. Chem. Res.*, **31,** 535 (1998); c) D. J. Sherlock et al., *Inorg. Chem.*, **37,** 93 (1998); d) A. Chandrasekaran et al., *Inorg. Chem.*, **37,** 459 (1998); e) P. Sood et al., *Inorg. Chem.*, **37,** 3747 (1998); f) N. V. Timosheva et al., *Inorg. Chem.*, **37,** 3862 (1998); g) P. Sood et al., *Inorg. Chem.*, **37,** 6329 (1998).

[5] a) S. D. Pastor et al., *J. Org. Chem.*, **49,** 1297 (1984); b) S. D. Pastor et al., *J. Heterocycl. Chem.*, **21,** 1285 (1984); c) S. D. Pastor et al., *Phosphorus Sulfur*, **32,** 105 (1987).

[6] a) C. Y. Wong et al., *Inorg. Chem.*, **35,** 325 (1996); b) H. Lau et al., *Angew. Chem. Int. Ed.*, **37,** 1098 (1998).

[7] S. D. Pastor et al., *Phosphorus, Sulfur, Silicon Relat. Elem.*, **115,** 169 (1996).

[8] S. D. Pastor et al., *Phosphorus, Sulfur, Silicon Relat. Elem.*, **139,** 87 (1998).

[9] S. D. Pastor et al., *Inorg. Chem.*, **36,** 5966 (1997).

[10] T. Thompson et al., *Inorg. Chem.*, **38,** 4163 (1999).

[11] a) J. B. Hendrickson, *J. Am. Chem. Soc.*, **86,** 485 (1964); b) R. R. Fraser et al., *Can. J. Chem.*, **53,** 167 (1975); c) F. A. L. Anet and I. Yavari, *J. Am. Chem. Soc.*, **99,** 6986 (1977); d) J. A. Moore and F. A. L. Anet, In *Comprehensive Heterocyclic Chemistry*, edited by W. Lwowski (Pergamin Press, Oxford, 1984), vol. 7, pp. 653–707; e) R. P. Arshinova et al., *Phosphorus Sulfur Silicon Relat. Elem.*, **34,** 1 (1987); f) R. P. Arshinova, *Russian Chem. Rev.*, **57,** 1142 (1988).

[12] L. P. Burke et al., *J. Am. Chem. Soc.*, **119,** 8313 (1997).

[13] a) R. P. Arshinova, *Phosphorus Sulfur Silicon Relat. Elem.*, **68,** 155 (1992); b) B. A. Arbusov et al., *Dokl. Akad. Nauk SSSR (Engl. Transl.)*, **305,** 80 (1989).

[14] a) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85,** 1899 (1963); b) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42,** 1339 (1965); c) M. Barfield and S. Sternhell, *J. Am. Chem. Soc.*, **94,** 1905 (1972); d) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **83,** 4726 (1964).

[15] E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, (Wiley: New York, 1994) 2nd ed., pp. 641–647.

[16] L. S. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* (Pergamon, Oxford, UK, 1969), 2nd ed., pp. 270–279.

[17] P. Hug et al., *Helv. Chim. Acta*, **73,** 618 (1990).

[18] G. M. Sheldrick, *Acta Crystallogr.*, **A46,** 467 (1990).

[19] G. M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Gottingen (Gottingen, Germany, 1997).

[20] L. J. Farrugia, ORTEP-III for Windows, *J. Appl. Cryst.*, **30,** 565 (1997).

[21] D. J. Beaver and P. J. Stoffel, *J. Am. Chem. Soc.*, **74,** 3410 (1952).