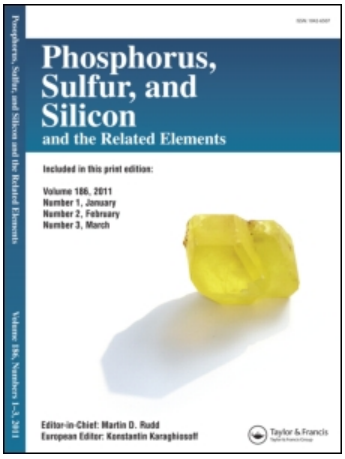

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The Conformation of Sterically Congested Seven-Membered Rings Containing Tetracoordinate Germanium(IV): A First X-Ray Crystallographic Structure Determination

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The X-ray crystallographic analysis of 6,6-dimethyl-2,4,8,10-tetra-tert-*octyl-dibenzo[*d,f*][1,3,2]dioxagermepin,* ***1*** *is reported. In the solid-state conformation of* ***1****, the dihedral angle about the C—C* sp^2-sp^2 *σ bond connecting the two aryl rings is 50.1°. The observed* C_2 *symmetry in the solid-state conformation of* ***1*** *is consistent with the previously suggested solution conformation.*

Keywords Conformational analysis; dibenzo[*d*, *f*][1,3,2]dioxagermepin; germanium; seven-membered rings; solid-state conformation; x-ray crystal structure

INTRODUCTION

Recently, a significant amount of research has focused on the synthesis and conformational analysis of hetero-substituted medium-sized rings.[1] In particular, studies on the spectral characteristics[2,3] and ligand properties[4] 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.[5] A crystallographic study of dibenzo[*d*, *f*][1,3,2]dioxaphosphepin derivatives by Malen et al.[6] elucidated the effect of substitution upon the conformation of the ring. The synthesis of the

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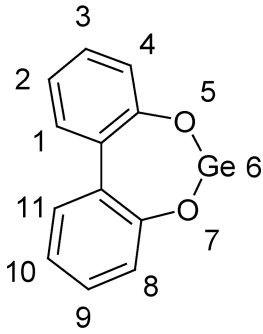


FIGURE 1 *Chem. Abstr.* numbering system for the dibenzo[*d*, *f*][1,3,2]dioxagermepin ring system.

corresponding dibenzo[*d*, *f*][1,3,2]dioxasilepin ring system has been reported[7–9] and Swamy et al.[10] prepared anionic five-coordinate silicates containing a dibenzo[*d*, *f*][1,3,2]dioxasilepin ring.

In their pioneering studies, Silcox and Zuckerman,[7] Zuckerman,[11] and Müller and Heinrich[12] reported the first synthesis and characterization of the dibenzo[*d*, *f*][1,3,2]dioxagermepin ring system (Figure 1). Recently, we reported the synthesis and characterization of sterically congested mono- and spirocyclic dibenzo[*d*, *f*][1,3,2]dioxagermepin derivatives.[13] The solution VT NMR spectral data is consistent with the rapid ring inversion ($\Delta G^*_{288.15} = 13.8$ kcal $\cdot$ mol^{-1}) of the seven-membered dibenzo[*d*, *f*][1,3,2]dioxagermepin ring (atropisomerism about the sp^2-sp^2 single bond connecting the two aryl rings) at an ambient temperature. We report herein the first X-ray crystallographic characterization of a sterically congested dibenzo[*d*, *f*][1,3,2]dioxagermepin ring.

RESULTS AND DISCUSSION

A C_2 symmetric conformation was found in the solid-state crystallographic structure of **1** (Scheme 1, Table I, Figure 2). Given the posit that tetrahedral geometry is achieved when the sum of the requisite bond angles about germanium is 328.5° (for "pure" sp^3 character), the sum of the O(1)—Ge—O(1′), C(1)—Ge—O(1′), and C(1)—Ge—O(1) bond angles (106.9°, 112.5°, and 102.3°, respectively) is consistent with the tetrahedral geometry at Ge ($\sum$ bond angles = 321.7°) (Table II). The Ge—O bond length in **1** [Ge—O(1) = 1.77 Å] is in the range previously observed for a Ge—O bond.[14–16] The Ge—C(1) bond length (1.89 Å) is slightly shorter than those previously observed for a Ge—C single bond (1.92–1.94 Å).[15,17–18]

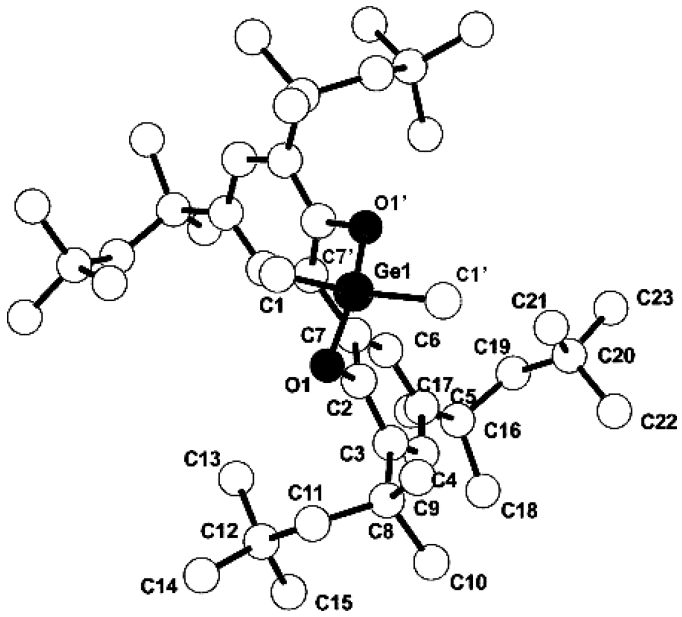


FIGURE 2 Molecular structure of **1** showing the crystallographic numbering scheme.

The dihedral angle [C(6)—C(7)—C(7′)—C(6′)] about the C—C sp^2-sp^2 σ bond connecting the two aryl rings is 50.1°. The C(7)—C(7′) sp^2-sp^2 bond length is 1.485 Å, which is in the range reported for C—C sp^2-sp^2 bond lengths in biphenyls.[19] The observed C_2 symmetry in the solid-state crystallographic data of **1** is consistent with the previous suggestion based upon VT NMR spectral data in a solution of rapid atropisomerism at an ambient temperature about the C—C single bond connecting the two aryl groups in the seven-membered dibenzo[*d*, *f*][1,3,2]dioxagermepin.[13] The magnitude of the dihedral angle connecting the aryl ring in the seven-membered germanium heterocycle **1** is similar in magnitude to the corresponding phosphorus system that has bulky substituents on the annulated aryl rings (47.4–52.0°).[3,5,20,21]

EXPERIMENTAL

The 6,6-dimethyl-substituted dibenzo[*d*, *f*][1,3,2]dioxagermepin derivative **1** was prepared as previously reported by Pastor et al.[13] by the reaction of the corresponding *tert*-octyl-substituted 1,1′-biphenyl-2,2′-diol with dimethylgermanium dichloride using triethylamine as a hydrogen chloride acceptor.

TABLE I Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for Germepin 1. U(eq) Is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

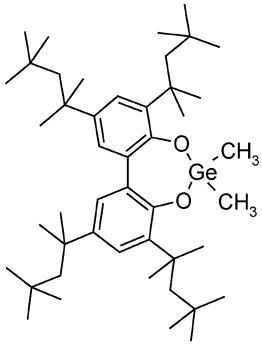
	x	y	z	U (eq)
Ge(1)	5000	4386(1)	7500	102(1)
O(1)	4532(1)	5320(2)	7914(1)	62(1)
C(11)	3388(1)	5567(3)	8496(2)	68(1)
C(9)	3437(2)	4316(3)	7285(2)	92(1)
C(2)	4334(1)	6305(3)	7487(2)	55(1)
C(8)	3352(1)	5601(3)	7568(2)	70(1)
C(10)	2758(1)	5910(4)	7189(2)	107(2)
C(3)	3773(1)	6446(3)	7274(2)	61(1)
C(5)	3963(1)	8311(3)	6610(2)	63(1)
C(16)	3760(2)	9379(3)	6090(2)	78(1)
C(1)	5326(2)	3550(7)	8409(6)	286(6)
C(6)	4507(1)	8175(3)	6887(2)	62(1)
C(7)	4708(1)	7178(3)	7329(2)	55(1)
C(4)	3608(1)	7444(3)	6836(2)	67(1)
C(12)	3397(2)	6675(4)	9040(2)	82(1)
C(18)	3133(2)	9469(5)	5980(4)	179(3)
C(13)	3947(2)	7323(4)	9105(3)	113(2)
C(14)	3314(2)	6183(5)	9870(2)	123(2)
C(19)	3965(3)	9355(3)	5282(3)	115(2)
C(20)	3935(2)	8388(4)	4674(3)	110(2)
C(21)	4200(2)	7253(4)	4952(3)	130(2)
C(15)	2931(2)	7556(4)	8782(3)	131(2)
C(17)	3971(4)	10493(4)	6506(4)	180(3)
C(22)	3370(4)	8100(12)	4325(7)	400(11)
C(23)	4188(7)	8813(8)	3972(5)	349(9)

2,4,8,10-Tetrakis(1,1,3,3-tetramethylbutyl)-6,6-dimethyldibenzo[*d,f*][1,3,2]dioxagermepin (1) *Crystallographic Data*

Suitable crystals for X-ray analysis were grown by a slow diffusion acetonitrile vapor into a toluene solution of **1**. Formula: $C_{46}H_{78}GeO_2$; formula weight (g/mol) = 735.67; crystal size (mm) $0.30 \times 0.30 \times 0.25$;

TABLE II Selected Bond Lengths (Angstroms) and Bond Angles (Degrees) for Germepin 1

Ge(1)—O(1)	1.770(2)	O(1)—Ge(1)—O(1′)	106.85(13)
Ge(1)—C(1)	1.889(6)	O(1′)—Ge(1)—C(1)	112.54(19)
O(1)—C(2)	1.381(3)	O(1)—Ge(1)—C(1)	102.3(3)
C(7)—C(7′)	1.485(5)	C(1)—Ge(1)—C(1′)	120.0(6)
		C(2)—O(1)—Ge(1)	118.84(17)



1

SCHEME 1

crystal system is monoclinic; cell measurement temp = 293 (2). Cell parameters: a = 24.7032 (18) Å, b = 11.2959 (9) Å, c = 16.8116 Å (13); $\alpha = 90.00^\circ$; $\beta = 97.179$ (2)$^\circ$ $\gamma = 90.00^\circ$; V = 4654.4 (6) Å^3; space group = C2/c; $d_{calc} = 1.050$ Mg · m^{-3}; Z = 4. Data collection: Bruker AXS diffractometer; MoKα ($\lambda = 0.71073$ Å) radiation; graphite monochromator; R indices [I > 2sigma(I)]: R = 0.0616, $R_w = 0.1731$; goodness-of-fit on $F^2 = 0.813$; largest diff. Peak and hole = 0.354 and −0.546 e.A^{-3}. Refinement method: Full-matrix least-squares on F^2, Program: SHELXS-97. Dihedral angles of **1** were measured from the crystallographic information file (CIF file) using the program Mercury version 1.3, which is a copyright work belonging to the Cambridge Crystallographic Data Center (CCDC).

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