94. The Conformation of Medium-Sized Organosilicon Heterocycles: First Evidence for the Existence of a Boat-Boat Conformation in a 12*H*-Dibenzo[*d*,*g*][1,3,2]dioxasilocin

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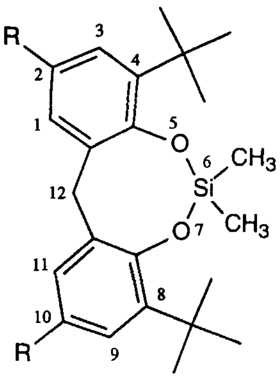
X-Ray crystal-structure analysis of 2,4,8,10-tetrakis(1,1-dimethylethyl)-6,6-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]-dioxasilocin showed that its eight-membered organosilicon heterocycle adopts a boat-boat (*BB*) conformation in the solid state (*Figs. 2* and *3*).

Although the conformational analysis of both carbocyclic and small-membered heterocyclic compounds has played a key role in the development of mechanistic and synthetic chemistry, the conformational analysis of medium-sized heterocycles has not received much attention until very recently[1]). The synthesis of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring system was described in the pioneering work of *Zuckerman* [2][2]). In 1984, we reported a solution ^{1}H-NMR study of **1** [4], for which the $\Delta G^{\neq}_{279}$ for ring inversion (13.9 kcal/mol) was obtained by variable-temperature NMR[3]). The ^{1}H- and ^{13}C,^{1}H-NMR spectrum below the coalescence temperature requires that a σ plane of symmetry pass through C(12) and the Si-atoms of the ring [4]. We suggested that the



1 R = *t*-Bu
2 R = Me

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[1]) For a review of recent activity, see [1].

[2]) For other ref., see [3].

[3]) For a review on methods to determine thermodynamic parameters by dynamic NMR, see [5].

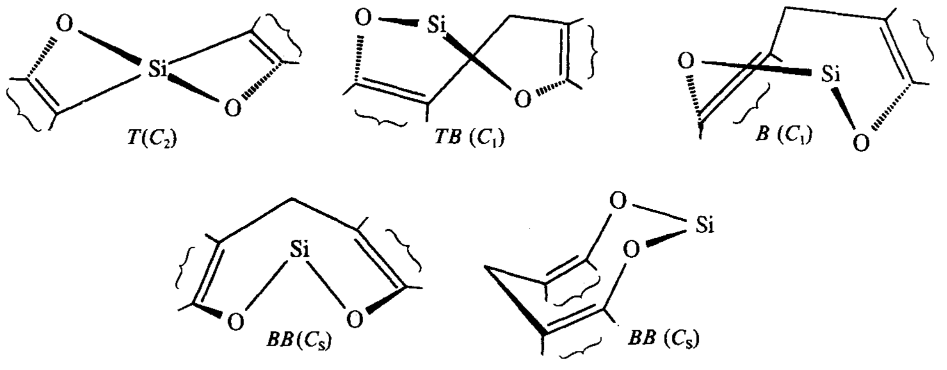

Fig. 1. *Conformations of the 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin ring system.* For convenience, the annulated benzo moieties and substituents on the Si-atom are emitted. The *TB* conformation illustrated represents only one member of a family of *TB* forms.

spectral data was consistent with either a boat-chair (*BC*) or boat-boat (*BB*) conformation for **1** (*Fig. 1*)[4]. The dynamic NMR data, however, did not exclude twisted conformations that rapidly pass through the required symmetry plane.

In a recent dynamic NMR study of **2**, *Arbuzov et al.* suggested that **2** existed in a *BC* conformation in solution and further excluded consideration of the *BB* conformation based upon arguments that suggest a high ground-state energy for this conformation [7]. Similar arguments for excluding the *BB* conformation in the 12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin ring system were forwarded by *Arshinova* based upon MO calculations and a consideration of molecular models[5]. For the first time, in this communication crystallographic data are presented demonstrating the existence of the *BB* conformation in the 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin ring system[6].

Results and Discussion. – The tetra(*tert*-butyl)-substituted 12*H*-dibenzo[*d,g*][1,3,2]-dioxasilocine **1** was prepared by the previously reported methodology [4], and suitable crystals of **1** were grown for X-ray analysis. A nearly perfect *BB* conformation was observed for the eight-membered ring in the X-ray crystal structure of **1** (*Figs. 2* and *3*) [11]. The intramolecular distance between the bridging C(12) and the pseudoaxial C(5) bonded to the Si-atom is 3.15 Å (see *Fig. 2* for numbering) [12]. The Si–O bond lengths (1.62 Å) are within the normally observed range (1.621 Å; $\sigma = 0.022$) [13]. Steric interactions within the *BB* conformation are reduced by a widening of the Si–O–C(arom.) bond angle to 144°. Given the posit that tetrahedral geometry is obtained when the sum of the relevant bond angles approaches 327°, the Si-atom in **1** is tetrahedral (334°).

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[4] For an explanation of these conformational designations, see [6].

[5] For a review of this work, see [8].

[6] For the original suggestion on the possibility of a *BB* conformation in 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins, see [9]. For recent solution NMR studies that suggest the existence of the *BB* conformation in 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocines, see [10].

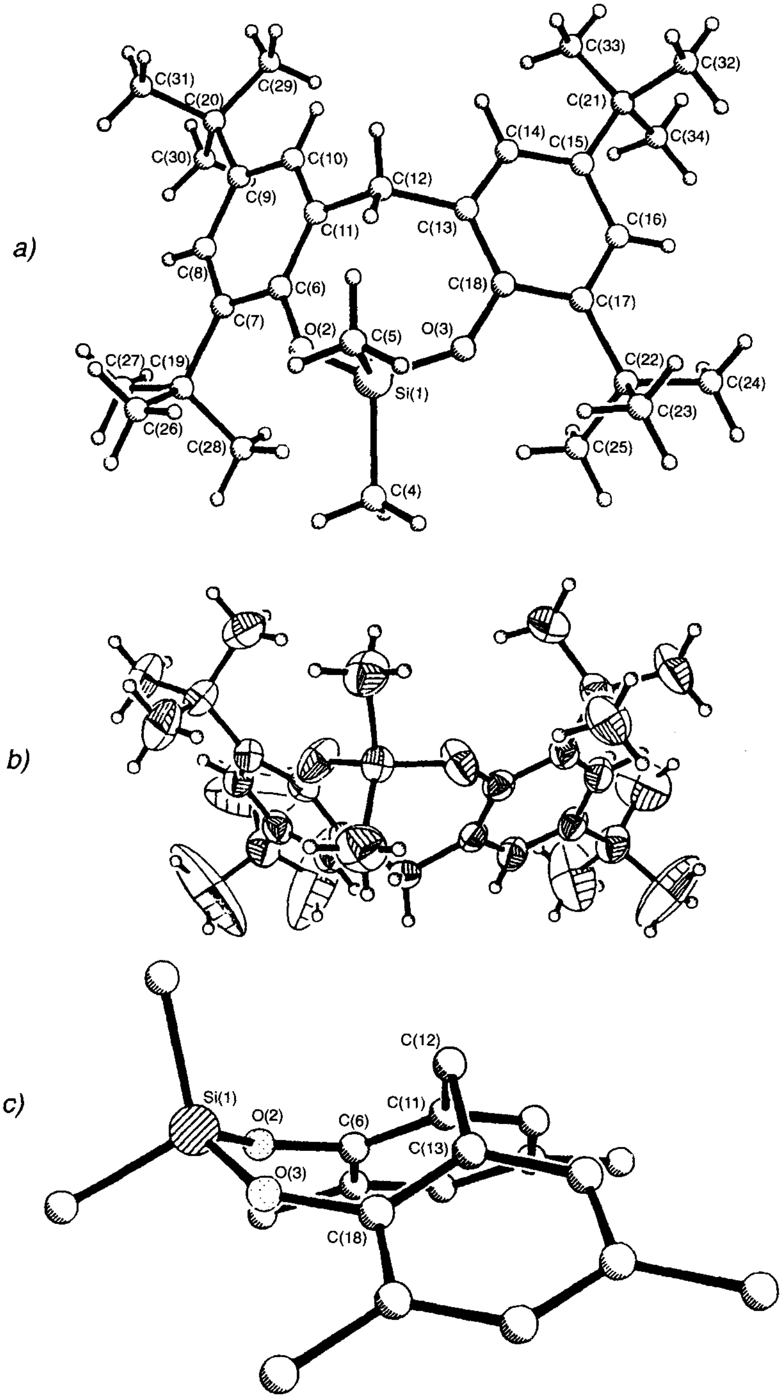
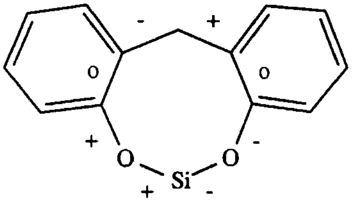


Fig. 2. a) *Ball-and-stick view of* 1 *showing the crystallographic numbering scheme* (arbitrary), b) *molecular structure of* 1 *showing thermal ellipsoids, and* c) *perspective of* 1 *without* tert-*butyl Me groups*



Boat-Boat (C_S)

-	+	- 87	+ 89
o	o	0	0
+	-	+ 8	- 16
+	-	+ 42	- 36

Observed torsional angles in **1**

Fig. 3. *Boat-boat conformation of the 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin ring specified by the signs of the torsional angles following the formalism of* Hendrickson [11]

Conclusions. – The demonstration of the existence of the *BB* conformation in solution is problematic, because extrapolation of the solid-state conformation to solution is complicated by lattice-energy and crystal-packing effects, which may render the conformations different. *Anet* and *Yavari* cautioned that the geometry of flexible conformations can be strongly influenced by crystal-packing forces in the solid state and considerable differences between solution and solid-state conformations may exist [14]. However, the unambiguous observation of a *BB* conformation for the 12*H*-dibenzo[*d,g*][1,3,2]-dioxasilocin ring of **1** in the solid state is a clear warning that the existence of a *BB* conformation cannot be dismissed *a priori*. Earlier pretensions that dismiss the presence of *BB* conformers for 12*H*-dibenzo[*d,g*][1,3,2]dioxametallocin ring systems may in certain cases require re-examination. Indeed, *BB* conformations were observed for certain transition-metal-containing 12*H*-dibenzo[*d,g*][1,3,2]dioxametallocins [15–17].

At present, the preference of **1** for assuming a *BB* conformation can be explained by steric arguments based upon a consideration of both the substitution on the Si-atom and the substituents on the aromatic ring adjacent to the Si-atom. Supportive solid-state and solution studies on an extensive series of 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocine analogues will be reported in due course.

Experimental Part

General. Reagents were purchased from commercial laboratory-supply houses. When necessary, solvents were dried prior to use with appropriate drying agents. Tetrahydrofuran (THF) was distilled immediately prior to use from a deep-blue soln. of sodium ketyl (Na/benzophenone). Reactions were carried out in a flame-dried apparatus under a dry inert atmosphere of either N_2 or Ar. NMR Spectra: *Varian*, model *Unity-500*; ^{29}Si-NMR (99.29 MHz) with full ^{1}H-decoupling and chromium(III) actylacetonate added to increase the relaxation rate; δ (^{29}Si) in ppm rel. to tetramethylsilane, where a positive sign is downfield from the standard.

*2,4,8,10-Tetrakis(1,1-dimethylethyl)-6,6-dimethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin* (**1**). Compound **1** was prepared by the procedure previously reported [4]. ^{29}Si-NMR ($CDCl_3$): −16.8.

X-Ray Crystal Structure of **1**. Suitable crystals (colorless prisms) for X-ray analysis were grown in butan-2-one. Data collection provided 4468 reflections of which 135 were standards and none were rejected. The initial structure solution provided positions for all of the non-H-atoms with CFOM = 0.071. Refinement indicated that a least one *t*-Bu group was disordered, and in the final solution, occupancy for one set of disordered atoms was set at 80%.

Tables of atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, bond lengths, bond angles, and torsion angles were deposited with the *Cambridge Crystallographic Data Center*.

Crystal data: $C_{31}H_{48}O_2Si$; formula weight 479.0 g·mol^{-1}; crystal size 0.1 × 0.1 × 0.3 mm; crystal system, triclinic; $P\bar{1}$ space group; cell parameters $a = 6.260(1)$ Å, $b = 13.305(2)$ Å, $c = 18.909(3)$ Å, $\alpha = 94.04(1)°$, $\beta = 90.02(1)°$, $\gamma = 102.51(1)°$, $V = 1533.7(5)$ Å^3; $Z = 2$; $d_{calc} = 1.037$; absorption coefficient 0.818 mm^{-1}, $F(000) = 524.40$.

Data collection: temp. 32°; *Siemens-R3m/V* diffractometer; CuK_α (λ = 1.54178 Å) radiation; highly orientated graphite crystal monochromator; 2Θ range 3.15 to 115.0°; scan type 2Θ–Θ, scan range (ω) 0.50° plus $K\alpha$ separation scan speed variable; 3.00–14.65° in ω; background measurement, stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time; standard reflections 3 measured every 100 reflections; index ranges, $-6 \leq h \leq 6, -14 \leq k \leq 14, 0 \leq l \leq 20$; reflections collected, 4333; number of observed reflections 3073 ($F > 3.0\sigma(F)$); independent reflections, 4182 (R_{int} = 1.62%).

Solution and refinement: system used, *Siemens* SHELXTL PLUS (VMS); solution, direct methods; refinement method, full-matrix least-squares; quantity minimized, $\Sigma w(F_0-F_c)^2$; H-atoms, riding model, fixed isotropic U; weighing scheme, $w^{-1} = \sigma^2(\mathrm{F}) + 0.0040F^2$; number of raremeters refined, 319; R indices (observed), R = 0.0655, R_w = 0.0925; goodness-of-fit 1.16, largest and mean Δ/σ 2.734 and 0.217, resp.: data-to-parameter ratio 9.6:1; largest difference peak 0.30 eÅ^{-3}, largest difference hole –0.31 eÅ^{-3}.

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