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Communication

Cyclophanes

Synthesis and Conformational Analysis of 2,11-Disila[3.3]metacyclophanes

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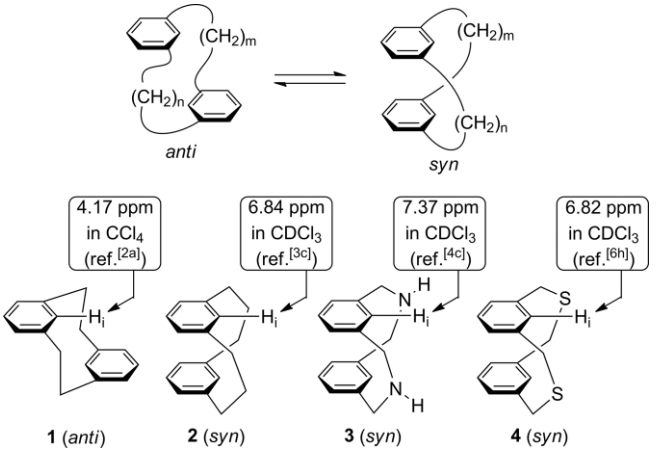
Abstract: Silyl-tethered [3.3]metacyclophanes were prepared and subjected to conformational analysis. The results show that these compounds exist in unprecedented *anti*-rich metacyclophane forms. In the case of 2,2,11,11-tetrasubstituted 2,11-disila[3.3]metacyclophanes, *anti* conformers are lower in energy than their *syn* counterparts. Evidence for this assignment comes from the results of ^{1}H NMR spectroscopic and X-ray crystallographic analyses, along with molecular orbital calculations. However, the 2,2,11,11-tetrahydro derivative displays the opposite behavior, which means that the *syn* conformer is thermodynamically most stable. The *syn*/*anti* ratios of these compounds in solution are governed by temperature and solvent polarity in a manner that can be explained by considering the mixed contributions of $\Delta\Delta G$ and dipole moments.

Introduction

Cyclophanes have been the subject of numerous studies because of their unique properties that are not only reflected in their structures but also in their host–guest characteristics.[1] Among these compounds, particular attention has been given to [*m.n*]metacyclophanes, because they exist as equilibrium mixtures of *syn* and *anti* conformers (Scheme 1). For example, ethylene-bridged [2.2]metacyclophane **1** exists predominantly in the *anti* conformation, as reflected in its ^{1}H NMR spectrum, which contains an unusually upfield-shifted resonance corresponding to its inner hydrogen atoms (H_i) as a consequence of the benzene ring current effect.[2] In contrast, [3.3]metacyclophanes in which the arene rings are bridged by three carbon atoms,[3] nitrogen-,[4] oxygen-,[5] sulfur-[6] (compounds **2**, **3**, **4**, respectively), or selenium-[7] containing linkages, all exist in the *syn* conformation; therefore, such upfield shifts were not observed in the ^{1}H NMR spectra.

In an earlier effort, we described the synthesis, properties, and chemical reactivities of selected cyclic benzylic silanes.[8] Continuing interest in this family of compounds prompted us to undertake an investigation aimed at the synthesis and conformational analysis of previously unknown silyl-tethered [3.3]metacyclophanes.[9] The results of this effort, described below, have demonstrated that these compounds exist in unexpected *anti*-rich [3.3]metacyclophane conformations.



Scheme 1. Conformations (*anti* and *syn*) of [*m.n*]metacyclophanes.

Results and Discussion

The preparative method used to synthesize the silyl-tethered [3.3]metacyclophanes involves Grignard reactions between *m*-xylylene dichloride (**5**) and dichlorosilanes (Scheme 2). For example, the reaction of magnesium with a mixture of **5** (50 mmol) and dichlorodimethylsilane (**6a**, 60 mmol) in THF gives a product mixture containing cyclic dimer **7a**, cyclic trimer **8a**, and unidentifiable cyclic oligomers. HPLC (GPC) separation of the mixture generates **7a** and **8a** in 36 and 25 % isolated yields, respectively. Reaction of **5** with dichlorodiphenylsilane (**6b**), performed in a similar manner, gives cyclic dimer **7b**, trimer **8b**, and tetramer **9b** in 19, 7, and 2 % yield, respectively. Finally, reaction of **5** with dichloromethylphenylsilane (**6c**) leads

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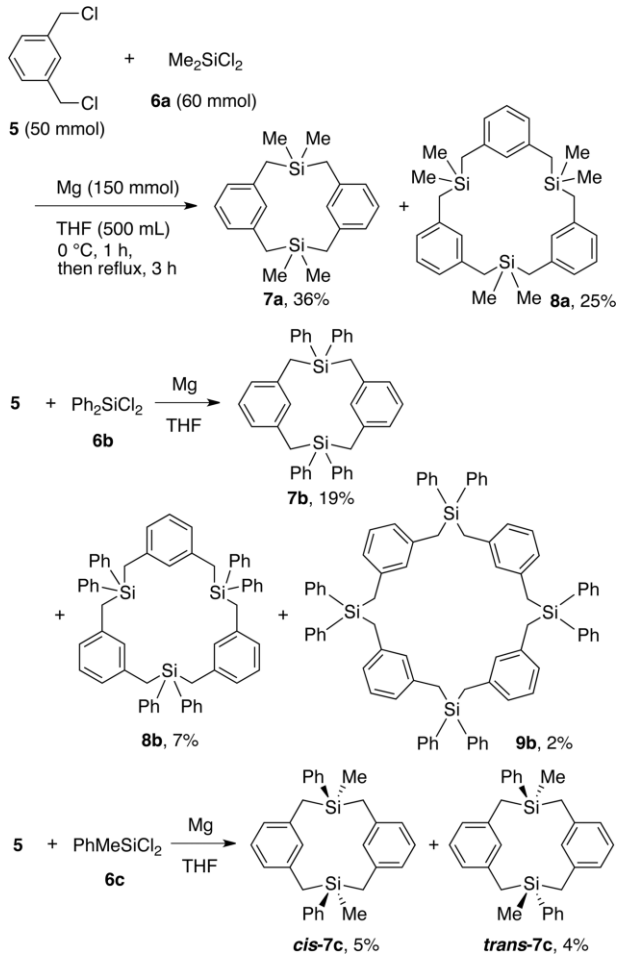
to production of two cyclic dimers, ***cis*-7c**, ***trans*-7c**, along with two stereoisomeric trimers.



Scheme 2. Synthesis of 2,11-disila[3.3]metacyclophanes.

As described above, the chemical shifts of inner hydrogen atoms in the ^{1}H NMR spectra of metacyclophanes aid in the determination of conformational preferences in these compounds. Interestingly, the ^{1}H NMR spectrum of **7a** in $CDCl_3$ contains an unusual resonance at 6.02 ppm (s, 2 H), which is assigned to inner aromatic hydrogen atoms at C-9 and C-18. For comparison, the inner aromatic protons of cyclic trimer **8a** and *m*-bis[(trimethylsilyl)methyl]benzene (**10**) resonate at more downfield positions (6.63 and 6.69 ppm, respectively). Similarly, resonances for two sets of aromatic protons in **7b** (5.97 ppm), ***cis*-7c** (6.22 ppm), and ***trans*-7c** (6.03 ppm) are also shifted upfield relative to those of **8b** (6.76 ppm), **9b** (6.62 ppm), and *m*-bis[(methyldiphenylsilyl)methyl]benzene (**11**, 6.51 ppm). These observations indicate that **7a**, **7b**, ***cis*-7c**, and ***trans*-7c** exist either predominantly or exclusively in *anti* conformations in $CDCl_3$ at room temperature. This is a surprising finding, because all previously described [3.3]metacyclophanes exist as *syn* structures under comparable conditions.

In order to gain information about the solid-state structures of the new disila[3.3]metacyclophanes, single-crystal X-ray diffraction analyses were performed (Figure 1).[10] The results show that tetraphenyl (compound **7b**) and *trans*-dimethyldiphenyl (compound ***trans*-7c**) derivatives have *anti* structures in the crystalline state and that the two benzene rings in each are aligned in a parallel fashion with the inner aromatic hydrogen atoms located on the faces of the opposing benzene rings [Figure 1(a),(b)]. To explore the reasons for these unusual conformational preferences, related metacyclophanes were subjected to analysis. The tetraphenyl-digerma analog **12**, a previously unknown compound, was prepared by Grignard reaction of **5** with Ph_2GeCl_2. X-ray crystallographic analysis showed that **12** also exists in an *anti* conformation in the crystalline state [Figure 1(c)]. The related sulfur-tethered metacyclophane **4**, which is known to exist in a *syn*-rich form,[6] was synthesized. We have confirmed that the *syn* structure of this compound exists in both the crystalline state [Figure 1(d)] and in $CDCl_3$ at room temperature (inner protons at 6.83 ppm).

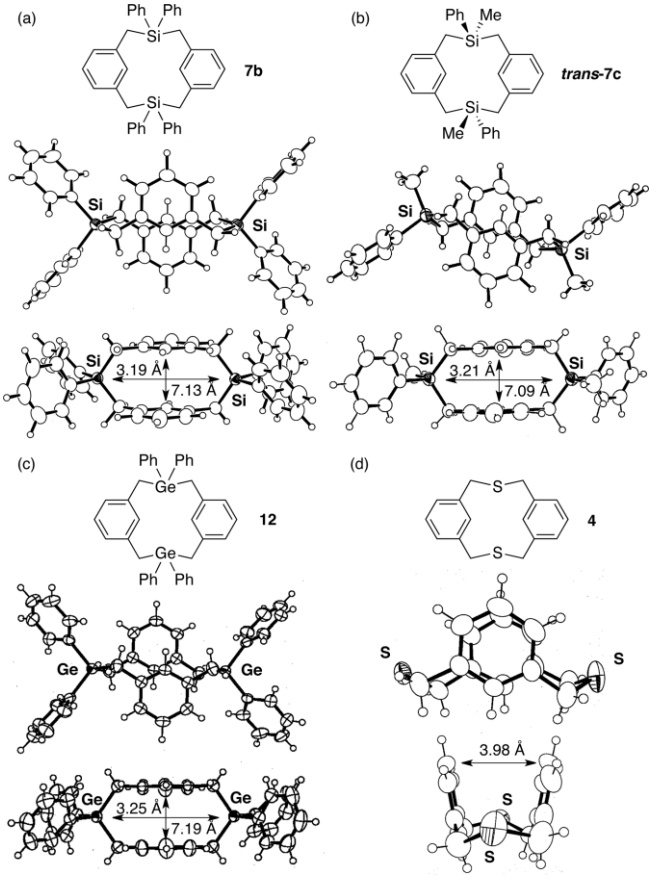
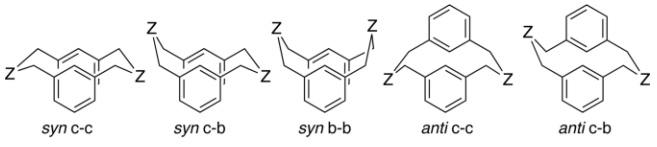


Figure 1. ORTEP drawings of 2,11-disila[3.3]metacyclophanes and the related compounds. (a) **7b**: $C_{40}H_{36}Si_2$; monoclinic; *C*2/*c* (#15); a = 13.666(1) Å; b = 12.2024(9) Å; c = 19.219(1) Å; β = 94.468(5)°; V = 3184.4(4) Å^3; Z = 4; D_{calcd} = 1.195 g cm^{-3}; R = 0.056; R_w = 0.058. (b) ***trans*-7c**: $C_{30}H_{32}Si_2$; monoclinic; *C*2/*c* (#15); a = 17.213(1) Å; b = 6.3969(6) Å; c = 24.605(2) Å; β = 109.423(5)°; V = 2555.1(3) Å^3; Z = 4; D_{calcd} = 1.166 g cm^{-3}; R = 0.059; R_w = 0.069. (c) **12**: $C_{40}H_{36}Ge_2$; monoclinic; *C*2/*c* (#15); a = 13.7000(7) Å; b = 12.3253(5) Å; c = 19.1235(7) Å; β = 96.373(1)°; V = 3209.2(2) Å^3; Z = 4; D_{calcd} = 1.370 g cm^{-3}; R = 0.055; R_w = 0.065. (d) **4**: $C_{16}H_{16}S_2$; monoclinic; $P2_1/n$ (#14); a = 9.155(2) Å; b = 7.9497(9) Å; c = 18.883(4) Å; β = 100.055(4)°; V = 1353.2(4) Å^3; Z = 4; D_{calcd} = 1.337 g cm^{-3}; R = 0.066; R_w = 0.082.

The preference for the *anti* conformation, observed for the silyl- and germyl-tethered metacyclophanes, has been explored by using theoretical methods. Earlier, Mitchell carried out calcu-

lations with metacyclophanes that led to theoretical heats of formation of *syn*-chair-chair, *syn*-chair-boat, *syn*-boat-boat, *anti*-chair-chair, and *anti*-chair-boat conformations.[6v] Referring to the report, we calculated heats of formation of silyl-tethered metacyclophanes and related compounds (Table 1). These results demonstrate that *syn*-chair-chair conformers are the most stable when the metacyclophanes possess carbon-, oxygen-, and sulfur-containing bridges. However, we found that the situation is different in silicon- and germanium-tethered cyclophanes, for which the *anti*-chair-chair forms are calculated to be thermodynamically most stable. Interestingly, theoretical methods show that the *syn*-chair-chair form of the dihydrosilyl-tethered metacyclophane **7d** is of lowest energy. Intrigued by this observation, we prepared **7d** by using HCl promoted dephenylation of the tetraphenyl derivative **7b** (Figure 2). X-ray analysis (Figure 2) showed that, as predicted, this compound possesses a *syn* structure in the crystalline state.

Table 1. Heats of formation of [3.3]metacyclophanes.[a]



Conformer	Relative heats of formation [kcal/mol]							
	Z = CH_2	CMe_2	SiH_2	$SiMe_2$	$SiPh_2$	$GePh_2$	O	S
syn c-c	0	0	0	1.4	2.0	2.4	0	0.1
syn c-b	1.3	4.4	1.5	1.2	2.2	2.5	1.8	0
syn b-b	2.3	2.8	2.9	2.4	3.3	3.5	3.6	0.3
anti c-c	2.7	0.4	0.7	0	0	0	2.5	2.6
anti c-b	2.4	4.0	2.5	2.8	4.4	4.3	4.0	2.0

[a] Relative energies to thermodynamically most stable conformers, calculated by PM3 in MOPAC Ver. 94.10.

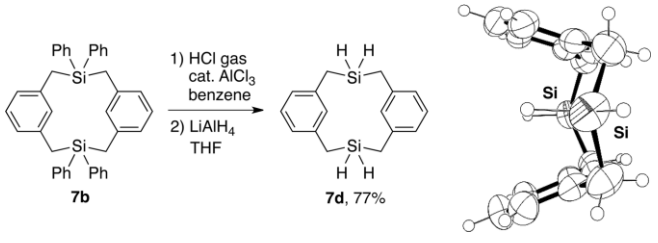


Figure 2. Synthesis and ORTEP drawing of tetrahydro derivative **7d**: $C_{16}H_{20}Si_2$; monoclinic; $P2_1/c$ (#14); a = 11.085(5) Å; b = 10.187(4) Å; c = 13.930(6) Å; β = 93.15(4)°; V = 1570(1) Å^3; Z = 4; D_{calcd} = 1.135 g cm^{-3}; R = 0.060; $R1$ = 0.054.

Variable-temperature ^{1}H NMR spectroscopy was employed to investigate the effect of temperature on the conformational equilibrium of the sila-linked metacyclophanes. Inspection of the spectra shows that the chemical shift of the inner hydrogen atoms (H_i) of tetraphenyl derivative **7b** is 5.97 ppm at room temperature both in $CDCl_3$ and CD_2Cl_2 [Figure 3(a),(b)]. The signal gradually migrates upfield when the CD_2Cl_2 solution is cooled, reaching 5.91 ppm at –90 °C [Figure 3(h)]. On the other hand, the inner hydrogen atoms of tetrahydro derivative **7d** shift in the opposite direction upon cooling, the H_i signal appearing at 6.28 ppm at room temperature in CD_2Cl_2 [Figure 3(k)] and 6.67 ppm at –90 °C [Figure 3(q)]. ^{1}H NMR spectra of CD_2Cl_2 solutions of the reference compounds, *m*-bis[(methyldiphenylsilyl)methyl]benzene (**11**) and *m*-bis[(dihydromethylsilyl)-methyl]benzene (**13**), at room temperature are shown in Figure 3(i) and (r). The chemical shifts of the benzylic protons remain nearly the same when solutions of these compounds are cooled to –90 °C. The difference in chemical shift ($\Delta\delta$) for H_i between tetraphenyl derivatives **7b** at –90 °C and **11** at room temperature is 0.65 ppm, whereas $\Delta\delta$ for the related tetrahydro derivative pair at the same temperatures is 0.15 ppm. These observations are in accord with the assumption that at lower temperature the conformational equilibrium of **7b**, already biased toward the *anti* form at room temperature, shifts to favor the *anti* form even more. However, in the case of **7d**, the equilibrium shifts in the opposite direction to favor the *syn* form more at lower temperature.

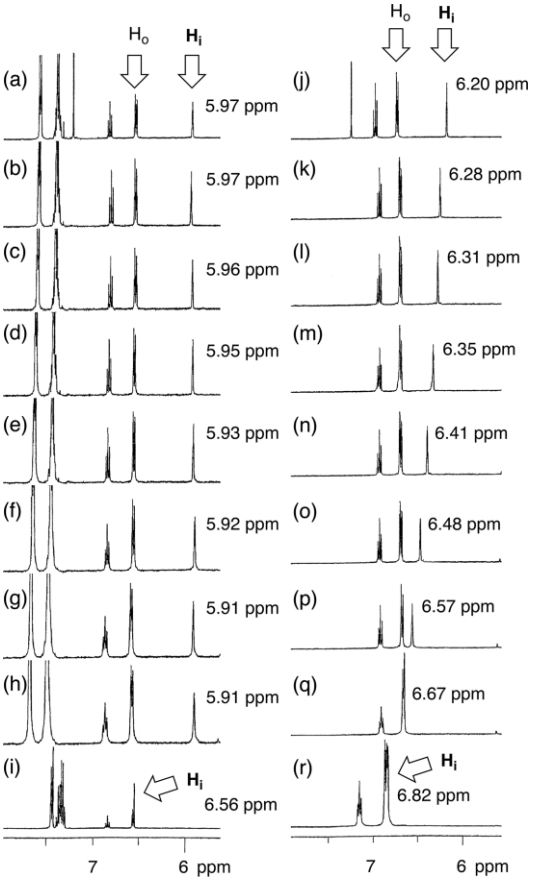


Figure 3. Variable-temperature ^{1}H NMR spectra of **7b** and **7d**. Left: ^{1}H NMR spectra of **7b** in $CDCl_3$ at room temperature (a), in CD_2Cl_2 at room temperature (b), 10 °C (c), –10 °C (d), –30 °C (e), –50 °C (f), –70 °C (g), –90 °C (h), and that of *m*-bis[(methyldiphenylsilyl)methyl]benzene (**11**) in CD_2Cl_2 at room temperature (i). Right: ^{1}H NMR spectra of **7d** in $CDCl_3$ at room temperature (j), in CD_2Cl_2 at room temperature (k), 10 °C (l), –10 °C (m), –30 °C (n), –50 °C (o), –70 °C (p), –90 °C (q), and that of *m*-bis[(dihydromethylsilyl)methyl]-benzene (**13**) in CD_2Cl_2 at room temperature (r). H_i indicates signals of inner aromatic hydrogen atoms. H_o indicates signals of hydrogen atoms at 5,7,14,16-positions of **7b** and **7d**.

The effect of solvents on the ^{1}H NMR chemical shifts of the sila-linked metacyclophanes was investigated. The resonance for the inner hydrogen atoms in **7d**, appearing at 6.06 ppm in [D_{12}]cyclohexane (Figure 4), shifts downfield in the following

solvents: $CDCl_3$ (6.20 ppm), CD_2Cl_2 (6.28 ppm), and CD_3CN (6.51 ppm), while the other proton resonances in this compound remain nearly unchanged. Similarly, the chemical shift of the inner hydrogen atoms of **7a** experiences a solvent-dependent downfield shift in the following manner: [D_{12}]cyclohexane (5.89 ppm), $CDCl_3$ (6.02 ppm), CD_2Cl_2 (6.06 ppm), and CD_3CN (6.23 ppm) (see Supporting Information). The results suggest that, while the *anti* conformer is favored in less polar solvents, the proportion of the *syn* conformer increases in polar solvents. This solvent effect is perhaps related to differences in the dipole moments of the conformers (Scheme 3). Because the *anti* structure can cancel the dipole moments, it is stabilized in less polar solvents. On the other hand, the *syn* structure amplifies the dipole moments, so it will be stabilized in polar solvents.

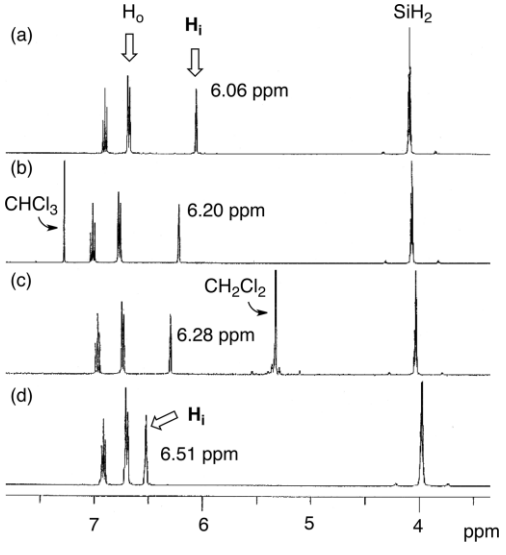
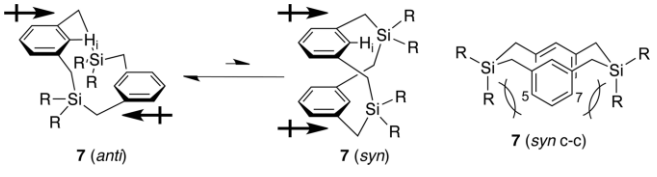


Figure 4. ^{1}H NMR spectra of **7d** in [D_{12}]cyclohexane (a), $CDCl_3$ (b), CD_2Cl_2 (c), and CD_3CN (d), at room temperature.



Scheme 3. Dipole moments and steric repulsion in the 2,11-disila[3.3]metacyclophane conformers.

For all previously studied [3.3]metacyclophanes that are linked by 3-atom chains containing carbon, nitrogen, oxygen, sulfur, and selenium, *syn* conformers have been shown to be thermodynamically stable. Only three exceptions to this general rule exist. Specifically, [3.3]metacyclophane-2,11-diones,[3m,3n,3p,3s] [3.3]metacyclophane-2,2,11,11-tetracarboxylate,[3a] and a dithia[3.3]metacyclophane, which contain extremely bulky and electron-donating substituents on both benzene rings,[6p] prefer to exist in *anti*-favored conformations. Analysis of these compounds suggests that the factors governing the *anti* preference in [3.3]metacyclophanes include (1) substitution on the 2 and 11 positions and (2) the presence of electron-donating and bulky groups that cause electrostatic and steric repulsion between the two benzene rings in the *syn* conformation.

The findings of the present study demonstrate that mere replacement by silyl groups at C-2 and C-11 in the tether can alter the preference in favor of the *anti* conformation. The typical energy difference between *syn* and *anti* conformers of [3.3]metacyclophanes is roughly 2–3 kcal/mol. However, the presence of substituted sila centers in the tether is sufficient to reverse this energetic ordering. Two factors might be responsible for this phenomenon. One is a consequence of two axial-type substituents at the silicon centers, which, in the *syn*-chair-chair conformation, create steric repulsion with hydrogen atoms at the 5, 7, 14, and 16 positions on the benzene rings (Scheme 3). The second factor is associated with the electropositive character of silicon. Thus, interaction between C(benzyl)–Si σ electron orbitals and benzene π^* orbitals[11] should lead to an increase in electron density on the benzene rings that causes a greater degree of electrostatic repulsion in the *syn* conformation. The observed temperature effects in the ^{1}H NMR spectra of the sila-linked metacyclophanes are consistent with the proposal that the proportion of the enthalpically lower energy conformation increases with decreasing temperature. Therefore, the temperature and solvent effects on the conformational equilibria of these compounds in solution can be understood in terms of a mixed contribution of $\Delta\Delta G$ and dipole moments.

Conclusion

We synthesized silicon- and germanium-tethered [3.3]metacyclophanes, and we found that, in the case of 2,2,11,11-tetrasubstituted derivatives, these are *anti*-rich [3.3]metacyclophanes. However, for the 2,2,11,11-tetrahydro derivative the *syn* conformer is thermodynamically stable. The temperature and solvent dependence of ^{1}H NMR spectra, as well as molecular orbital calculations, indicated that the *syn*/*anti* ratios of these compounds in solution can be explained by considering mixed contributions of $\Delta\Delta G$ and dipole moments. X-ray crystallographic analyses support this behavior. This phenomenon seems to be useful for switching devices, so further studies are now in progress.

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Keywords: Cyclophanes · Silicon · Germanium · Synthetic methods · Conformation analysis

[1] a) P. M. Keehn, S. M. Rosenfeld, *Cyclophanes*, Academic Press, New York, **1983**; b) F. Vögtle, *Cyclophane Chemistry*, Wiley, Chichester, **1993**; c) E.

Weber, *Top. Curr. Chem.* **1994**, *172*, 1–210; d) F. Vögtle, G. Hohner, *Top. Curr. Chem.* **1978**, *74*, 1–29; e) L. Ernst, *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *37*, 47–190.

[2] a) D. J. Wilson, V. Boekelheide, R. W. Griffin Jr., *J. Am. Chem. Soc.* **1960**, *82*, 6302–6304; b) T. Sato, S. Akabori, M. Kainosho, K. Hata, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 218–221; c) F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 274; *Angew. Chem.* **1969**, *81*, 258; d) T. Umemoto, T. Otsubo, Y. Sakata, S. Misumi, *Tetrahedron Lett.* **1973**, *14*, 593–596; e) T. Takemura, T. Sato, *Can. J. Chem.* **1976**, *54*, 3412–3418; f) T. Otsubo, D. Stusche, V. Boekelheide, *J. Org. Chem.* **1978**, *43*, 3466–3470; g) D. Kamp, V. Boekelheide, *J. Org. Chem.* **1978**, *43*, 3470–3475; h) T. Sato, K. Torizuka, R. Komaki, H. Atobe, *J. Chem. Soc. Perkin Trans. 2* **1980**, 561–568; i) K. Torizuka, T. Sato, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2411–2412; j) M. Tashiro, T. Yamato, *J. Org. Chem.* **1981**, *46*, 1543–1552; k) H. A. Staab, L. Schanne, C. Krieger, V. Taglieber, *Chem. Ber.* **1985**, *118*, 1204–1229; l) M. Tashiro, T. Yamato, *J. Org. Chem.* **1985**, *50*, 2939–2942; m) R. H. Mitchell, T. K. Vinod, G. W. Bushnell, *J. Am. Chem. Soc.* **1985**, *107*, 3340–3341; n) R. H. Mitchell, G. J. Bodwell, T. K. Vinod, K. S. Weerawarna, *Tetrahedron Lett.* **1988**, *29*, 3287–3290; o) M. Tashiro, S. Mataka, Y. Takezaki, M. Takeshita, T. Arimura, A. Tsuge, T. Yamato, *J. Org. Chem.* **1989**, *54*, 451–458; p) M. Tashiro, H. Fujimoto, A. Tsuge, S. Mataka, H. Kobayashi, *J. Org. Chem.* **1989**, *54*, 2012–2015; q) R. H. Mitchell, T. K. Vinod, G. W. Bushnell, *J. Am. Chem. Soc.* **1990**, *112*, 3487–3497; r) A. Longen, M. Nieger, F. Vögtle, K. H. Dötz, *Chem. Ber./Recueil* **1997**, *130*, 1105–1111.

[3] a) T. Shinmyozu, T. Inazu, T. Yoshino, *Chem. Lett.* **1976**, 1405–1406; b) T. Otsubo, M. Kitasawa, S. Misumi, *Chem. Lett.* **1977**, 977–980; c) T. Otsubo, M. Kitasawa, S. Misumi, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1515–1520; d) D. Krois, H. Lehner, *J. Chem. Soc. Perkin Trans. 1* **1982**, 477–481; e) D. Krois, H. Lehner, *Tetrahedron* **1982**, *38*, 3319–3324; f) H. Sasaki, T. Kitagawa, *Chem. Pharm. Bull.* **1983**, *31*, 2868–2878; g) M. F. Semmelhack, J. J. Harrison, D. C. Young, A. Gutiérrez, S. Rafii, J. Clardy, *J. Am. Chem. Soc.* **1985**, *107*, 7508–7514; h) J. Nishimura, A. Ohbayashi, Y. Horiuchi, Y. Okada, S. Yamanaka, A. Oku, *J. Org. Chem.* **1987**, *52*, 1409–1413; i) K. Sako, T. Hirakawa, N. Fujimoto, T. Shinmyozu, T. Inazu, H. Horimoto, *Tetrahedron Lett.* **1988**, *29*, 6275–6278; j) Y. Fukazawa, Y. Takeda, S. Usui, M. Kodama, *J. Am. Chem. Soc.* **1988**, *110*, 7842–7847; k) K. Sako, T. Shinmyozu, H. Takemura, M. Suenaga, T. Inazu, *J. Org. Chem.* **1992**, *57*, 6536–6541; l) S. Osada, Y. Miyahara, N. Shimizu, T. Inazu, *Chem. Lett.* **1995**, 1103–1104; m) Y. Fukazawa, T. Hayashibara, Y. Yang, S. Usui, *Tetrahedron Lett.* **1995**, *36*, 3349–3352; n) T. Shinmyozu, T. Hirakawa, G. Wen, S. Osada, H. Takemura, K. Sako, J. M. Rudzinski, *Liebigs Ann.* **1996**, 205–210; o) K. Sako, H. Tatemitsu, S. Onaka, H. Takemura, S. Osada, G. Wen, J. M. Rudzinski, T. Shinmyozu, *Liebigs Ann.* **1996**, 1645–1649; p) Y. Fukazawa, Y. Yang, T. Hayashibara, S. Usui, *Tetrahedron* **1996**, *52*, 2847–2862; q) H. Isaji, M. Yasutake, H. Takemura, K. Sako, H. Tatemitsu, T. Inazu, T. Shinmyozu, *Eur. J. Org. Chem.* **2001**, 2487–2499; r) T. Yamato, K. Tsuchihashi, N. Nakamura, M. Hirahara, H. Tsuzuki, *Can. J. Chem.* **2002**, *80*, 207–215; s) T. Yamato, K. Tsuchihashi, N. Nakamura, M. Hirahara, K. Tanaka, *Can. J. Chem.* **2002**, *80*, 510–516; t) H. Takemura, M. Kotoku, M. Yasutake, T. Shinmyozu, *Eur. J. Org. Chem.* **2004**, 2019–2024; u) M. Shibahara, M. Watanabe, T. Iwanaga, K. Ideta, T. Shinmyozu, *J. Org. Chem.* **2007**, *72*, 2865–2877; v) M. Shibahara, M. Watanabe, K. Aso, T. Shinmyozu, *Synthesis* **2008**, 3749–3754; w) M. Shibahara, M. Watanabe, M. Suenaga, K. Ideta, T. Matsumoto, T. Shinmyozu, *Tetrahedron Lett.* **2009**, *50*, 1340–1344.

[4] a) S. Pappalardo, F. Bottino, M. D. Grazia, P. Finocchiaro, A. Mamo, *Heterocycles* **1985**, *23*, 1881–1884; b) F. Bottino, M. D. Grazia, P. Finocchiaro, F. R. Fronczek, A. Mamo, S. Pappalardo, *J. Org. Chem.* **1988**, *53*, 3521–3529; c) T. Shinmyozu, N. Shibakawa, K. Sugimoto, H. Sakane, H. Takemura, K. Sako, T. Inazu, *Synthesis* **1993**, 1257–1260; d) W. Josten, D. Karbach, M. Nieger, F. Vögtle, K. Hägele, M. Svoboda, M. Przybylski, *Chem. Ber.* **1994**, *127*, 767–777; e) W. Josten, S. Neumann, F. Vögtle, M. Nieger, K. Hägele, M. Przybylski, F. Beer, K. Müllen, *Chem. Ber.* **1994**, *127*, 2089–2096; f) H.-J. Krüger, *Chem. Ber.* **1995**, *128*, 531–591; g) S. Breidenbach, S. Ohren, M. Nieger, F. Vögtle, *J. Chem. Soc., Chem. Commun.* **1995**, 1237–1238; h) S. Breidenbach, S. Ohren, F. Vögtle, *Chem. Eur. J.* **1996**, *2*, 832–837; i) H. Plenio, J. Hermann, R. Diodone, *Inorg. Chem.* **1997**, *36*, 5722–5729; j) H. Schwierz, F. Vögtle, *Synthesis* **1999**, 295–305; k) H. Takemura, H. Kariyazono, N. Kon, T. Shinmyozu, T. Inazu, *J. Org. Chem.* **1999**, *64*, 9077–9079; l) H. Takemura, H. Kariyazono, M. Yasutake, N. Kon, K. Tani, K. Sako, T. Shinmyozu, T. Inazu, *Eur. J. Org. Chem.* **2000**, 141–148; m) T. Satou, T. Shinmyozu, *J. Chem. Soc. Perkin Trans. 2* **2002**, 393–397; n) H. Takemura, G. Wen, T. Shinmyozu, *Synthesis* **2005**, 2845–2850.

[5] G. R. Newkome, S. Pappalardo, F. R. Fronczek, *J. Am. Chem. Soc.* **1983**, *105*, 5152–5153.

[6] a) T. Sato, M. Wakabayashi, M. Kainosho, K. Hata, *Tetrahedron Lett.* **1968**, *9*, 4185–4189; b) F. Vögtle, L. Schunder, *Chem. Ber.* **1969**, *102*, 2677–2683; c) V. Boekelheide, J. L. Mondt, *Tetrahedron Lett.* **1970**, *11*, 1203–1206; d) B. R. Davis, I. Bernal, *J. Chem. Soc. B* **1971**, 2307–2313; e) T. Sato, M. Wakabayashi, K. Hata, M. Kainosho, *Tetrahedron* **1971**, *27*, 2737–2755; f) F. Vögtle, W. Wieder, H. Förster, *Tetrahedron Lett.* **1974**, *15*, 4361–4364; g) F. Vögtle, K. Böckmann, *Chem. Ber.* **1979**, *112*, 1400–1409; h) W. Anker, G. W. Bushnell, R. H. Mitchell, *Can. J. Chem.* **1979**, *57*, 3080–3087; i) K. Böckmann, F. Vögtle, *Chem. Ber.* **1981**, *114*, 1065–1073; j) R. H. Mitchell, W. Anker, *Tetrahedron Lett.* **1981**, *22*, 5135–5138; k) R. H. Mitchell, R. V. Williams, T. W. Dingle, *J. Am. Chem. Soc.* **1982**, *104*, 2560–2571; l) W. Anker, K. A. Beveridge, G. W. Bushnell, R. H. Mitchell, *Can. J. Chem.* **1984**, *62*, 661–666; m) R. H. Mitchell, K. S. Weerawarna, G. W. Bushnell, *Tetrahedron Lett.* **1984**, *25*, 907–910; n) R. H. Mitchell, K. S. Weerawarna, *Tetrahedron Lett.* **1988**, *29*, 5587–5588; o) R. H. Mitchell, T. K. Vinod, G. J. Bodwell, G. W. Bushnell, *J. Org. Chem.* **1989**, *54*, 5871–5879; p) J. Breitenbach, R. Hoss, M. Nieger, K. Rissanen, F. Vögtle, *Chem. Ber.* **1992**, *125*, 255–258; q) L. Ernst, K. Ibrom, K. Marat, R. H. Mitchell, G. J. Bodwell, G. W. Bushnell, *Chem. Ber.* **1994**, *127*, 1119–1124; r) T. Yamato, M. Shigekuni, H. Kunugida, Y. Nagano, *J. Chem. Res. Synop.* **1997**, 192–193; s) M. Ashram, D. O. Miller, J. N. Bridson, P. E. Georghiou, *J. Org. Chem.* **1997**, *62*, 6476–6484; t) G. J. Bodwell, J. N. Bridson, T. J. Houghton, B. Yarlagadda, *Tetrahedron Lett.* **1997**, *38*, 7475–7478; u) T. Moriguchi, K. Sakata, A. Tsuge, *Chem. Lett.* **1999**, 167–168; v) R. H. Mitchell, *J. Am. Chem. Soc.* **2002**, *124*, 2352–2357; w) J. Xu, Y.-H. Lai, *Org. Lett.* **2002**, *4*, 3211–3214; x) Y. Morisaki, T. Ishida, Y. Chujo, *Polym. J.* **2003**, *35*, 501–506; y) J. Xu, Y.-H. Lai, W. Wang, *Org. Lett.* **2003**, *5*, 2781–2784; z) Y. Ting, Y.-H. Lai, *J. Am. Chem. Soc.* **2004**, *126*, 909–914.

[7] a) R. H. Mitchell, *Tetrahedron Lett.* **1975**, *16*, 1363–1364; b) R. H. Mitchell, *Can. J. Chem.* **1980**, *58*, 1398–1406; c) G. W. Bushnell, R. H. Mitchell, *Can. J. Chem.* **1982**, *60*, 362–367; d) H. Higuchi, S. Misumi, *Tetrahedron Lett.* **1982**, *23*, 5571–5574; e) H. Higuchi, K. Tani, T. Otsubo, Y. Sakata, S. Misumi, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4027–4036; f) R. H. Mitchell, K. S. Weerawarna, G. W. Bushnell, *Tetrahedron Lett.* **1987**, *28*, 5119–5120; g) R. H. Mitchell, K. S. Weerawarna, *Tetrahedron Lett.* **1988**, *29*, 5587–5588; h) S. Muralidharan, M. Hojjatie, M. Firestone, H. Freiser, *J. Org. Chem.* **1989**, *54*, 393–399; i) M. Hojjatie, S. Muralidharan, H. Freiser, *Tetrahedron* **1989**, *45*, 1611–1622; j) J. Thomas, W. Maes, K. Robeyns, M. Ovaere, L. Van Meervelt, M. Smet, W. Dehaen, *Org. Lett.* **2009**, *11*, 3040–3043.

[8] a) K. Nakanishi, K. Mizuno, Y. Otsuji, *J. Chem. Soc. Perkin Trans. 1* **1990**, 3362–3363; b) K. Nakanishi, K. Mizuno, Y. Otsuji, *J. Chem. Soc., Chem. Commun.* **1991**, 90–92; c) Y. Inoue, A. Sugimoto, K. Mizuno, *J. Chem. Res. Synop.* **2000**, 528–529; d) K. Mizuno, K. Nakanishi, Y. Otsuji, T. Hayamizu, H. Maeda, T. Adachi, A. Ishida, S. Takamuku, *J. Photosci.* **2003**, *10*, 121–126; e) H. Maeda, K. Nishimura, K. Mizuno, M. Yamaji, J. Oshima, S. Tobita, *J. Org. Chem.* **2005**, *70*, 9693–9701; f) H. Maeda, R. Hiranabe, K. Mizuno, *Tetrahedron Lett.* **2006**, *47*, 7865–7869.

[9] A [3.3]metacyclophane having silicon atoms at other positions is known. C. Dutan, S. Choua, T. Berclaz, M. Geoffroy, N. Mézailles, A. Moores, L. Ricard, P. Le Floch, *J. Am. Chem. Soc.* **2003**, *125*, 4487–4494.

[10] CCDC 1483311 (for **7d**), 1483312 (for ***trans*-7c**), 1483313 (for **8b**), 1483314 (for **4**), 1483315 (for **7b**), and 1483316 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[11] K. Hassall, S. Lobachevsky, J. M. White, *J. Org. Chem.* **2005**, *70*, 1993–1997.

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Cyclophanes

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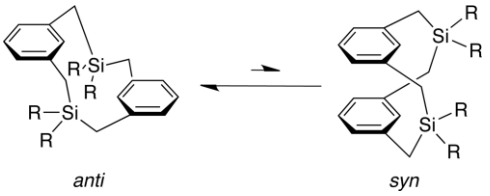
Synthesis and Conformational Analysis of 2,11-Disila[3.3]metacyclophanes



Until now, carbon-, nitrogen-, oxygen-, sulfur-, and selenium-tethered [3.3]-metacyclophanes have been synthesized, and their conformation is known to be biased to *syn* conformers. In this work, we first synthesized silicon- and germanium-tethered [3.3]metacyclophanes, and we found that their conformations are unexpected *anti*-rich [3.3]metacyclophanes!

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