

The ring inversion of silacycloheptatriene and cycloheptatriene. Comparison of the 'aromaticity' of planar and boat conformers estimated by nucleus-independent chemical shift

Tohru Nishinaga,* Yoshiteru Izukawa and Koichi Komatsu*

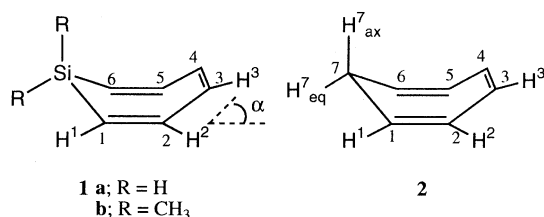
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

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ABSTRACT: Nucleus-independent chemical shifts (NICS) of boat and planar structure of silepins (**1**) and cycloheptatriene (**2**) were calculated at the HF/6-31+G* level for the Becke3LYP/6-31G* optimized geometries in order to investigate the correlation between the inversion barrier and aromatic nature in the boat and planar forms of **1** and **2**. The NICS of unsubstituted silepin **1a** indicated that there is almost no stabilization in the boat form (NICS, -0.5) and that the planar form (NICS, 3.5) is relatively destabilized in comparison with the boat form. On the other hand, the NICS of **2** showed that there is considerable homoconjugative stabilization in the boat form (NICS, -4.2) and destabilization in the planar form (NICS, 8.2). In addition to the geometrical effects resulting from angle strain, these electronic effects are considered to affect the energy barriers for ring inversion, which have been calculated to be 0.9 kcal mol⁻¹ for **1a** and 5.2 kcal mol⁻¹ for **2**. © 1998 John Wiley & Sons, Ltd.

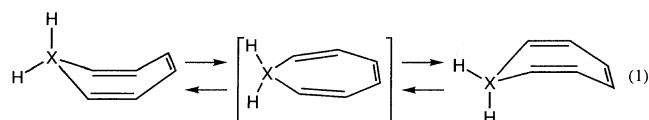
KEYWORDS: cycloheptatriene; silacycloheptatriene; ring inversion; aromaticity; *ab initio* calculation; nucleus-independent chemical shift

Silacycloheptatriene (silepin) (**1**) has the possibility of achieving 6 π aromatic stabilization if it takes a planar conformation and if the six π -electrons of the triene part constitute a cyclic conjugated system by delocalization through the vacant d-orbital of the silicon atom. In reality, silepin takes a boat form, which undergoes rapid ring inversion just like cycloheptatriene (**2**).¹ Although



unsubstituted silepin (**1a**) is not yet known, the 1,1-dimethyl derivative (**1b**) has been synthesized and the energy barrier for the ring inversion ($\Delta G_{\text{inv}}^{\ddagger}$) has been found to be too low to be measured by NMR.¹ On the other hand, the value of $\Delta G_{\text{inv}}^{\ddagger}$ of cycloheptatriene has

been determined to be 6.1 kcal mol⁻¹ (1 kcal = 4.184 kJ) at -143 °C² and 5.7 kcal mol⁻¹ at -152 °C³ by the low-temperature NMR technique. Simply from comparison of these results, the planar transition-state structure of silepin may appear to be more stabilized than that of cycloheptatriene. However, from comparison of the particular derivatives of silepin and the cycloheptatriene annelated with three bicyclo[2.2.2]octene units, no significant cyclic conjugation for the silepin was observed.⁴ In order to estimate the effects of possible π -electron delocalization in these systems, we performed *ab initio* calculations⁵ at the Becke3LYP/6-31G* level to obtain the optimized structures and computed the 'nucleus-independent chemical shifts' (NICS) proposed by Schleyer *et al.*⁶ by calculations at the HF/6-31+G* level, with regard to the planar and boat structures for each of the silepins **1a** and **1b** and cycloheptatriene (**2**).



In the present study, the optimized structures for the boat forms of **1a** and **1b** were calculated to have the bending angles α of 21.5 and 20.7°, respectively, which are in fair agreement with the value (25°) estimated from the ¹H NMR coupling constants for **1b**.¹ *Ab initio*

*Correspondence to: T. Nishinaga or K. Komatsu, Inst. for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan.
E-mail: nishinaga@scl.kyoto-u.ac.jp

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Table 1. Calculated and observed NMR chemical shifts of **1b** and **2**

Compound	NMR chemical shift (ppm)												
	H-1	H-2	H-3	H-7 _{ax}	H-7 _{eq}	CH ₃	C-1	C-2	C-3	C-7	CH ₃	Si	
1b	Calcd	5.98	7.14	6.46	—	—	-0.23, -0.24	129.2	140.3	130.8	—	-1.1, -0.2	-10.2
	Obsd ^a	5.79	6.89	6.41	—	—	0.09	131.2	140.4	132.1	—	-3.0	-17.2
2	Calcd	5.61	6.34	6.83	1.57	2.69	—	120.0	123.8	130.5	25.5	—	—
	Obsd ^b	5.26	6.09	6.50	1.57 ^c	2.78 ^c	—	120.4	126.8	131.0	28.1	—	—

^a Ref. 1.^b Ref. 12.^c Observed at -158°C; Ref. 3.

calculations on **2** at the Becke3LYP/6-31G* level were reported recently⁷ and we obtained the same results. The comparison between the calculated and observed results has also been discussed.⁷ Since the transition-state structure for ring inversion is considered to be planar, the energy barrier for ring inversion can be estimated from the calculated energy difference between the planar and boat forms. The calculated values for **2** have previously been reported to range from 4 to 10 kcal mol⁻¹.⁷⁻¹¹ In the present study, we obtained a calculated value of 5.2 kcal mol⁻¹ (the same value as has been reported⁷) for **2**, in agreement with the experimental values (see above), and much lower values of 0.9 and 1.0 kcal mol⁻¹ for **1a** and **1b**, respectively.

These calculated values for ring inversion appear to be correlated with the geometrical change in the σ -framework as exemplified by the change in averaged C—C—C angle of sp² carbons of the Becke3LYP/6-31G* geometry. Upon going from the boat form to the planar form, the averaged angle changed from 128.3 to 131.4° for **1a** (from 128.6 to 131.7° for **1b**) whereas it changed more, i.e. from 124.4 to 129.8°, for **2**. The averaged C—C—C angle of **1** is larger for both the planar and boat forms owing to both the electrostatic effect of Si and the longer C—Si bond. In order to gain a deeper insight into the cause of these inversion barriers, it seemed of particular importance to estimate the extent of conjugative stabilization for planar and boat forms of **1** and **2** using the recently reported index of aromaticity, NICS.⁶

The values of the ¹H and ¹³C NMR chemical shifts that we obtained by the GIAO calculations are in fairly good agreement with the experimental values, as shown in

Table 1, indicating that the magnetic properties obtained by the present method are reliable. The NICS values calculated for the boat and planar forms of **1a**, **1b** and **2** are shown in Table 2. The values for the planar forms of these compounds are all positive, implying that these have an antiaromatic character according to the definition of NICS,⁶ although the values for **1** are small. In contrast, whereas the boat form of **1** is almost non-aromatic, the boat form of **2** has a negative NICS value and is classified as a weakly aromatic species.

Previously, the NICS of cyclopentadiene has been calculated as -3.2 at the HF/6-31+G* level.⁶ The presence of aromaticity in this system has been controversial, and cyclopentadiene has been described as 'borderline' aromatic 'at best',¹³ based on the aromatic stabilization energy¹³ and the diamagnetic susceptibility exaltation.¹⁴ Such aromaticity in cyclopentadiene and antiaromaticity in the planar form of cycloheptatriene (**2**) can be assumed only when the 2 π hyperconjugative contribution of the CH₂ group is taken into account.¹³

On the other hand, the weak aromaticity of the boat form of **2**, suggested by NICS calculations, could only be interpreted by assuming homoconjugative interaction between the p orbitals of C-1 and C-6 in the triene moiety. The presence of weak but appreciable conjugative stabilization in **2** has been shown experimentally by measurements of the heat of hydrogenation¹⁵ and the diamagnetic susceptibility exaltation.¹⁴ In the case of silepin, the distance between C-1 and C-6 is calculated to be longer (2.982 Å for **1a** and 3.002 Å for **1b**) than that of **2** (2.446 Å), and this would be the cause of the decrease in homoconjugative aromaticity.

Hence, according to the results of NICS calculations, no significant (p-d) π conjugation would be operating in silepins **1a** and **1b**, and the planar forms of **1a** and **1b** were found to be not electronically stabilized but rather relatively destabilized in comparison with the boat form, from the result of increased NICS values upon going from the boat to the planar form. In the case of **2**, such destabilization in the planar form compared with the boat form is even larger than that of silepin. These effects seem to be contributing to the energy barrier for ring inversion of these systems in addition to geometrical effects.

Table 2. NICS of **1** and **2**

Compound	NICS (ppm)	
	Boat	Planar
1a	-0.5	3.5
1b	-0.5	3.1
2	-4.2	8.2

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