Bowl-to-bowl inversion of sumanene derivatives†‡

Toru Amaya, Hiroyuki Sakane, Toshiko Muneishi and Toshikazu Hirao*

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The bowl-to-bowl inversion of the non-planar bowl-shaped compounds derived from sumanene as a fullerene C_{3v} fragment was found to be slow and tuned by a solvent, and the benzylic mono- and di-anions inverted even more slowly.

Bowl-to-bowl inversion is one of the characteristic behaviors for some flexible concave polyaromatic hydrocarbons (PAHs). This intriguing dynamics has been exclusively studied with corannulene (**2a**, Fig. 1(b)), which is the smallest C_{5v} symmetric fragment of fullerenes with a bowl depth of 0.87 Å,[1] and its derivatives. Scott *et al.* demonstrated for the first time that the bowl-to-bowl inversion of the corannulene derivative **2b** occurs rapidly with an activation barrier of 10–11 kcal mol^{-1}.[2] Further elaboration of the structure gave more detailed insight into the inversion dynamics, for example, the introduction of a rigid five-membered ring to the rim of corannulene was found by Sygula, Rabideau and co-workers to slow the inversion.[3] Siegel and co-workers investigated the relationship between the inversion energy barrier and the bowl depth.[4] In this regard, sumanene (**1**, Fig. 1(a)) with a deeper C_{3v} symmetric bowl (1.11 Å) is another candidate molecule to investigate the inversion behavior.[5,6] Furthermore, the facile functionalization using three benzylic positions permits the structural elucidation.[6,7] Preliminary results using variable-temperature ^{1}H NMR implied that **1** inverts much slowly than corannulene.[5] A theoretical study using the DFT method suggested that the inversion barrier of **1** is 16.9 kcal mol^{-1} (B3LYP/cc-pVTZ//B3LYP/cc-pVDZ, Gaussian 94).[8] Control of the dynamics is envisioned not only to contribute to the enantioselective synthesis of sumanene-based curved molecules, but also to afford a new building block for molecular machines, molecular devices and molecular switches. We report here the dynamics of the trideuteriosumanene **3**, hexasubstituted derivatives **6** and **7**, and the benzylic monoanion **4** and dianion **5**.

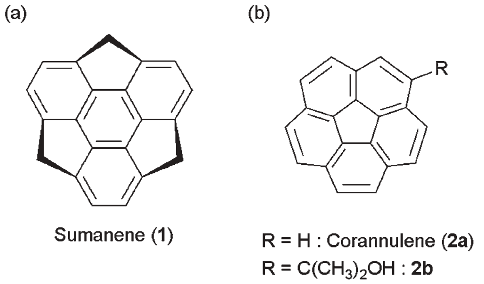


Fig. 1 (a) Sumanene **1**, (b) corannulenes **2a** and **2b**.

Using the 2D-EXSY NMR method, the chemical exchange of the protons in close proximity cannot be observed due to cancelling of the crosspeaks by the nuclear Overhauser effect.[9] To investigate the inversion dynamics of sumanene, trideuteriosumanene **3** can be used, where the bowl-to-bowl inversion is equivalent to the isomerization between the diastereomers **3a** and **3b** (Fig. 2(a)). Accordingly, the bowl-to-bowl inversion rate of **3** is determined by measurement of the chemical exchange rate for the benzylic protons.

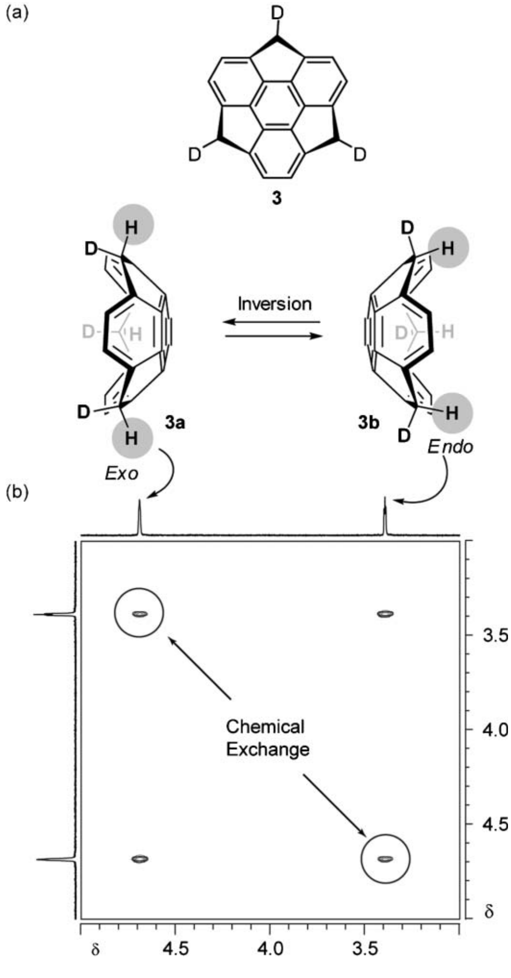


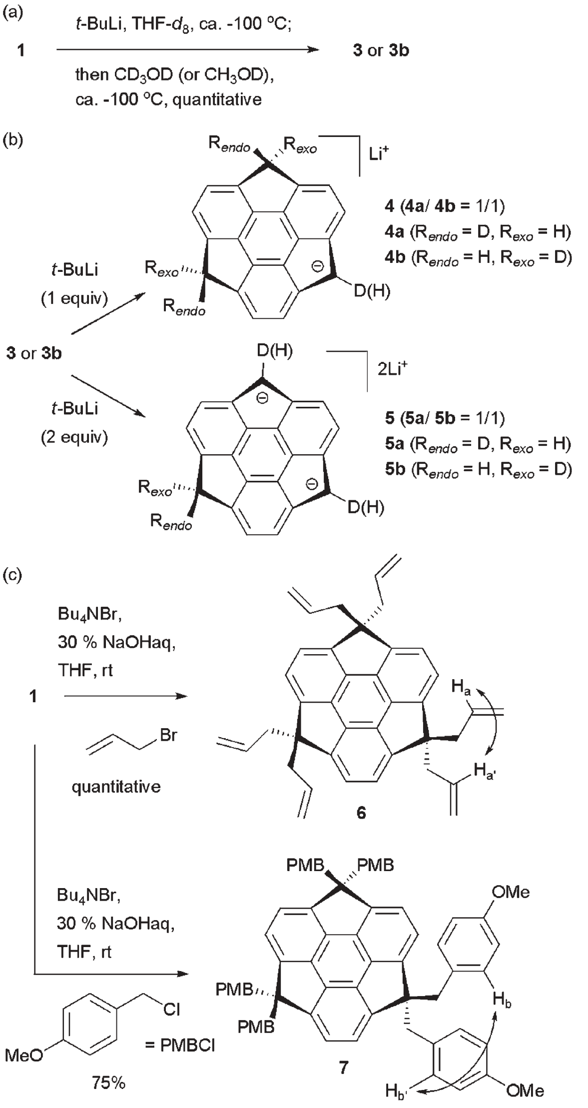
Fig. 2 (a) Trideuteriosumanene **3** and schematic representation of its bowl-to-bowl inversion. (b) A selected region of the EXSY spectrum of **3** in $CDCl_3$.

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka, 565-0871, Japan.
E-mail: hirao@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7415;
Tel: +81-6-6879-7413

† This paper is dedicated to the memory of Professor Yoshihiro Matsumura.

‡ Electronic supplementary information (ESI) available: Preparation procedure and compound characterization data (^{1}H, ^{13}C, 2D-EXSY, HMBC and HMQC NMR with spectra, IR and HRMS). See DOI: 10.1039/b712839h

The trideuteriosumanene **3** was prepared as shown in Scheme 1(a). The benzylic trianion was generated by the treatment of **1** with excess amount of *t*-BuLi and then trapped with CD_3OD at approximately −100 °C. The obtained crude product was purified by usual column chromatography on silica gel to give **3** quantitatively (Scheme 1(a)). The deuteration ratio of **3** was >99%. ^1H NMR showed two broad singlets in the benzylic proton region. Selective decoupling ^{13}C NMR and HMBC experiments indicated only two equally abundant C_3 symmetric species (see ESI‡). If the deuterium trapping occurred with no selectivity, four species should be observed after reaching equilibrium. Thus it is likely that the selective *exo*-deuteration gave **3b**, which was confirmed by its isolation (described in the next paragraph). Further characterization of these species by chemical exchange spectroscopy (EXSY) identified the chemical exchange process between two sets of protons located at *exo*- and *endo*-benzylic positions of sumanene (Fig. 2(b)), which provides direct evidence for the bowl-to-bowl inversion of sumanene and its derivatives. The EXSY cross-peak was subsequently quantified to compute the rate of inversion and activation energy.[10] This process was repeated using various solvents as summarized in Table 1.§ In $CDCl_3$, the rate constant and activation energy ($\Delta G^{\ddagger}$) were 0.066 s^{-1} (318 K) and 20.4 kcal mol^{-1}, respectively (Table 1, entry 1). This result is 3.5 kcal mol^{-1} higher than the value estimated by DFT calculation,[8] and approximately twice as high as that of the corannulene derivative **2b**.[2] At room temperature (298 K), the rate constant (k) was calculated to be 0.007 s^{-1}, that is, 143 s are required for one inversion in $CDCl_3$. This is in sharp contrast that the corannulene derivative **2b** which inverts about 200 000 times each second.[2] Similar inversion dynamics was observed when the EXSY experiments were repeated in CD_2Cl_2 and THF-d_8 (Table 1, entries 2 and 3). On the other hand, the use of methylated benzene-based solvents (toluene-d_8, *p*-xylene-d_{10}, and mesitylene-d_{12}) reduced the energy barrier of **3** (Table 1, entries 6, 7 and 8). It should be noted that the difference between the highest and the lowest barriers was 0.7 kcal mol^{-1}, and the inversion of **3** can be accelerated up to three times by simply exchanging the solvent (0.066 s^{-1} for entry 1, 0.21 s^{-1} for entry 7). These findings suggest an electronic and/or steric interaction between sumanene and solvent.



Scheme 1 Synthesis of (a) trideuteriosumanene **3**; (b) the monoanion **4**, and the dianion **5**; (c) the hexasubstituted derivatives **6** and **7**.

The dynamic behaviors of the monoanion **4** and dianion **5** were also investigated. Treatment of **3** with the requisite amount of *t*-BuLi generated **4** and **5** (Scheme 1(b)). The inversion behavior was studied using a similar method. In both cases, no crosspeak was observed even with increased temperature. This suggests that the anions **4** and **5** maintain a relatively rigid bowl-shape in THF-d_8.[11] So, we planned to monitor the equilibration of *exo*-deuterated **4b** and **5b** by simple ^1H NMR measurement to investigate such slow inversion. Selective deuteration of the trianion was achieved to give **3b** by precipitation with CH_3OD at approximately −100 °C. Keeping **3b** as a solid at room temperature did not induce bowl-to-bowl inversion. To generate monoanion **4b** and dianion **5b**, **3b** was treated with the requisite amount of *t*-BuLi at approximately −100 °C in THF-d_8 (Scheme 1(b)), then the equilibration was monitored. The ^1H NMR spectra are shown in Fig. 3. Growing of the *exo*-protons (4.46 and 3.88 ppm for **4** and **5**,

Table 1 Rate constant (k/s^{-1}) and activation energy ($\Delta G^{\ddagger}$/kcal mol^{-1}) for the bowl-to-bowl inversion (600 MHz, 318 K, 20 mM)[a]

Entry	Compound	Solvent	k^b	$\Delta G^{\ddagger\ c}$
1	**3**	$CDCl_3$	0.066	20.4
2		CD_2Cl_2	0.015 (303 K)	20.3
3		THF-d_8	0.075	20.3
4		1,4-Dioxane-d_8	0.10	20.1
5		Benzene-d_6	0.089	20.2
6		Toluene-d_8	0.13	19.9
7		*p*-Xylene-d_{10}	0.21	19.7
8		Mesitylene-d_{12}	0.15	19.9
9	**4**	THF-d_8	9.10×10^{-5} (283 K)	21.8[d]
10	**5**	THF-d_8	3.40×10^{-5} (273 K)	21.5[d]
11	**6**	$CDCl_3$	0.40	19.2
12	**7**	$CDCl_3$	2.0	18.2

[a] All experiments were carried out twice, and the errors did not exceed 0.1%. The 2D-EXSY spectra were clear enough to quantify the area of cross peaks, and are shown in ESI. [b] The integrations for the exchange cross-peak were processed using the EXSYCalc program[10] to give the rate constant (k). [c] $\Delta G^{\ddagger} = -RT\ln(hk/k_BT)$: T is temperature, k_B is the Boltzmann constant, and h is Planck's constant. [d] Determined by monitoring the equilibration using ^1H NMR (22 mM).

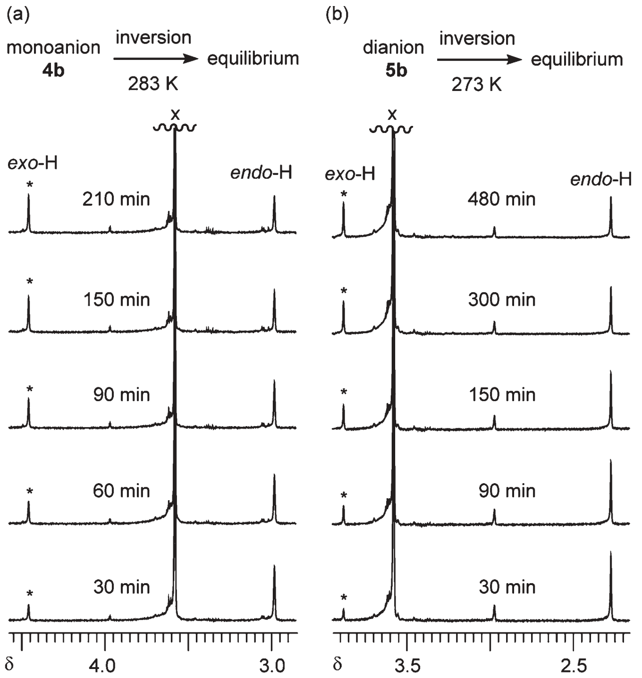


Fig. 3 Selected ^{1}H NMR spectra of equilibration for (a) monoanion **4** at 283 K and (b) dianion **5** at 273 K (600 MHz, 22 mM, THF-d_8). (*) *Exo*-protons; (x) residual THF.

respectively) was observed at longer times in both spectra (Fig. 3(a) and (b)). The half-life times were 2985 s for **4** at 283 K and 7547 s for **5** at 273 K. The rate constants (k) for the reversible equilibration of **4** and **5** were 9.10×10^{-5} s^{-1} at 283 K and 3.40×10^{-5} s^{-1} at 273 K, respectively (Table 1, entries 9 and 10), determined by regression analysis using the equation $2kt = \ln[a/(a - 2x)]$ where a is the initial concentration of **4a** (or **5a**) and x is the concentration of **4b** (or **5b**) at time t. Correlation coefficients of the linear regressions were 0.999 and 0.978 (for **4** and **5**, respectively, see Fig. S1 and S2, ESI‡). $\Delta G^{\ddagger}$ values were 21.8 and 21.5 kcal mol^{-1} for **4** and **5**, respectively (Table 1, entries 9 and 10), calculated from the Eyring equation. Monoanion **4** and dianion **5** show a 1.5 and 1.2 kcal mol^{-1} higher barrier than that of **1**, respectively.

Further studies were carried out with hexasubstituted sumanenes. The hexaallylated and hexa-*p*-methoxybenzylated sumanenes **6** and **7** were obtained by nucleophilic substitution reaction of **1** with aqueous 30% NaOH solution as a base in the presence of tetrabutylammonium bromide and a minimum amount of THF in quantitative and 75% yields, respectively (Scheme 1(c)). Full characterization for all protons and carbons was carried out by ^{1}H NMR, ^{13}C NMR, 2D-NOESY, HMBC and HMQC experiments (all spectra were shown in ESI‡). The chemical exchange of H_a–$H_{a'}$ and H_b–$H_{b'}$ was analyzed for **6** and **7**, respectively. The inversion barriers of **6** and **7** were 19.2 and 18.2 kcal mol^{-1} (Table 1, entries 11 and 12), which are 1.2 and 2.2 kcal mol^{-1} lower than that of **3**, respectively. In terms of the inversion rate, these values are approximately 7 and 35 times as fast as that of **3**, respectively. The facile inversion of hexasubstituted sumanenes may be due to the steric repulsion of the bulky *endo*-substituents.

In summary, the bowl-to-bowl inversion of sumanene derivatives were experimentally investigated using 2D-EXSY NMR, which showed much slower inversion compared to that of corannulene. $\Delta G^{\ddagger}$ of the deuteriosumanene **3** was 19.7–20.4 kcal mol^{-1}, depending on the solvent. In bowl-to-bowl inversion of PAHs, solvent effect was first addressed. The mono- and di-anions of **3** showed a relatively rigid structure in solution. Hexasubstituted derivatives **6** and **7** were successfully synthesized, where a low inversion barrier was observed. Further structure–dynamics relationships are now under investigation.

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Notes and references

§ The NMR experiments for the measurement of the bowl-to-bowl inversion were conducted with 20 mM of sumanene derivatives. First, the longitudinal relaxation time T_1 at the corresponding protons was measured for each spectrum using the inversion–recovery method with the 180–τ–90° pulse sequence. 1D NOE experiments were carried out at various values of mixing time t_m. The optimum t_m was evaluated to be that at which the value of [integration for chemical exchange at 1D NOE experiment] × [S/N ratio] reaches a maximum. Relaxation decay d_1 was determined from eqn (1) where t_{ac} = acquisition time. Values of T_1 and t_m are summarized in Table S1, ESI.‡1

$$3T_1 = t_{ac} + t_m + d_1$$

2D EXSY (2D NOESY) experiments were performed with a spectrum width of 8 ppm, with acquisition time of 0.213 s, using 1024 data points in the t_2 dimension and 512 in t_1, with subsequent weighting with the sinebell function with 16 scans for each t_1 increment. Exchange cross-peaks were integrated, which were then processed using EXSYCalc[10] to give the chemical exchange rate constant (k). The rate constant k was further substituted to the Eyring equation to derive the activation energy ($\Delta G^{\ddagger}$).

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