

A theoretical study of the bowl-to-bowl inversion of sumanene derivatives*

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Abstract: A theoretical study was conducted on the bowl-to-bowl inversion of sumanene: its benzylic mono-, di-, and trianion species and its mono-, di-, and trinaphthosumanenes. The use of B3LYP/6-311+G(2d,p) for the B3LYP/6-31G(d,p)-optimized geometries approximately reproduced the experimental values for the bowl-to-bowl inversion of sumanene, and its benzylic mono- and dianion species. The value for the trianion was estimated to be around 21 kcal/mol using the above levels. The investigation of naphthosumanenes clearly indicated a noted increase in the inversion barrier with additional fused rings. The calculated inversion barrier for mononaphthosumanene also correctly reproduced the experimental value (32.2 kcal/mol) using the above levels (31.4 kcal/mol). The calculated barrier for trinaphthosumanene reached 63.8 kcal/mol, therefore, the bowl-to-bowl inversion is less likely to occur under realistic conditions.

Keywords: bowl structure; bowl-to-bowl inversion; calculation; inversion barrier; sumanene.

INTRODUCTION

Interest in the science of nonplanar π -conjugated carbon molecules, represented by C_{60} and carbon nanotubes, has greatly expanded due to their potential for application in interdisciplinary fields such as electrical materials science, catalysis, and pharmaceuticals [1]. In this context, bowl-shaped polyaromatic hydrocarbons, or π -bowls, are now considered to be another group of key materials in the science of curved π -conjugated carbon systems. Bowl-to-bowl inversion is one of the characteristic behaviors of some shallow π -bowls. Such intriguing dynamics have been studied exclusively using the C_{5v} symmetrical fullerene fragment, corannulene (**1**) (Fig. 1) [2,3]. Sumanene (**2**), with a C_{3v} symmetrical deeper bowl, is another compound that is a candidate for investigation of these types of dynamics (Fig. 1). We have already achieved the synthesis of **2** [4], and studied its structure [5a], followed by derivatizations [5], syntheses of deeper π -bowls [6], complexation with a transition metal [7], and application to organic electrical materials [8].

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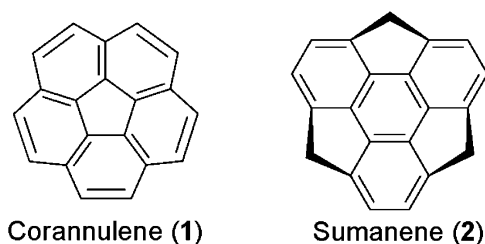


Fig. 1 Corannulene (1) and sumanene (2).

Facile generation of the benzylic anions **3–5** is possible with **2** (Fig. 2), and their electrophilic trapping permits the stereoselective introduction of various substituents [5a]. Therefore, the dynamics of the anion species may contribute to the stereoselectivity control. Recently, we investigated the bowl-to-bowl inversion of **2** and its derivatives including the benzylic monoanion **3** and dianion **4** by ^1H NMR and 2D exchange spectroscopy (EXSY) NMR [9]. Consequently, the inversion barriers of **2–4** were found to be 19.7–20.4, 21.8, and 21.5 kcal/mol, respectively [9]. Thus far, the theoretical studies have been performed with **2**. The semi-empirical method (MNDO) significantly overestimated the barrier of the bowl-to-bowl inversion for **2** (24.2 kcal/mol) [10]. A popular density functional theory (DFT) method using the B3LYP function predicted the barrier for **2** more accurately (16.9 kcal/mol with cc-pVTZ and 16.8 kcal/mol with 6-31G(d) basis sets) [11]. The inversion dynamics of the benzylic trianion **5** ($\text{C}_{21}\text{H}_9^{3-}$) were also investigated theoretically using B3LYP/6-31+G(d) [12].

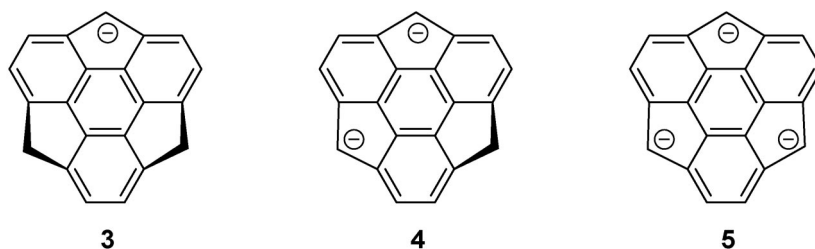


Fig. 2 Benzylic monoanion **3**, dianion **4**, and trianion **5** of sumanene (2).

We are also engaged in the question of how many additional fused rings on the sumanene structure are required to lock the bowl conformation. In the study of the inversion dynamics for corannulenes, the additional five-membered ring effectively slowed the inversion (ca. 27.65 kcal/mol) [2b,d]. For this reason, mono- **6**, di- **7a**, and **7b**, and tri-annulated sumanene **8** (Fig. 3a) were designed and synthesized from **2** in a few steps (Fig. 3b) [6]. Tri-annulated sumanene **8** possesses a hemifullerene ($\text{C}_{30}\text{H}_{12}$) skeleton. Dynamic NMR study of the benzylic dideuterated derivative of mononaphtho-sumanene gave the ΔG^\ddagger value for the bowl-to-bowl inversion [6].

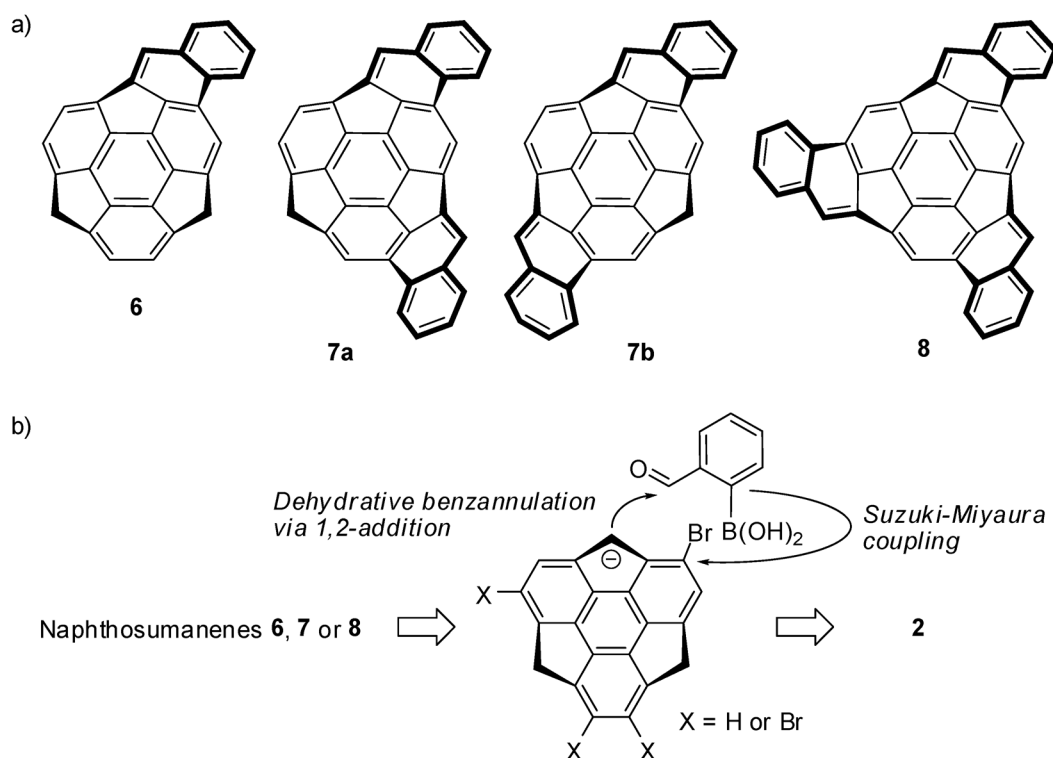


Fig. 3 (a) Naphthosumanenes **6**, **7a**, **7b**, and **8**. (b) Retrosynthesis for naphthosumanenes **6**, **7**, or **8**.

With some experimental values in hand, we report here a theoretical study of the bowl-to-bowl inversion of **2**, its benzylic monoanion **3** ($C_{21}H_{11}^-$), dianion **4** ($C_{21}H_{10}^{2-}$), and trianion **5** ($C_{21}H_9^{3-}$), and its annulated derivatives **6**, **7a**, **7b**, and **8**.

STRATEGY FOR THE ESTIMATION OF BOWL-TO-BOWL INVERSION

Bowl-to-bowl inversion barriers in the present study were estimated from the energy difference between the optimized bowl structure and the planar structure for a transition state, as reported previously (Fig. 4) [11a]. All calculations were conducted using a Gaussian 03 suite program. All the bowl-shaped compounds were structurally optimized at the B3LYP/6-31G(d,p) level. Planar conformers for the transition states were optimized at the same level of theory, and the structures were checked using the corresponding frequency calculation [13].

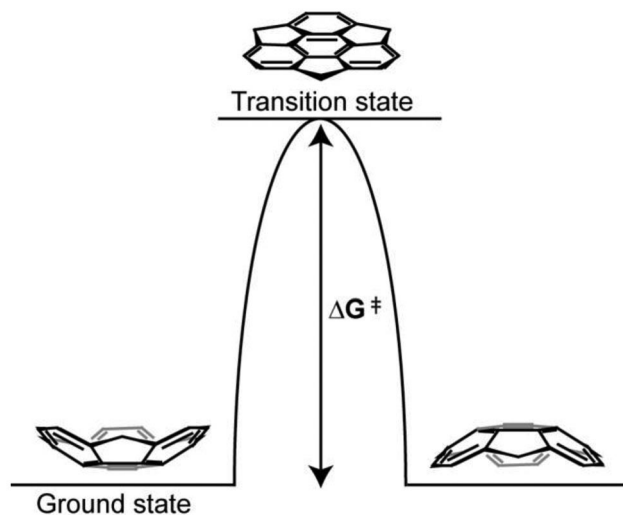
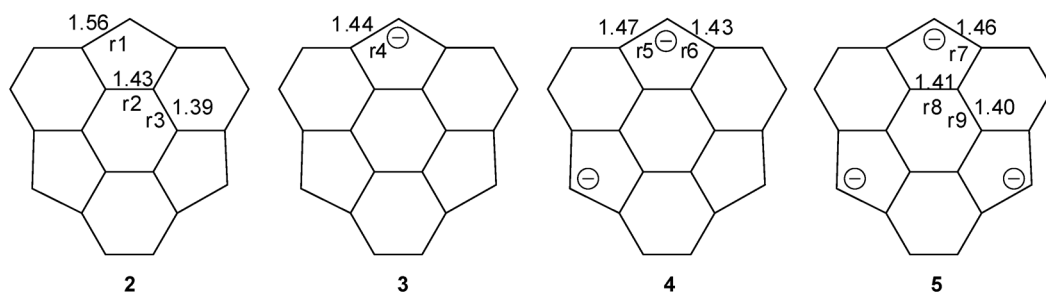


Fig. 4 Schematic representation of the bowl-to-bowl inversion barrier ΔG^\ddagger for sumanene.

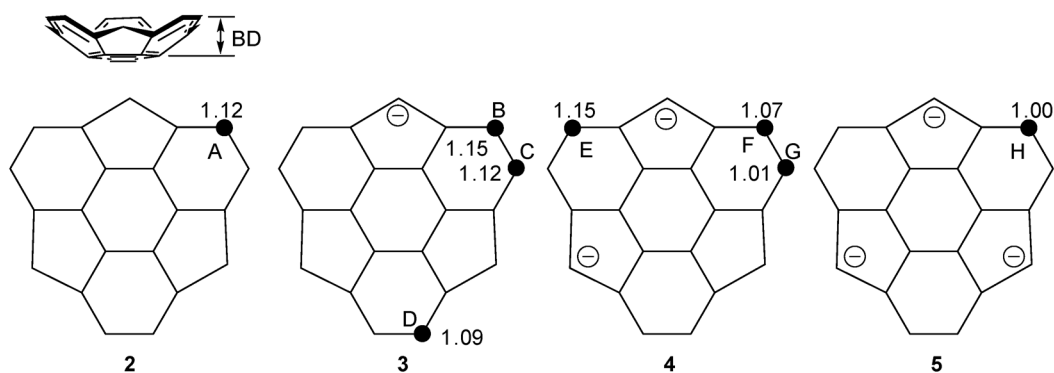
CALCULATED STRUCTURES OF SUMANENE AND ITS BENZYLIC ANION SPECIES

The selected bond lengths of **2–5** are shown in Fig. 5a. The bowl depth (BD) and the π -orbital axis vector (POAV) angle [14] were employed to evaluate the curvature. The BD is defined as the distance between the plane of the hub benzene ring and the aromatic carbon rim. The POAV angle is defined as $\theta_{\sigma\pi}-90^\circ$, which indicates the extent of the pyramidalization. Selected values for sumanene compounds are depicted in Fig. 5b and 5c. The optimized structure of **2** is quite similar to the crystal structure [5a]. In the optimized structure of **3**, the bond length, r_4 , is 1.44 Å, which is shorter than the r_1 of **2** (1.56 Å) probably due to the sp^2 hybridization. The BDs of **3** from the carbon rims of B, C, and D are 1.15, 1.12, and 1.09 Å, respectively. They become gradually smaller as the distance from the benzylic anion increases. A slight deepening was observed at the carbon rim of B in **3**, but a small shallowing was observed at the carbon rim of D, as compared with the carbon rim of A in **2** (1.12 Å). POAV angles at the carbon hubs of J, K, and L are 9.7, 8.3, and 8.4°, respectively. The value of J is larger than that of I for **2** (8.7°) [15], whereas the smaller values are obtained for K and L. Accordingly, the degree of curvature increases around the benzylic anion. Similar trends were observed for dianion **4**. The bond lengths of r_5 and r_6 are 1.47 and 1.43 Å, respectively. The BD from the carbon rim of E is 1.15 Å, which is the same value as for B in **3**. On the other hand, smaller values were obtained for F and G (1.07 and 1.01 Å, respectively). Carbons M and N exhibited large POAV angles of 9.4 and 9.5°, respectively. In contrast, a significantly smaller value was observed for O (7.3°). Thus, the side of the benzylic methylene is flattened and the opposite side becomes deeper for dianion **4**. With the optimized structure of C_{3v} symmetric trianion **5**, the hub benzene ring showed a small bond alternation (r_8 and r_9 : 1.41 and 1.40 Å, respectively) in contrast to **2** (r_2 and r_3 : 1.43 and 1.39 Å, respectively). The bond length of r_7 is similar to the corresponding bonds for **3** and **4**. The BD at H is 1.00 Å, which is the smallest value for sumanene and its anion species.

a) Selected bond lengths (Å)



b) Selected bowl depths (Å)



c) Selected POAVs (°)

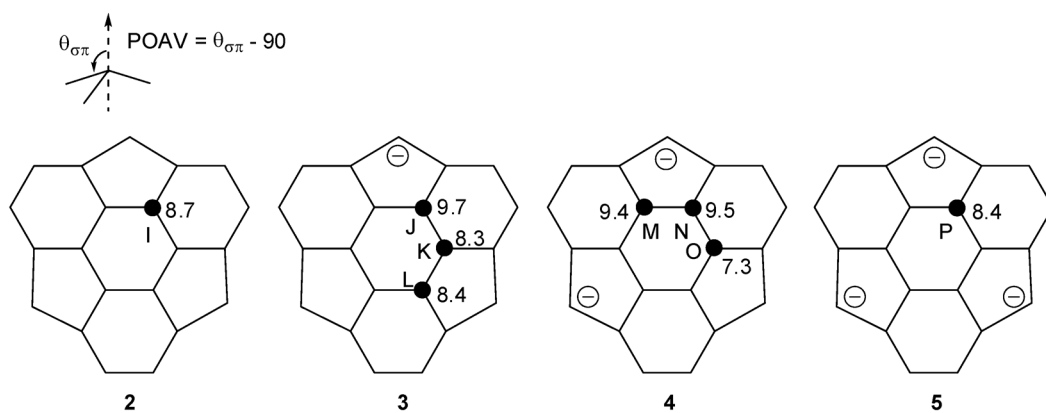


Fig. 5 Selected (a) bond lengths (Å), (b) BDs (Å), and (c) POAVs (°) in the optimized structures of sumanene (**2**), and its benzylic mono-, di-, and trianion species **3–5** based on B3LYP/6-31G(d,p).

CALCULATED BOWL-TO-BOWL INVERSION BARRIERS OF SUMANENE AND ITS BENZYLIC ANION SPECIES

Single-point energy calculation was conducted for these optimized structures to evaluate the bowl-to-bowl inversion barriers. The experimental and calculated inversion barriers ΔG^\ddagger (kcal/mol) are shown in Table 1. Based on the experimental values for trideuteriosumanene [9], inversion barriers ΔG^\ddagger for **2** should be around 20 kcal/mol, depending on the solvents. The B3LYP/6-31G(d,p) underestimated the barrier by ca. 3 kcal/mol. A well-estimated value (19.0 kcal/mol) was obtained by use of a triple- ζ basis set with a polarization and a diffuse function. The additional polarization function and/or diffuse function are insignificant [19.0 kcal/mol at B3LYP/6-311++G(2d,p) and 18.9 kcal/mol at B3LYP/6-311++G(3df,3pd)]. The use of an aug-cc-pVTZ basis set showed a smaller value (18.3 kcal/mol). The MP2/6-311+G(2d,p) estimated 19.1 kcal/mol, which is similar to the corresponding B3LYP functional. The electron correlation appears to be unimportant for this inversion process. The experimental values for **3** and **4** are 21.8 and 21.5 kcal/mol for tetrahydrofuran (THF), showing a slightly higher barrier for monoanion **3** [9]. The use of the polarizable continuum model (PCM) method to include the solvent effect did not improve the calculation results. The best conditions for **3** were obtained with B3LYP/6-311+G(2d,p) and MP2/6-311+G(2d,p) levels (21.6 kcal/mol each), which differs from the experimental value by a mere 0.2 kcal/mol. On the other hand, a slight overestimation (1 kcal/mol) was observed for dianion **4** (22.5 and 22.6 kcal/mol) under the best conditions for **3**. This could have been due to the effect of the solvents and/or to the counter cations. Exploring the appropriate structure for the transition state may also be necessary to improve the accuracy. The closest value, 21.4 kcal/mol, for **4** was obtained for the B3LYP/aug-cc-pVTZ level in contrast with **3**. In the investigation of trianion **5**, the diffuse function has a strong effect. This tendency is consistent with the reported one, where the diffuse function also has a strong effect for **5** [12]. The inversion barrier ΔG^\ddagger for **5** is estimated to be around 21 kcal/mol for B3LYP/6-311+G(2d,p) with/without a self-consistent reaction field (SCRF) parameter and MP2/6-311+G(2d,p) levels. Thus, the calculated values of the inversion barrier for **5** are larger than those of sumanene **2** (18.3–19.1 kcal/mol), although trianion **5** has a shallower optimized structure than **2** (1.12 Å for **2** and 1.00 Å for **5**, Fig. 5b). The experimental value is required for further discussion of the theoretical result.

Table 1 Bowl-to-bowl inversion barrier ΔG^\ddagger (kcal/mol) for sumanene (**2**) and its benzylic mono-, di-, and trianion species **3–5**.

Level	ΔG^\ddagger (kcal/mol)			
	2	3	4	5
Experimental	19.7–20.4 ^a	21.8	21.5	— ^d
B3LYP/6-31G(d,p)	17.0	18.3	17.2	12.1
B3LYP/6-311+G(2d,p)	19.0	21.6	22.5	20.9
B3LYP/6-311+G(2d,p) SCRF ^b	— ^c	21.1	22.4	21.2
B3LYP/aug-cc-pVTZ	18.3	20.9	21.4	— ^c
MP2/6-311+G(2d,p)	19.1	21.6	22.6	21.0

^aDepends on solvents [9].

^bPCM model with THF.

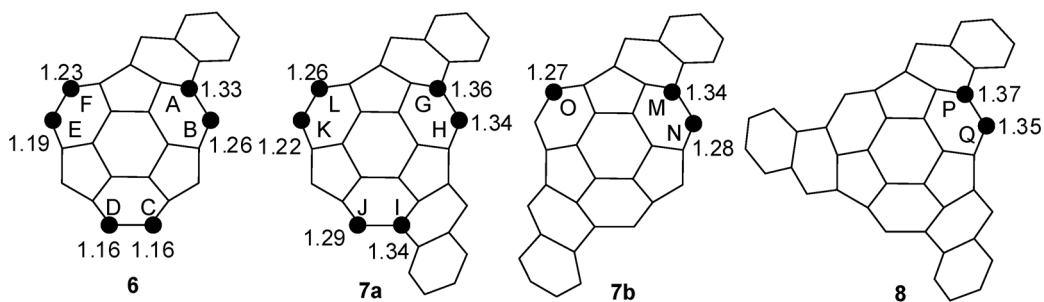
^cNot tried.

^dNo experimental value is obtained.

CALCULATED STRUCTURES OF NAPHTHOSUMANENES

The optimized structures of naphthosumanenes **6**, **7a**, **7b**, and **8** using B3LYP/6-31G(d,p) level are described in terms of the BD and the POAV. The selected BDs and POAVs are shown in Figs. 6a and 6b, respectively. Here, the BD is defined as the distance between the plane of the six-membered ring at

a) Selected bowl depths (Å)



b) POAVs (°)

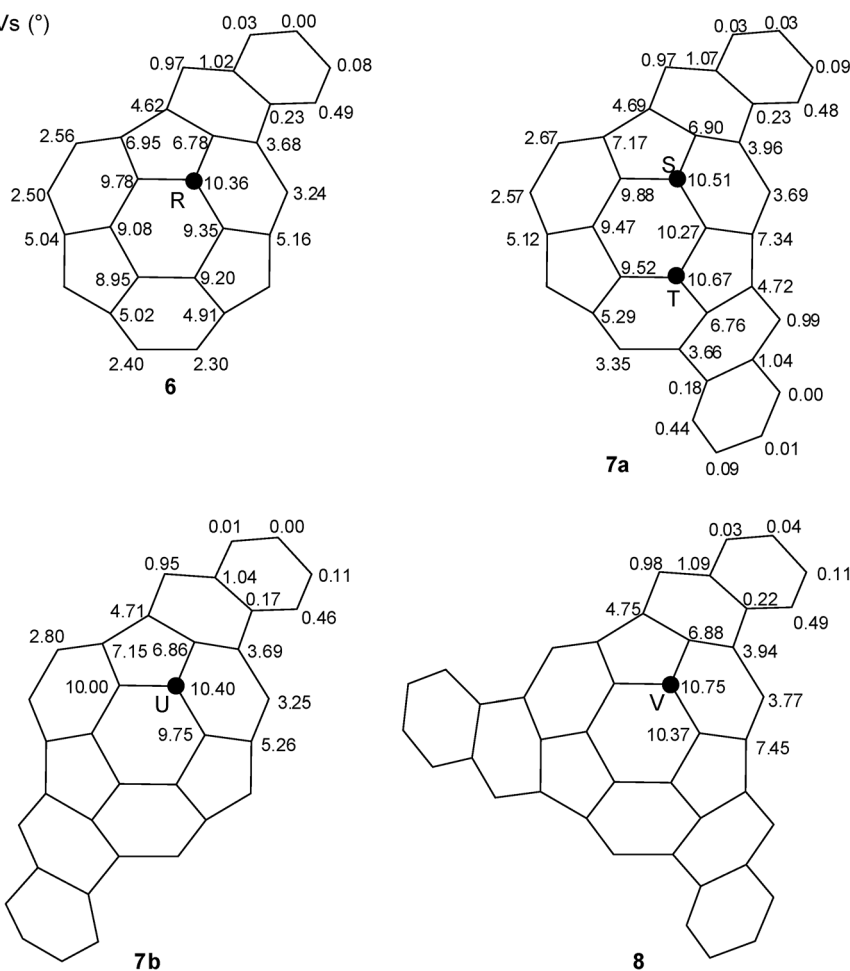


Fig. 6 Selected (a) BDs (Å), and (b) POAVs (°) for the optimized structures of naphthosumanenes **6**, **7a**, **7b**, and **8** based on B3LYP/6-31G(d,p).

the base and the aromatic carbon rim on the sumanene skeleton in the structure. In the mononaphthosumanene **6**, the BD at A is 1.33 Å, which is much deeper than that of **2**. A small deepening compared to **2** was also observed from the carbon rims of C and D (1.16 Å). The carbons G, I, and M for **7a** and **7b** showed somewhat larger BDs (1.36, 1.34, and 1.34 Å, respectively) than that of the corresponding one for **6**. The BDs are greater than 1.22 Å for carbons G to O in **7a** and **7b**, thus, the bowl structure seems to possess a larger strain on the whole. Trinaphthosumanene **8** exhibited a more strained structure, where the BDs are 1.37 and 1.35 Å for P and Q, respectively. These values are comparable to hemifullerene [16]. As for the POAVs, the degree of the curvature was found to increase from the carbon rims to the hub benzene ring for all compounds, **6**, **7a**, **7b**, and **8**. The carbons of the hub benzene ring closest to the annulated naphthene moieties are the most curved, such as 10.36° at R for **6**, 10.51 and 10.67° at S and T for **7a**, and 10.40° at U for **7b**. The POAV at V for trinaphthosumanene **8** reaches 10.75°, but is still smaller than the corresponding one in fullerene C₆₀ (11.6°) [17].

CALCULATED BOWL-TO-BOWL INVERSION BARRIERS OF NAPHTHOSUMANENES

Single-point energy calculation was conducted for these optimized structures to evaluate the bowl-to-bowl inversion barriers. The values for the experimental and calculated inversion barrier ΔG^\ddagger (kcal/mol) are shown in Table 2. Based on the experimental value for the benzylic dideuterated mononaphthosumanene in mesitylene-*d*₁₂ [6], the inversion barrier ΔG^\ddagger for **6** should be around 32.2 kcal/mol. Similar to the estimate for sumanene and its anion species, B3LYP/6-31G(d,p) underestimated the barrier by ca. 3 kcal/mol. A well-estimated value for **6** (31.4 kcal/mol) was obtained by use of B3LYP/6-311+G(2d,p). The values for **7a** and **7b** are 46.4 and 45.2 kcal/mol, respectively [B3LYP/6-311+G(2d,p)]. Thus, the ΔG^\ddagger for **7a** is somewhat larger than that for **7b**, which is accounted for by the above-mentioned results that **7a** has somewhat larger values for both POAVs and BDs compared with those of **7b** (Fig. 6). Finally, the inversion barrier ΔG^\ddagger for **8** was estimated to be 63.8 kcal/mol [B3LYP/6-311+G(2d,p)]. Apparently, the bowl structure is difficult to invert.

Table 2 Bowl-to-bowl inversion barriers ΔG^\ddagger (kcal/mol) for naphthosumanenes **6**, **7a**, **7b**, and **8**.

Level	ΔG^\ddagger (kcal/mol)			
	6	7a	7b	8
Experimental	32.2 ^a	— ^b	— ^b	— ^b
B3LYP/6-31G(d,p)	29.1	43.7	42.5	61.0
B3LYP/6-311+G(2d,p)	31.4	46.4	45.2	63.8

^aMesitylene-*d*₁₂.

^bNo experimental value is obtained.

CONCLUSIONS

A theoretical study was conducted for the bowl-to-bowl inversion of sumanene (**2**), its benzylic anion species **3–5**, and naphthosumanenes **6–8**. Use of B3LYP/6-311+G(2d,p) for the B3LYP/6-31G(d,p)-optimized geometries approximately reproduced the experimental values for **2–4**. The value for the trianion **5** was estimated to be around 21 kcal/mol using the above level. The investigation of naphthosumanenes **6–8** clearly indicated that the inversion barrier increases due to additional fused rings. The calculated inversion barrier of mononaphthosumanene **6** also correctly reproduced the experimental value (32.2 kcal/mol) using the above level (31.4 kcal/mol). Thus, the single-point energy calculation at the B3LYP/6-311+G(2d,p) level for the B3LYP/6-31G(d,p) optimized geometries seems the best conditions to estimate the bowl-to-bowl inversion of the sumanene derivatives so far. The

calculated barrier for trinaphthosumanene **8** reached 63.8 kcal/mol, so the bowl-to-bowl inversion of **8** is less likely to occur under realistic conditions.

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