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Synthesis of Hydroxysumanene and Substituent Effect of Hydroxy Group on Bowl Inversion Dynamics and Electronic Structure

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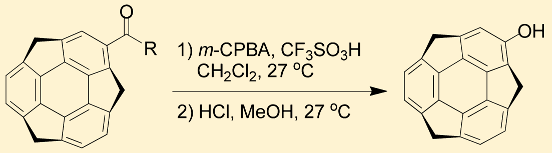
S Supporting Information



ABSTRACT: Hydroxysumanene was synthesized from acylsumanenes by Baeyer–Villiger oxidation. DFT calculation predicted the higher bowl inversion energy and deeper bowl structure of hydroxysumanene than those of pristine sumanene. The bowl inversion energy of hydroxysumanene was experimentally determined by 2D-EXSY NMR measurement as 21.2 kcal/mol. The energy was larger than that of pristine sumanene (20.3 kcal/mol), which agreed with the calculation result. Electrochemical measurement indicated the higher HOMO level of hydroxysumanene than that of sumanene, which confirmed the electron-rich character of the phenolic function in the bowl skeleton.

Sumanene (**1**) is a C_{3v} symmetric bowl-shaped buckybowl.[1] After the successful synthesis of pristine sumanene,[1c] substituted sumanene derivatives with a variety of functional groups have been synthesized.[1−3] They exhibited various unique properties such as bowl inversion,[4,5] columnar packing structure in the solid state,[3,5,6] bowl chirality,[5,7] electron conductivity,[5,8] curved face-dependent stereoelectronic effect,[9] and unprecedented coordination ability.[10] Among its interesting properties, we extensively studied the substituent effects on the bowl inversion energy barrier and the correlation between the bowl structure and the bowl inversion energy by means of DFT calculation and experiments.[4b,5] We have previously proposed by calculation that the hydroxy group causes deeper bowl depth and higher bowl inversion energy than those of the pristine sumanene.[4b] In addition, hydroxysumanene could be a useful synthetic intermediate to prepare substituted sumanene derivatives owing to the reactive phenolic functional group. Herein, we report the synthesis of hydroxysumanene by Baeyer−Villiger oxidation of acylsumanenes derived from sumanene and the experimental determination of the bowl inversion energy by the NMR measurement. The electronic state of hydroxysumanene was also investigated by UV absorption and electrochemical measurements.

Hydroxysumanene (**6**) was synthesized by Baeyer−Villiger oxidation of acylsumanenes, prepared by electrophilic acylation of sumanene (**1**) (Scheme 1).[3a] The oxidation of formylsumanene (**2**) or acetylsumanene (**3**) by *m*-chloroperbenzoic acid (*m*-CPBA) in the presence of trifluoromethanesulfonic acid (TfOH)[11] afforded acyloxysumanenes **4** and **5** in 84% and 61% yields, respectively. The acid-catalyzed alcoholysis of **4** or **5** using 10% HCl/MeOH gave **6** in 78% or 54% yields in two steps from **2** or **3**, respectively.

For the determination of bowl inversion energy of **6** by the 2D-EXSY NMR method, **6**-d_3 was necessary to avoid the scrambling of the signals of chemical exchange of the *exo* and *endo* protons at the benzylic position with the NOE signals between them.[4a] Therefore, **6**-d_3 was prepared from **1**-d_3[4b] by the same method without loss of deuterium, and the bowl inversion energy of **6**-d_3 was determined to be 21.2 kcal/mol by 2D-EXSY NMR measurement (ESI). The experimental and calculated bowl inversion energies and the calculated bowl depths of **1** and **6** are shown in Table 1. In calculations, the bowl depth of **6** was slightly deeper than that of **1**. Accordingly, the calculated bowl inversion energy of **6** was 0.3 kcal/mol higher than that of **1** owing to the correlation between the bowl depth and bowl inversion energy.[4b,5] The experimental bowl inversion energy (21.2 kcal/mol) of **6** was also 0.9 kcal/mol higher than 20.3 kcal/mol of **1**, which agreed with the calculated higher bowl inversion energy of **6** than that of **1**. In the previous report regarding the trisubstituted sumanene derivatives,[5] we proposed that the origin of the deeper bowl depth and the higher bowl inversion energy caused by the hydroxy group comes from the difference of the steric repulsion of the hydroxy group between the ground state bowl structure and the flat transition state. The optimized bowl structure and flat transition structure by DFT calculation were shown with the distance between the hydroxy group and *ortho*-hydrogen atom in Figure 1. In the flat transition state, the distance becomes shorter than that of the bowl structure, which destabilizes the transition state, leading to the higher bowl inversion energy of **6** than **1**.

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Scheme 1. Synthesis of Hydroxysumanene 6 and Trideuterohydroxysumanene 6-d_3

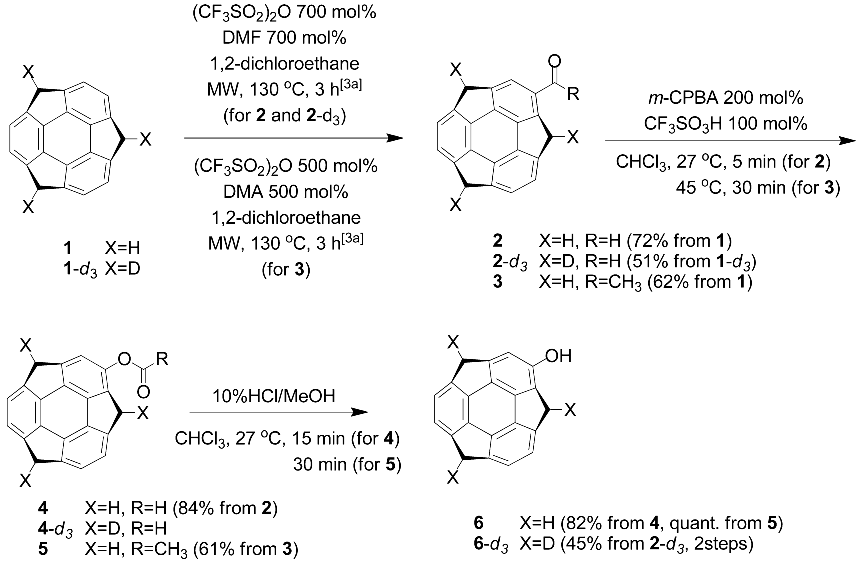

Table 1. Bowl Inversion Energy and Calculated Bowl Depth of 1 and 6

	bowl inversion energy (kcal/mol)		
	experiment[a]	calculation[b]	calculated bowl depth (Å)[b]
1	20.3	19.7	1.155
6	21.2	20.0	1.159

[a] The experimental error is less than 0.1% which can be negligible. [b] Calculated at ωB97XD/6-311++G(d,p) level.

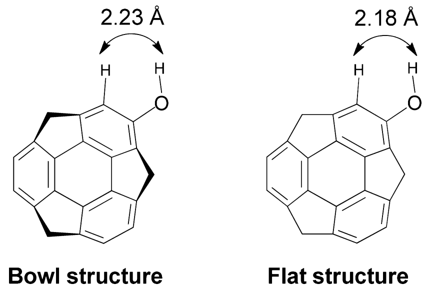

Figure 1. Distance between hydrogen of hydroxy group and the neighboring hydrogen in the optimized bowl and flat structures of **6** by DFT calculation [ωB97XD/6-311++G(d,p)].

Absorption and emission spectra of **1** and **6** are shown in Figure 2.[12] **6** showed the absorption band at λ_{max} = 280 nm, which was slightly red-shifted from that of **1** at λ_{max} = 277 nm. The absorption edge (392 nm) of **6** also showed a slight red shift from that (371 nm) of **1**, suggesting the narrower HOMO−LUMO gap of **6** than **1**. The emission spectrum (λ_{max} = 397 nm) of **6** also showed a slight red shift than that of **1** (λ_{max} = 375 nm). The electrochemical property of **6** was investigated by cyclic voltammetry (CV) (Figure 3) and differential pulse voltammetry (DPV; ESI).[13] Both **1** and **6** showed two irreversible oxidation waves. **6** showed a lower first oxidation potential (0.54 V) than **1** (0.89 V) due to the higher HOMO level of **6** caused by the electron-donating ability of the hydroxy group. The trend of experimental HOMO−LUMO gaps and HOMO levels was consistent with that from calculations (Figure 4).

In summary, hydroxysumanene **6** was synthesized from formyl- and acetyl-sumanenes **2** and **3** by Baeyer−Villiger oxidation. The bowl inversion energy of **6** was experimentally determined by 2D-EXSY NMR measurement as 21.2 kcal/mol. The energy was larger than the 20.3 kcal/mol of sumanene **1**, which agreed with the calculation result. Absorption spectra, cyclic voltammetry, and DFT calculation indicated that **6** has a higher HOMO level and narrower HOMO−LUMO gap than

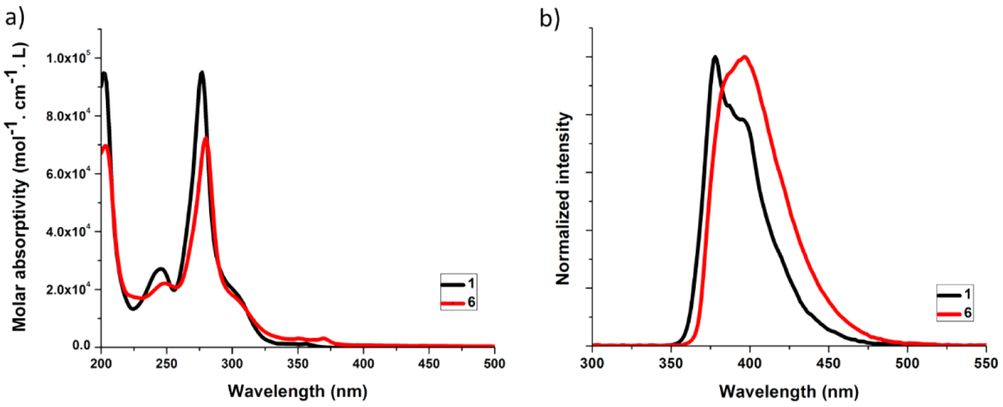

Figure 2. (a) Absorption and (b) emission spectra (excited at the absorption maxima) of **1** and **6** (1.0×10^{-5} M in CH_3CN).

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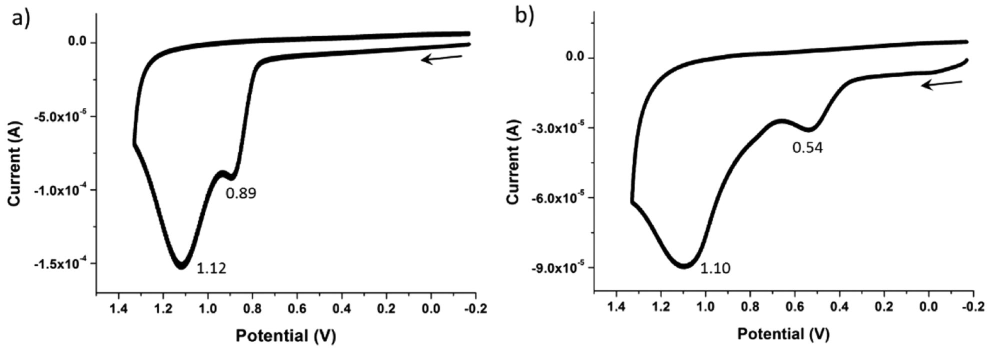

Figure 3. Cyclic voltammogram of (a) **1** and (b) **6** in CH_3CN containing 0.1 M Bu_4NClO_4 (vs Fc/Fc^+).

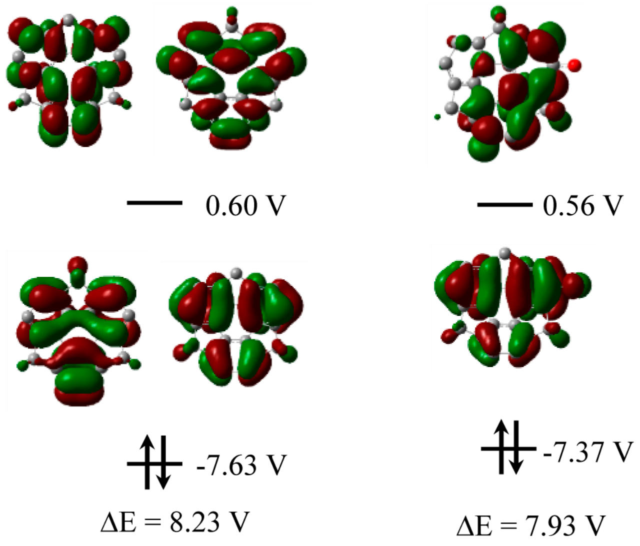

Figure 4. Calculated HOMOs and LUMOs of **1** (left) and **6** (right) [ωB97XD/6-311++G(d,p)].

1. The synthesized hydroxysumanene would be a useful synthetic intermediate for the syntheses of diverse substituted sumanene derivatives by further functionalization as well.

■ EXPERIMENTAL SECTION

General Information. All chemicals were reagent grade and used as received if not mentioned. Commercially available *m*-chloroperbenzoic acid was recrystallized from dichloromethane. The purity of recrystallized peracid was determined to be 83 wt % by iodometric titration. Na_2SO_4 was dried at 100 °C under vacuum before use. CH_3CN for electrochemical measurements was freshly distilled from CaH_2 prior to use. ^1H and ^{13}C NMR spectra were measured at 23 °C at 400 and 100 MHz, respectively. A residual solvent peak was used as an internal standard (^1H NMR: $CDCl_3$ 7.24 ppm; ^{13}C NMR: $CDCl_3$ 77.0 ppm). High resolution mass spectra (HRMS) were measured using electron impact mode (EI) and fast atom bombardment mode (FAB) with a double-focusing magnetic sector analyzer. Gel permeable chromatography (GPC) was conducted with $CHCl_3$ as eluent.

Acyloxysumanenes (4 and 5). Trifluoromethanesulfonic acid (3.0 μL, 0.034 mmol) was added to dry $CHCl_3$ (0.5 mL) containing anhydrous Na_2SO_4 (100.0 mg) at room temperature under an argon atmosphere. *m*-Chloroperbenzoic acid (83% activity, 14.2 mg, 0.068 mmol) was added to the mixture. After stirring for 5 min at room temperature, acylsumanene **2** or **3**[3a] (10.0 mg of **2**, 0.034 mmol or 10.0 mg of **3**, 0.033 mmol) was added. The reaction mixture was stirred at room temperature for 5 min for **2** or at 45 °C for 30 min for **3**. Dimethyl sulfide (13.0 μL, 0.177 mmol) was added, and the mixture was stirred at room temperature for 5 min. The reaction mixture was filtered through Celite, and the solvent was evaporated to afford the crude **4** and **5**. The crude product was purified by GPC to give **4** (8.9 mg, 84% yield) as a pale yellow solid or **5** (6.4 mg, 61% yield) as a pale yellow solid.

Formyloxysumanene (4). Mp: 219 °C (dec.); ^1H NMR ($CDCl_3$): δ 8.37 (*s*, 1H), 7.14−7.08 (*m*, 4H), 6.81 (*s*, 1H), 4.70 (*d*, *J* = 19.6 Hz, 1H), 4.69 (*d*, *J* = 20.0 Hz, 1H), 4.58 (*d*, *J* = 19.6 Hz, 1H), 3.43 (*d*, *J* = 20.0 Hz, 2H), 3.29 (*d*, *J* = 19.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 159.0, 151.6, 149.11, 149.10, 149.0, 148.9, 148.8, 148.7, 148.2, 148.0, 147.8, 146.4, 144.3, 138.0, 124.0, 123.392, 123.390, 123.35, 116.8, 41.7, 41.6, 40.4 ppm; IR (KBr): *υ* 2885, 1760, 1721, 1389 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{22}H_{12}O_2$ $[M]^+$ 308.0837, found 308.0837.

Acetyloxysumanene (5). Mp: 182 °C (dec.); ^1H NMR ($CDCl_3$): δ 7.12−7.05 (*m*, 4H), 6.76 (*s*, 1H), 4.69 (*d*, *J* = 19.6 Hz, 1H), 4.67 (*d*, *J* = 19.2 Hz, 1H), 4.55 (*d*, *J* = 19.6 Hz, 1H), 3.42 (*d*, *J* = 19.2 Hz, 1H), 3.41 (*d*, *J* = 19.6 Hz, 1H), 3.40 (*d*, *J* = 19.6 Hz, 1H), 2.30 (*s*, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 169.0, 151.3, 149.0, 148.94, 148.90, 148.8, 148.6, 148.4, 148.1, 148.0, 146.1, 145.1, 138.4, 123.8, 123.32, 123.30, 123.2, 117.2, 41.7, 41.6, 40.4, 21.0 ppm; IR (KBr): *υ* 2885, 1754, 1205 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{23}H_{14}O_2$ $[M]^+$ 322.0994, found 322.0988.

Hydroxysumanene (6). Crude acyloxysumanene **4** or **5**, prepared from acylsumanene **2** or **3** (10.0 mg of **2**, 0.034 mmol or 10.0 mg of **3**, 0.033 mmol), was dissolved in dry $CHCl_3$ (1 mL). Under an argon atmosphere, 10% HCl in methanol (150.0 μL) was added. The reaction mixture was stirred under an argon atmosphere at room temperature for 15 min for **4** and 30 min for **5**. After evaporation of solvent, the residue was purified by PTLC (CH_2Cl_2) to give **6** (6.6 mg, 69% yield in two steps from **2**, 5.7 mg, 62% in two steps from **3**) as a white solid. Mp: 230 °C (dec.); ^1H NMR ($CDCl_3$): δ 7.09−7.01 (*m*, 4H), 6.55 (*s*, 1H), 4.93 (*brs*, 1H), 4.67 (*d*, *J* = 19.2 Hz, 1H), 4.63 (*d*, *J* = 19.2 Hz, 1H), 4.56 (*d*, *J* = 19.6 Hz, 1H), 3.49 (*d*, *J* = 19.2 Hz, 1H), 3.39 (*d*, *J* = 20.0 Hz, 1H), 3.34 (*d*, *J* = 20.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 153.0, 151.7, 150.3, 149.2, 149.1, 148.9, 148.8, 148.2, 148.07, 148.06, 147.7, 142.3, 130.1, 123.6, 123.3, 123.2, 122.2, 112.4, 41.6, 41.5, 39.1 ppm; IR (KBr): *υ* 3263 (br), 2886, 1559, 1396 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{21}H_{12}O$ $[M]^+$ 280.0888, found 280.0883.

Trideuteroformylsumanene (2-d_3). **2-d_3** was prepared from trideuterosumanene **1-d_3**[4b] by following the reported method to prepare **2** from **1**.[3a] Trifluoromethanesulfonic anhydride (90.0 μL, 0.529 mmol) and 1,2-dichloroethane (4 mL) were added to dimethylformamide (41.0 μL, 0.529 mmol) at 0 °C in a microwave test tube. The reaction mixture was stirred at 0 °C for 5 min. Trideuterosumanene (20.0 mg, 0.075 mmol) was added, and the mixture was stirred at 130 °C for 3 h by microwave irradiation. The reaction mixture was quenched by 1 M aq. NaOH. The mixture was extracted by CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered using a Kiriyama funnel, and evaporated under vacuum. The crude product was purified by PTLC (CH_2Cl_2) to afford **2-d_3** (11.3 mg, 51% yield). Mp: 205 °C (dec.); ^1H NMR ($CDCl_3$): δ 10.03 (*s*, 1H), 7.64 (*s*, 1H), 7.21−7.13 (*m*, 4H), 4.90 (*brs*, 0.5H), 4.75 (*brs*, 0.5H), 4.70 (*brs*, 0.5H), 3.80 (*brs*, 0.5H), 3.52 (*brs*, 0.5H), 3.42 (*brs*, 0.5H) ppm; ^{13}C NMR ($CDCl_3$): δ 191.9, 152.76, 152.74, 151.97, 151.92, 150.0, 149.72, 149.70, 149.21, 149.16, 149.09, 149.06, 149.01, 148.98, 148.77, 148.75, 148.64, 148.0, 147.20, 133.1, 133.0, 127.23, 127.20, 125.09, 125.02, 124.23, 124.16, 123.59, 123.53, 123.50, 42.2 (*t*, J = 20.1 Hz, D), 41.6 (*t*, J = 20.1 Hz, D), 41.4 (*t*, J = 20.6 Hz, D) ppm; IR (KBr): υ 2930, 2887, 1681, 1634, 1253, 768 cm^{-1} ; HRMS (FAB) m/z: calcd for $C_{22}H_9D_3O$ [M]$^+$ 295.1076, found 295.1080.

Trideuterohydroxysumanene (6-*d*$_3$). **6-*d*$_3$** (4.3 mg, 0.015 mmol) was prepared in 45% yield from **2-*d*$_3$** (10.0 mg, 0.034 mmol) by following the same method for **6** from **2**. ^{1}H NMR ($CDCl_3$): δ 7.10−6.99 (*m*, 4H), 6.55 (*s*, 1H), 4.88 (*brs*, 1H), 4.67 (*brs*, 0.5H), 4.62 (*brs*, 0.5H), 4.54 (*brs*, 0.5H), 3.48 (*brs*, 0.5H), 3.38 (*brs*, 0.5H), 3.33 (*brs*, 0.5H) ppm; ^{13}C NMR ($CDCl_3$): δ 152.9, 151.74, 151.70, 150.36, 150.34, 149.25, 149.1, 149.07, 148.9, 148.2, 148.1, 148.06, 148.03, 147.7, 142.3, 130.07, 130.03, 123.6, 123.5, 123.3, 123.27, 123.22, 123.16, 122.19, 122.14, 112.4, 112.38, 41.4 (*t*, J = 20.1 Hz, D), 41.2 (*t*, J = 19.7 Hz, D), 38.8 (*t*, J = 20.1 Hz, D) ppm; IR (KBr): υ 3354 (br), 2928, 2886, 2354, 1339, 1225, 1191, 768 cm^{-1} ; HRMS (FAB) m/z: calcd for $C_{21}H_9D_3O$ [M]$^+$ 283.1076, found 283.1068.

■ COMPUTATIONAL DETAILS

All the theoretical calculations were conducted by Gaussian09.[14] The ground state structures were obtained by full optimization at the ωB97XD/6-311++G(d,p) level, and frequency calculations were performed to confirm the exact minimum of potential energy. The flat transition structures were also calculated at the same level and were confirmed by one imaginary frequency which corresponds to bowl inversions. The difference between the subtotal energies + ZPEs of bowl and flat structures of corresponding compounds are reported as bowl inversion energies in the table.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02046.

> ^{1}H and ^{13}C NMR of new compounds, bowl-to-bowl inversion energy measurement of **6-*d*$_3$**, DPV of **6** and calculated atom coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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(12) Solvent dependent absorption and emission spectra of **1** and **6** are shown in the SI.

(13) Condition of CV: 0.1 M Bu_4NClO_4 in CH_3CN containing 0.1 M Bu_4NClO_4, scan rate 100 mV/s (vs Fc/Fc$^+$) with glassy carbon as working electrode, platinum electrode, and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The initial direction is anodic.

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