

## Heterobuckybowls

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## Redox-Dependent Transformation of a Hydrazinobuckybowl between Curved and Planar Geometries

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**Abstract:** A red-fluorescent heterobuckybowl with an embedded hydrazine structure was synthesized from a cyclobiphenothiazine derivative via a strained cyclobicarbazole. The hydrazinobuckybowl was found to possess bowl and twist structures in the neutral state, a shallow bowl structure in the monocation state, and a planar structure in the dication state by means of X-ray crystallographic analysis, DFT calculations, and a comparison of experimental and calculated  $^{13}\text{C}$  NMR chemical shifts. The hydrazinobuckybowl is the first bucky-bowl that changes its geometry between curved bowl/twist structures and a planar structure depending on the oxidation state. The drastic geometrical change was possible as a result of the presence of two heteroatoms in the bowl skeleton and the multiple reversible redox reactions of the compound. Owing to the two kinds of bowl and twist conformations, the bowl-inversion dynamics of the hydrazinobuckybowl were found to follow a triple-well potential model.

In the expanding scientific field of nonplanar  $\pi$ -conjugated organic molecules, bowl-shaped aromatic compounds (buckybowls, geodesic polyarenes,  $\pi$ -bowls) have fascinated many chemists owing to their unique properties derived from their  $\pi$ -conjugated bowl structure.<sup>[1]</sup> Among buckybowls,  $C_3$ -symmetric corannulene and  $C_3$ -symmetric sumanene have been studied extensively,<sup>[1,2]</sup> including their heterobuckybowl derivatives containing heteroatoms in the bowl skeleton.<sup>[3]</sup> Heterobuckybowls are attractive molecules owing to their synthetic challenges as well as their expected properties that are characteristic of embedded heteroatoms and heterocycles. For example, the introduction of heteroatoms into the carbon skeleton of buckybowls has been reported to lead to a deeper, shallower, or flatter bowl shape and slower or faster bowl-inversion kinetics.<sup>[3,4]</sup> A homochiral heterobuckybowl with a deep bowl and a high bowl-inversion/racemization barrier was obtained by embedding nitrogen atoms in the sumanene skeleton.<sup>[3c]</sup> In this study, we synthesized  $C_2$ -symmetric red-fluorescent hydrazine-embedded heterobuckybowls **1** (Figure 1) possessing the novel property that their geometry is transformed between curved bowl/twist structures and

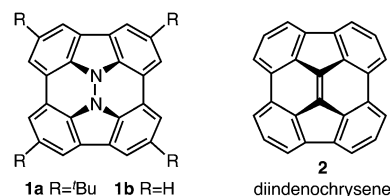


Figure 1. Hydrazinobuckybowls **1** and diindenochrysene (**2**).

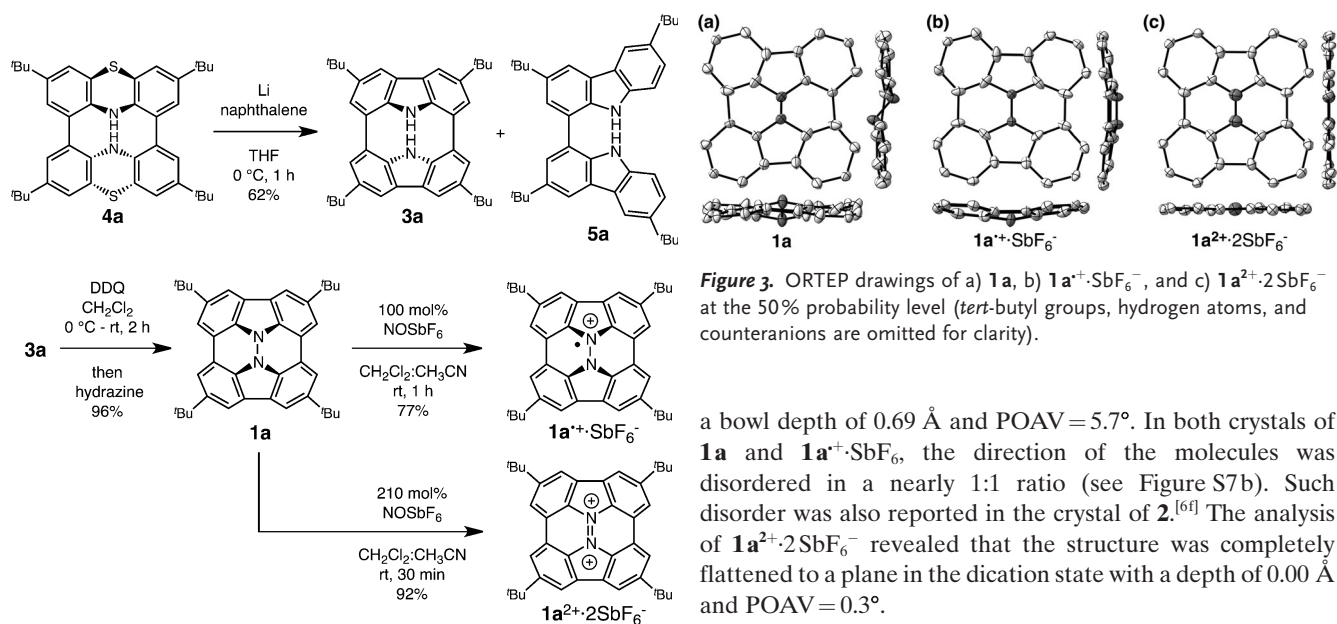
a planar structure depending on the oxidation state.<sup>[5]</sup> Compounds **1** are the first hydrazine-embedded buckybowls with the diindenochrysene<sup>[6]</sup> skeleton **2** and a partial structure of the unidentified hydrazine-embedded fullerene  $C_{58}N_2$ .<sup>[7]</sup> We succeeded in synthesizing **1a** via the strained cyclobicarbazole **3a**, which was obtained by the reductive desulfurization of a phenothiazine to form a carbazole skeleton. Owing to the hydrazine-embedded polyarene structure,<sup>[8]</sup> the stable monocation and dication were generated by stepwise two-electron oxidation. Bowl and twist structures in the neutral state, a shallower bowl structure in the monocation state, and a planar structure in the dication state were determined by means of X-ray crystallographic analysis, DFT calculations, and comparison of experimental and calculated  $^{13}\text{C}$  NMR chemical shifts. The drastic geometrical change was possible as a result of the combination of two heteroatoms and multiple redox processes. Because of the two kinds of bowl and twist conformations, the bowl-inversion dynamics of **1a** were also found to follow a triple-well potential model: the second example of such behavior among reported buckybowls. The strain energy of cyclobicarbazole **3a** was also evaluated by DFT calculations. Herein, we report the synthesis, structures, and properties of **1a**, the cationic species, and **3a**.

For the synthesis of hydrazinobuckybowl **1a**, we used our previously described compound **4a** with a double-butterfly structure<sup>[8k]</sup> as the starting material (Scheme 1). Compound **4a** underwent a modified reductive desulfurization reaction with Li powder and naphthalene<sup>[9]</sup> to give **3a** in 62% yield. Compound **5a**<sup>[8h]</sup> was also formed as a major by-product in 12% yield through reductive C–C bond cleavage of **3a**. A prolonged reaction time resulted in the complete conversion of **3a** into **5a**. This unusual C–C bond-cleavage reaction is considered to be due to the highly strained structure of **3a**, as indicated by DFT calculations.<sup>[10]</sup> The strain energy of **3** was estimated as  $62.5 \text{ kcal mol}^{-1}$  [B3LYP/6-31G(d)], which is comparable to the reported energies of [6]–[9]cycloparaphenylenes.<sup>[10,11]</sup> The oxidation of **3a** with DDQ, followed by reductive quenching with hydrazine, afforded hydrazinobuckybowl **1a** in 96% yield. The cyclic voltammogram of **1a** showed two reversible redox waves at 0.06 and

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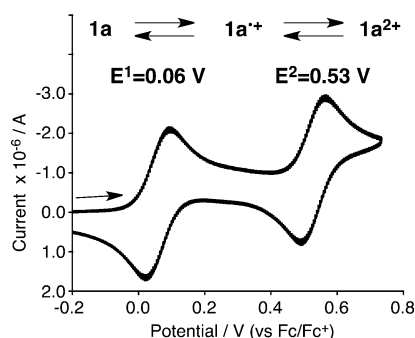
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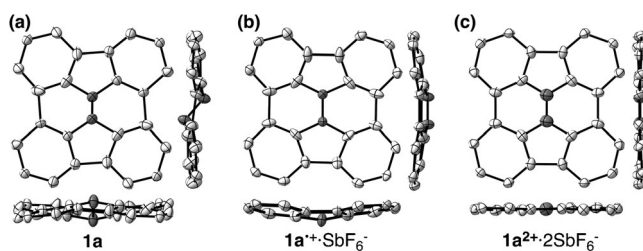


0.53 V (vs. Fc/Fc<sup>+</sup>; Figure 2) and indicated the generation of the stable monocation and dication of **1a**. Thus, the monocation **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup> and dication **1a**<sup>2+</sup>·2SbF<sub>6</sub><sup>−</sup> were synthesized and isolated in high yields by chemical oxidation with 1 and 2 equivalents of NOSbF<sub>6</sub>, respectively (ESR analysis of **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup>, the photophysical properties of **1a** and the cationic species, and the aerobic oxidation of **1a** to **1a**<sup>+</sup> under acidic conditions are described in the Supporting Information). Notably, **1a** exhibited a long-wavelength absorption ( $\lambda_{\text{edge}} = 630$  nm) and red fluorescence at  $\lambda_{\text{max}} = 610$  nm (see Figure S4 in the Supporting Information). The hydrazine-embedded polyarene structure was found to be a good fluorophore for long-wavelength emission in conjunction with our previously reported hydrazinopolyarenes.<sup>[8k]</sup>

Single crystals of **1a**, **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup>, and **1a**<sup>2+</sup>·2SbF<sub>6</sub><sup>−</sup> were obtained for X-ray crystallographic analysis (Figure 3; see also Figure S7). The analysis of **1a** at 50 K did not show a bowl shape but a twist shape (or S shape), in which the two nitrogen atoms were directed toward opposite sides with a  $\pi$ -orbital axis vector (POAV) of 18.3°. On the other hand, **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup> exhibited a shallow bowl shape in the monocation state with



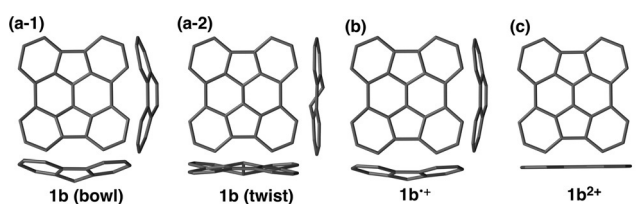
**Figure 2.** Cyclic voltammogram of **1a** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>.



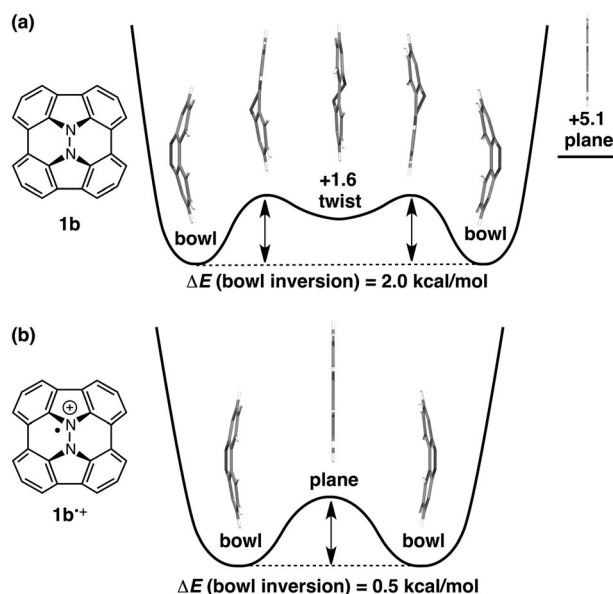
**Figure 3.** ORTEP drawings of a) **1a**, b) **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup>, and c) **1a**<sup>2+</sup>·2SbF<sub>6</sub><sup>−</sup> at the 50% probability level (*tert*-butyl groups, hydrogen atoms, and counteranions are omitted for clarity).

a bowl depth of 0.69 Å and POAV = 5.7°. In both crystals of **1a** and **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup>, the direction of the molecules was disordered in a nearly 1:1 ratio (see Figure S7b). Such disorder was also reported in the crystal of **2**.<sup>[6f]</sup> The analysis of **1a**<sup>2+</sup>·2SbF<sub>6</sub><sup>−</sup> revealed that the structure was completely flattened to a plane in the dication state with a depth of 0.00 Å and POAV = 0.3°.

Whereas X-ray crystallographic analysis revealed the structures in the crystal states, we conducted DFT calculations [wB97X/d6-311 + G(d,p); see the Supporting Information for details] to elucidate the stable structures and thermal dynamics of a single molecule in the gas or solution phase (Figures 4 and 5; see also Tables S3–S5 in the Supporting



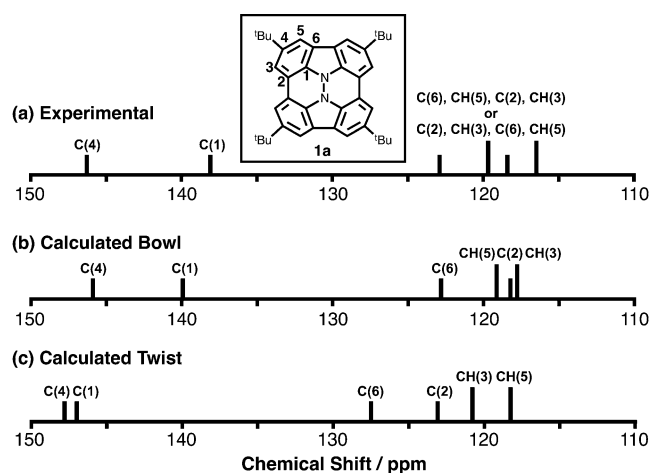
**Figure 4.** Calculated structures of a-1) **1b** (bowl), a-2) **1b** (twist), b) **1b**<sup>+</sup>, and c) **1b**<sup>2+</sup>.



**Figure 5.** Calculated energy diagram for the bowl inversion of a) **1b** on a triple-well potential and b) **1b**<sup>+</sup> on a double-well potential.

Information). The calculations revealed that nonsubstituted **1b** possessed a bowl shape as the most stable conformer and a twist shape as a less stable conformer with an energy difference  $\Delta E = 1.6 \text{ kcal mol}^{-1}$  (Figure 4a, 5a). Consequently, bowl inversion of **1b** occurred via the twist intermediate on a triple-well potential surface, and the calculated bowl-inversion energy was extremely low ( $2.0 \text{ kcal mol}^{-1}$ ). The calculated planar transition state ( $5.1 \text{ kcal mol}^{-1}$ ) was higher in energy than that of the twist structure. Stable structures of **1b**<sup>+</sup> and **1b**<sup>2+</sup> were calculated to be a shallow bowl shape and a planar shape, respectively (Figure 4b,c). The calculated transition state of the bowl inversion of **1b**<sup>+</sup> was a planar structure ( $0.5 \text{ kcal mol}^{-1}$ ) on a double-well potential surface (Figure 5b). The twist shape of **1b**, bowl shape of **1b**<sup>+</sup>, and planar shape of **1b**<sup>2+</sup> were consistent with those observed by X-ray crystallographic analysis of **1a**, **1a**<sup>+</sup>·SbF<sub>6</sub><sup>−</sup>, and dication **1a**<sup>2+</sup>·2SbF<sub>6</sub><sup>−</sup> (see Table S3). Comparison of the bond lengths of the calculated structures (see Figure S8) indicated significant shortening of the N–N bond length in the order from **1b** (bowl:  $1.37 \text{ \AA}$ , twist:  $1.38 \text{ \AA}$ ) to **1b**<sup>+</sup> ( $1.31 \text{ \AA}$ ) and **1b**<sup>2+</sup> ( $1.27 \text{ \AA}$ ), thus showing the same trend as the X-ray crystal structures of **1a** (twist), **1a**<sup>+</sup>, and **1a**<sup>2+</sup>, which is responsible for the flattening of the structure. We further checked the effects of substituents and solvents on the energy difference between bowl and twist structures by calculations (see Table S4). Bowl and twist shapes of **1a** with *tert*-butyl groups were calculated, and a slightly larger difference of  $\Delta E = 2.7 \text{ kcal mol}^{-1}$  was found as compared to  $1.6 \text{ kcal mol}^{-1}$  for **1b**. No significant solvent effect on the energy (NMR solvent: CHCl<sub>3</sub>) was observed by using the polarizable continuum model (PCM) calculation. The ratio of bowl and twist conformers of **1a** at 298 K was calculated to be 99:1 from  $\Delta G = 2.6\text{--}2.7 \text{ kcal mol}^{-1}$ , thus showing that the bowl conformer is predominant in the gas or solution phase in the calculations.

The employed DFT methods are reliable enough for us to believe the predominant existence of the bowl conformer of **1a** in the gas or solution phase, as judging from the good correlation between experimental and calculated parameters of other buckybowl as well as the twist shape of **1a**, the bowl shape of **1b**<sup>+</sup>, and the planar shape of **1b**<sup>2+</sup> (see Table S3). Nevertheless, we sought further confirmation of the correlation between the experimental data of **1a** in solution and the calculated parameters of the bowl conformer. Since observation of the kinetics by variable-temperature NMR spectroscopy was not applicable for **1a** (see the Supporting Information for details), we focused on the comparison of NMR chemical shifts between experiment and calculation. The prediction of NMR chemical shifts, particularly of the <sup>13</sup>C nucleus, has enough accuracy to allow structure elucidation with confidence.<sup>[4,12]</sup> This accuracy was already demonstrated for corannulene derivatives,<sup>[4,12c]</sup> and we also confirmed the accuracy of this method by comparing experimental and calculated <sup>13</sup>C NMR shifts of buckybowl by using the gauge-independent atomic orbital (GIAO) method at  $\omega\text{B97XD}/6\text{-}311++\text{G}(3\text{d},3\text{p})$  (see the Supporting Information). <sup>13</sup>C NMR chemical shifts of bowl and twist structures of **1a** were calculated by the same method (see Table S7). A schematic diagram of experimental and calculated <sup>13</sup>C NMR spectra of



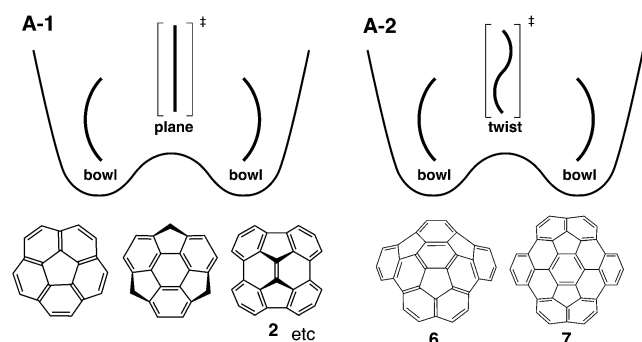
**Figure 6.** Schematic diagram of experimental and calculated [GIAO/ $\omega\text{B97XD}/6\text{-}311++\text{G}(3\text{d},3\text{p})//6\text{-}311+\text{G}(\text{d},\text{p})$ ] <sup>13</sup>C NMR chemical shifts of **1a** between 110 and 150 ppm.

**1a** in the 110–150 ppm region is shown in Figure 6. From a comparison of the spectral patterns of calculated bowl and twist structures, several distinct differences were observed: I) the chemical shifts of C(1), C(6), and C(2); and II) the order of the chemical shifts of CH(5), C(2), and CH(3). The calculated spectrum of the bowl conformer showed much more resemblance to the experimental spectrum than that of the twist conformer. Thus, we concluded that the bowl structure is the stable and predominant conformer in CHCl<sub>3</sub> solution on the basis of computation-assisted NMR spectral assignment.

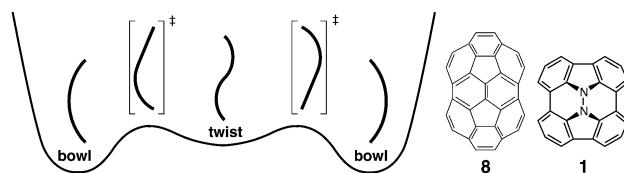
On the basis of reported theoretical studies, the bowl-inversion process of buckybowl is classified into two types, depending on the shape of the potential: A) double-well potential and B) triple-well potential (Figure 7). Depending on the shape of the transition state, type A is further divided into type A-1 with a planar transition state and type A-2 with a twist (S-shaped) transition state. The transition state is planar in most buckybowl, including corannulene, sumanene, and **2**,<sup>[2b,c,6i,13]</sup> whereas Wu et al. recently reported two buckybowl, **6** and **7**, with twist transition states, as determined by calculation.<sup>[14]</sup> In type B, a buckybowl has two conformers: a bowl conformer with a global minimum energy and a twist conformer with a local minimum energy, and they are inverted via a nonplanar transition state. Semibuckminsterfullerene **8** has been found to have type B inversion behavior by calculation.<sup>[13b,15]</sup> Compound **1a** is the second reported buckybowl of type B and the first example of an intermediate twist shape with a local minimum energy that appears in the crystal state as shown by X-ray crystallographic analysis.

In summary, hydrazinobuckybowl **1a**, the monocation, and the dication were synthesized from cyclobiphenothiazine **4a** via the strained cyclobicarbazole **3a** by reductive desulfurization from a phenothiazine to a carbazole skeleton. Compound **1a** was determined to possess bowl and twist structures in the neutral state, a shallow bowl structure in the monocation state, and a planar structure in the dication state. The calculation of NMR chemical shifts was demonstrated to

## Type A Double-well potential



## Type B Triple-well potential



**Figure 7.** Types of bowl inversions of buckybowl: Type (A-1) planar transition state and (A-2) twist transition state on a double-well potential and type (B) twist intermediate and nonplanar transition state on a triple-well potential.

be a strong tool for the determination of the conformation of flexible aromatic compounds. Compound **1a** is the first buckybowl whose geometry is transformed between curved bowl/twist structures and a planar structure depending on the oxidation state. The bowl-inversion dynamics of **1a** were found to follow a triple-well potential model. The drastic geometrical change of the bowl was possible as a result of the two heteroatoms and the multiredox system. The hydrazine-embedded bicarbazole structure of red-fluorescent **1a** was also found to be a good fluorophore for long-wavelength emission. The combination of the characteristics of curved  $\pi$ -conjugated molecules and heteroatoms has potential for the development of compounds with new properties.

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**Keywords:** cations · conformation analysis · heterobuckybowls · heterocycles · redox chemistry

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- [1] a) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868; b) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843; c) A. Sygula, *Eur.*

*J. Org. Chem.* **2011**, 1611; d) S. Higashibayashi, H. Sakurai, *Chem. Lett.* **2010**, 39, 122; e) T. Amaya, T. Hirao, *Chem. Commun.* **2011**, 47, 10524; f) *Fragments of Fullerenes and Carbon Nanotubes* (Eds.: M. A. Petrukhina, L. T. Scott), Wiley, Hoboken, **2012**; g) Y.-T. Wu, J. S. Siegel in *Topics in Current Chemistry* 349, *Polyarenes I* (Eds.: J. S. Siegel, Y.-T. Wu), Springer, Heidelberg, **2014**, pp. 63–120.

- [2] a) W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380; b) L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920; c) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldrige, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 1921; d) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878.
- [3] a) K. Imamura, K. Takimiya, Y. Aso, T. Otsubo, *Chem. Commun.* **1999**, 1859; b) S. Furukawa, J. Kobayashi, T. Kawashima, *J. Am. Chem. Soc.* **2009**, *131*, 14192; c) M. Saito, T. Tanikawa, T. Tajima, J.-D. Guo, S. Nagase, *Tetrahedron Lett.* **2010**, *51*, 672; d) T. Tanikawa, M. Saito, J.-D. Guo, S. Nagase, *Org. Biomol. Chem.* **2011**, *9*, 1731; e) Q. Tan, S. Higashibayashi, S. Karanjit, H. Sakurai, *Nat. Commun.* **2012**, *3*, 891; f) T. Tanikawa, M. Saito, J.-D. Guo, S. Nagase, M. Minoura, *Eur. J. Org. Chem.* **2012**, 7135; g) X. Li, Y. Zhu, J. Shao, B. Wang, S. Zhang, Y. Shao, Z. Jin, X. Yao, R. Fang, X. Shao, *Angew. Chem. Int. Ed.* **2014**, *53*, 535; *Angew. Chem.* **2014**, *126*, 545; h) S. Ito, Y. Tokimaru, K. Nozaki, *Angew. Chem. Int. Ed.* **2015**, *54*, 7256; *Angew. Chem.* **2015**, *127*, 7364; i) H. Yokoi, Y. Hiraoka, S. Hiroto, D. Sakamaki, S. Seki, H. Shinokubo, *Nat. Commun.* **2015**, *6*, 8215.
- [4] For an example of a change in bowl depth and inversion kinetics through redox chemistry, see: S. Nishida, Y. Morita, A. Ueda, T. Kobayashi, K. Fukui, K. Ogasawara, K. Sato, T. Takui, K. Nakasuji, *J. Am. Chem. Soc.* **2008**, *130*, 14954.
- [5] For the deformation of heteronanographenic structures of a hexagonal lattice between curved and planar structures through redox reactions or coordination, see: a) M. Kuratsu, M. Kozaki, K. Okada, *Angew. Chem. Int. Ed.* **2005**, *44*, 4056; *Angew. Chem.* **2005**, *117*, 4124; b) Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 4529; c) T. Kushida, S. Yamaguchi, *Organometallics* **2013**, *32*, 6654; d) S. Osumi, S. Saito, C. Dou, K. Matsuo, K. Kume, H. Yoshikawa, K. Awaga, S. Yamaguchi, *Chem. Sci.* **2016**, *7*, 219.
- [6] a) S. Hagen, U. Nuechter, M. Nuechter, G. Zimmermann, *Polycyclic Aromat. Compd.* **1995**, *4*, 209; b) S. Hagen, H. Christoph, G. Zimmermann, *Tetrahedron* **1995**, *51*, 6961; c) L. T. Scott, *Pure Appl. Chem.* **1996**, *68*, 291; d) U. Chen, S. Ma, R. G. Cooks, H. E. Bronstein, M. D. Best, L. T. Scott, *J. Mass Spectrom.* **1997**, *32*, 1305; e) R. Shenhar, R. Beust, R. E. Hoffman, I. Willner, H. E. Bronstein, L. T. Scott, M. Rabinovitz, *J. Org. Chem.* **2001**, *66*, 6004; f) H. E. Bronstein, N. Choi, L. T. Scott, *J. Am. Chem. Soc.* **2002**, *124*, 8870; g) R. Shenhar, R. Beust, S. Hagen, H. E. Bronstein, I. Willner, L. T. Scott, M. Rabinovitz, *J. Chem. Soc. Perkin Trans. 2* **2002**, 449; h) H. E. Bronstein, L. T. Scott, *J. Org. Chem.* **2008**, *73*, 88; i) H.-I. Chang, H.-T. Huang, C.-H. Huang, M.-Y. Kuo, Y.-T. Wu, *Chem. Commun.* **2010**, 46, 7241; j) H. Y. Cho, R. B. M. Ansems, L. T. Scott, *Beilstein J. Org. Chem.* **2014**, *10*, 956.
- [7] The formation of diazafullerene  $C_{58}N_2$  in the gas phase during mass spectrometry of a precursor was proposed: H. Huang, G. Zhang, D. Wang, N. Xin, S. Liang, N. Wang, L. Gan, *Angew. Chem. Int. Ed.* **2013**, *52*, 5037; *Angew. Chem.* **2013**, *125*, 5141.
- [8] a) F. A. Neugebauer, S. Kuhnhauser, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 596; *Angew. Chem.* **1985**, *97*, 589; b) H. Fischer, C. Krieger, F. A. Neugebauer, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 374; *Angew. Chem.* **1986**, *98*, 341; c) M. Dietrich, J. Heinze, H. Fischer, F. A. Neugebauer, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1021; *Angew. Chem.* **1986**, *98*, 999; d) M. Dietrich, J. Heinze, *J. Am. Chem. Soc.* **1990**, *112*, 5142; e) M. Dietrich, J. Heinze, S. Kuhnhauser, F. A. Neugebauer, *J. Am. Chem. Soc.* **1996**, *118*,

- 5020; f) K. Shiraishi, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**, *127*, 9312; g) A. W. Franz, F. Rominger, T. J. J. Müller, *J. Org. Chem.* **2008**, *73*, 1795; h) P. Pandit, K. Yamamoto, T. Nakamura, K. Nishimura, Y. Kurashige, T. Yanai, G. Nakamura, S. Masaoka, K. Furukawa, Y. Yakiyama, M. Kawano, S. Higashibayashi, *Chem. Sci.* **2015**, *6*, 4160; i) K. Yamamoto, T. Nakamura, S. Higashibayashi, *Chem. Lett.* **2015**, *44*, 1229; j) P. Pandit, T. Nakamura, S. Higashibayashi, *Chem. Lett.* **2015**, *44*, 1336; k) K. Yamamoto, S. Higashibayashi, *Chem. Eur. J.* **2016**, *22*, 663.
- [9] a) E. Lieber, S. Somasekhara, *Chem. Ind.* **1958**, 1367; b) H. Gilman, J. J. Dietrich, *J. Am. Chem. Soc.* **1958**, *80*, 380; c) R. B. Miller, S. C. Farmer, *Molecules* **2001**, *6*, 668; d) S. C. Farmer, S. H. Berg, *Molecules* **2008**, *13*, 1345.
- [10] For details, see the Supporting Information.
- [11] Y. Segawa, H. Omachi, K. Itami, *Org. Lett.* **2010**, *10*, 2262.
- [12] a) P. Cimino, L. Gomez-Paloma, D. Duca, R. Riccio, G. Bifulco, *Magn. Reson. Chem.* **2004**, *42*, S26; b) S. D. Rychnovsky, *Org. Lett.* **2006**, *8*, 2895; c) K. K. Baldridge, J. S. Siegel, *Theor. Chem. Acc.* **2008**, *120*, 95.
- [13] a) T. J. Seiders, K. K. Baldridge, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **2001**, *123*, 517; b) P. U. Biedermann, S. Pogodin, I. Agranat, *J. Org. Chem.* **1999**, *64*, 3655; c) U. D. Priyakumar, G. N. Sastry, *J. Phys. Chem. A* **2001**, *105*, 4488; d) S. Higashibayashi, R. Tsuruoka, Y. Soujanaya, U. Purushotham, G. N. Sastry, S. Seki, T. Ishikawa, S. Toyota, H. Sakurai, *Bull. Chem. Soc. Jpn.* **2012**, *85*, 450.
- [14] a) T.-C. Wu, M.-K. Chen, Y.-W. Lee, M.-Y. Kuo, Y.-T. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 1289; *Angew. Chem.* **2013**, *125*, 1327; b) M.-K. Chen, H.-J. Hsin, T.-C. Wu, B.-Y. Kang, Y.-W. Lee, M.-Y. Kuo, Y.-T. Wu, *Chem. Eur. J.* **2014**, *20*, 598.
- [15] P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, R. Sygula, *J. Am. Chem. Soc.* **1994**, *116*, 7891.

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