Penrose Stairs

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Illusory Molecular Expression of “Penrose Stairs” by an Aromatic Hydrocarbon[**]

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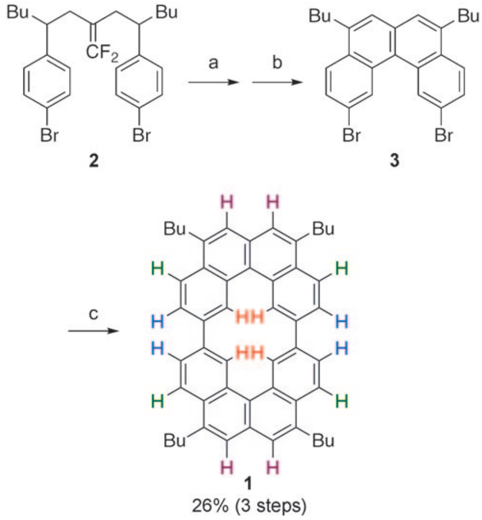
Conveying three-dimensional objects in the form of two-dimensional line drawings is an important skill, especially in scientific and technological fields.[1] Ever since the invention of the symbolic and ingenious representation of benzene as a hexagon, line drawings of chemical substances are among the most indispensable means to depict molecules.[2] Line drawings, however, can sometimes deceive and amuse the viewers by representing impossible objects, as pointed out by Penrose and Penrose.[1,3] The Penrose stairs, endlessly descending stairs in a continuous circle, were expressed in art by M. C. Escher in his famous lithograph, *Ascending and Descending*.[4] We found that such an illusory structure emerged from a molecule with unique caracole topology.[5] Notably, the molecular Penrose stairs, cyclobis[4]helicene **1**, deceive us in a manner different from the original proposal of Penrose. The dynamic behavior of **1** in solution has been observed to show a possible combination of covalent and noncovalent chemistry to explore unique molecular topologies in future.

We started the synthesis of **1** by preparing the helicene subunit by an intramolecular cyclization reaction of difluoroalkene **2**.[6] As we reported previously,[7] difluoroalkene with halogenated phenyl groups was prone to a skeletal rearrangement, but the desired dihalo[4]helicene **3** was obtained under milder cyclization conditions. Thus, **2** was subjected to a Friedel–Crafts type cyclization with magic acid ($FSO_3H{\cdot}SbF_5$) at 0 °C and was further converted to **3** by dehydrogenation with trityl tetrafluoroborate (Ph_3CBF_4) without isolation of the cyclized intermediate (Scheme 1). NMR spectroscopical analysis of **3** showed that the compound was obtained in 53 % yield from **2** after purification by silica gel column chromatography; however, it was also contaminated with a trace amount of byproducts including chrysene and uncyclized compounds.



Scheme 1. Synthesis of cyclobis[4]helicene **1**. Reagents and conditions: a) $FSO_3H{\cdot}SbF_5$ (2.5 equiv), HFIP/CH_2Cl_2, 0 °C; b) Ph_3CBF_4 (4.0 equiv), $ClCH_2CH_2Cl$, reflux; c) [Ni(cod)$_2$] (2.4 equiv), 1,5-cyclooctadiene (2.4 equiv), 2,2′-bipyridine (2.4 equiv), toluene/DMF, 60 °C. The colors of the hydrogen atoms indicate the assignment of proton resonances shown in Figure 3.

The convergent homocoupling of subunit **3** proceeded smoothly by Ni-promoted biaryl coupling to afford cyclobis[4]helicene **1**.[8] Thus, **3** (ca. 60 % purity, NMR analysis) was mixed with [Ni(cod)$_2$], 1,5-cyclooctadiene, and 2,2′-bipyridine to give **1** in 26 % yield (yield of isolated product after 3 steps from **2**) after purification by recrystallization and GPC (Scheme 1). As a byproduct, a small amount of a cross-coupling product between **3** and the uncyclized contaminant was also isolated.[9] Although the coupling reaction also took place with oxidative coupling of the corresponding cuprate,[10] the yield of **1** was not improved despite the formidable procedure that requires a stepwise conversion by metalation.

The molecular structure of **1** was established unequivocally by X-ray crystallographic analysis of a single crystal.[11] Two helicene subunits with the same helical configuration are coupled in one molecule, and the crystal is composed of a mixture of two enantiomers (see below). Taking into account the helical chirality of the subunits and the axial chirality at the linkages,[12] we can assign the absolute configurations of the enantiomers as (*P*,*P*,*R*,*R*) and (*M*,*M*,*S*,*S*), respectively (*P*,*P*,*R*,*R*-form shown in Figure 1). In each helicene subunit, the decrement distances of the middle helix measure 0.95 and 0.63 Å, and the interplanar angles at the terminus are 23° and

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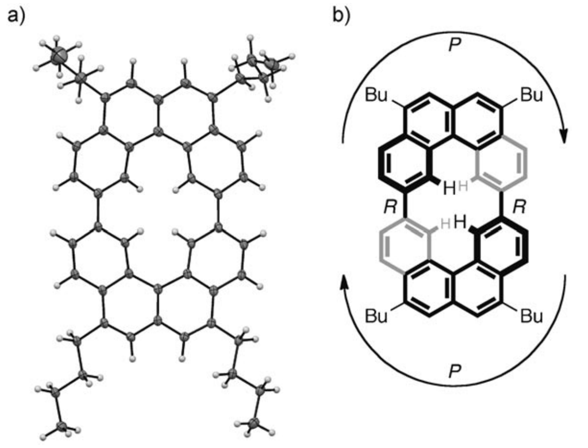

Figure 1. Molecular structure of cyclobis[4]helicene **1**. a) ORTEP drawing with thermal ellipsoids at 50% probability showing a representative structure of (*P*,*P*,*R*,*R*)-**1**. The structure was determined by X-ray crystallographic analysis. b) Line drawing with the absolute configurations of the helical chirality (*P*) and the axial chirality (*R*).

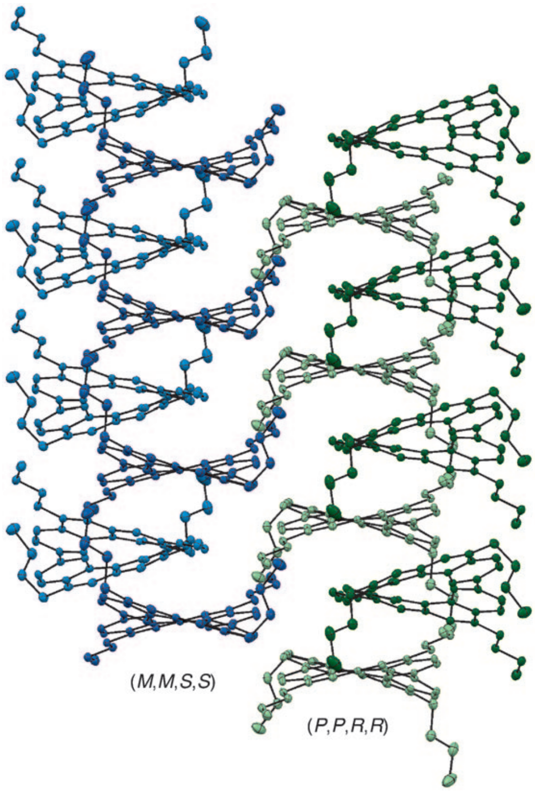

Figure 2. Packing structure of cyclobis[4]helicene **1**. Structures are viewed along the longitudinal direction of **1**, showing two neighboring columns.

19° (Figure S1). The hydrogen atoms attached to the inner 14-membered ring are packed in an overcrowded environment.[13] Four out of six interatomic distances among four hydrogen atoms are less than the sum of the van der Waals radii (< 2.4 Å) and the other two are of the same order (ca. 2.4 Å; Figure S2).

The peculiarity of the molecular topology of **1** became apparent and perplexed us, when we depicted the structure in line drawings especially with depth-cue effects and configuration assignments as shown in Figure 1 b. According to the definition,[12,14] (*P*)-helicene is the right-handed helix in which, when viewed perpendicular to the central aromatic rings, the viewer would track the aromatic stairs downward by circling in a right-handed direction. Each of the helicene subunits of **1** obeys this definition: the *P*-form stairs lead the viewer downward in a right-handed manner (Figure 1 b, with the decrement distance of 0.95 and 0.63 Å, see above). However, when one tracks the overall circle of the molecule that bears two *P*-form subunits in the right-handed manner, one unexpectedly reaches the original position without descending (Figure 1 b). The situation is, conceptually, a molecular expression of a well-known impossible object, the Penrose stairs.[3,4] As is often the case with illusions in art,[1] the deliberate examination of **1** from the side reveals a simple trick; the axial twists of the single bond linkages enable the tilted orientation of the central naphthalene moieties of the subunits (see Figure 2 for the side view).[15] Interestingly, we noticed that the trick can also be disclosed by applying another, well-conceived chemical terminology for the configuration assignments.[12] When we apply *P* and *M* helical notions to the axial chirality of the (*P*,*P*,*R*,*R*)-isomer, for instance, the molecule shows left-handedness (*M*,*M*) for the two pillaring axes that bridge two right-handed helicenes (*P*,*P*). The alternative assignment, (*P*,*P*,*M*,*M*), indeed indicates that the stairs are quadruply helical and both ascending and descending in one travelling direction.[16]

We also noticed that **1** forms columns of a single enantiomer in crystals. Stacking on top of a molecule with the same configuration, each of the enantiomers segregates into a separate column. As shown in Figure 2, the columns of (*P*,*P*,*R*,*R*)-**1** and (*M*,*M*,*S*,*S*)-**1** appear alternately in the crystal. Chiral segregation is most likely prompted to maximize the intermolecular contact area by assembling molecules of structural complementarity, that is, molecules of the same configuration.

Theoretical calculations indicate that the unique topology of **1** may be conjured away in the monomeric form in solution. Thus, the epimerization, a conformational change from (*P*,*P*,*R*,*R*) to (*M*,*M*,*S*,*S*) or vice versa, proceeds through a transient intermediate of the *meso* form (7.5 kcal mol^{-1} higher in energy than chiral forms) and requires an activation energy of 10.1 kcal mol^{-1} (see Figure S4). The activation barrier is lower than that required for the racemization of [5]helicene,[17] which suggests that the time-averaged structure of **1** may be regarded as a flat plane without peculiar topology.[18] Note also that such a dynamic structural change may be inherent to the 14-membered sp^2-carbon ring and may normally take place at the defects of the nanocarbon materials.[19,20]

However, the ^{1}H NMR analysis shows that the large aromatic hydrocarbon skeleton facilitates the self-aggregation of **1** in solution. We observed upfield shifts of proton resonances by increasing the concentration of **1** in chloroform (Figure 3 and Figure S5). We applied the isodesmic model of indefinite self-aggregation to the concentration-dependent shifts of the aromatic resonances[21] and obtained the associ-

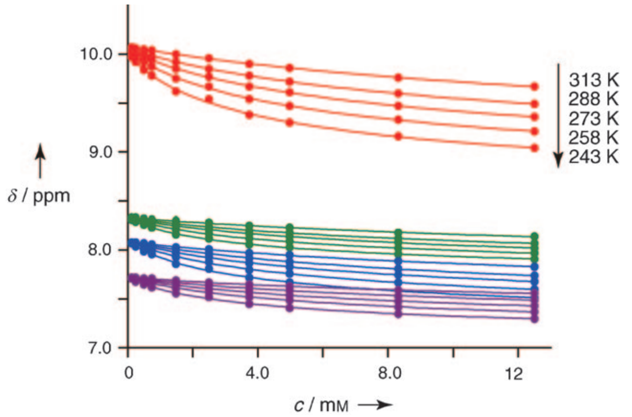

Figure 3. Concentration- and temperature-dependent shifts of aromatic NMR resonances. See Scheme 1 for the color-code assignments of the protons. The curves are derived from the fit obtained from the isodesmic model.

ation constant K_{assoc} of $64.9 \pm 5.1\,\mathrm{M}^{-1}$ at 288 K (see Table S10). In addition, the van't Hoff analysis further revealed the enthalpy-driven character of the aggregation with values of $\Delta H = -3.82\,\mathrm{kcal\,mol^{-1}}$ and $\Delta S = -4.91\,\mathrm{cal\,mol^{-1}\,K}$ (Figure S6). The observation of aggregation suggests that the dynamic conformational behavior of **1** in reality may not exactly follow the theoretical picture of monomeric species. Although the precise structure of the aggregate is not clear at this stage, the upfield shift is consistent with the π-stacking aggregation that is expected from the crystallographic analysis. Considering that the segregation of enantiomers took place upon crystallization, investigations of symmetry-breaking systems with the molecular Penrose stairs, for instance in liquid crystalline phase, may be an interesting subject in the future.[22]

According to a theorem in line drawings,[1] Penrose stairs such as in M. C. Escher's lithograph can be categorized as the anomalous images that are generically reconstructible and uncorrectable. However, the molecular Penrose stairs, which display eight hexagons with two pillaring lines, deceive us in a different manner, by being generically reconstructible and correct with their quadruply helical structure. Although the peculiar topology of molecular entities has been explored by using dynamic noncovalent chemical bonds,[23] the ever-increasing variety of chemical reactions for covalent bond formations may further add to this intriguing repertoire with severe structural constraints and could stimulate intellectual amusement. The convergent synthesis of rigid aromatic hydrocarbons with mobile π electrons may also be beneficial for the molecular design of organic materials,[24] and the combination of unique covalent topologies with noncovalent assembly should be explored in the near future.[25,26]

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