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Structures and Conformational Analysis of 1,8-Bis(9-triptycylethynyl)anthracene and Its Derivatives as Prototypes of Molecular Spur Gears

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The title compounds having two 9-triptycyl rotors, two acetylene shafts, and an acene base were synthesized by coupling reactions as molecular spur gears. Their molecular structures were compared to evaluate the meshing of rotor moieties and the orientation of the two gear shafts. The mechanism of rotation of three-toothed rotors was explored by NMR spectroscopy and DFT calculations in terms of gear rotation and slippage.

Molecular gears are a fundamental feature of molecular machines that possess rotor moieties, where two or more rotors mesh with each other and transmit rotary motion from one gear shaft to another via correlated rotation.[1] Gear wheels are required to have a rigid framework bearing several cogs, and aromatic units have been occasionally adopted as building units.[2] A typical three-toothed wheel is the 9-triptycyl (Trip) group, which has a bicyclic core and three benzeno cogs.[3] Iwamura and Mislow proposed the pioneering design for molecular gears **1**, which consists of two Trip groups connected by a methylene or other linkers (Figure 1).[4] These gears are called bevel gears, a kind of gear with intersecting axes, because the two gear shafts are not parallel but rather intersect each other. Since then, Trip groups have been extensively utilized as wheel components in various molecular gears.[5]

As for molecules with two Trip groups, their orientation determines the function of molecular gears and related machines.[4b,5a] Structures with two wheels at both ends of an axis work as an axle–wheel component in molecular vehicles, such as di(9-triptycyl)ethynes and their derivatives, where the two wheels rotate readily and independently.[6] When large substituents are introduced into the ethyne derivatives, the rotation about the acetylene axes is restricted by steric hindrance.[7,8] The most common type of gear is a spur gears, where the axes of two rotors are parallel and the gears have straight teeth relative to the axes. Cyclic compounds with two triptycene-9,10-diyl groups and ethylene glycol chains were reported as candidates for spur gears.[9] However, there was no evidence of gearing between the rotors because of the flexibility of the chain moieties. For molecules to mimic mechanical spur gears, the two gear axes should be mounted on a rigid base in the same direction, as proposed by Siegel and co-workers.[10] We have been investigating the structures and dynamic behavior of alkyne compounds with triptycene and anthracene groups,[7,11] and the information we have gained has prompted us to use these units for the construction of new gear systems. As a prototype of molecular spur gears, we designed **2**, which consisted of three components: an anthracene base, two acetylene shafts, and two Trip rotors (Figure 1). The two rotors are connected at the 1,8-positions of the base in the same direction at an appropriate distance (5.0 Å). The incorporation of linear shafts is essential to avoid steric interactions between the base and the rotors. This model is suitable for the evaluation of the geometric orientation of the two gear axes, because the structures of each component can be easily modified in various ways. We synthesized compound **2a** and its derivatives with different rotors, shafts, and bases shown in Figure 1. Then, we compared their structures and dynamic behavior and propose a molecular design for switching bevel gears to spur gears by using the triptycene wheel system.

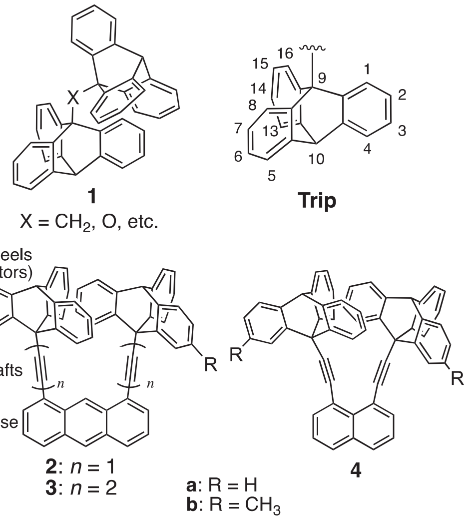
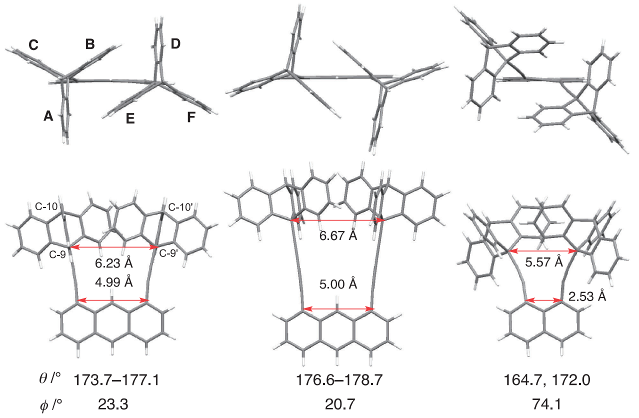


Figure 1. Typical examples of molecular gears **1** and target compounds **2**–**4** as prototypes of molecular spur gears.

Compounds **2a** and **4a** were synthesized by the Sonogashira coupling of 9-ethynyltriptycene[7b] with the corresponding diiodoacenes.[12] Compound **3a** with diacetylene linkers was prepared from 1,8-diethynylanthracene[11b] and 9-(bromoethynyl)triptycene by Pd-catalyzed cross coupling. We also synthesized compounds **2b**–**4b** with 2-methyl-9-triptycyl rotors in a similar manner, in which one tooth in each rotor was labeled by a substituent to control the rate and mode of rotation to values suitable for dynamic NMR study.[13] In the ^{1}H NMR spectra of **2a**–**4a**, the six benzeno groups in the two Trip groups were equivalent at room temperature to give one set of ABCD systems in the aromatic region. Compounds **2b**–**4b** also gave symmetric ^{1}H NMR signals. Some of the signals were observed at a high magnetic field due to the ring current of the nearby benzeno groups. In particular, a large shielding was observed for the H-2, H-7, and H-15 (δ 5.9–6.5).

The molecular structures of **2a**–**4a** were investigated by X-ray analysis[14] and DFT calculations[15] (Figure 2). In **2a**, benzeno groups **A** and **D** are nearly perpendicular to the average plane of the base anthracene at the opposite sides. Inside teeth **B** and **E** are nearly parallel at the separation of ca. 3.8 Å and mesh with



2a (X-ray) **3a** (DFT) **4a** (X-ray)

Figure 2. Two views of molecular structures of **2a**–**4a** by X-ray analysis or DFT calculation (M05/6-31G). θ: Bond angles at sp carbons. ϕ: Shaft angles are the angles formed by the two lines passing C-9 and C-10 (C-9′ and C-10′).

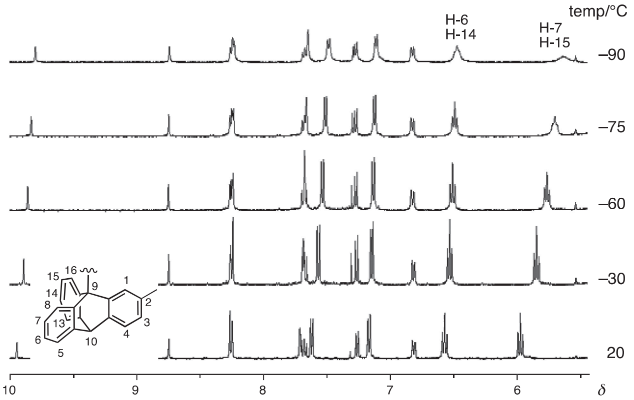
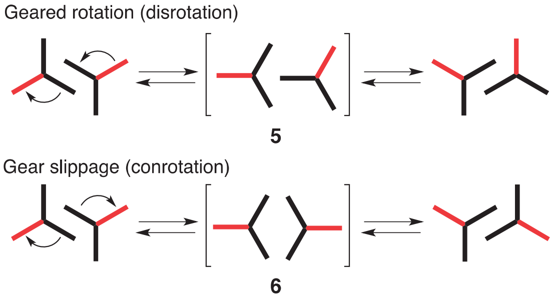


Figure 3. Variable temperature ^{1}H NMR spectra of **2b** in CD_2Cl_2.



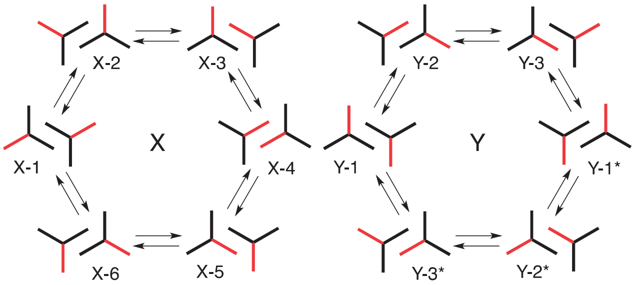
Scheme 1. Two mechanisms of rotation of two Trip rotors in **2**–**4** as schematically presented along the shaft axes from the rotor side. Black and red bars show teeth without and with Me groups, respectively, for **2b**–**4b**.

each other. The two shaft moieties are slightly deformed by the bending deformations at the alkyne carbons to avoid steric interactions between the rotors. As a result, whereas the distance between the two shafts is 5.0 Å at the base joints, it is widened to 6.2 Å at the rotor joints. Gear orientation was evaluated by the shaft angle (ϕ), which was calculated from the two lines passing C-9 and C-10. The shaft angle of **2a**, 23°, suggests that the two axes are nearly parallel compared with those in conventional bevel gears, although it is not an ideal spur gear. In **3a**, the bending deformations of the shaft moieties are smaller than those in **2a**, leading to a small shaft angle. Severe steric hindrance is noted between the rotor moieties in **4a** having a naphthalene base. The bond angles of the alkyne carbons (θ) attached to the base is 165°, and the bending deformations of the shaft moieties out of the naphthalene plane are also significant. The shaft angle of **4a** is increased to 74°. Accordingly, the anthracene base is a much better choice than the naphthalene base and the long linkers are more suitable to approach the parallel axes than the short linkers.

Not only the static structure but also the dynamic motion is a key aspect in evaluating gear function. The dynamic processes of **2b**–**4b** with labeled teeth were investigated by NMR spectroscopy and DFT calculations. The ^{1}H NMR spectra of these compounds were measured at low temperatures in CD_2Cl_2, and the spectra of **2b** are shown in Figure 3. As the temperature was lowered, the signal due to H-7 and H-15 in the Trip rotors at δ 6.0 shifted to a high magnetic field and broadened at −90 °C. This means that conformational exchange takes place as fast as the NMR time scale at the low temperature with the changing of populations. Conformational search of **2b** gave five conformers that differed in the positions of the two Me groups.[13] The conformers with an inside Me group are less stable by 4–5 kJ mol^{-1} than those with the others at the M05/6-31G level.

We also calculated some models of transition states for the geared rotation and the gear-slippage mechanisms for **2a** (Scheme 1). The optimum transition state of the geared rotation is shown as structure **5**, where the inside tooth of one rotor is directed toward the axis of the other rotor. This structure is less stable by 16 kJ mol^{-1} than the global minimum. Any other processes that change the gear-meshing phase are regarded as gear slippage. A possible mechanism of such process is shown in Scheme 1, where the tips of two inside teeth of one rotor pass over those of the other rotor in **6**. Calculations revealed that this process required an energy of ca. 23 kJ mol^{-1}. This means that the barrier to the gear slippage is higher than that to the geared rotation. For **2b**, the transition states with one or two Me groups in the inside teeth should be further destabilized due to steric hindrance, although the estimation of their energies by calculation has been unsuccessful so far.

We then discuss the rotational mechanism from the available data. There are 18 possible conformers of **2b**, which can be classified into three rotational circuits correlated by the geared rotation (Scheme 2). Group **X** involves a conformer with two outside Me groups (**X-1**) and another circuit, the mirror image of **X**, is not shown in Scheme 2. In group **Y**, there is one pair of enantiomeric conformers (**Y-1**/**Y-1***) with two perpendicular Me groups. We first assume that the populations of conformers with the inside Me group are negligible, and thus the rotation via the transition state with the inside Me group can be ruled out. In this case, the molecules would exist as **Y-1**/**Y-1*** or rapidly equilibrating **X-1**, **X-2**, and **X-6**. As long as the rotation takes place via the geared mechanism, this compound would give two sets of signals in the ^{1}H NMR spectrum. Hence, we need to consider the interconversion across the circuits. For instance, the gear-slippage process in Scheme 1 converts **X-2** into **Y-2*** via the transition state with one inside Me group, which should then



Scheme 2. Rotational circuits of geared rotation in **2b**–**4b**. Another circuit, the mirror image of X, is not shown. Red bars are Me-substituted teeth. Enantiomer pairs: Y-2/Y-2*, Y-3/Y-3*. Topomer pairs: X-2/X-6, X-3/X-5, Y-2/Y-3*, Y-3/Y-2*.

readily isomerize into **Y-1*** by the geared rotation. The observed signal broadening in the ^{1}H NMR spectra is attributable to the gear slippage via a less stable transition state, although the course of isomerization is not fully established yet. While similar lineshape changes were observed for **4b**, all the aromatic signals remained sharp at −90 °C for **3b** (see Supporting Information). The latter observation means that the long shafts increase the mobility of the rotor moieties. Further investigations will reveal the rotational mechanism of the molecular gears and their substituent effects in detail.

In summary, we synthesized six compounds with two Trip rotors attaching to an acene base as the prototypes of spur gears. An investigation of their molecular structures revealed that the orientation of the two rotors could be tuned by the kind of component, and a 1,8-anthrylene unit was found to be good for this purpose. The rotation process can be discussed in terms of geared rotation and gear slippage by using derivatives with labeled teeth, although the mechanisms could not be fully determined. In order to construct ideal spur gears with parallel shafts, we need to modify the fundamental structures by changing the structure of each component. Furthermore, the bridging of the other sides of rotors with another base moiety shows promise in terms of the parallel alignment of the two shafts. The syntheses of such molecules are in progress to realize the structures and functions of spur gears on the molecular scale.

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13 Supporting Information (spectroscopic data of the final products, calculated structures, and VT NMR spectra) is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

14 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-802618 (**2a**) and -802619 (**4a**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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