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How Does the Flexibility of Molecules Affect the Performance of Molecular Rotors?

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Abstract

In research on molecular machines, the flexibility of the molecules has been shown to significantly affect the performance of such “soft” machines and thus lead to unexpected phenomena that differ from rigid machines in the macroscopic world. Taking several typical rotational molecules as examples, we examine how the deformation of the molecule (commonly caused by curving parts of a molecule due to its interaction with other molecules) affects the effectiveness of a molecular machine system, such as a chain of molecular gears. From the viewpoint of quantum chemistry and classical mechanics, we introduce a torque analysis strategy to quantitatively analyze the strength of the repulsion/attraction force induced by the deformation of such molecules. By comparing different types of chemical bonds, we show that a bond connecting to an aromatic ring exhibits a larger stiffness than bonds that do not directly connect to an aromatic ring. We thereby highlight that the inclusion of aromatic rings in a molecular machine can considerably increase the stiffness of the machine, which is an important factor in designing effective molecular machines.

Introduction

Molecular machines (both muscle-like1-4 and rotational5-8) have drawn considerable attention in the past decades, including the 2016 Nobel Prize in Chemistry,9 due to their prominent potential in nanoscience, which may lead to a blossoming of the development of nanoscale molecular robotics. While in the past 20 years a wide variety of molecular devices (e.g. rotors,5-8, 10-12 switches,13-17 pumps,4,14 and logic gates18,19) have been synthesized and investigated, the logical next step in this development is to extend to more complex machine systems that consist of multiple mechanically linked smaller “machines”. To that end it is necessary to explore the cooperative motions among an interlocking collection of such molecules. One example is the design of molecular gears (cogwheels), as they are indispensable components for connecting different parts of such linked machines, analogous to macroscopic machines: they permit transferring rotational movement from a source (e.g. a molecular motor) to a point of application.20, 21

Interestingly, we found in our earlier research that the coupling/interlocking behavior between
molecular devices (such as motors and gears) is quite different from that in the macroscopic world, and may sometimes be problematic.\textsuperscript{21} This mainly comes from the flexibility of the molecules, viz. the machine itself – at molecular scale – is not rigid, and thus may be deformed due to the interaction with other machines or other components of the same machine system. Note that such deformation is different from molecular vibration in chemistry: the latter is a rapid periodic motion of the atoms in a normal, stable molecule, while deformation here denotes much larger and slower changes in the shape of the molecule, which is usually seen as causing an unstable geometric state and is confined by certain external constraints, e.g. intermolecular forces, external fields, etc.

The flexibility and stiffness of molecules has been explored mainly in biochemical systems (e.g. proteins), because their structural flexibility is usually associated with various biological processes such as molecular recognition and catalytic activity.\textsuperscript{22, 23} Here we demonstrate that such flexibility of molecules also plays an important role in molecular machines as it can induce sometimes exotic behavior, but occasionally also fail to perform desired functions. This is usually determined by the extent of the induced deformation (and thus its stiffness): if we imagine a molecule that is deformed by the interaction with other molecules, then the distorted chemical bonds in the deformed molecule provide an equivalent resistance – a counterforce causing stiffness. An evaluation of the magnitude of such stiffness will help us understand and better predict the behavior of interlocking molecular machines, as deformation is so common in these systems at the nanoscale.

In the present paper, we firstly simulate three model gear systems (shown in Figures 1, 2, and 3) which would easily and faithfully transmit rotations if they were composed of rigid gears in ideal macroscopic machinery: by contrast, we demonstrate the degree to which the molecular-scale models transmit or fail to transmit rotational motion under the influence of the flexibility of the molecules. Then, in the following section, we propose a torque-curvature analysis scheme to quantitatively analyze the magnitude of driving forces contributed by the deformation (due to the flexibility) of the molecules. By doing so, we deduce several conclusions that are helpful for designing molecular gears by taking proper account of the flexibility of molecules. These conclusions are also extendable to other molecular machines that contain intermolecular linkages between their different components.

**Modeling and computational methods**

Calculations for the present paper were performed within first-principles density functional theory (DFT)\textsuperscript{24}. For structures adopting periodic boundary conditions (Figures 1-5), we applied the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{25} together with dispersion corrections\textsuperscript{26} to account for intermolecular van der Waals interactions. All the geometry optimizations were performed using the Vienna Ab-initio Simulation Package (VASP)\textsuperscript{27, 28} based on the projector-augmented wave (PAW) method\textsuperscript{29, 30}, with a maximum 400eV cutoff for the plane-wave basis set. The charge distribution was analyzed (Tables 1 and 2) using the Gaussian09 package\textsuperscript{31}. For Figures 1-3, $2 \times 1 \times 1$ \Gamma-centered k-points were sufficient for the Brillouin Zone sampling.

In the simulations studying the interlocking and rotation process between two or more molecular gears (as illustrated in Figures 1-3), we impose successive rotations on a “driver” molecule (at one end of the gear chain), so as to generate forces, torques and rotations on the other “slave” molecules driven by it. In each simulation, we start from an arbitrary “driver” orientation defined as 0°: for this initial driver orientation, while the structure of the driver is fixed as a rigid
body, the slaves and the graphene sheet are fully relaxed, yielding negligible net forces on all atoms and thus negligible net torques on all slave molecules. We then manually rotate the driver stepwise (10˚ clockwise in each step) to represent a smooth quasi-static motion, simulating a molecular motor. Next, we re-optimize the slave molecules (and the graphene sheet) while keeping the driver fixed at its 10˚ rotation geometry, such that the slaves can follow any appropriate energy-optimized pathway, including rotation, tilting, bending, slipping, skipping, breaking up, etc. After that, the driver goes on to reach its 20˚ orientation and this procedure is repeated in 10˚ steps.

Results & Discussion

Unexpected phenomena and even failure of performance caused by the flexibility of molecule.

In our earlier work, we explored the propagation of rotation along a chain of molecular gears built on a graphene sheet, as shown in Figure 1.\textsuperscript{21} Each gear is a 5-arm rotor made of a carbon ring (the carbon ring is extended with cyano groups) that can be attached to the graphene sheet with an intermediate manganese atom acting as the pivot between the rotor C-ring and the graphene C-ring. Such a sandwich structure has been proved to be stable according to the 18-electron principle in organometallic chemistry.\textsuperscript{32-36} Thus, a single gear can stand firmly but rotate almost freely (with a rotational barrier less than 0.005 eV) on the graphene sheet. To computationally examine how the rotation of an active “driver” molecule is transmitted through a chain of passive “slave” molecules, we built a model consisting of up to four such gears and defined one gear (at the right end in Figure 1) as the “driver”, and the others as the “slaves”. In our modeling, the driver molecule was rotated manually, representing a motor, and was expected to induce rotation of all the slave molecules, just like a gear chain. The interesting result is that in some situations the slaves did not follow the driver’s rotation simultaneously and smoothly, but instead exhibited a “creep-then-jump” (or “stick-slip”) motion: in those cases, while the driver rotated 10˚ clockwise at each step, slave #1 followed it by rotating counterclockwise, as expected, but with a slight delay in rotation; such a delay was more obvious for slave #2 and especially for slave #3, which underwent almost no rotation at first. However, as the delay (in rotation) accumulated, all the slaves made a sudden jump soon after the driver reached about 70˚, so that the slaves almost caught up with the driver. This “creep-then-jump” motion was repeated again and again periodically as the driver kept rotating smoothly. For detailed information, please refer to Figure 4 or Movie 1 of reference\textsuperscript{21}.

By examining the geometry, we realize that such irregular rotation in fact originates from the flexibility of the molecules and, to a lesser degree, the graphene, through the interplay of several factors: (1) as seen in Figure 1B, the gears (except for the driver whose geometry is always rigid in the simulation) are significantly tilted instead of staying parallel to the graphene surface, due to the intermolecular repulsion between the gears, which are attracted to “hollow” sites of the graphene by the strong metal-graphene interaction; (2) the relative tilting of the gears breaks their planar symmetry and allows the individual arms/teeth of the gears to be significantly bent out of the ring plane due to internal flexibility within the molecules, as also seen in Figure 1B; (3) both the tilting and the out-of-plane bending of the gears induce corrugation (non-planarity) of the graphene sheet through (a) the metal-graphene bonding, which attempts to keep the planes of the gear and graphene parallel to each other, (b) downward pressure through the metal atoms (the manganese atom of slave 1 is pushed sideways because the gear above it is shifted sideways by the driver, as well as pushed downward because the arms of the gear above it are bent downward by the two neighboring gears; both of these metal displacements push the graphene down); and (c) the direct force of the tilted
rotor arms on nearby C atoms of the graphene; (4) the intermolecular forces can also bend the gear arms in-plane (tangentially), so that the open angle between adjacent arms of a gear is somewhat distorted from the ideal 72° of 5-fold symmetry (this is most visible in Figure 1A for the two left-pointing arms of slaves 1 and 2, which show in-plane bending of the C-C-H alignment, repelled by the right-most arms of slaves 2 and 3, respectively). These four factors originate from the strong inter-gear repulsion or gear-graphene bonding and thus lead to a considerable chain-induced rotational barrier for each rotating gear: as evaluated, a single gear that is parallel to the graphene surface feels almost no rotational barrier, while a 30° tilted gear suffers from a rotational potential barrier of about 0.3 eV. As the tilted arms scrape against the uneven surface of the graphene sheet during their rotation, they tend to get stuck in this potential, thus leading to the delay in rotation of the gears.

![Figure 1. Chain of four adjacent molecular gears made of carbon rings substituted with cyano (-CN) groups, in which the gear at the right end acts as the driver, rotating clockwise as indicated by the black arrow, and the other three gears are slaves driven by it. Each gear is attached to the graphene sheet with a central manganese atom (magenta) acting as pivot. (A) is the top view while (B) is the corresponding side view.](image)

In this example, we observe no skipping between the interacting arms of different adjacent gears, i.e. arms do not slip past each other: all delayed rotations are later caught up and compensated by larger forward jumps.

The situation was different when we investigated the related gear chain shown in Figure 2. Each gear is now made of a 6-membered carbon ring substituted with six ethynyl groups, thus the arms in this gear are substantially longer than those shown in Figure 1; on the other hand, we have also increased the gear-gear distance (from 3 to 4 graphene lattice constants), which gives the gear arms a bit more space to move in. Based on the 18-electron principle in organometallic chemistry, we highlight that chromium and its congeners in the same column of the Periodic Table are the only
suitable intermediates for a 6-membered carbon ring to stand robustly while rotating nearly freely on a graphene sheet, so we adopted chromium here. While in this system a single driver can successfully drive a single slave through a 60° rotation and thus a 360° full rotation (see Figure S1 in the supplementary information for details), we find that a longer gear chain containing two slaves starts to become problematic, as illustrated in Figure 2. As the driver rotates from 0° to 30°, both slave #1 and slave #2 follow it but with an observable delay in rotation – as expected from the knowledge gained from the 5-arm gears in Figure 1. However, when the driver reaches 60°, slave #1 almost totally stops rotating and we observe that the interacting arm (denoted with a red ellipse) bends appreciably out of the ring plane: it curves away from the graphene sheet as seen in the side view in Figure 2; also, the open angle between that arm and the arm to its left is widened, due to in-plane bending of the interacting arm. At the rotation angle of 65°, it becomes obvious that this arm skips past the nearby arm of the driver. This process tells us: the bending of the arm does not produce a sufficiently strong driving force to make its entire rotor overcome the rotation barrier; instead, the gear follows a more energy-efficient pathway by bending its arm away from the graphene sheet, thus leading to a skipping of arms between gears; this is made possible to some extent by the additional space between gears but especially by the larger flexibility due to the increased length of the ethynyl vs. cyano arms. For comparison, in the corresponding “1 driver + 1 slave” case shown in Figure S1, we observe no significant bending of the arm away from the graphene sheet and thus no skipping of arms between gears: the reason is that slave 1 is freer to rotate in the absence of slave 2 (note how distorted the arms of slave 1 near slave 2 are in Figure 2, unlike the same arms in Figure S1), so that the arms of slave 1 can better mesh between those of the driver.

In our earlier work we discussed that a proper selection of gear-gear distance can help to improve the effectiveness of the gear chain. However, the gear-gear distance of 4 graphene lattice constants (viz. the distance of four carbon rings on the graphene sheet) used in Figure 2 is already the nearest practical choice in this system.

Figure 2. Chain of three adjacent molecular gears made of carbon rings substituted with ethynyl (-C≡CH) groups, in which the gear at the lower end acts as the driver, rotating clockwise as indicated by the black arrow; the other two gears are slaves driven by the driver. The C≡CH arms of slave #2 are labelled A-F to mark the rotation; besides, all molecules have one of their hydrogen atoms

...
highlighted in red to emphasize the rotations. Each gear is attached to the graphene sheet with a central chromium atom (blue) acting as pivot. The four left panels correspond to four orientations of the driver molecule: 0°, 30°, 60°, and 65°, respectively. The right panel gives a side view parallel to the graphene sheet at the driver orientation of 60°.

We have also explored a molecular “propeller” made of a hexaphenylbenzene, which can potentially also serve as a molecular gear, see Figure 3. This molecule contains six propeller blades connected by a central aromatic ring that is attached to the graphene sheet with a chromium pivot. In the simulation, we only kept the central six carbon atoms of the driver rigid at each rotation step and let the blades be optimized freely. The large size of the blades could in principle prevent the skipping between gears – observed in the last example. However, as we illustrate in Figure 3, such gears also suffer from the flexibility of the molecules: as the driver rotates, the blades of both the driver and slave are severely deformed and finally lead to skipping between the driver and slave (see the driver rotation from 30° to 90° in Figure 3, during which the slave barely rotates). Since these propeller blades are to some extent perpendicular to the central carbon rings, they can easily scrape against the uneven graphene surface, and thus easily get stuck in it: the distance between the stuck hydrogen atom and the graphene surface is ~2.3 Å, far more than a normal C-H bond length (~1.1 Å), thus they are not forming new chemical bonds. Very similar to the former case of the 6-arm ethynyl (-C≡CH) molecular gears, the intermolecular forces from the driver’s arms repel the slave’s arms, leading to their bending; such bending will subsequently provide a driving force to make the slave rotate; unfortunately, this driving force in the present case is again not strong enough to exceed the rotational barrier of the entire rotor – unlike the case shown in Figure 1. By contrast, a 5- or 4-blade rotor would have a smaller rotational barrier, since its blades would be more parallel to the surface; however, as we tested computationally, the interacting blades of two such rotors can easily bend away from or toward the graphene plane and thus skip past each other by sliding over each other.

Figure 3. Coupling of two adjacent molecular propeller gears made of 6-membered carbon rings, each bonded to six phenyl groups (driver and slave are marked). Each gear is attached to the graphene sheet with an intermediate chromium atom (blue) acting as pivot. The curved red arrow illustrates the slave’s expected rotation (counterclockwise) while the black arrow indicates the rotation of the driver molecules (clockwise). The hydrogen atoms on one blade of both the driver
and slave are painted red to emphasize the rotations. The four panels correspond to four orientations of the driver molecules: 0°, 30°, 60°, and 90°, respectively. The right panel gives a side view parallel to the graphene sheet at the driver orientation of 60°.

We thus come to realize that molecular machines can differ very much from the rigid machines in the macroscopic world due to the flexibility of molecules: molecules act more like toys made of rubber. As for rotational molecules, both small single-molecule motors\textsuperscript{5,7} and large rotors\textsuperscript{13,38} suffer from this problem: when a motor drives another component in the machine system, the largest resistance (due to the deformation) it can provide determines the upper limits of the power it can output; when a rotor transmits rotational motion, the largest resistance to the driving forces it can provide determines whether it qualifies as a gear, as investigated and explained above. Thus, an evaluation of the flexibility will be helpful for us to understand, estimate, and predict the capabilities of molecular machines.

**Quantitative evaluation of molecular stiffness using the torque-curvature relationship.** Most of the rotors synthesized experimentally up to now consist of a few typical chemical groups and bonds (mainly: aromatic ring, single, double, and triple carbon-carbon bond, carbon-nitrogen bond), and larger molecular assemblies composed of them.\textsuperscript{39,40} Therefore we here select such typical groups and bonds as examples to examine their flexibility.

The valence shell electron pair repulsion (VSEPR) theory\textsuperscript{41} in chemistry intuitively explains why a stable molecule adopts a distinct geometric shape: linear (e.g. CO\textsubscript{2}), trigonal planar (e.g. BCl\textsubscript{3}), tetrahedral (e.g. CH\textsubscript{4}), etc. The premise is that the valence electron pairs surrounding an atom tend to repel each other and will, therefore, adopt an arrangement that minimizes this repulsion, thus determining the molecule's geometry. This theory provides a qualitative prediction of the geometry, instead of a quantitative one, viz. how large the repulsion (between the electron pairs) is, and how large it will be when we break the equilibrium of the bond, i.e. when curving a chain of atoms. Some quantitative descriptions and algorithms\textsuperscript{42,43} were also proposed, such as those defining the concepts of molecular curvature, tension, flexibility index, etc.\textsuperscript{44,45} However, there is still a dispute over how to precisely describe the flexibility, since the definition of flexibility varies as the scope of our interest changes from a local bond to the whole molecule: the flexibility of a single bond is in fact a different concept from that of a set of bonds, and that of the entire molecule. We will not discuss the definition of such a concept in the present paper, but mainly focus on the specific systems (i.e. molecular machines, especially molecular rotors), in which the observation of flexibility is only confined to a small group of atoms.

The torque analysis scheme proposed in our previous work\textsuperscript{46} (see also further applications\textsuperscript{20,21,47}) is adopted here as a convenient way to evaluate the relationship between curvature and applied forces in a rotor molecule: the Pulay forces\textsuperscript{48} obtained from a single-point self-consistent field (SCF) calculation can serve to obtain this relationship. Taking the 5-arm gear shown in Figure 1 as an example, the rotational axis is chosen as the surface normal of the graphene sheet, passing through the manganese atom (the pivot); then the total torque acting on the whole rotor (thus inducing its rotation) is summed as:

$$\vec{T} = \sum_i \vec{n}_i \times \vec{F}_i,$$

where the index $i$ runs over all the atoms that constitute the rotor (here 10 C atoms and 5 N atoms),
\( \vec{F}_i \) is the Pulay force acting on atom \( i \), and \( \vec{r}_i \) is the corresponding vector from the pivot (the Mn atom) to the position of atom \( i \). When the whole system is in equilibrium (e.g. as in Figure 1), the total torque acting on each gear is zero. But when the driver alone rotates (for example by 10° clockwise), the equilibrium is broken and the atoms of slave #1 start to be affected by the repulsion from the driver’s arms: the total torque on slave #1 is now not zero, and the torque direction is (approximately) normal to the graphene sheet, making slave #1 tend to rotate counterclockwise as shown in Figure 1.21 (The torque direction can also be tilted from the surface normal, causing tilting of the rotor and off-normal bending of rotor arms, as seen in Figure 1(B). The same approach can be used to evaluate these effects, but we will here focus on the in-plane bending of rotor arms.)

**Figure 4.** The bending of several typical chemical groups with a curvature of roughly 0.35 A\(^{-1}\), 0.35 A\(^{-1}\), 0.28 A\(^{-1}\), 0.30 A\(^{-1}\), and 0.39 A\(^{-1}\) for A, B, C, D, and E, respectively. Groups D and E are derived from the rotors A and B by replacing most of each rotor by a straight C-H group (atoms 2 and 3 in graphs D and E) pointing directly at the rotor center. The dashed black lines denote the relaxed directions before the groups are bent, while the solid black curves indicate the situation after the deformation – these curves also correspond to certain curvatures (the reciprocal values of the radii), see text. The black arrows denote the direction of the resistant forces of the deformed bonds.

In gears with longer arms, like those shown in Figures 2 and 3, the imposed torques typically cause stronger bending of those arms. We illustrate several examples of in-plane bent rotor arms in Figure 4: each group indicated with a solid black line is curved (for instance, due to the interaction of external intermolecular forces from a neighboring gear molecule) to deviate away from its relaxed shape, which is indicated with a straight dashed black line, tangential to the curved black line. Curvature is a convenient index to quantify such bending: we set the curvature as \( 1/r \), where the radius \( r \) defines a circle on which the atoms are constrained to lie in our calculations. We then stepwise increase the curvature (thus simulating an increasing force on and bending of the rotor arms) and calculate the resulting torques on the rotors (relative to the rotor’s rotational axes). This information is plotted in Figure 5.

We see that for rotors A, B, and C, the torques increase with the curvature almost equally. The flexibility (and thus elasticity) of these arms thus seems to be largely independent of the bond type (C-H, C≡N, C≡C, C-C, C-F). We then further conducted calculations for the simplified structures in Figures 4(D) and 4(E), which do not contain aromatic rings, for comparison: the results indicate that the single -C≡CH and -C≡N groups actually bend very easily. A control group A’ related to A (with only one of the six -C≡CH arms, the others being replaced by H) is also examined: the single arm of rotor A’ is about 20-40% more flexible than the rotor with 6 arms, largely due to the
Figure 5. Torques generated as a function of the curvature $1/r$ for several typical molecular rotors or groups (A-E illustrated in Figure 4), together with a control group A’ for A (rotor A’ has only one -C≡CH arm, compared to the 6 -C≡CH arms of A). For rotors A, B, and C, the rotational axes for the torque calculations are normal to the graphene sheet and pass through the central chromium atoms; for groups D and E, which are related to A and B, respectively, the rotational axes are positioned at the centers of the original C₆ rings of A and B, respectively. All the groups are bent in-plane with all the bond lengths fixed to their equilibrium value in the straight alignment. We also include a control group A’ to compare with A: it has only one instead of six arms, so as to exclude the influence from other arms.

From the results plotted in Figure 5, we realize that a bond that is directly connecting to an aromatic ring yields much larger resistance to bending: its stiffness is about 2-3 times that generated from bending a set of bonds not connected to an aromatic ring – compare A(A’)-C to D-E in Figure 5. Although the other unbent arms in A-C definitely contribute some resistance to the bent arm through intramolecular interaction, Figure 5(A’) shows that the stiffness of a single arm is still much larger than in the absence of the aromatic ring, as in Figure 5(D).

A possible reason is that the bending of the bonds leads to charge redistribution and consequently affects the electrostatics between atoms. Thus, we examined the charge distribution and charge transfer of these examples and list them in Tables 1 and 2. Interestingly, the magnitude of charge transfer in the explored linear bonds (not including the aromatic rings) does not have much influence on the magnitude of the resistance that is reflected from the torque (see Tables 1 and 2, together with Figure 5 at the curvature of ~0.45 Å⁻¹), and we do not observe marked differences in stiffness between different types of chemical bonds, i.e. C-H, C≡N, C≡C, C=C, C-C: C₆H₂ yields clearly more charge transfer (from 0.17-0.26, excluding the hydrogen atoms) than C₃NH (from 0.06-
denote the electrons transfer away from individual atoms due to the bending process. The atom indices 1 and 5. The curvature of the bonds

As the bonds are bending, the central atom (atom #1 in (A), (B), and (C)) tends to lose electrons or keep stable – we see that the degree is different: (A) loses 0.24, (B) loses 0.05 – almost negligible, while (C) even obtains a negligible portion (0.04) of electrons. However, atom #2 appreciably loses a large portion of electrons in all the three compounds, and thus should now exhibit a strong electrostatic repulsion to atom #1. In the meantime, atom #3 appreciably obtains electrons and consequently tends to attract atom #1. As a comparison, compounds (D) and (E), which do not contain an aromatic ring in them, exhibit no such induced electrostatic repulsion or attraction. And the conclusion is: the inclusion of aromatic rings tends to stiffen the chemical bonds connecting to them.

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Table 1. Mulliken charges of atoms of the deformed molecular rotors A, B, and C shown in Figures 4 and 5. The curvature of the bonds is set at 0.45 Å⁻¹, a little bit tighter than illustrated in Figure 4. The atom indices 1-8 correspond to those marked in Figures 4 and 5. The numbers in parentheses denote the Mulliken charges for atoms in normal undeformed bonds; the numbers in the brackets denote the electrons transfer away from individual atoms due to the bending process.

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<td>[0.09]</td>
<td>-</td>
<td>[-0.06]</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Mulliken charges of atoms of the deformed linear molecules D and E shown in Figures 4 and 5. The curvature of the bonds is set at 0.45 Å⁻¹, a little bit tighter than illustrated in Figure 4. The atom indices 1-7 corresponds to those marked in Figures 4 and 5. The numbers in parentheses denote the Mulliken charges for atoms in normal undeformed bonds; the numbers in the brackets denote the electrons transfer away from individual atoms due to the bending process.
In summary, our simulations of bending effects in molecular rotors and gears lead to the following observations: (1) longer rotor arms containing a long linear group (like those illustrated in Figure 2) actually produce no stronger driving forces (to adjacent rotors) than shorter arms (like those illustrated in Figure 1); (2) the driving forces generated in all the studied typical rotors are actually mainly contributed by the single bond (C-C_6 or F-C_6 here) connecting to the aromatic ring, instead of by the C≡N or C≡C triple bond, or any others; (3) there is no substantial difference between various chemical groups in the magnitude of generated resistance/stiffness; (4) we observe almost no deformation of the planar aromatic rings, as bending a π bond is believed to be generally more difficult;\(^4\) (5) we have found no cases in which the rotors are destroyed – although this may indeed happen in certain cases, as observed in previous studies\(^{20, 21}\). Therefore, we suggest that, in designing molecular machines, aromatic rings be included in the molecules so as to enhance the stiffness of the machine, and conversely: replacing aromatic rings with other groups may reduce the machine’s stiffness.

**Conclusions**

In earlier research about molecular machines, we found that the flexibility/elasticity affects their performance very significantly, bringing about quite different phenomena from those occurring in rigid machines in the macroscopic world. Neglecting such flexibility may lead to failure by the machines to perform desired functions. In the present paper, taking several model molecular rotors built on surfaces as examples – especially when they are coupled to form interlocking gears – we demonstrate how the flexibility may affect their performance through bending, skipping, sticking, jumping, etc. We also propose and apply a torque-curvature function to measure the extent of the flexibility of typical molecular bonds, thus providing a general understanding about such properties. Conclusions and understandings obtained here can also be extended to other similar molecular machine systems and are expected to enlighten the design of molecular machines – both in theoretical prediction or experimental realization. In particular, there is the prospect of devising equations of motion, at least semi-classically but beyond molecular dynamics, so as to describe the multi-component motion of molecular machinery, including vibrational, flexing and dissipative effects. Also, further systematic analysis of the relative flexibility of different categories of molecular bonds would be of great use.

**Supporting Information**

A 6-arm gear chain (consisting of 1 driver and 1 slave) with chromium pivots.

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