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Interruption of the inner rotation initiated in isolated electron-driven molecular rotors

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An anthracene molecule substituted at the central ring by two aniline moieties able to rotate about the C-N bonds can be considered to be a prototype molecular rotor. Electron attachment into the lowest empty orbitals of this molecule leads to formation of long-lived (microseconds) negative ions. Elimination of a hydrogen molecule from these anions was observed in the gas phase by means of dissociative electron attachment spectroscopy. The experimental findings were interpreted using density functional theory calculations. It was shown that the decay process must be accompanied by formation of a new covalent bond in which one aniline moiety is fixed to the adjacent carbon atom of the anthracene ring. The observed irreversible interruption of the rotational motion could occur in other artificial electron-driven molecular machines provided that suitable atoms approach each other under the rotation.

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I. INTRODUCTION

Molecular species made of interlocked components can be viewed as molecular machines operating via electronic and nuclear rearrangements driven by a suitable conversion of chemical or light energy into movement [1]. Examples from biology are presented by the complex protein assemblies which are responsible for most forms of movements encountered in the cellular world [2,3]. Simpler single organic molecule-based artificial mechanisms mimicking the functions of mechanical devices are receiving particular attention owing to their possible applications in new nanoscale devices [1]. In addition to the most studied case of light-driven molecular mechanisms [4,5], electron-driven nanoscale machines [6] represent another important class of such devices. This includes also the case of resonance electron transfer through a single molecule (or molecular wire) junction, usually accompanied by excitation of rotational [7] or vibrational [8] motions. Electron tunneling from a scanning tunneling microscope tip is found to drive a prototype nanocar, a four-wheeled molecule, across a metal surface [9] and also is able to cause excitation of directional rotational motion in a single chiral molecule, butyl methyl sulfide, connected to a Cu(111) surface via its sulfur atom [10]. Molecular rotors have already demonstrated applications as probes for microviscosity [11] and fluid flow in real time [12]. Surface-anchored rotors important for applications [13] are easily accessible by surface analysis methods. Such devices are capable of reproducing the behavior of natural molecular machines which usually operate at interfaces [3,14]. Nevertheless, investigations of a simple isolated molecular system are desirable to model the behavior of structures attached to more complex environments [15].

The present paper reports on an unexpected result, namely that, upon excitation of the rotational motion initiated in 9,10-dianilindoanthracene (DAA) single molecules by electron attachment, an irreversible interruption of their motion subsequently occurred. The process schematically shown in Fig. 1 is driven by a mechanism referred to as dissociative electron attachment (DEA) [16,17]. It was investigated under gas-phase conditions by dissociative electron attachment spectroscopy [17] and the findings were interpreted using density functional theory calculations. Initially, the temporary negative ion, DAA$^-$, is produced by electron attachment to DAA, which then dissociates via elimination of a neutral hydrogen molecule, forming the doubly dehydrogenated anion, dda$^-$ and competing with simple reemission of the captured electron. Although reported under gas-phase conditions, the present results give some more insight into operation of electron-driven artificial molecular rotors. The observed effect should thus be taken into account for any artificial molecular machines operating under conditions of excess negative charge.

II. EXPERIMENTAL AND COMPUTIONAL DETAILS

Low-energy (0–5 eV) resonance electron capture by gas-phase DAA was investigated using dissociative electron attachment spectroscopy [17]. A schematic representation of the magnetic mass spectrometer and a description of specific conditions may be found elsewhere [18]. Briefly, a magnetically collimated electron beam of defined energy was passed through a collision cell containing a vapor of the substance under investigation, under single-collision conditions. Currents of mass-selected negative ions formed by DEA were recorded as a function of the incident electron energy. The electron energy scale was calibrated with the SF_6^- signal at zero energy, generated by attachment of thermal electrons to SF_6. The full width at half maximum of the electron energy distribution was 0.4 eV, and the accuracy of the measured peak positions was estimated to be ±0.1 eV. A procedure for experimental evaluation of the electron detachment time from mass-selected negative ions modified for magnetic mass filters was described elsewhere (see Ref. [19] and references therein) and is based on detection of neutral particles formed by electron detachment from the anions in the field-free area (40 cm length) before the detector. Under the present experimental conditions, the reference electron detachment time from the SF_6^- anions formed at zero electron energy was estimated to be 100 μs at 170 °C (the temperature used to evaporate DAA) and the time of flight for DAA$^-$ from the

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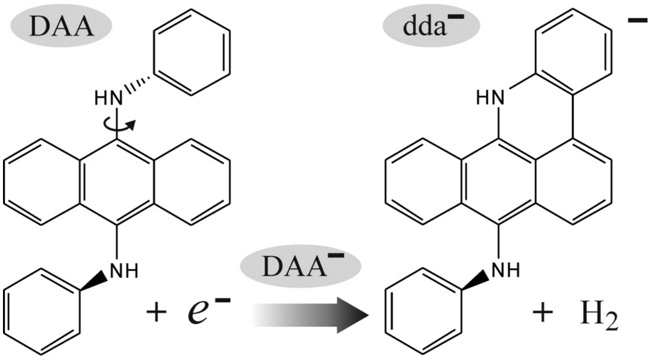

FIG. 1. Elimination of H_2 molecule from the temporary negative ion (DAA^-) generated by electron attachment to gas-phase dianilindoanthracene (DAA) is accompanied by formation of a new C-C bond in the dehydrogenated species (dda^-). The process leads to irreversible fixation of "a rotor" (aniline moiety) to "a stator" (anthracene core) in a prototype simple molecular machine.

point of its formation inside the collision cell to the detection system is estimated to be 41 μs.

III. RESULTS AND DISCUSSION

Mass-selected currents of the long-lived (microseconds) molecular negative ions DAA^- ($m/e = 360$), as well as the dda^- ($m/e = 358$) species associated with loss of two hydrogen atoms from DAA^- as a function of incident electron energy, are reported in Fig. 2(a) by solid lines. Three resonant bands with maxima at 0 (thermal energy), 0.7, and 1.9 eV, are clearly observed in the dda^- current, whereas the DAA^- current reveals no contribution around 1.9 eV. It should be noted that doubly dehydrogenated species are rarely formed by DEA to aromatic molecules at such low incident electron energies. The $m/e = 359$ anion formed by rupture of the single N-H bond (usually caused by DEA at electron energies close to 1 eV [20]) is the more expected dehydrogenated fragment in the present case. However, the $m/e = 359$ anion signal at the electron energies below 5 eV is completely masked by the isotopic contribution from the dda^- current.

Signals of the neutral species formed by electron detachment from DAA^- and dda^- during their straightforward flight through the field-free space located between the mass analyzer and the detector are shown in Fig. 2(a) by open symbols. The ratio of these signals to the yields of DAA^- and dda^- reflects the rate of electron detachment from the mass-selected negative ions. The evaluated [19] electron detachment time as a function of incident electron energy is reported in Fig. 2(b). Electron detachment times from both the DAA^- (formed at 0 and 0.7 eV) and dda^- (formed at 1.9 eV) lie in the microseconds range. The dda^- species formed below 1 eV holds the extra electron for much longer times, quite outside the experimental time window (the neutral counterpart was not observed in this electron energy range). Therefore, the corresponding electron detachment time lies in the milliseconds range.

Spectral features observed at low electron energies are usually associated with rapid (vertical) electron attachment into the empty molecular orbitals by a shape resonance mechanism [16]. An empirical linear scaling procedure [21] was applied to the Becke three-parameter Lee-Yang-Parr (B3LYP)/6-31G(d) virtual orbital energies of DAA to locate the corresponding negative ion states within the Koopmans' theorem [22] approximation. This approach was found (see, for instance, Refs. [23,24] and references therein) to be adequate for the description of the negative ion states. Predicted positions of the lowest π^* orbitals obtained by the scaled B3LYP/6-31G(d) orbital energies for the most stable conformer of DAA (both aniline moieties are turned to the same side of the anthracene core; see Fig. 3) are indicated in Fig. 2(a) by vertical bars. It should be noted that the σ^* anion states are not considered here because they are usually more short lived in comparison with π^* states. Thus their contribution to formation of the anions through the DEA mechanism is expected to be small. Several anion states can likely make a contribution to the DEA band peaked at 0.7 eV, the closest in energy being the π_3^* [see Fig. 2(a)]. A maximum observed in the anion current around 1.9 eV coincides well with the position of the π_9^* orbital.

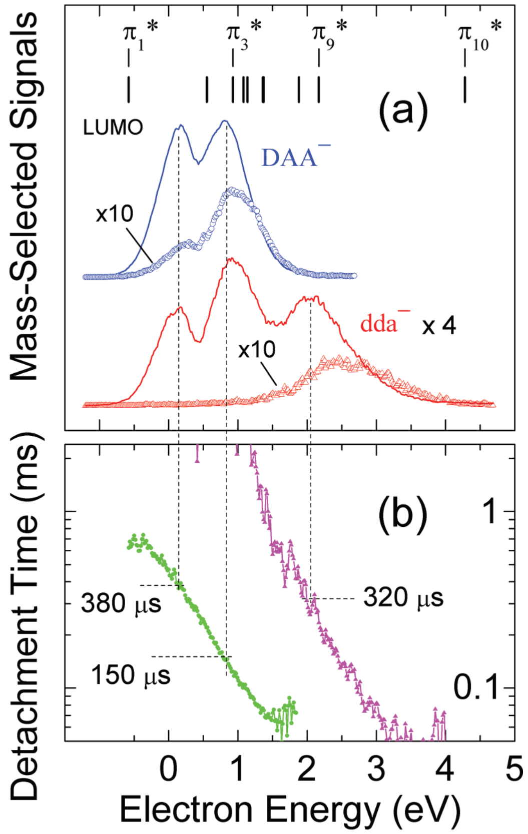

FIG. 2. (Color online) (a) Currents of mass-selected negative ions DAA^- and dda^- (× 4) formed by electron attachment to DAA as a function of incident electron energy (solid lines). Signals of corresponding neutral species (× 10 relatively to corresponding anion currents) formed by electron detachment are shown by open symbols. Vertical bars locate the predicted positions of the lowest empty $\pi*$ orbitals of DAA. (b) Electron detachment times from DAA^- (left curve) and dda^- (right curve) as a function of incident electron energy. The values corresponding to the maxima at 0, 0.7, and 1.9 eV are reported.

The DEA signal peaking at zero (thermal) electron energy is usually associated with electron attachment into vibrationally

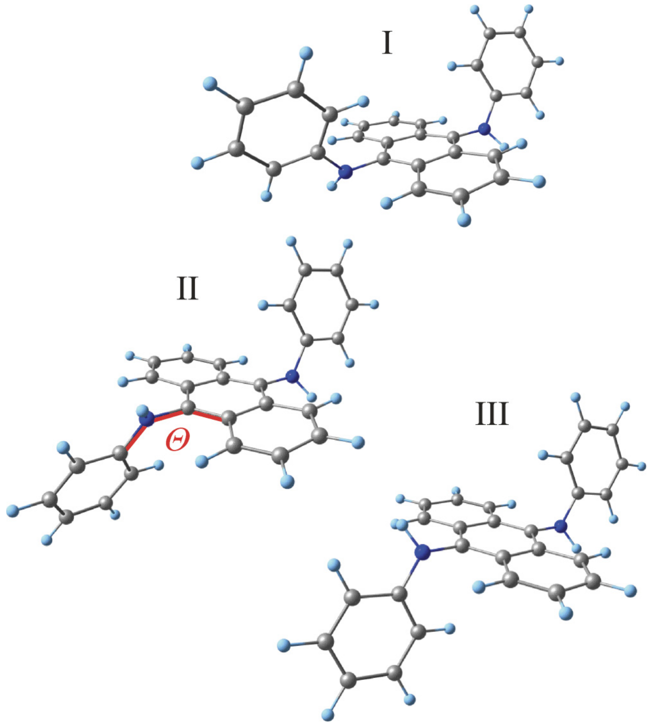

FIG. 3. (Color online) B3LYP/6-31 + G(d) optimized geometries of three stable DAA conformers. Aniline moieties in the most stable conformer I are in their "staggered" conformation. Conformers II and III (0.0027 and 0.019 eV, respectively, less stable than I) have the aniline moieties turned to different sides of the anthracene plane. Aniline moieties in conformer III are in their "eclipsed" conformation. Anthracene core in III is planar, whereas in I and II it is helical.

excited levels of stable anion states by a mechanism referred to as vibrational Feshbach resonances [16]. The scaling procedure predicts the lowest empty molecular orbital (LUMO, π_1^*) of DAA to be bound (with energy -0.58 eV below the electron continuum; see Fig. 2) and corresponding to a vertical electron affinity (EA) of 0.58 eV. Alternatively, estimating the vertical electron affinity of DAA as the B3LYP/6-31 + G(d) total energy difference between the neutral and the lowest anion state, both in the optimized geometry of the neutral state, gives a slightly higher value of 0.9 eV. The adiabatic electron affinity (EA_a) of DAA estimated at the same level of theory as the total energy difference between the neutral and the lowest anion state, each in its optimized geometry, is found to be 1.0 eV.

The B3LYP/6-31 + G(d) threshold for abstraction of a hydrogen atom from the N site of DAA$^-$ by DEA is calculated here to be 1.33 eV. This value is in close agreement with the energy (around 1 eV) of the incident electron required to rupture the N-H bond in gas-phase uracil and thymine by DEA [20]. Evidently, abstraction of a hydrogen atom from the C site of the aromatic rings requires even more energy. Abstraction of two hydrogen atoms (both from the N sites of DAA$^-$) and their elimination as a radical species requires 4.48 eV according to the present B3LYP/6-31 + G(d) calculations. Given that the N-H sites in DAA are spatially separated, the possibility to form molecular hydrogen as a neutral counterpart could be excluded. Therefore, formation of dda$^-$ by rupture of both the N-H bonds can hardly be expected at incident electron energies below 4 eV. A possible way for this to occur is schematically presented in Fig. 1 and can take place from formation of additional bonds that reduce the total energy of the products. Provided that a molecular hydrogen is eliminated from DAA$^-$ and a new C-C bond is formed, the total energy of the products becomes significantly lower [the B3LYP/6-31 + G(d) threshold is negative, -0.28 eV]. In this case, formation of the dda$^-$ by DEA is possible even at thermal energy.

Figure 3 shows the B3LYP/6-31 + G(d) optimized geometry of three stable DAA conformers differing from each other by a value of the dihedral angle (labeled Θ in Fig. 3) responsible for the rotation of the aniline moieties. The most stable conformer (labeled I in Fig. 3) has both aniline rings turned to the same side of the anthracene plane. Two other conformers (labeled II and III) are only slightly (0.0027 and 0.019 eV, respectively) less stable. Oppositely to III, the anthracene core in I and II is predicted to be "helical." The value of Θ is also responsible for the principal geometry change on going from the neutral DAA to its negative ion. Namely, Θ (in conformer I) is changed from 79.7° in the optimized neutral state to 86.9° in the optimized negative ion according to the present B3LYP/6-31 + G(d) calculations. Therefore, it is reasonable to assume that the incoming electron acts as a "trigger mechanism," such that the electron capture by DAA leads to excitation of the rotational motion of the aniline moieties relative to the anthracene core. This leads to a close approach of the H atoms to each other and their elimination as a H_2 molecule, leaving the excess negative charge on the dda$^-$. The potential energy stored in the helical state of the core is also available.

It is worth speculating if elimination of a hydrogen molecule occurs at the very first approach of the H atoms or, alternatively, it takes place after several rotational cycles. The answer should address the rate of the rotational motion or, in other words, to the amount of energy deposited into the rotational degrees of freedom. If the rotation is slow, the molecule has time to "tune" its geometry so that the hydrogen atoms can avoid the collision. Figure 4 shows the calculated relative energy (only electronic

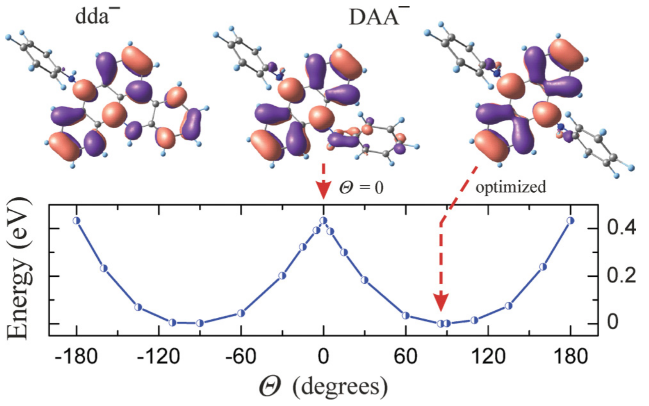

FIG. 4. (Color online) B3LYP/6-31G(d) total energy (only electronic contribution) of DAA$^-$ relative to that of its optimized state as a function of dihedral angle Θ. Single-occupied molecular orbital (SOMO) of anionic species, dda$^-$, DAA$^-$ in their optimized geometry and DAA$^-$ at Θ = 0 are schematically shown.

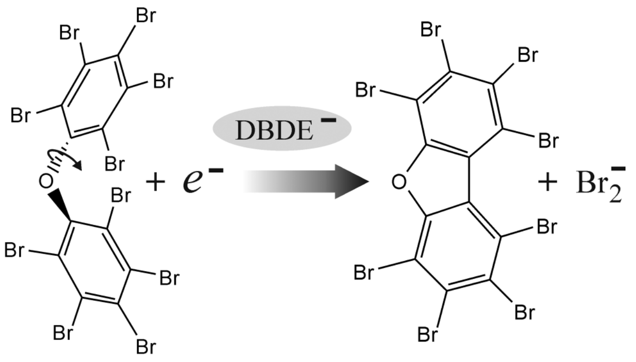

FIG. 5. Elimination of Br_2^- anion from the temporary negative ion (DBDE$^-$) generated by electron attachment to gas-phase decabromodiphenyl ether (DBDE) is accompanied by formation of a new C-C bond. Octabromodibenzofuran is produced as a neutral counterpart. Br-substituted benzene moieties able to rotate about the C-O bond become irreversible fixed to each other.

contribution) of DAA$^-$ as a function of Θ under rotation of one aniline moiety. The other moiety as well as the anthracene core were allowed to relax to the most energetically favored state in order to model "a tuning" of the geometry under the rotation. A potential barrier about 0.5 eV (see Fig. 4) for rotational motion of an aniline substitute in DDA$^-$ is predicted by the present B3LYP/6-31 + G(d) calculations. The energy to overcome this barrier could be derived from the excess energy stored in DAA$^-$. Actually, the excess energy stored in a negative ion formed by thermal electron attachment is equal to the EA$_a$ of the target molecule. A contribution (usually small) arising from a difference between the vibrational frequencies of a molecule and its anion (the so-called zero-point energy correction) should also be included. Incoming electron energy as well contributes to the excess energy under DEA above zero energy (0.7 and 1.9 eV in the present case).

It is reasonable to assume that the DAA$^-$ excess energy is partly redistributed into the rotational degrees of freedom. Indeed, the long-lived molecular anions formed at incident electron energies above zero are rarely observed [25]. Formation of such anions at thermal energy is attributed to molecules with EA$_a$ above 0.5 eV. DAA is predicted to be not planar in its optimized geometry (see Fig. 3), so that it does not possess a broad conjugated π system. Correspondingly DAA is expected to behave under DEA similarly to a single anthracene molecule (EA$_a$ = 0.530 eV [26]), although the predicted EA$_a$ of DAA is somewhat higher (1.0 eV). Molecular negative ions of anthracene were only observed at thermal energy of the incident electrons, and the electron detachment time was estimated to be 25 μs [27]. In contrast, the DAA$^-$ current reveals a pronounced maximum above zero energy (at 0.9 eV). The corresponding electron detachment time is much higher (see Fig. 2). Delayed electron detachment is attributed to fast redistribution of the anion excess energy among the available degrees of freedom [25]. In the present case we speculate that the DAA$^-$ excess energy could (at least partly) be transferred into rotational motion of the aniline moieties. This assumption is in line with the predicted change of the DAA geometry due to the extra electron attachment. Correspondingly, a contribution from the aniline moieties to a single occupied molecular orbital (SOMO) of DAA$^-$ becomes significant under their turning about the C-N bond into the plane of the anthracene core (see Fig. 4). The excess negative charge in dda$^-$ resides in the SOMO located on the both anthracene and aniline aromatic rings.

IV. SUMMARY

In conclusion, molecular species possessing the inner rotational degrees of freedom can be dissociated by low-energy electron attachment. Approach of suitable atoms to each other may lead to their elimination as a neutral two-atom molecule from the temporary negative ion due to the rotational motion initiated by extra electron capture. In turn, the rotational parts in the negative charged fragment are fixed by a new covalent bond. The incoming electron influences the molecular system by (i) bringing an additional energy and (ii) initiating the rotational motion. It finally leads to breaking of the prototype molecular machine by a dissociative event. The extra electron could also escape from the "broken machine" during milliseconds or microseconds after the attachment depending on its initial energy. Although the effect was observed under gas-phase conditions, it implies a possibly unwanted behavior of molecular rotors operating under conditions of excess negative charge.

It should be noted that the observed fixation of rotational motion stimulated by DEA in isolated molecule is not a single case. Figure 5 shows an almost identical example reported earlier [28] in DEA to decabromodiphenyl ether (DBDE). This molecule, sufficiently nonplanar in its optimized geometry, consists of two bromine-substituted benzene rings attached to a central oxygen atom. Electron capture to DBDE leads to elimination of the Br_2^- anion accompanied by formation of the planar octabromodibenzofuran molecule (see Fig. 5). The observed (under gas-phase conditions) behavior of prototype molecular rotors could be considered as a challenge for investigations of solid-state or surface-anchored tiny mechanisms with the objective to support or reject the proposed mechanism of disruption of nanodevices by excess negative charge. The most obvious difference to be taken into account on going from the gas to condensed state is stabilization of the molecular orbitals by approximately 1 eV [29].

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