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Towards a symmetric reversible single-molecule switch: Amino-imino-cyclo-n-enes

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ABSTRACT

We propose cyclic 5- and 7-ring structures with alternating single and double bonds and adjacent imino and amino groups as candidates for switches in molecular electronics, with amino-imino tautomerisation as the switching mechanism. Due to the C_{2V}-symmetric transition state, the molecules exhibit a symmetric double-well potential with identical energies for the two states, which is a desirable property for a functioning molecular switch. Calculations at the double hybrid mPW2PLYP-D2/def2-TZVP level show barriers of 1.07 and 0.52 eV for the 5-ring and 7-ring, respectively (zero-point corrected: 0.97 and 0.41 eV, respectively). The corresponding 9-ring structure is not suitable as a molecular switch, due to ring puckering and the existence of multiple minima. Attachment of ethyne groups to the nitrogens and the opposite carbon, as models for molecular wires, only slightly changes the barrier heights. The 5- and 7-ring structures are promising switch candidates for further investigation.

1. Introduction

The computer and semi-conductor industry has been one of the main drivers of innovation in the 20th and 21st century. One of its key enablers has been the ongoing miniaturisation of electronic components and devices, as epitomised by Moore's Law [1], which postulates a doubling of the number of transistors per area every 18 months. However, Moore's Law is approaching its physical limits, and a marked slow-down has already been observed [2]. As a result, companies developing electronic devices are seeking alternative approaches to packing even more functionality into smaller volumes. One possible way of achieving an even higher density of components is the development of molecular electronics, using single molecules as switches or transistors. Once industrially accessible, these will revolutionise the electronics and computer industry.

The main requirement for a molecule to be used for such a purpose is the existence of two distinct states that display different conductance behaviour, and a means of rapidly switching between those. A switch needs to be reversible; it is therefore desirable that the two states are of similar or the same energy. We have recently proposed a molecular switch based on tautomerisation of an amino and imino group, attached to adjacent carbon atoms of a quinone-like ring molecule [3]. Near-symmetry of the barrier was achieved through binding to an iron atom coordinated to the quinone ring. This would in practice cause problems, as a mechanism would have to be found to keep the metal atom in place. A different approach to creating a symmetric barrier, without the need for a coordinated metal, is the use of an odd-numbered ring, where the two states are related by symmetry. This is the option we will investigate in this publication.

We first consider a 7-membered ring, with alternating single and double bonds, and adjacent amino and imino groups: aminotroponimine (IUPAC name 7-iminocyclohepta-1,3,5-trien-1-amine). Aminotroponimine is the nitrogen analogue of tropolone. Aminotroponimine and various derivatives have been synthesised [[4–9]. Claramunt et al. studied aminotroponimines with the imino hydrogen and the outer amino hydrogen replaced by bulkier groups such as phenyl and pyrrole rings, using multinuclear NMR and electrospray mass spectroscopy [5, 6]. Machiguchi et al. succeeded in synthesising pure aminotroponimine [9]. Aminotroponimimes have also been used as ligands for boron and metal complexes [4,7,8]. Sanz et al. studied the properties of the intramolecular hydrogen bond in tropolone, aminotropone and aminotroponimine using density functional theory. They found that compounds in which the 7-membered ring is unsaturated have stronger hydrogen bonds, mainly due to enhanced intrinsic acidity and basicity of the hydrogen-bond donor and acceptor groups [10].

To investigate the effect of ring size, we also consider rings consisting

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of 5 and 9 carbon atoms (5-iminocyclopenta-1,3-dien-1-amine, and 9-iminocyclonona-1,3,5,7-tetren-1-amine). Aminotroponimine, the cyclopentadiene and cyclononatetrene will hereafter simply be referred to as the 5-, 7- and 9-rings.

Another question that needs to be addressed is if the switching behaviour of the molecule changes when it is part of a network, where it would be connected to other components with "molecular wires", such as conjugated organic chains. The simplest such wire would be an ethyne molecule, which can form a conjugated bridge to double bonds in the ring or the C-N bond of the imino group, as shown in Fig. 1.

2. Methodology

The ring molecules were first optimised using the BLYP [11,12] density functional augmented with Grimme's D3 dispersion correction [13] in conjunction with the 6-31+G(d) basis set, followed by optimisation using mPW2PLYP-D2 (double hybrid functional mPW2PLYP [14] with Grimme's D2 dispersion term [15]) in combination with the def2-TZVP [16] basis set. We used this functional as dispersion-corrected double hybrid functionals were recently identified to be the most accurate DFT methods for ground-state thermochemistry [17]. Both minimum and transition state optimisations were performed. Starting structures for the transition state optimisations were either estimated (by placing the hydrogen involved in the tautomerisation midway between the two nitrogens) or taken as the maximum in the profile of a relaxed scan calculated by increasing the (amino)NH distance or reducing the (amino)H•••(imino)N distance. Harmonic vibrational frequencies were calculated to verify the structures are true minima and transition states.

As the 9-ring is not planar, there are several local minima due to different possibilities of twisting the ring out of plane. It was found that all the lowest-energy conformations are variations of the "boat" form. We optimised structures with the amino and imino groups on any two adjacent carbons of the boat conformation, at both levels of theory. The two levels of theory obtained the same lowest-energy minimum. The maximum in the profile of a relaxed scan calculated at the BLYP-D3/6-31+G(d) level was used as the starting point for a transition state optimisation. The optimised transition state, verified to be a true transition state by the presence of one imaginary frequency, was used as the starting structure of a transition state optimisation at the mPW2PLYP-D2/def2-TZVP level.

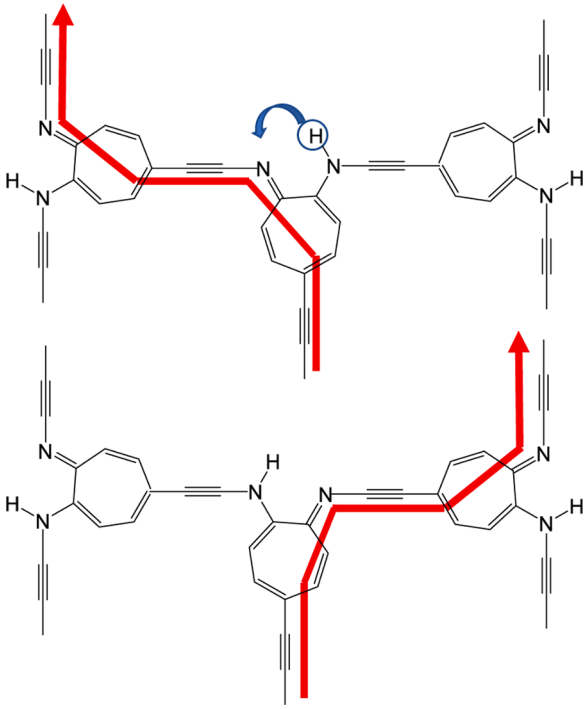

Fig. 1. Network of molecular switches, showing the change in flow of current (indicated by the red arrows) upon switching the circled hydrogen as indicated by the arching arrow.

Geometry optimisations on the minimum and transition state were also carried out for the 5- and 7-rings with -C≡CH substituents attached to the two nitrogens and the opposite carbon, modelling molecular wires.

Intrinsic Reaction Coordinate (IRC) [18] calculations were carried out to confirm that the transition state links the correct minima. These employed a step size along the reaction path of 0.1 Bohr, with the Hessian being calculated analytically every 10 predictor steps. In the profiles presented in Figs. 3 and 5, the reaction coordinate was scaled to ±1.0 to make it easier to compare the energetics. Energies are relative to the lowest minimum.

All DFT calculations were carried out with Gaussian 09 [19].

The switch rate r_{switch} was computed using the Boltzmann distribution:

$$r_{switch} = fe^{-\Delta E/kT} \tag{1}$$

Here, ΔE is the barrier height (in J), f is the switching frequency (in s^{-1}), k is Boltzmann's constant ($k = 1.38064852 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$) and T is the temperature (in K). f is obtained by converting the frequency of the symmetric NH_2 stretch (or the NH stretch for the molecules with wires), from cm^{-1} to s^{-1} (by multiplying by the speed of light; $c = 2.998 \times 10^{-10}$ cm s^{-1}). The frequencies were calculated at the mPW2PLYP-D2/def2-TZVP level.

3. Results and discussion

Fig. 2 shows the optimised structures of the minimum energy and transition state of the 5-, 7- and 9-rings. The tautomerisation barriers at the mPW2PLYP-D2 level are 1.07, 0.52 and 1.00 eV, respectively. Zero-point energy correction decreases these to 0.97, 0.41 and 0.86 eV, respectively. Claramunt et al. calculated the barrier for the 7-ring at the B3LYP/6-31G* level [6]. They obtained a value of 0.52 eV (0.41 eV after zero-point energy correction), in close agreement with our result. The corresponding IRCs are shown in Fig. 3. The 5- and 7-rings are planar, with a C_{2V}-symmetric transition state. The planarity of the 7-ring is in agreement with the B3LYP calculations of Sanz et al. [10]. In the case of the 9-ring, the structure is non-planar and the transition state does not show mirror symmetry. The non-planarity is presumably due to reduced strain caused by unfavourably large C-C-C angles (which would be around 140° in the planar structure), which counterbalances the loss of favourable conjugation in the nonplanar structure. The IRC connects the lowest-energy minimum to a higher-lying one. Reaching the lowest-energy structure on both sides of the transition state would require a twist of the ring in addition to the hydrogen exchange. This added complexity likely makes the 9-ring unsuitable as a switch in a network, and we therefore did not consider it further.

With wires attached to the 5- and 7-rings (Figs. 4 and 5), the transition states retain their C_{2V} symmetry. The barriers are slightly reduced, to 0.98 and 0.41 eV, for the 5- and 7-ring, respectively (0.85 and 0.29 eV zero-point energy corrected). This indicates that being attached to a network or electrodes will not change the switching behaviour of these molecules significantly.

The barrier height must be sufficient to prevent thermally induced spontaneous switching. The thermal switch rate can be estimated using the Boltzmann distribution as described in the Methodology section. Fig. 6 shows the switch rate calculated from the barriers and vibrational frequencies for the 5- and 7-ring with and without wires. Due to the higher barrier, the 5-ring is more resistant to spontaneous switching, indicating that such a switch could be operated at higher temperatures. At liquid nitrogen temperature (77 K), the switch rate of the 7-ring with

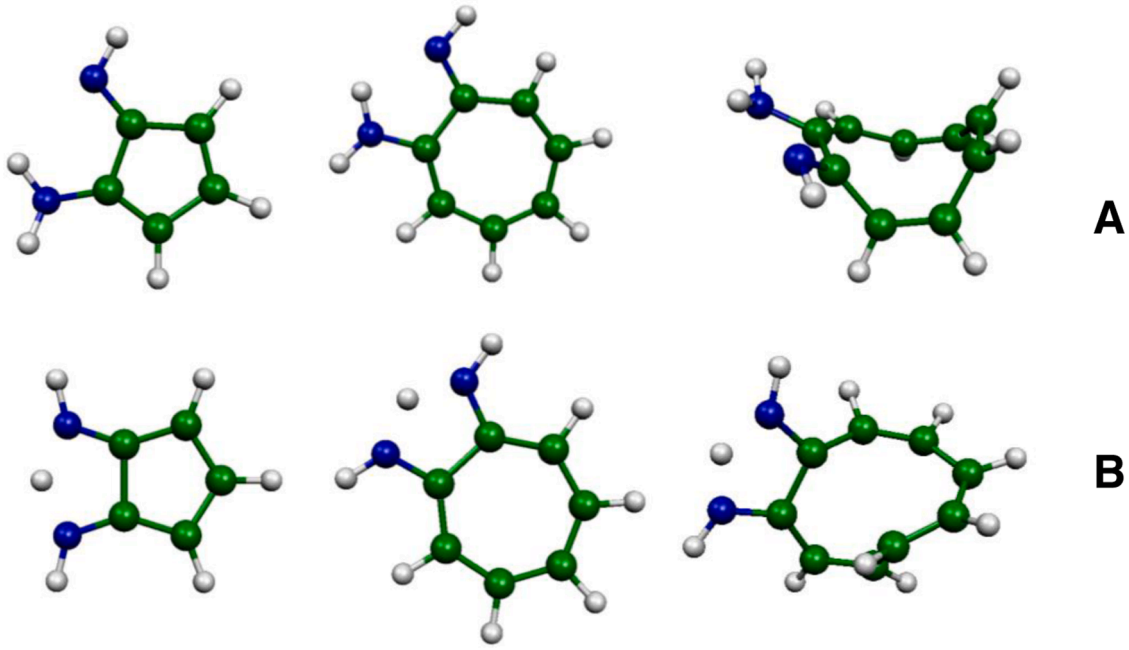

Fig. 2. mPW2PLYP-D2/def2-TZVP optimised structures of the minima (A) and transition states (B) of the 5-, 7- and 9-ring.

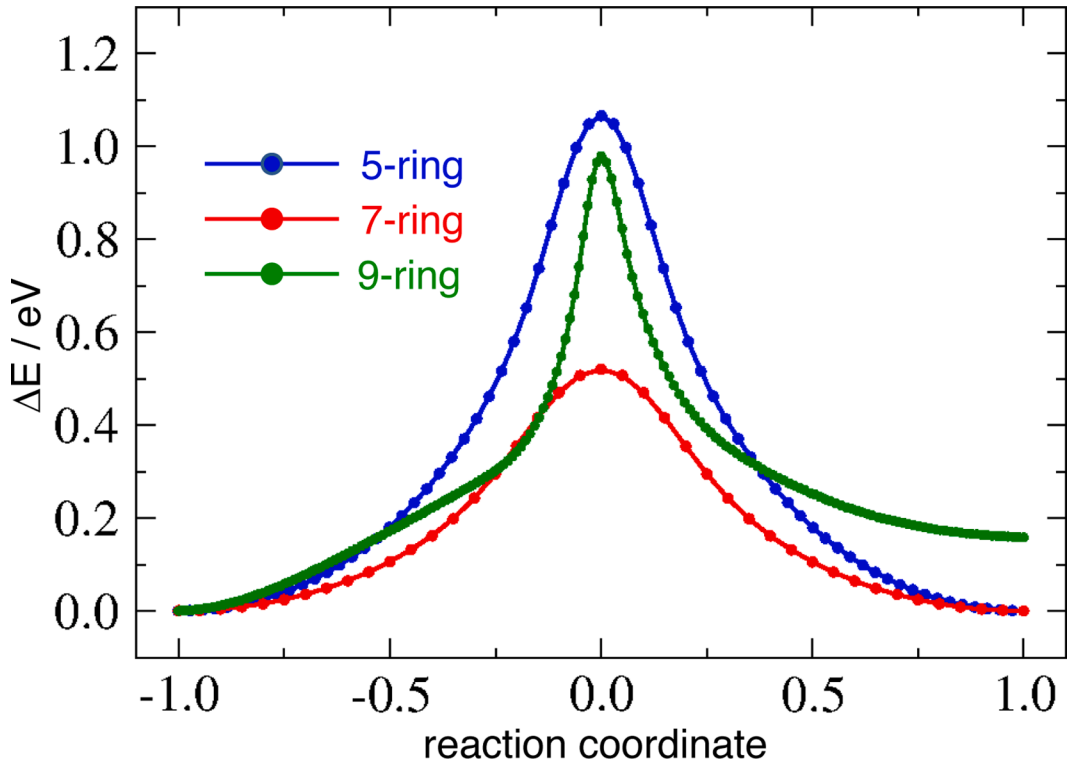

Fig. 3. IRCs of the 5, 7- and 9-ring calculated at the mPW2PLYP-D2/def2-TZVP level.

wires is in the order of 10^{-13} and that of the 5-ring with wires is 10^{-50}. This indicates that no spontaneous switching would take place in the 5-ring under these temperature conditions. In the case of the 7-ring, the larger switch rate indicates that some molecules can be expected to change configuration in a macroscopic assembly. Whereas this is not desirable in a traditional electronic device, it may be acceptable in a system where the final state is measured statistically. This would be particularly interesting for neural networks and similar machine learning applications, where fault tolerance is an intrinsic advantage of the method [20–22].

4. Conclusions

We propose odd-membered carbon ring structures with adjacent amino and imino substituents as switches for molecular electronics. The switching mechanism would be the transfer of a hydrogen from the amino to the imino group. We computed the minima, transition states and barriers for amino→imino hydrogen transfer for 5-, 7- and 9-

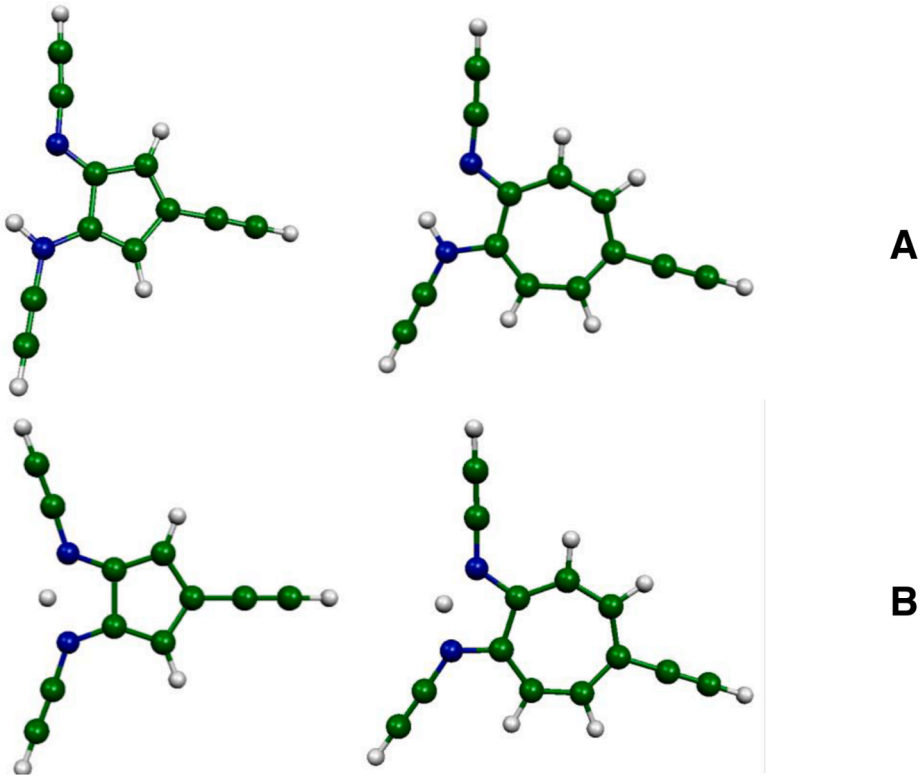

Fig. 4. mPW2PLYP-D2/def2-TZVP optimised structures of the minima (A) and transition states (B) of the 5- and 7-rings with wires attached.

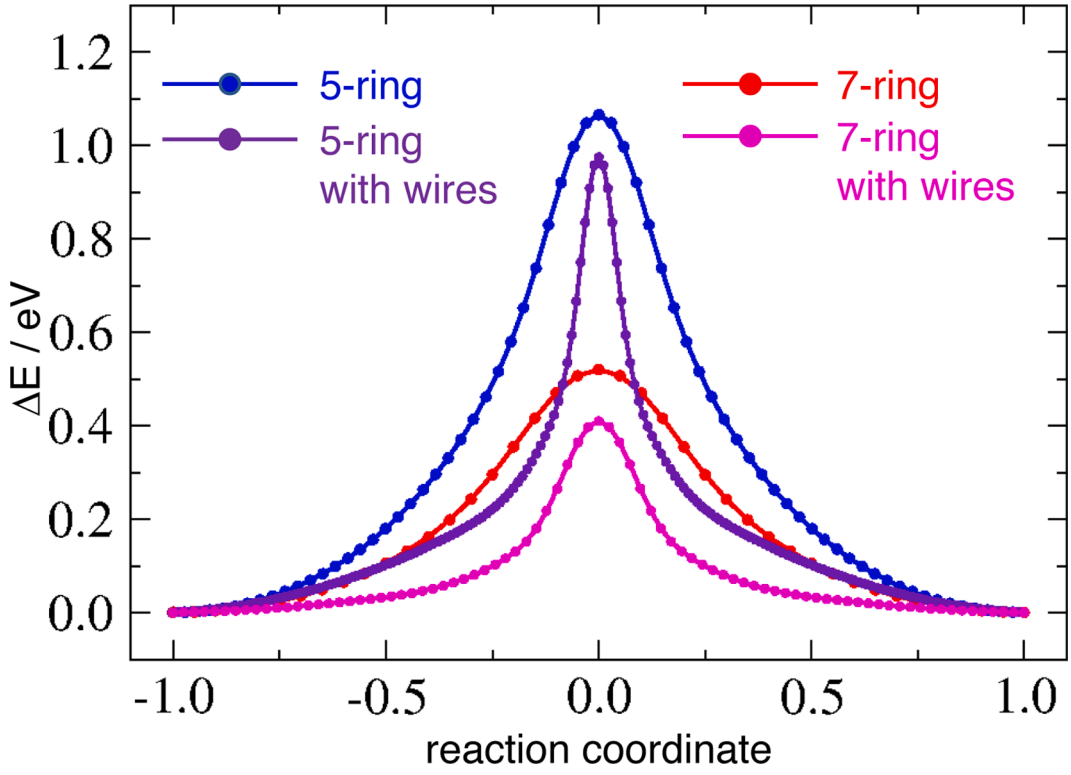

Fig. 5. IRCs of the 5, 7- and 9-ring with wires attached calculated at the mPW2PLYP-D2/def2-TZVP level.

membered rings (5-iminocyclopenta-1,3-dien-1-amine, 7-iminocyclohepta-1,3,5-trien-1-amine and 9-iminocyclonona-1,3,5,7-tetren-1-amine, respectively) at the dispersion-corrected double hybrid density functional theory level. We find that the 5- and 7-membered rings exhibit symmetric double-well potentials with a C_{2V}-symmetric transition state, due to the planarity of the ring. This symmetry remains upon attachment of ethyne "wires" to the two nitrogens and the opposite carbon. The barriers are slightly reduced in this case. The 9-membered

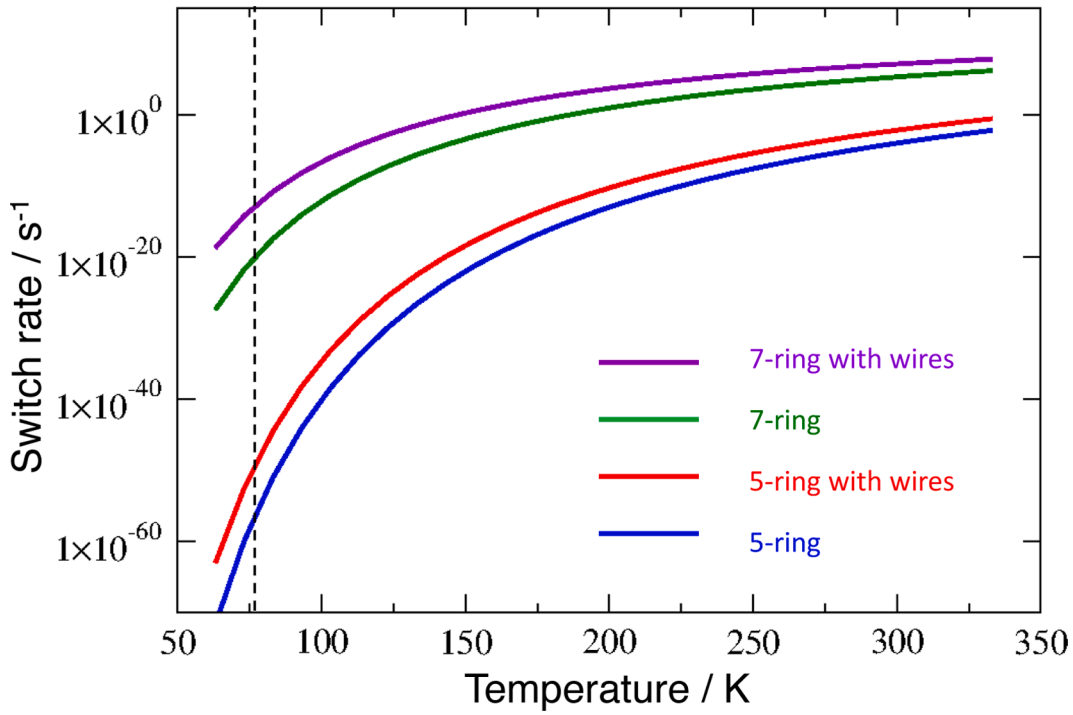

Fig. 6. Calculated thermal switch rate as function of temperature for the 5- and 7-ring with and without wires. The vertical dashed line indicates the temperature of liquid nitrogen.

ring exhibits puckering, which destroys the symmetry and creates multiple local minima. These properties make this molecule less suitable for incorporation into a network.

The results suggest that the 5- and 7-ring structures are viable candidates for molecular switch networks. Whereas to the best of our knowledge, there is no mention of the 5-ring in the literature, the 7-ring has been synthesised before [9]. For the molecule to operate as a switch, a mechanism to trigger the tautomerisation would have to be found. This could be an external electric field, as proposed in Ref. [3], or an optical excitation. The latter has been investigated by Akai et al. [23,24]. In conclusion, we find that molecules such as those investigated in the current study are promising candidates for use in molecular electronics. The ultimate goal is a network of a large number of interconnected and interacting switches, just as an electronic circuit is an assembly of semiconductor-based transistors. Initial experimental realisation may focus on individual switches or small networks on surfaces, where they can be studied and manipulated with established techniques such as scanning tunnelling spectroscopy. This would also facilitate exposure to external stimuli to trigger switching.

CRediT authorship contribution statement

Tanja van Mourik: Writing – review & editing. **Herbert Früchtl:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability statement

Cartesian coordinates of the minima and transition states are available in Supplementary Materials. The research data supporting this publication can be accessed at https://doi.org/10.17630/4908b94e-d478-4d1a-8f05-0d85851abab8.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chphi.2021.100035.

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