

Tautomerism in Reduced Pyrazinacenes

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Abstract: Monoprotic and diprotic NH tautomerism in reduced oligoazaacenes, the pyrazinacenes, was studied by using first principles simulations. Stepwise reductions in the metadynamics-sampled free energy profile were observed during consecutive monoprotic tautomerizations, with energy barriers gradually reducing with increasing proton separation during monoprotic processes. This is accompanied by an increasing contribution from the quinoidal electronic structure, as evidenced by the computed highest occupied molecular orbital (HOMO) structure. An unusual odd–even effect in the free energy profiles is also observed upon changing the length of the pyrazinacene. Calculated HOMO structures reveal an increasing tendency for delocalization of pyrazine lone pairs with an increasing number of ring annelations. The influence of tautomerism on the pyrazine lone pair delocalization was also observed. Tautomers with protons situated centrally on the pyrazinacene backbone are predicted to be more stable due to a combination of (enamine) delocalization and a loss of Clar sextet resonance stabilization in tautomers with protons at terminal pyrazine rings. Experimental evidence suggesting the structure of pyrazinacene tautomers is included and discussed as a support to the calculation.

Introduction

The acenes represent an important class of molecular materials which possess properties suitable for applications in organic semiconducting devices, including organic field effect transistors.¹ Pentacene (**1**),² the quintessential acene, has been extensively studied because of its high field effect mobility (up to $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ultrapure samples³) but

also in the development of the synthesis of more easily processable derivatives, since pentacene itself is a rather intractable and unstable substance. Thus, soluble, substituted pentacenes have been prepared, and improved stability against aerobic oxidation has also been obtained in several cases.⁴ Because of their importance as organic electronic materials, the acenes have also attracted attention from a predictive point of view, and computational methods have been applied extensively in order to assess the benefits of preparing higher-order oligoacene structures.⁵

Our interest in oligoacenes stems from the synthesis of higher annulated oligopyrazines, which we term “pyrazinacenes”. Heteroacenes, including the pyrazinacenes, are important as *n*-type counterparts of the *p*-type semiconducting CH pentacenes.⁶ During development of the synthetic methods, we were intrigued by the possibility of protic

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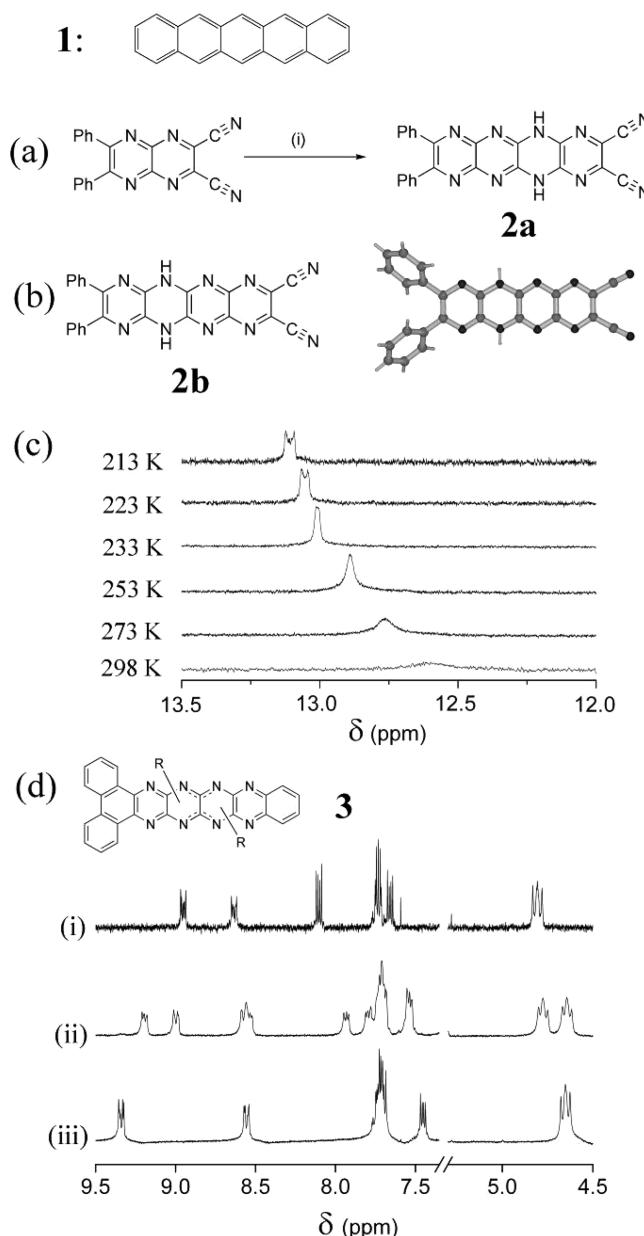


Figure 1. Chemical structure of pentacene, **1**, and (a) synthesis of **2a**, (i) 2,3-dicyano-5,6-diaminopyrazine, dimethylsulfoxide, Na_2CO_3 , 100 °C. (b) Chemical structure of **2b** and its molecular structure obtained by single-crystal X-ray crystallographic analysis. (c) VT- ^1H NMR spectra of **2a**· Na^+ showing the splitting of the NH resonance at low temperatures. (d) Proposed chemical structure and ^1H NMR spectra (i–iii) of compounds obtained by the *N*-alkylation of dihydro-5,6,7,8,13,14,15,16-octaza-[*n,p*]-dibenzohexacene.

tautomerism in the reduced pyrazinacenes that does not have an analog in the CH pentacenes.⁷ Thus, this feature might be a significant determinant of the physical properties of the pyrazinacenes. Initially, we studied dihydro-substituted compounds, the 2H-pyrazinacenes (Figure 1). The existence of tautomerism in the 2H-pyrazinacenes first became apparent during single-crystal X-ray crystallographic analysis of the compound that was expected to be 2,3-dicyano-5,12-dihydro-8,9-diphenyl-1,4,5,6,7,10,11,12-octazatetracene, **2a**. Actually, its tautomeric analogue **2b** containing the 6–11-dihydro moiety was obtained (Figure 1b), having been formed during

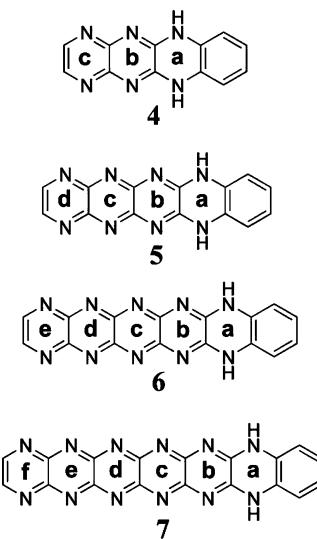


Figure 2. Structures of the proposed compounds **4**–**7** studied for their tautomeric processes.

synthesis or at crystallization. A preliminary variable-temperature (VT) ^1H NMR study on the monosodium salt of **2a** (**2a**· Na^+ ; used to avoid the appearance of too many tautomers; Figure 1c) revealed splitting of the resonance due to exchangeable amine protons at a depressed temperature consistent with the existence of two isomers of **2a**. Other, more circumstantial evidence for the tautomerism came from attempts to *N*-alkylate **2a/b** analog **2H-3** using alkyl halides, which gave a mixture of several compounds of identical mass but with differing ^1H NMR spectra, as illustrated in Figure 1d. Tautomerism should also influence the properties of the compounds. In particular, semiconductivity will be most likely modulated, while bulk proton mobility would make these compounds interesting materials for proton conduction applications (e.g., in fuel cells).

While investigations on the synthesis and structural analysis of the dihydropyrazinacenes continue in our laboratory, questions regarding their NH tautomerism and how this influences aromaticity and electronic properties of the molecules are addressable by using computational methods. We were especially curious about the energetics of potential tautomeric processes and how this might translate into proton delocalization. Furthermore, we were keen to determine what factors might delineate the relative yields of products of *N*-alkylation at the pyrazinacene nitrogen atoms. With this aim, we applied molecular dynamics simulations to study the deprotonation/reprotonation processes necessary for tautomerism in an isolated 2H-pyrazinacene molecule. For our computational study, we chose compounds **4**–**7** (containing a number of fused six-membered rings corresponding to their designated compound number), which possess one terminal benzene ring and, respectively, three, four, five, or six fused pyrazine rings (Figure 2). Pyrazine rings are labeled alphabetically, and monoprotic or diprotic tautomerism is denoted by “1H” and “2H”, respectively. For example, if **6** undergoes a monoprotic shift from ring *a* to ring *d*, then the resulting compound is named **6d(1H)**, while a similar diprotic shift would result in **6d(2H)**. The fused benzo ring present in all of the compounds was placed as a fixed nontautomerizing group so that the effect on tautomerism of having a pyrazino

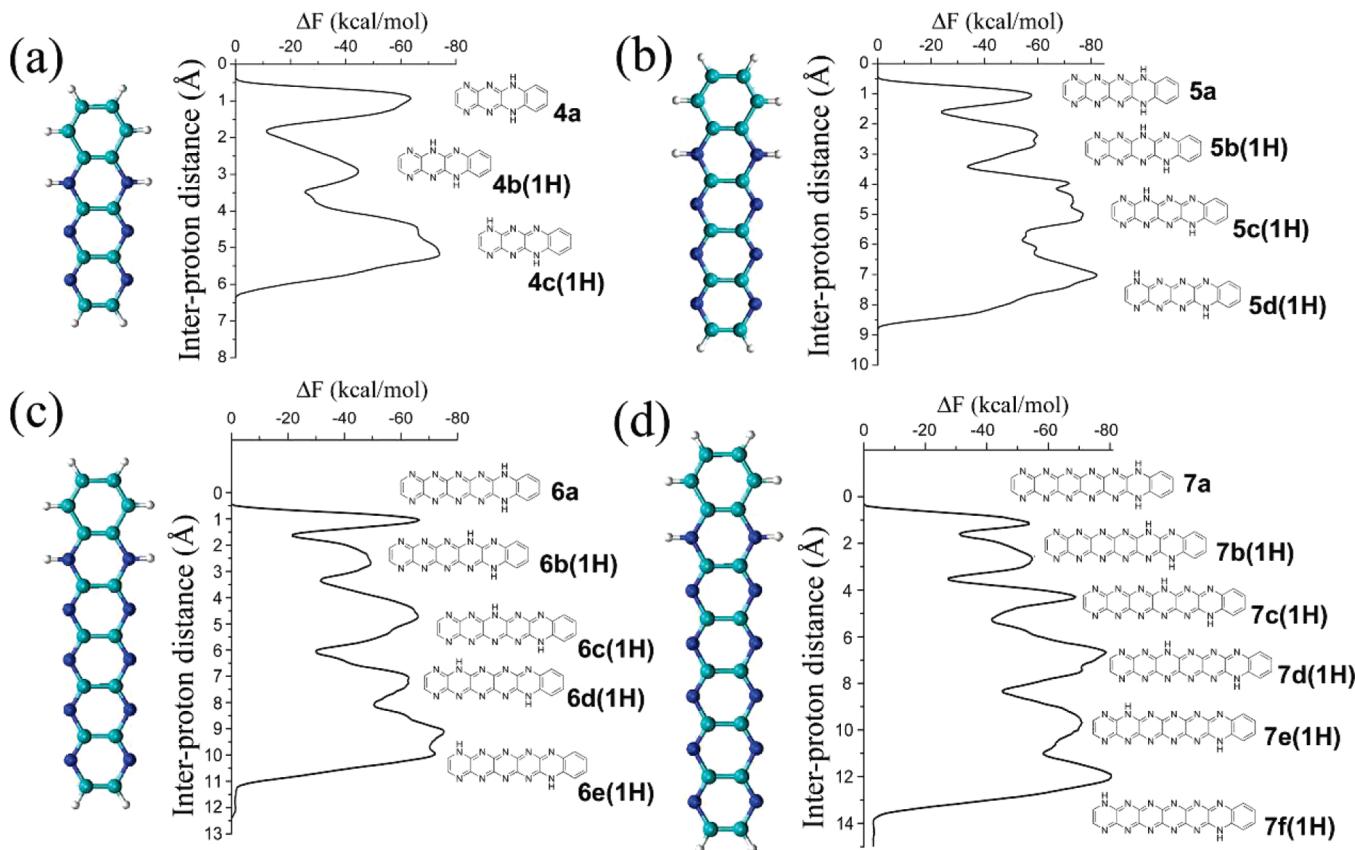


Figure 3. Variation of free energy (ΔF) with distance between exchangeable protons.

group in a terminal position could be evaluated. This benzo group is also present since our real synthetic procedures often result in pyrazinacene molecules containing such a group.

Computational and Experimental Details

Computational. All calculations were performed using the CPMD code.⁸ The first principles molecular dynamics version adopted is the Car–Parrinello⁹ approach; the density functional¹⁰ used to describe the total energy included generalized gradient corrections to the exchange and correlation functionals after Becke¹¹ and Lee–Yang–Parr,¹² respectively. The core–valence interaction was described in terms of norm-conserving Troullier-Martins pseudopotentials,¹³ and valence electron wave functions were represented in a plane-wave (PW) basis set with an energy cutoff of 70 Ry. All simulations were performed in an isolated cell according to the prescription of Barnett and Landman¹⁴ for the release of periodic boundary conditions in PW approaches. The simulation of the displacement of a proton along the molecule and the related calculations of free energy barriers were done within the metadynamics approach,¹⁵ which has already been extensively discussed in the literature and has been shown to be particularly suited to this class of problem.¹⁶ The metadynamics collective variable (CV) used in the present set of simulations was the distance between one of the N atoms of the molecule and the proton which has to be displaced, $CV = [\mathbf{R}(H) - \mathbf{R}(N)]$. This collective variable is included in the Lagrangean equations of motion with a fictitious mass $M_{CV} = 25$ au and a force constant $k_{CV} = 0.25$ au for the harmonic term. The penalty potential

adopted was a superposition of small Gaussian functions, of amplitude $W(t)$, sampled uniformly between 0.02 and 0.18 kcal mol⁻¹, and each new Gaussian function was introduced after 100 steps of dynamics amounting to 10 fs. Further information on the computational procedure can be found in the Supporting Information. The total energies of the various molecules were obtained with a standard geometry optimization performed until the forces became lower than 0.001 eV/Bohr. The highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) structures were computed by exact diagonalization of the Kohn–Sham matrix on the final optimized geometries.

Synthesis. Compounds **2** and **3a–c** were synthesized as previously reported.¹⁷ Details are provided in the Supporting Information.

Results and Discussion

Free energy changes on the tautomerization of **4–7** are shown in Figure 3. The various minima in the plots of free energy versus the interproton distance are due to different tautomeric forms of the molecules, while the less negative peaks represent the barrier against the tautomerization process. We can observe one main effect in the free energies, namely, that the energy barrier for displacing the proton from its initial position systematically decreases by increasing the number of fused pyrazinacene rings in going from **4** to **7**. However, there is also a peculiar odd–even effect between molecules with even and odd numbers of rings. If we compare (see Figure 3) the free energy barriers for molecules **a** and **c**, we see that they decrease in passing from **a** to **c**.

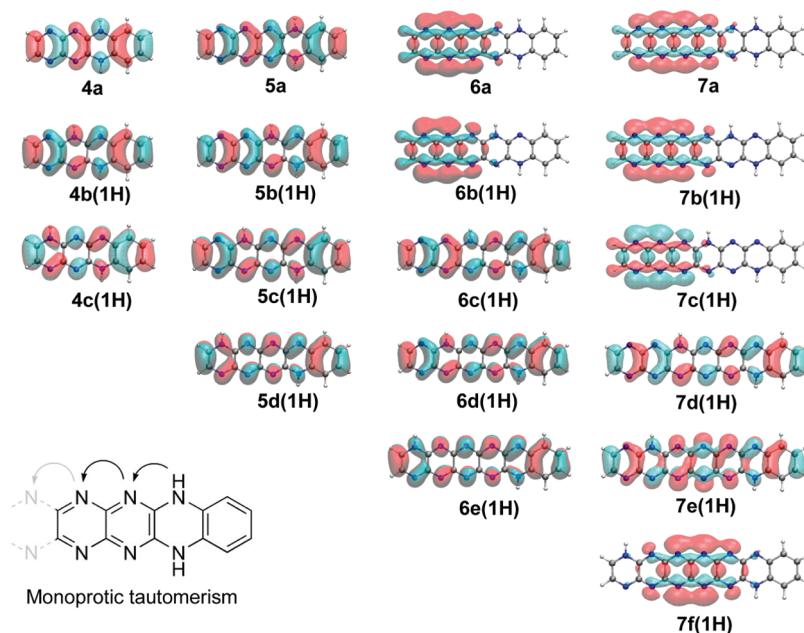


Figure 4. Calculated structures of HOMOs of tautomers of **4–7** due to monoprotic migration (“1H” denotes one proton process).

However, they also decrease in going from even to odd, and in fact, molecules **b**, despite being composed of fewer rings, have a lower energy barrier for the first deprotonation than molecules **c**. There are therefore two effects: first, molecules with an odd number of total rings have energy barriers for first deprotonation, which are systematically lower (~20 kcal/mol), and, second, increasing the number of rings leads to a reduction of the energy barriers. While the second effect can be explained by the fact that the longer molecules can more easily mesomerize in response to the proton shift, the peculiar odd–even effect does not have an immediate explanation. It may be a result of the combination of several different factors including symmetry, competition between aromaticity and antiaromaticity, and the role of entropic effects, including the fact that, as the molecule becomes longer, nonplanar geometries may be favored, although deviations from planarity were found to be small.

For the subsequent deprotonation steps, a combination of different effects occurs, and a different behavior is observed between odd and even ring molecules. For example, respective tautomerizations of **4a–7a** to **4b(1H)–7b(1H)** do not result in a reduction in the free energy activation barrier, and for **4a** and **6a**, an increase is observed, indicating that this is not a favored process. This is not entirely unexpected, since there are no mesomeric advantages apparent during this procedure. In fact, it is likely that formation of the **b** tautomers actually obstructs conjugation relative to the starting **a** tautomers (i.e., there are fewer fused aromatic six-membered rings). As the proton migrates toward the nonbenzo-substituted end of the molecule, tautomers at each nitrogen “station” exhibit lower activation energies in comparison with the starting tautomer, which we attribute to the increasing conjugated quinoidal character of the fused pyrazine unit situated between singly reduced pyrazines, which can be seen in the calculated HOMO structures of compounds **4a–7a** to **4c(1H)–7f(1H)**, shown in Figure 4. However, there is the additional feature of pyrazino nitrogen

atom lone pair delocalization¹⁸ in the longer pyrazinacenes. In particular, where tautomers of **6** and **7** have at least three fused (and nonreduced) pyrazine rings, then delocalization occurs, as shown in **6a(1H)**, **6b(1H)**, **7a(1H)**, **7b(1H)**, **7c(1H)**, and **7f(1H)**.

In **4** and **5**, as monoprotic tautomerization occurs, an increasing quinoidal character appears, whereas in **6** and **7**, a similar tautomerization occurs at the expense of delocalization and is accompanied by increasing quinoidal character. Interestingly, in **7** the quinoidal character appears in **7d(1H)** and **7e(1H)** but is destroyed upon transfer of the single proton to the terminal pyrazine, giving **7f(1H)** in favor of a nitrogen-lone-pair delocalized structure. The structure of HOMO **7e(1H)** appears to be a chimera with an unusual structure between the delocalized and quinoidal forms. This structure occurs despite the presence of three fused pyrazine rings, which is thought to favor nitrogen atom lone pair delocalization. HOMO **7e(1H)** bears features of both quinoidal and delocalized orbitals, while, conversely, diprotic tautomerization does not yield such a structure, so that it is likely due to a mixing of quinoidal and delocalized nitrogen lone pair orbitals.

A very interesting phenomenon occurs in the case of diprotic tautomerism, graphically summarized in Figure 5, involving migration of the π -electron cloud in compounds **4–7**. We found that, when there are three fused pyrazine rings, a delocalization of the HOMO occurs along these rings with no (or just minor) contributions due to the remaining portion of the molecule. The shift of protons along the molecule in a certain direction causes a reduction of delocalization in the same direction or a transfer of electronic density in the opposite direction. This is a fundamental result that might have far-reaching consequences regarding the application of these molecules and their derivatives in molecular electronics and condensed matter devices. Thus, it can be argued that multiple tautomerizations or “conduction” of protons along a pyrazinacene backbone in one

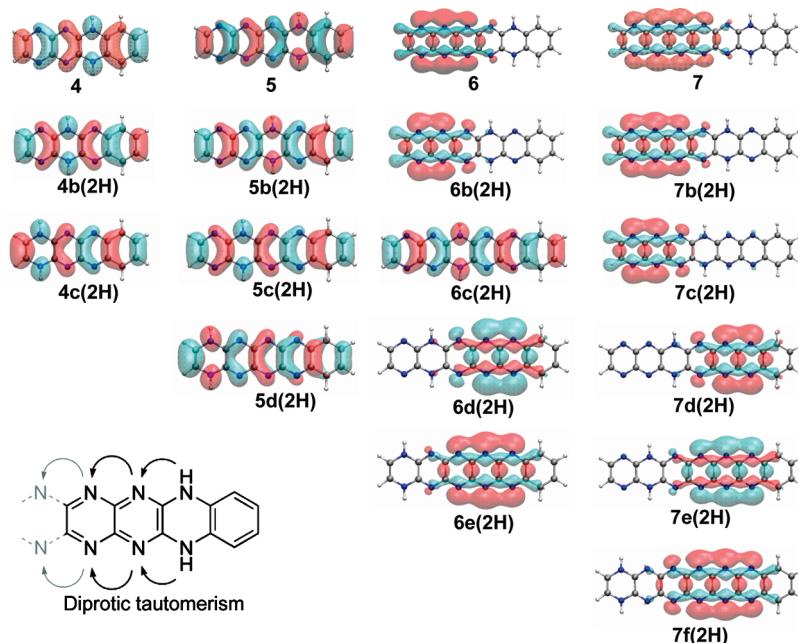


Figure 5. Calculated structures of HOMOs of tautomers of **4–7** due to diprotic migration (“2H” denotes two proton process).

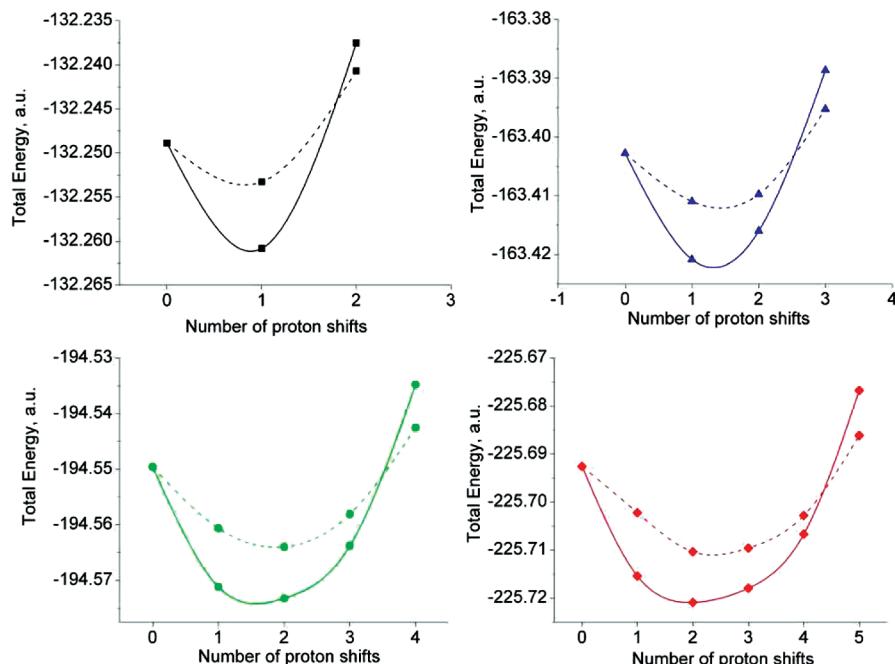


Figure 6. Total energies of the tautomers from monoprotic/diprotic shifts. Dashed lines, monoprotic (1H); solid lines, diprotic (2H). Black line, **4**; blue line, **5**; green line, **6**; red line, **7**.

direction results in a net transfer of electron density in the opposite direction. If we consider a single extended pyrazinacene, then the result would be an accumulation of protons and electron density at opposing ends of the molecule. Finally, it should be noted that not all of the possible tautomers have been considered here. That is, tautomers due to mixed monoprotic/diprotic processes have been neglected for clarity. However, the tautomers on which we focused in this work exhibit the most important phenomena due to proton migration and HOMO structure so that the other tautomers, although certainly of interest, do not provide any further insight into this system.

Total Energy Stability. Next, we considered the stabilities, in terms of relative total energies, of the individual tautomers depending on mono- or diprotic tautomerization. The result of this analysis is summarized in Figure 6. Basically, shifting two protons (i.e., dihydropyrazine ring migration) yields a species of greater stability in all cases for **4–7**. A single proton migration results in a lower stability. There is an exception in that tautomers with two protons at the terminal pyrazine ring (i.e., **4c(2H)**, **5d(2H)**, **6e(2H)**, and **7f(2H)**) are all less stable than the corresponding monoprotic-shifted tautomers, although those compounds (i.e., **4c(1H)**, **5d(1H)**, **6e(1H)**, and **7f(1H)**) are still less stable than their

respective parents (a symptom of the aforementioned fused benzo group). Tautomers with protons located toward the center of the molecule are more stable, and there is some precedent for this from our laboratory investigations and from the work of others.^{5c,d} The molecules considered here are formally antiaromatic according to the Hückel rule, which classifies aromatic molecules as having $4n + 2 \pi$ electrons, while those with $4n \pi$ electrons are antiaromatic. In this case, the resulting electronic structure is influenced by the fact that the molecule is composed of fused and partly reduced nitrogen heterocycles, so that delocalization may be also affected by polarity, electronegativity, and more crucially, tautomerism. The increased stability of the tautomers bearing protons at central rings of the molecules is an indication that these formally antiaromatic molecules can gain stabilization through structural rearrangements involving proton shifts. In longer molecules, π electrons of the dihydropyrazine moieties can be more easily displaced to adjacent pyrazine rings, and this is one of the reasons why tautomers with protons at central positions are more stable. Furthermore, the shift of protons to a terminal pyrazine ring lowers the stabilities of the molecules because of a reduction in resonance stabilization as a result of the loss of a Clar six-membered benzenoid ring. This occurs in both monoprotic and diprotic processes, giving rise to the above tautomers characterized by highest energies. On the other hand, starting tautomers **4a–7a** are more stable than those with terminal mono- or dihydropyrazine groups, but they are less stable than those with centrally situated mono- or dihydropyrazines because of the presence of the stabilizing terminal benzenoid group (see Figure 6a). To determine which of the central rings is preferably reduced, there are two effects that must be considered. First, there should be a repulsive interaction between the electron-rich terminal benzo group and an adjacent electron-rich dihydropyrazine moiety. Second, dihydropyrazine groups are better accommodated at centrally positioned rings because of resonance stabilization effects.^{5d} Thus, in **5** and **7**, where an odd number of fused rings is present, the most stable tautomer is the one with protons located at the central ring. In **6**, with two central rings, the one remote from the fused benzo group is favored. Energies of tautomers due to monoprotic processes reflect this observation, although the energetic benefits are less important, suggesting that diprotic tautomerism is preferred. Finally, if tautomerism of the pyrazinacenes can be modulated (or frozen, for instance, by *N*-alkylation), then they present an excellent opportunity for the study of how aromaticity (or antiaromaticity) varies depending on subtle variations in the structure of the molecules. Previous studies focused on this feature have given invaluable insights into the role of aromaticity on the stabilities of particular electronic structures.^{5c,d}

Initially, we isolated compounds assigned the structures **2** and **3**, which we subjected to alkylation using simple alkyl halides at elevated temperatures (this was originally for purposes of derivatization to facilitate chemical analysis). *N*-alkylation of octaazatetracenes **2** and **3** gave simple mixtures, each of three compounds (with traces of other compounds of the same mass) which could be separated and

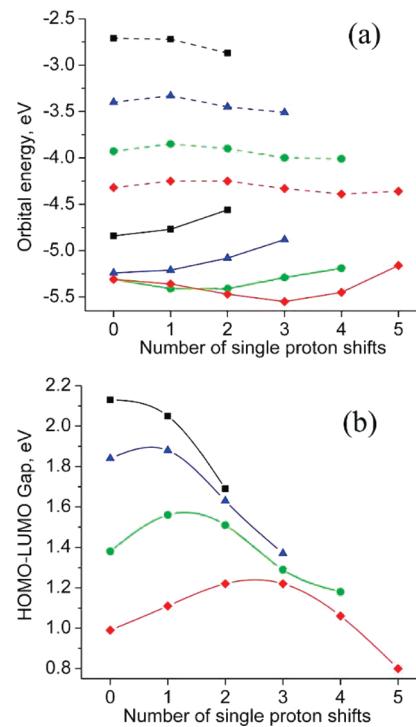


Figure 7. (a) Proton location dependency of energies of highest occupied and lowest unoccupied molecular orbitals for tautomers of **4** (black), **5** (blue), **6** (green), and **7** (red) following consecutive single proton shifts. (b) Variation in HOMO–LUMO energy gap depending on the number of single proton shifts in **4** (black), **5** (blue), **6** (green), and **7** (red).

identified as isomers of *N,N'*-dialkyl-octaazatetracenes. Proton NMR spectroscopy (see Figure 2) indicates which of the isomers is unsymmetrically substituted (i.e., *N*-alkyl groups on different pyrazine rings rather than on the same one). The evidence for existence of the di-*N*-alkylated pyrazinacenes is consistent with data from our calculations and also suggests that mono- and diprotic processes can both occur and that tautomers with protons located on central pyrazine rings are more stable. Hence, only three tautomers were isolated, presumably with alkyl groups on the central nitrogen atoms.¹⁹ On the basis of the mixture of isomers obtained from the *N*-alkylation of octaazatetracene type compounds, **4**, we had expected that they might bear delocalized electronic (or delocalized protonic) systems, although this is not the case obtained from calculations (see Figure 4). Since the *N*-alkylation reaction is performed at elevated temperatures (100–140 °C), we believe that it is possible that formation of the delocalized state might be thermally activated, although it is probably not required for tautomerization to occur (since the *N*-alkylation reaction is performed under mildly basic conditions in a polar medium, e.g. dimethylsulfoxide, both of which are known to facilitate intra- and intermolecular protic reactions).

HOMO–LUMO Levels and Gap. Energy levels of HOMOs are somewhat influenced by the tautomerization processes, while those of the LUMOs are less affected (see Figures 7 and 8 for monoprotic and diprotic tautomerizations, respectively). During monoprotic shifts, HOMOs of tautomers of **4** and **5** increase gradually in energy, while **6** and

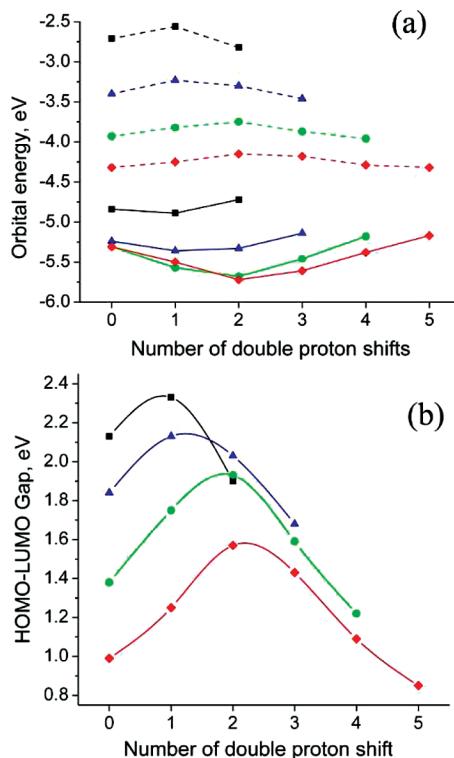


Figure 8. (a) Proton location dependency of energies of highest occupied and lowest unoccupied molecular orbitals for tautomers of **4** (black), **5** (blue), **6** (green), and **7** (red) following consecutive double proton shifts. (b) Variation in HOMO–LUMO energy gap depending on the number of double proton shifts in **4** (black), **5** (blue), **6** (green), and **7** (red).

7 go through a minimum after two and three proton shifts, respectively. For diprotic shifts, **4** and **5** tautomers have a slight minimum after a single shift, while **6** and **7** both reach their minimum orbital energy after two shifts. The curious uniting feature of these observations is that, for **6** and **7**, the degree of HOMO delocalization is at a minimum (according to the HOMO structures in Figures 4 and 5) in the HOMOs of lowest energy. However, this does not necessarily disagree with the statement of increased delocalization of the inner ring because, in the HOMO, we have contributions from all of the π electrons of the molecule.

In 2H-pyrazinacenes **4–7**, the HOMO level is slightly stabilized with an increasing number of fused rings, while the LUMO level undergoes a much more significant stabilization. The latter has the effect of reducing the HOMO–LUMO gaps for **4–7**, which are also shown in Figures 7 and 8. The magnitude of the HOMO–LUMO gap gradually decreases with an increasing number of fused rings, as expected.²⁰ Tautomerism in the individual systems has the effect of increasing the HOMO–LUMO gap for molecules with centrally placed reduced pyrazine rings. This is due to an interruption in the standard conjugation and the occurrence of the Clar rule, as discussed before. These molecules possess properties appropriate for their incorporation into thin film FET devices or similar.²¹

Tautomerism in aza-acenes has been discussed as far back as the 1890s, when dihydro-5,7,12,14-tetraazapentacene **8** was erroneously ascribed a quinonoid structure, **8a**.²² Proton

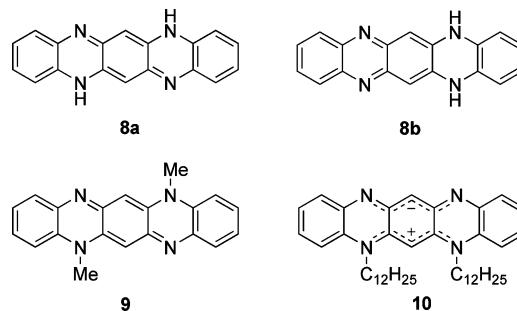


Figure 9. Chemical structures of compounds **8a,b**, **9**, and **10**.

NMR measurements subsequently revealed the benzenoid form **8b**^{7a} in solution, although other studies have found that the quinonoid form can be stabilized by **8**'s N-methylation, giving **9** (see Figure 9).^{7b} Actually, direct or indirect introduction of N-alkyl groups into aza-acene compounds has been shown as a method for obtaining products with unusual zwitterionic electronic structures such as **10**.²³ In the case of the pyrazinacenes, the situation is complicated by the ability of the corresponding molecules to undergo tautomerization through proton transfer(s) to an adjacent pyrazine ring, and N-alkylation also results in unsymmetrically substituted products. The uniqueness of these compounds originates from the fusion of several pyrazine rings and the absence of interrupting carbon-only six-membered rings. Prior to the pyrazinacenes, only a few examples of fused pyrazines were available, and all contained bulky N-substituent side groups.²⁴ The potential importance of the pyrazinacenes and their relations has been emphasized by several recent computational investigations on their electronic structures.^{5,13} Also, certain reduced derivatives, such as the dihydriodiazatetracene of Miao et al.,^{5c} have provided insight into questions regarding the influence of reduced pyrazine rings on the aromaticity and stability of these compounds. Other studies have found that the introduction of a dihydropyrazine ring into oligoacenes can improve their properties (i.e., stability against oxidation) with regard to device preparation and operation.²² This can be extended to the pyrazinacenes since we know that they have much greater stabilities and solubilities than the corresponding CH-only analogs.

NH tautomerism is a peculiarity of the present dihydropyrazinacene system that, at the same time as being scientifically important, has potential in some applications. One can imagine isolated lengthy reduced pyrazinacenes acting as discrete proton transporters in protonic devices or polymeric derivatives being used in proton-conducting membranes inside fuel cells. Also, the increased number of heteroatoms with smaller atomic radii in these systems allows for close intermolecular contacts when stacking, which should favor charge transport in their thin films and improve their potential as organic semiconducting materials.

Conclusions

We have investigated protic tautomerism in a series of reduced nitrogen-rich oligoazaacenes, the pyrazinacenes, starting with experimental structures and using computational

approaches to access information on proton shift and electronic structure not directly accessible to experimental probes. We found that the energy barrier for the displacement of a proton from an initial position systematically decreases by increasing the number of fused pyrazinacene rings. The energy barrier is also subject to a peculiar odd–even effect whose origin, although partly unknown, can be related to resonance effects depending on the ring multiplicity. Moreover, we found that both monoprotic and diprotic tautomerism in the pyrazinacenes influences strongly the structures of the highest occupied molecular orbital, especially in the acenes containing five or more fused rings. The latter is as a result of disruption of delocalization. However, in longer molecules, another effect appears: π electrons of the intrinsically antiaromatic rings of the dihydropyrazine in the center of molecules can be more easily delocalized, partly accounting for the increased stability of the compounds with protons at central positions. Tautomers with terminal dihydropyrazine groups are destabilized by the loss of Clar resonance stabilization. At least three fused pyrazine rings are necessary for proper delocalization of the HOMO levels, and this feature is consistent with our experimental observation that the tautomerization of protons at reduced pyrazine rings of pyrazinacenes only occurs significantly in compounds containing at least four fused rings, such as *N,N*-dihydrooctaazatetracene (e.g., **2a,b**). Because of this feature, we suggest that protic tautomerization in pyrazinacenes containing a reduced ring is strongly associated with delocalization of the π electrons of the remaining pyrazine groups. Thus, it might be inferred that multiple tautomerizations or “conduction” of protons along a pyrazinacene backbone in one direction results in a net transfer of electron density in the opposite direction. The connotations of the peculiarities of proton and electron transport for the properties of the pyrazinacenes remain to be seen, especially since intermolecular processes would be likely also involved in the operation of any condensed matter devices assembled using these compounds. However, the enhanced stability of these compounds over other acenes (and even other reduced heteroacenes) means that they are amenable to development as materials for thin film transistor electronics or as proton conductors. We expect to report other experimental observations of these compounds shortly.

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Supporting Information Available: Structures of lowest unoccupied molecular orbitals (LUMOs) of tautomers of compounds **4**, **5**, **6**, and **7**. Cartesian coordinates of calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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