

Tetraazaacenes Containing Four-Membered Rings in Different Oxidation States. Are They Aromatic? A Computational Study

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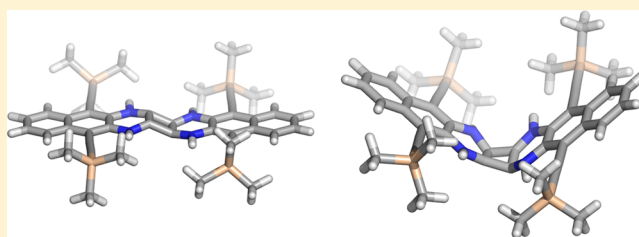
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S Supporting Information

ABSTRACT: A symmetrical tetraazaacene incorporating a central cyclobutadiene ring was calculated in different oxidation (hydrogenation) states, displaying different tautomers and conformers. Geometries, thermodynamics, and electronic properties were computed, and the aromaticity of all these species was calculated on a per ring basis by NICS-scans and NICS-X-scans. The results unveil unexpected and fascinating insights into the complex aromaticity of those compounds, including a formally aromatic (!) cyclobutadiene ring.



INTRODUCTION

Aromaticity is a nonmeasurable quantity, yet it is one of the most frequently used concepts in chemistry. Usually it is used to describe a family of compounds—aromatic compounds—which consists of cyclically conjugated π bonds with $(4n + 2)$ π electrons which show certain energetic, structural, and magnetic properties. However, aromaticity is also used in other cases. Terms like polycyclic aromatic compounds, aromatic transition states, aromatic interactions (e.g., stacking, H-aromatic interactions), σ aromaticity, and more are in frequent use in the chemical and biological literature. However, strangely enough, the term “aromaticity” is not well-defined in the qualitative or quantitative sense.¹ In recent years, aromaticity is mainly estimated by nucleus-independent chemical shift (NICS).² Indeed, NICS does not always give the best answer regarding aromaticity,^{3,4} but improvements to the method are constantly being developed.^{5,6} In this paper, we use methods which are based on many NICS values at each ring and represent only the π contribution to these values (see the Computational Methods). These methods overcome most of the NICS-associated problems and should give a fairly accurate representation of aromaticity.

The relative stability and aromaticity of a series of cyclobutadiene-annulated azaacenes was computed. Thermodynamic and magnetic changes of their properties upon hydrogenation were calculated. The question of aromaticity in acenes and related species is still acute as new topologies appear and are examined. Vollhardt et al. have prepared and investigated acene-types, in which benzene and cyclobutadienes, the epitomes of aromaticity and antiaromaticity, respectively, are juxtaposed in compounds called the [N]-phenylenes.⁷ Also, Swager et al. have prepared some related

acenocyclobutadienes and analyzed their properties and potential applications.⁸ However, there are only very few reported cases (Hünig, **1**, and Vollhardt, **2**)^{9,10} in which pyridines or pyrazines are juxtaposed to cyclobutadiene units, such as **3** (Figure 1).¹¹

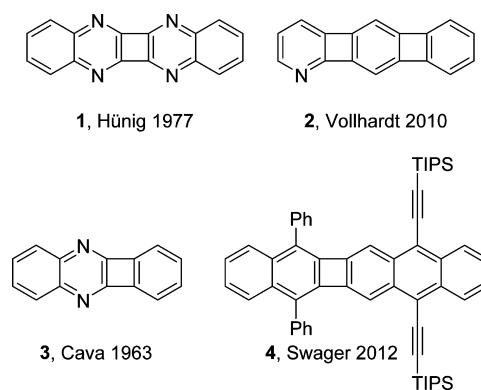


Figure 1. Molecules containing cyclobutadienes synthesized by Hünig, Vollhardt, Cava, and Swager.^{2–5}

Compound **3**, made by Cava in 1963,¹¹ was only characterized by its melting point (238 °C) and correct elemental analysis. In the case of **1**, it was observed that the fully oxidized form **1** and the reduced form **1-H₂** both were isolable and could be interconverted. The attempt to reduce **1-H₂** further into its tetrahydro compound was apparently not

Received: October 7, 2014

Published: November 11, 2014

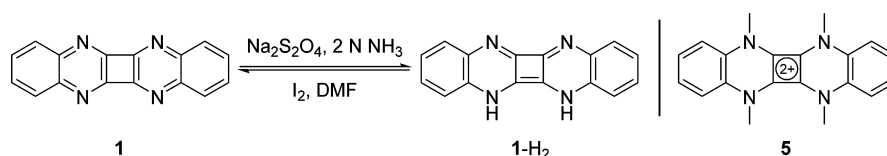


Figure 2. Redox system of **1** and **1-H₂** (left). Tetramethylated dication **5** was reported as an equivalent for a tetrahydro species (right).

successful, but the isolable salt **5** was described as being sensitive toward nucleophiles (Figure 2). Compound **5** does have an absorption band in the range of 700 nm, suggesting that it is highly conjugated. Incidentally, **1** was described to form as yellow crystalline needles, and **1-H₂** was obtained as green powder.

Azaacenes featuring cyclobutadiene rings are a fascinating class of compounds due to the growing interest displayed in the azaacenes and **1–3**, and cyclobutadienoazaacenes should move into the spotlight. For the simple azaacenes, there are fundamentally important questions that have been looked at, particularly the question of aromaticity of the compounds like **6** and **7** and that of their *N,N'*-dihydrocongeners **6-H₂** and **7-H₂**. Abnormally large heats of hydrogenation were observed in these substances, as their reduction into the formally antiaromatic dihydro compounds proceeds with exothermicity. The thermochemical and NICS data were interpreted by Bunz and Schleyer (Figure 3).^{12,13}

RESULTS AND DISCUSSION

Geometries. We first calculated the geometries of the compounds **8–11c** (Figures 4 and 5) using the B3LYP/6-

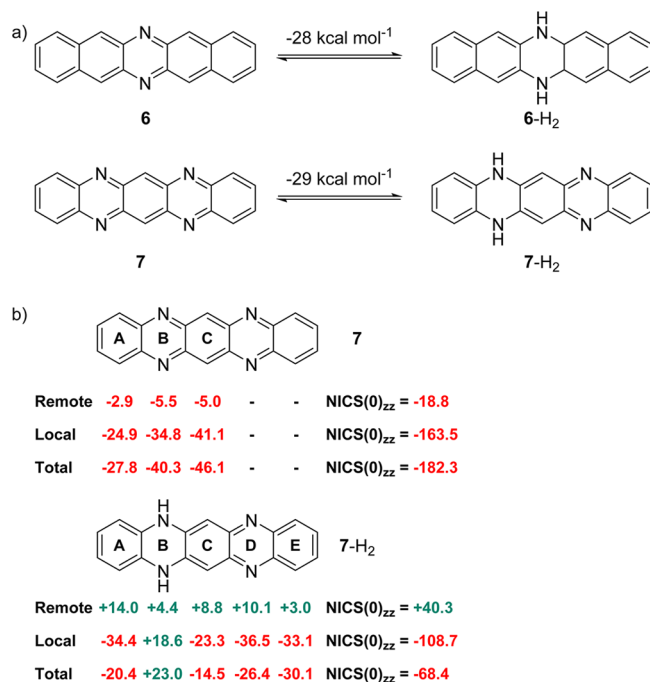


Figure 3. (a) Exothermicity of the hydrogenation of **6** and **7**. (b) NICS calculations for **7** and **7-H₂** by Bunz and Schleyer.¹² Local refers to NICS(0)_{zz} values including only π MOs that belong to the designated ring. The remote NICS(0)_{zz} are defined by the π MO contributions that are not directly involved with the designated ring. The total NICS(0)_{zz} incorporates all of the individual LMO contributions. NICS points were computed at each of the individual heavy atom ring centers of the polycyclic compounds.

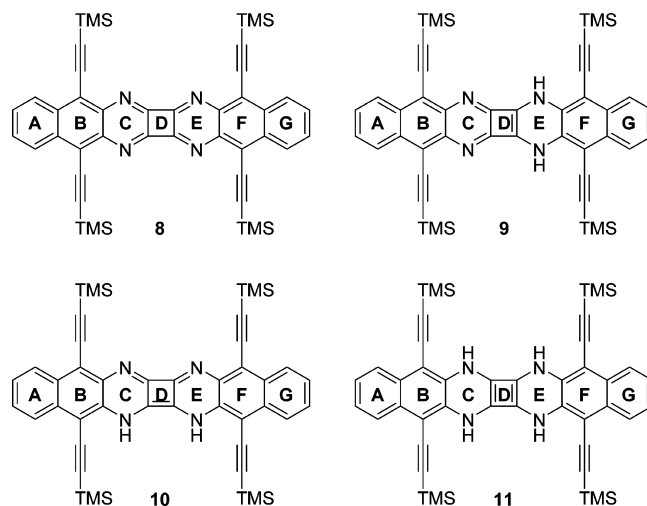


Figure 4. Structures of **8–11** with labeling of the rings.

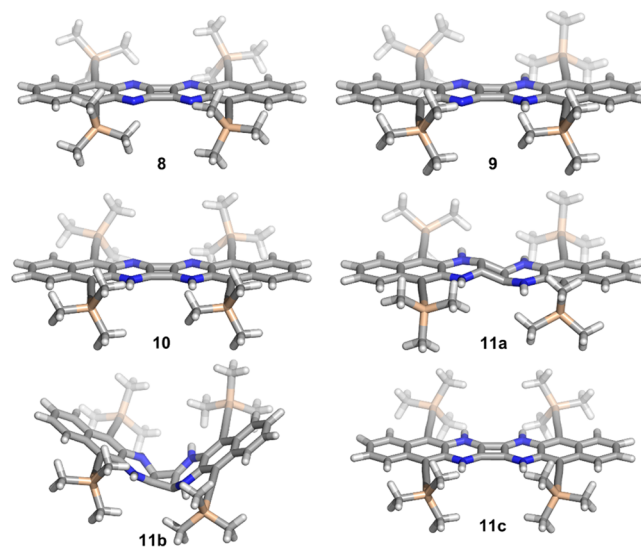


Figure 5. Geometries of all calculated compounds: **8** (top, left), **9** (top, right), **10** (middle, left), **11a** (middle, right), **11b** (bottom, left), and **11c** (bottom, right).

311G* combination. The oxidized compound **8** shows a planar geometry of the aromatic core with alternating (calculated) bond lengths. The “horizontal” bonds in the middle ring are not very elongated with a length of 1.50 Å, considering the formally antiaromatic character, and they are a bit shorter than the ones reported in the crystal structure of **1** by Allmann,¹⁴ while the “vertical” bonds are a bit longer. Calculated and X-ray crystal structure-obtained bond lengths are in good agreement (see Figure 6). We did a geometry optimization of **1** under the same conditions as for **8**. The bond lengths and angles for the pyrazine and cyclobutadiene rings match perfectly with those obtained for **8**. Allmann’s structure of **1** is a good guess for the

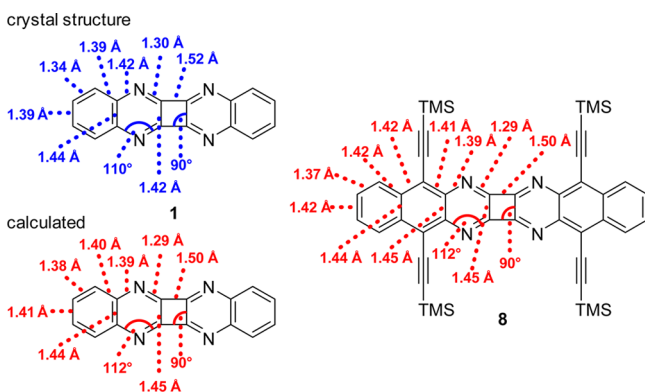


Figure 6. Comparison of bond lengths and angles of the crystal structure (left, top) and calculated structures (left, bottom) of **1** and **8** (right). All bond lengths are measured in angstroms.

structure of **8**; the calculations easily reproduce the experimental data. Both dihydro compounds **9** and **10** show a planar calculated geometry (Figure 7). In **9**, the aromatic

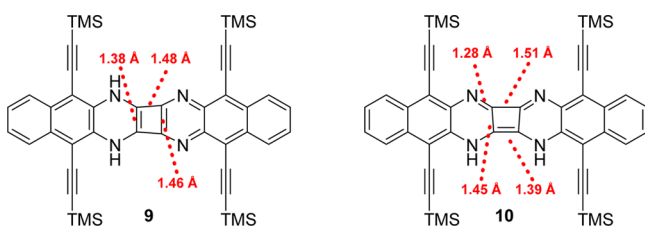


Figure 7. Distortions of the four-membered ring in **9** and **10**.

pyrazine and the formally localized double bond in the dihydropyrazine ring lead to a trapezoid shape of the four-membered ring with opposing bond lengths of 1.46 and 1.38 Å. In the case of **10**, the central ring also shows a trapezoid shape because of the formally localized double bond. The opposing bond lengths are 1.39 and 1.51 Å. The nitrogen-containing rings show a localized double bond of 1.28 Å at the sp^2 -nitrogen side. While the topologically different dihydro compounds **9** and **10** only display one stable ground-state structure, the structural landscape of the tetrahydro compound **11** is more complex. A detailed view of the bond lengths and angles of **11a–c** are shown in the Supporting Information. Here, both the parallel **11a** and the unsymmetrically kinked isomer **11b** are ground-state minima. The geometry of **11a** displays two parallel halves connected by the central ring (Figure 8). The offset of the two halves is 0.32 Å, and the angle between the dihydropyrazine and the four-membered ring is 31°. The dihydropyrazine rings are not completely coplanar with the aromatic rings, but bent. The bonds of the central ring that connect the two halves are 1.54 Å long, i.e. single bonds. The shape of **11a** unveils an inner and an outer side of the core with the inner side facing toward the other parallel half. The

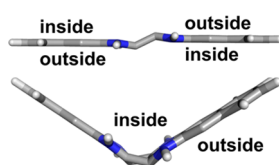


Figure 8. Side view of parallel **11a** (top) and kinked **11b** (bottom). For clarity side chains were omitted.

other stable conformer **11b** is kinked. Two linear halves are connected by a distorted, central ring forming an angle of 66°. Thus, **11b** also shows an inner and an outer side. As in **11a**, the dihydropyrazine rings are not completely coplanar with the 6-membered rings. We contemplated the best way to think about the nonplanar geometry of the four carbons in the central cyclobutadiene in compounds **11a,b**. These are stable conformers as closed-shell singlets (the stabilities of the wave functions were checked). Thus, radical-type resonance structures probably do not contribute much. Perhaps the best way to look at these rings is as tetramethylenecyclobutane (see Figure 10). In this case, the nonplanar geometry has a minimal effect on the conjugation, and strain can be better accommodated. The nonplanar geometry of **11a,b** might also suggest that these rings are formally antiaromatic. We are not at all sure that there is a good answer to this question. Formal electron count is valid for single ring systems. To the best of our knowledge, there is no formal method to assign aromaticity/antiaromaticity for systems that contain global, semiglobal, and local ring current. Of course, one can write single and double bonds and resonance structures, but the validity of these to the properties of the compounds is questionable. There is one thing that we are sure of: These rings do not have ring currents of their own (or only small ones). The NICS-X-scan of the hypothetical **11c** suggests that this is true also for the planar systems.

The planar third conformer **11c** is not an energy minimum but was calculated for comparison. The central ring is stretched in the east–west direction, whereas the other two bonds are localized double bonds of 1.34 Å length. The compounds **8–11b** are calculated minima according to a vibration analysis. Conformer **11c** was found not to be a minimum; there are 14 imaginary vibrations left. Regardless, we calculated a zero-point energy for this geometry because the bare SCF energies do not reflect the relative energies of the other compounds reasonably.

Stability and Hydrogenation Enthalpies. This series of molecules shows fascinating electronic properties. Fully oxidized compound **8** displays a low LUMO energy of -3.68 eV, which is in the same range as that of TIPS-tetraazapentacene^{15,16} or PCBM. Hence, **8** meets one condition for potential use in n-channel applications in OFETs. The deep LUMO is attractive for a compound with formally only anthracene units and is made possible by the symmetric structure and the nonaromatic cyclobutadiene connection. As for the linear azaacenes, the hydrogenation of the oxidized species into the dihydro species is exothermic. Comparing those two dihydro compounds, **9** is 7.3 kcal/mol more stable than **10**. The energetic preference for 1,4- N,N' -dihydropyrazines is shared with other azaacenes.^{12,13} In contrast, further reduction to the tetrahydro compounds **11a,b** is endothermic, which is also known for the azaacenes. Parallel **11a** is only 2.2 kcal/mol more stable than kinked **11b**, while the energy of hypothetical planar **11c** is more than 20 kcal/mol higher. Remarkably, the HOMO energies of the isomers **9** and **10** and **11a,b**, respectively, do not differ much, even though the planar structure **11c** is very electron rich with a high-lying HOMO. The LUMO energies do change considerably (Table 1). For a comparison of calculated orbital energies and experimental reduction potentials in the case of azaacenes, we refer to Bunz et al.¹⁶

NICS-Scans and NICS-X-Scans. In polycyclic conjugated molecules, the ring currents are sometimes localized on each of the rings and sometimes spread over more than one ring or

Table 1. Results of the Energy Calculations^a

| property | 8 | 9 (-H ₂) | 10 (-H ₂) | 11a (-2H ₂) | 11b (-2H ₂) | 11c (-2H ₂) |
|------------------------------|-------|----------------------|-----------------------|-------------------------|-------------------------|-------------------------|
| HOMO energy (eV) | -5.82 | -5.12 | -5.11 | -4.31 | -4.31 | -3.56 |
| LUMO energy (eV) | -3.68 | -2.41 | -2.29 | -2.30 | -2.07 | -1.99 |
| Gap (eV) | 2.13 | 2.71 | 2.83 | 2.01 | 2.24 | 1.57 |
| Relative SCF +ZPE (kcal/mol) | 0 | -17.1 | -9.8 | 16.0 | 18.2 | 40.7 |

^aEnergies were calculated at the B3LYP/6-311+G* level of theory.

even over the whole molecule.^{17–19} Thus, in systems like those discussed here, the full picture cannot be obtained by examining only the NICS values of individual rings. Therefore, we calculated the NICS(1)_{πZZ} values, based on NICS-scan²⁰ and the σ-only model²¹ using the Aroma package.^{21–23} To obtain the type of ring currents (local/global), NICS-X-scans²³ were performed. Figure 9 shows the results of the NICS-X-scans.

Let us first examine the results obtained for theoretical compound **11c**. The planarity of this molecule allows for maximum interactions, and as a result, also maximal aromaticity/antiaromaticity interactions. Thus, **11c** is a good model for understanding the behavior of the induced magnetic field in **11a,b**. As shown in Figure 9, the compound is made up of two distinct and identical halves, which are separated by the four-membered ring at the center. In each half, rings A/G exhibit diatropicity, rings C/E exhibit paratropicity, and rings B/F exhibit almost no currents. These observations can be explained by the coexistence of several currents in the system: a global paratropic current, two naphthalenic currents (rings A + B and rings F + G, respectively), two local diatropic currents (rings A and G, respectively), and two local paratropic currents (in rings C and E, respectively). Indeed, closer inspection reveals that the diatropicity of the side rings A and G is much smaller than that of naphthalene (approximately -8 ppm, relative to approximately -16 ppm for naphthalene).²⁴ This indicates the existence of a paratropic contribution in these rings, which stems from the global paratropic current. The strength of this current can be estimated by the field above rings B and F. The fact that the NICS value is ~0 suggests that the naphthalenic diatropic current and the global paratropic current cancel each other out. Therefore, the global paratropic current creates an induced field of approximately 10 ppm. Using this estimate, we can deduce that the local (benzenic) current in rings A/G is responsible for approximately -8 ppm of the chemical shift there, and the local paratropic current in the dihydropyrazine rings (C/E) is responsible for approximately 8 ppm of the chemical shift there. The magnetic field at the center of the compound, above the cyclobutadiene ring, is almost nonexistent. Though the measured value is diatropic, this is most likely due to residual effects from the two neighboring paratropic currents. Support for this conclusion can also be found in the decrease of the NICS value when moving from 1.0 to 1.7 Å above the molecular plane. Namely, NICS(1)_{πZZ} is approximately -45 ppm, while the NICS(1.7)_{πZZ} (from the NICS-X-scan) is approximately -7.5 ppm. In benzene (an example of a ring with a diatropic ring current), the respective numbers are -34 ppm²⁰ and approximately -17 ppm,²³ respectively. With this under-

standing, it is now easier to study the results for the remaining compounds.

Compound **8** is also split into two halves, separated by the cyclobutadiene ring. The field above the cyclobutadiene moiety is paratropic, as expected, but it is much smaller than the usual values obtained for antiaromatic rings. This suggests a high degree of localization, which occurs in order to minimize antiaromaticity. In order to achieve this localization, the molecule must adopt resonance forms such as those shown in Figure 10 as the dominant canonic structures. As a result, the nitrogen-containing rings are also localized, which explains the very small field measured above them. What remains are two naphthalenic units (A + B and F + G, respectively), characterized by diatropic currents. The values calculated for the naphthalenic units are similar to those calculated for naphthalene itself, which substantiates this conclusion.

Compound **9** may be viewed as a combination of **8** (left side) and **11c** (right side). The main difference is observed above rings C, D, and E. Though the right-hand side shows the same paratropicity as observed in **11c**, the left-hand side is not identical to **8**. Rather, ring C has decreased aromaticity. A feasible explanation for this is that ring C now participates in a 12 π electron (i.e., paratropic) circuit with rings D and E. Its paratropicity is smaller than rings D and E due to an additional local current, which is diatropic.

For **10** we observe a different pattern. In addition to the naphthalenic currents seen in **8**, **9**, and **11c**, **10** exhibits a paratropic current (16 π electrons) that encompasses five rings: B, C, D, E, and F. As rings B and F participate in both this paratropic circuit and their respective naphthalenic circuits, they show decreased diatropicity relative to ring A, which participates only in the naphthalenic circuit. Compounds **11a,b** are identical to **11c**, except for their geometrical distortion. Both are interesting, because of their shapes, as two halves and the possibility to calculate NICS values on the inside and the outside (Figure 8). In both cases, the dihydropyrazines are strongly antiaromatic, but rings B and F show different behavior. While the inside value (ring F) is suggesting nonaromaticity, the outside value displays a strong aromaticity of -58 ppm (Figure 9). The outside values should be more realistic, because the ghost atoms (for the NICS measurement) are not influenced by the spatial proximity to the other half of the molecule. For the kinked isomer **11b** we only calculated the outside values, for this reason. Due to their lack of planarity, the interactions between the orbitals are attenuated, which results in lowered conjugation. Thus, both of these conformers exhibit patterns that are similar—qualitatively, but not quantitatively—to that of **11c**. It is possible that this compound avoids the planar structure **11c**, adopting instead the distorted structures **11a** and **11b**, in order to minimize antiaromaticity (as manifested by the global paratropic current). Their geometry also hinders accurate calculations of NICS_{πZZ}; therefore, only NICS_{ZZ} results for these two compounds are displayed in Figure 9. Noteworthy, the discontinuous profile of **11a** is basically a geometrical problem. If one supposes the probe is moved from left to right, above the bond that fuses the 6-membered ring and the 4-membered ring the BQ is 1.7 Å above the bond, with a 90° angle to the plane of the 6-membered ring. However, the 4-membered ring is not coplanar with the 6-membered ring, so that the BQ has to be rotated in order to be perpendicular to the 4-membered ring and at 1.7 Å above the bond, but then it is not perpendicular to the 6-membered ring. As a result, there are two BQs above that bond, and each

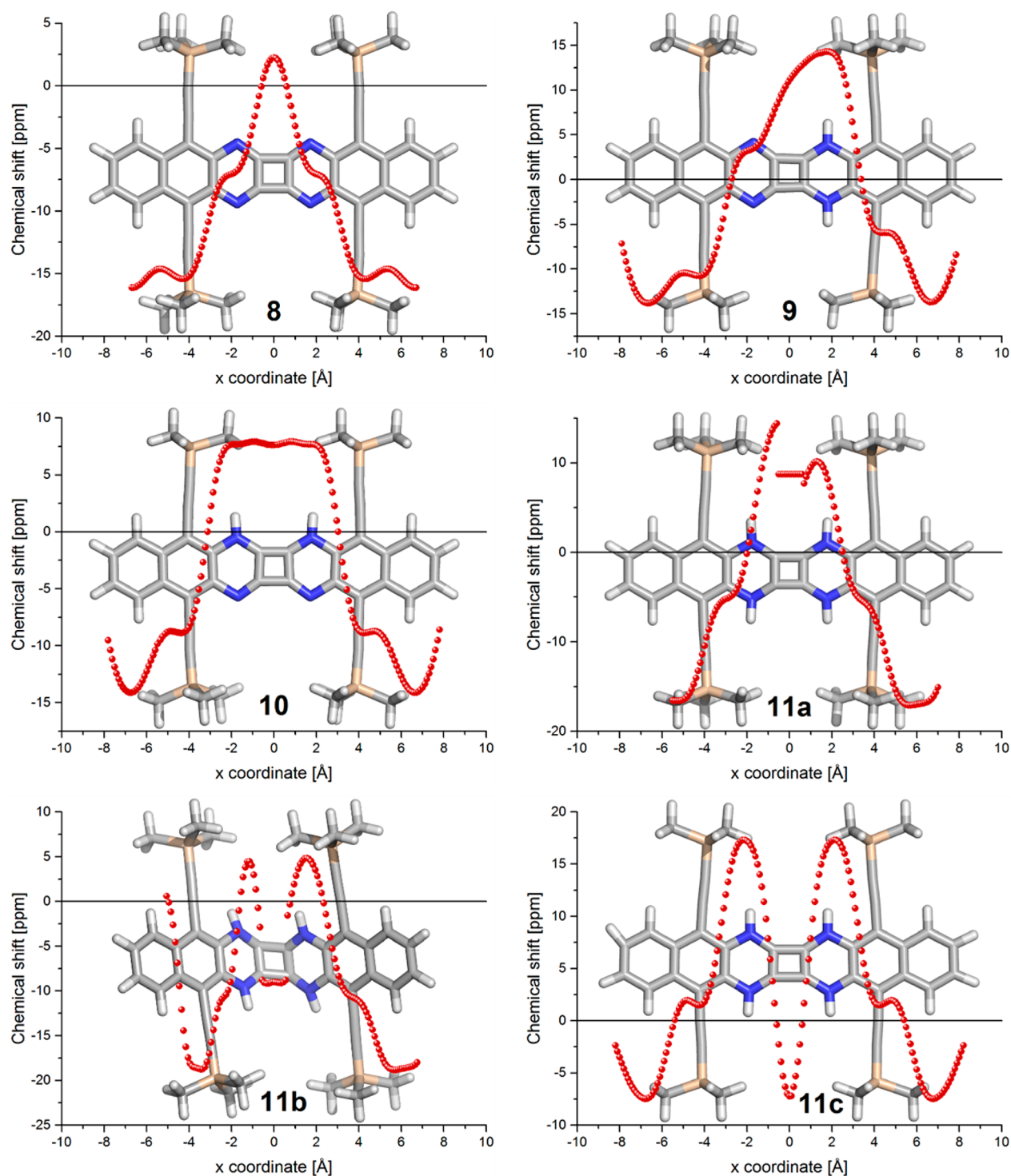


Figure 9. NICS-X-scan results of 8–11c, starting with rings A on the left side. For compounds 11a and 11b, only NICS_{ZZ} results are shown.

experiences a different magnetic environment. The very same geometrical problem happens when moving into the right 6-membered ring.

CONCLUSION

In conclusion, each of the systems studied here has different aromaticity properties. While 10 shows a high degree of localization, 11a,b (and their computational model, 11c) show high degrees of delocalization with global, semiglobal, and local currents. These differences are expected to be manifested in the

chemical properties of the different systems (such as different reactivity toward electrophiles and nucleophiles), as well as in their physical properties, such as their ability to act as organic semiconductors. Incorporating a cyclobutadiene ring may help to build enlarged, but stable azaacenes.^{25–28} These predictions are awaiting experimental results.

COMPUTATIONAL METHODS

All calculations were performed on a Gaussian09²⁹ platform. The NICS(1)_{πZZ} values were calculated according to published proce-

Table 2. Results of the NICS-Scan Calculations

| compd | ring A | ± | ring B | ± | ring C | ± | ring D | ± | ring E | ± | ring F | ± | ring G | ± |
|------------------|--------|------|--------|------|--------|-------|--------|-------|--------------------|------|---------------------|------|---------------------|------|
| 8 | -23.17 | 0.42 | -23.69 | 2.92 | -9.56 | 2.05 | 6.95 | 0.20 | -9.54 ^a | 2.05 | -23.69 ^a | 2.92 | -23.19 ^a | 0.42 |
| 9 | -28.24 | 3.70 | -23.10 | 2.70 | 4.56 | 4.37 | 5.96 | 16.43 | 28.68 ^b | 3.46 | -15.61 | 2.01 | -28.77 | 3.79 |
| 10 | -28.34 | 3.64 | -17.88 | 0.23 | 16.14 | 1.71 | 12.31 | 0.19 | 16.14 ^a | 1.70 | -18.20 ^a | 0.72 | -28.28 ^a | 3.55 |
| 11a ^c | -24.14 | 4.60 | -57.73 | 2.95 | 22.77 | 18.44 | 5.56 | 8.71 | 34.21 | 8.38 | -0.36 | 0.55 | -24.24 | 2.65 |
| 11b ^d | -23.69 | 3.68 | 16.52 | 1.47 | 25.81 | 0.53 | -7.16 | 1.15 | 27.80 | 1.16 | 14.17 | 2.16 | -23.03 | 3.55 |
| 11c | -16.72 | 3.51 | -3.08 | 2.24 | 30.35 | 2.02 | -45.11 | 11.18 | | | | | | |

^aRings A/G, B/F, and C/E should be identical. For control of the method all rings were calculated. ^bHere, ring E is the dihydropyrazine ring. ^cValues for rings A–C were calculated on the outside of the molecule and rings E–G on the inside (see Figure 8). Because the different sides affect the calculation probes only, the values for the outside are more realistic as they are not affected by the other half of the molecule and, especially, the middle ring. ^dNICS values were calculated on the outside of the molecule.

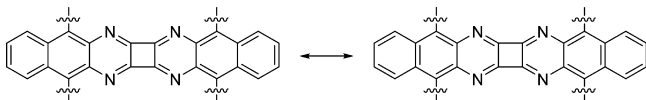


Figure 10. Resonance forms of 8.

dures^{20,21} using AroMa.^{21–23} As part of the procedure used in AroMa, each ring is calculated separately and therefore reoriented to the *xy* plane. For the NICS-X-scans,²³ trajectories along the long axes of the molecules were calculated and BQs were input manually using these equations at a height of 1.7 Å above the molecular plane. Since most of the compounds are not planar, only NICS_{zzz} results from the Sigma-Only Models³⁰ are presented here. For data analysis and plotting NumPy 1.8.0³¹ and OriginPro 9.1G³² were used. Geometries were fully optimized at the B3LYP/6-311G* level of theory and checked for imaginary frequencies, single-point and NICS calculations were done at B3LYP/6-311+G*.

■ ASSOCIATED CONTENT

📄 Supporting Information

Further information about the computational calculations including Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.S. and U.H.F.B. thank the DFG (Grant No. BU 771/7-1) for financial support. R.G.-P. thanks the Schulich Faculty of Chemistry at the Technion for a Ph.D. fellowship. A.S. thanks the ISF (Grant No. 1485/11) for financial support.

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