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Visualization of homoaromaticity in cations, neutral molecules and anions by spatial magnetic properties (through space NMR shieldings)—an $^1H/^{13}C$ NMR chemical shift study

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ABSTRACT

Prototypes for homoaromaticity in cations, neutral molecules, and anions are theoretically studied at the MP2 level of theory. For the global minimum structures on the potential energy surface both $^1H/^{13}C$ chemical shifts and spatial magnetic properties as through space NMR shieldings (TSNMRS) were calculated by the GIAO perturbation method. The TSNMRS are visualized as iso-chemical-shielding surfaces (ICSS) of different sign and size. Coincident experimental and computed $^1H/^{13}C$ chemical shifts afforded the possibility to decide from the TSNMRSs at hand on both the existence and the size of homoaromaticity in the molecules studied.

1. Introduction

Homoaromaticity is of continuous interest since Winstein's suggestion that aromatic stabilization of conjugated cyclic systems with $(4n+2)\,\pi$ electrons may be not interrupted by insertion of intervening groups.[1] Homoaromaticity has been evaluated through magnetic (significant equalization of the ^{13}C chemical shifts of the peripheral carbon atoms, highfield shifts of protons above/below the homoaromatic system, large negative NICS, and maximal values of magnetic susceptibility χ) and structural properties (approximately equal C,C bond lengths around the periphery of the system and diminished bond length alternation—the more the bond lengths alternate, the less aromatic the compound).[2] Reviews of homoaromaticity[2,3] report for similar compounds on unequivocal homoaromaticity, only minor impact from homoaromaticity up to lacking homoaromaticity.

This equivocal situation encouraged us to scrutinize the physical organic concept of 'homoaromaticity' by studying the spatial magnetic properties of representative, potentially homoaromatic cationic, neutral and anionic molecules. The spatial magnetic properties of molecules can be readily calculated as through space NMR shieldings (TSNMRS)[4] and visualized as iso-chemical-shielding surfaces (ICSS), and they have been successfully employed to quantify the anisotropic effects of functional groups (for determining the stereochemistry of nuclei proximal to the functional group/aromatic moiety)[4–19] and to separate the latter effect from 'steric compression' on the same protons,[20] to visualize and quantify also both planar[21–23] and spherical (*anti*)aromaticity,[23,24] the *endo-* and *exo*-hedral aromaticity of fullerenes[25] and the partial (*anti*)aromaticity of fulvalenes[26] and fulvenes,[27] and to visualize and quantify the partial '*push–pull*' and '*captodative*' aromaticity.[28] In this respect, the application of the spatial magnetic properties provided more effective information than the conventional interpretation of deshielded ^1H chemical shifts for aromatic protons. These shifts are not reliable measures of aromaticity because they are affected by factors other than deshielding due to the ring current effect.[29,30]

It is the aim of this paper to calculate the structures, the intramolecular flexibility and the $^1H/^{13}C$ chemical shifts of a variety of molecules with potential cationic, neutral and anionic homoaromaticity (Scheme 1) on the MP2/6-311+G** level of theory. The computed $^1H/^{13}C$ chemical shifts, thus obtained, were compared with the experimental δ-values; agreement is usually strong evidence for accurate calculated geometries of molecules.[31] As the next step, our approach[4] was applied, the TSNMRS of **1**–**21** were computed and visualized as ICSS of different size and direction. The corresponding TSNMRS of benzene and the cyclopropenylium cation, respectively, already published[4,21] are considered as spatial magnetic properties of prototype aromatic molecules and were employed as references for homoaromaticity in **1**–**21**. These

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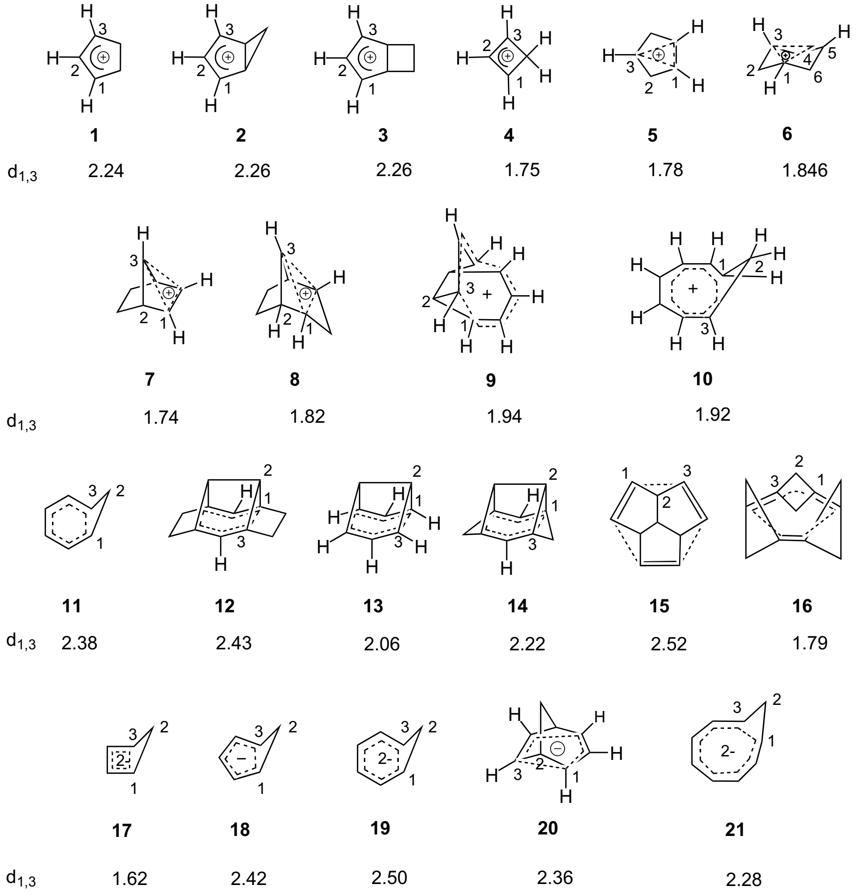


Scheme 1.

TSNMRS were evaluated at ICSS=$\pm$0.1 ppm and compared with the corresponding distances in Å from the center of the molecules **1**–**21**; differences will be discussed concerning the degree of homoaromaticity in **1**–**21** employing our approach.[4,21]

2. Computational details

The quantum chemical calculations were performed using the Gaussian 03 program package.[32] All compounds were fully optimized at the MP2/6-311+G** level of theory.[33] The spatial magnetic properties (TSNMRS) were constructed[4] using the NICS concept; the NICS values[34] were computed on the basis of the MP2/6-311+G** geometries of **1**–**21** applying the GIAO method[35] at the HF/6-311+G** theory level.[36] To calculate spatial NICS, ghost atoms were placed on a lattice of -10 Å to $+10$ Å with a step size of 0.5 Å in the three directions of the Cartesian coordinate system. The resulting 68,921 NICS values, thus obtained, were analyzed and visualized by the SYBYL 7.3 molecular modeling software;[37] different ICSS of -0.1 ppm (red) deshielding and 5 ppm (blue), 2 ppm (cyan), 1 ppm (greenblue), 0.5 ppm (green) and 0.1 ppm (yellow) shielding were used to visualize the TSNMRS of **1**–**21** in the following Figures.

Of significant note though, there have been some recent developments of the NICS index[38a] showing that not the average NICS but only the NICS(1)$_{zz}$ component could rigorously be used to quantify aromaticity[38b,39] and average NICS have proven to be not generally suitable for the quantitative evaluation of aromaticity.[40] For example, NICS analysis was shown to lead to an incorrect prediction of aromaticity for cyclopropane[41] and the cyclopropenyl anion.[42]

NMR chemical shifts were calculated by the GIAO method[43] at the MP2/6-311+G** level of theory (the reference compound TMS was calculated at the same level). All calculations were carried out on SGI workstations and LINUX clusters.

3. Results and discussion

Both structures and TSNMRS of the molecules **1**–**21** are given in the corresponding figures together with the TSNMRS of benzene and/or cyclopropenylium cation as prototype aromatic compounds; actually, **1**–**21** are subdivided into groups of molecules with potential *cationic* (**1**–**10**), *neutral* (**11**–**16**) and *anionic homoaromaticity* (**17**–**21**), respectively. Both computed and experimental ^{1}H and ^{13}C chemical shifts of these molecules (as far as accessible) are compiled in the respective tables. The results will be discussed consecutively applying the classification chosen by us.

3.1. Homoaromatic cations

The agreement between computed and experimental ^{1}H as well as ^{13}C chemical shifts proved to be sufficient [δ ($^{1}H_{exp}$)=0.9109 δ ($^{1}H_{calcd}$)+0.4356 (R^{2}=0.9563); δ ($^{13}C_{exp}$)=0.9398 δ ($^{13}C_{calcd}$)+7.3079 (R^{2}=0.9556)], particularly with regard to the fact that the theoretical δ-values have been computed for molecules in the gas phase but measured experimentally[1,45–51] in super acid, a medium difficult[44] to simulate theoretically (cf. Table 1). Obviously, the electronic structure of the ions studied, esp. due to the present charge(s), is dominating the magnetic properties and the medium proves to be of minor influence only. Furthermore, this correlation between computed and experimental ^{1}H and ^{13}C chemical shifts is strong evidence that the geometries calculated for the molecules are accurate.[3]

Beside experimentally established cations **1**, **2**, **4**, **6**, **7**, and **10**,[1,45–51] additionally, the 2π-1,2,3-cation **3**, the 2π-1,3,4-cation **5**, the 2π-1,3,5-cation **8**, and the 6π-1,3,4,5,7,8,9-cation **9** have been computed at the same level of theory. Olah,[52] carefully searching for **5** and **6**, found experimental evidence for **6** only,[53,54] compound **5** remains unknown; the norbornyl cation **7** and a number of derivatives of 3,5-bridged bishomocyclopropenyl cations **8**, however, were prepared.[55–61] Moreover, the existence of the bishomoheptafulvene cation **9** has been reported.[59] Both ^{1}H and ^{13}C chemical shifts computed for **3**, **5**, **8**, and **9** appear acceptable with a view to **1**, **2**, **4**, **6**, **7**, and **10**: in the cases of **5**, **6**, and **8**, the ^{13}C chemical shifts are strongly shifted to highfield as known from C-7 of the 7-norbornyl cation.[62]

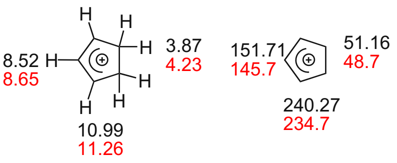
As criterion for homoaromaticity and the homoconjugative delocalization of [4 n+2] π-electrons, the spatial magnetic properties of molecules **1**–**21** were examined, calculated as TSNMRS; the corresponding values are visualized as ICSS of different size and direction and had been found to quantify aromaticity successfully.[21–28]

First, in Figure 1 the TSNMRS of benzene, as the prototype aromatic compound, and the 6π-electron potentially homoaromatic cations **9** and **10** are displayed. The similarity, actually almost identity, of the corresponding ICSS of benzene and the homotropylium cation **10** is impressive; if the ICSS are used as a quantitative measure of aromaticity,[21–26] homoaromaticity of **10** seems to be even larger than the aromaticity of benzene itself and ca. the same as estimated for the tropylium cation.[26] This might indicate an effect due to the positive charge in the tropylium cation **10**; alternatively, the size of the conjugated system might play a role since it is known that magnetic susceptibility exaltation is dependent upon the square of the ring area as are NICS.[63]

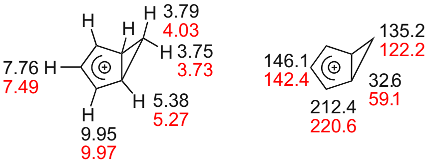
Simultaneously, because the various ICSS in **10** can be considered as visualization of the corresponding ring current effect of the

Table 1

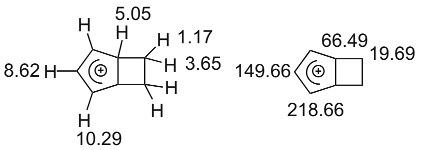
Computed[a] and experimentally determined[b] ^{1}H and ^{13}C chemical shifts of the potentially homoaromatic cations **1**–**10**[1,45–51,54,56,60,61]



1 [45]

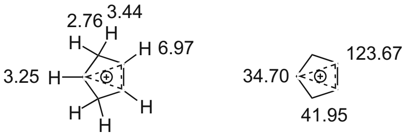


2 [46,47]

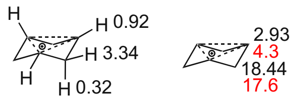


3

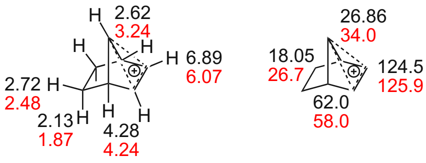
4 [45,48,49]



5

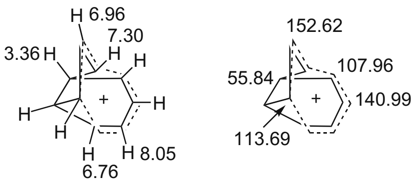


6[54]

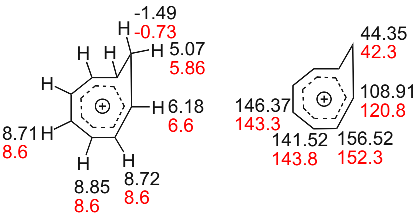


7 [56, 60, 61]

8



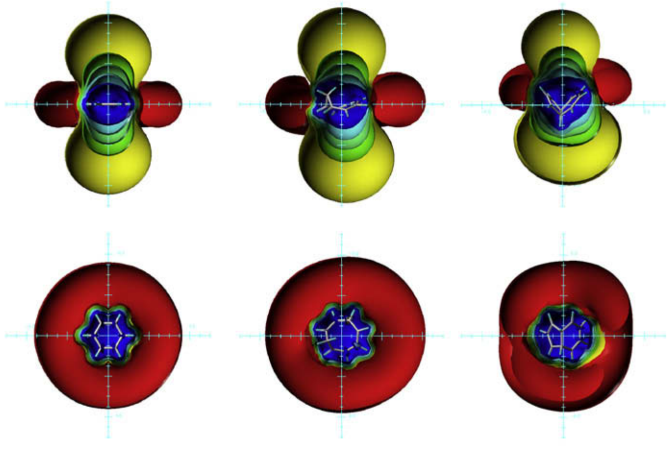
9



10 [1, 50, 51]

[a] This study.

[b] Reference given in brackets.

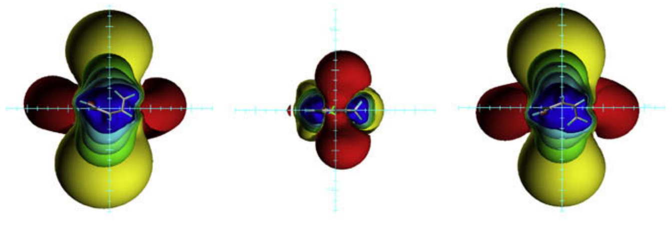


Benzene 10 9

Figure 1. Structures and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of benzene (as reference), the homotropylium cation **10** and bishomoheptafulvene cation **9** as potential candidates of 6π-*electron homoaromaticity*.

homoconjugatively delocalized 6π-electrons, the strong shielding of H_{syn} [δ (^{1}H) −0.73 ppm] due to the position just above the 6π-ring system of the homoaromatic compound **10** appears comprehensible. Because the chemical shift of H_{syn} in **10** has been employed as one of the main arguments for homoaromaticity in **10** and of the existence of the ring current of the homoconjugative delocalization of the 6π-electrons in **10**, both visualization and quantification of the spatial magnetic properties of **10** as TSNMRS unequivocally prove the existence of homoaromaticity in **10**, as concluded already previously employing different measures.[2,3,45,49,51,64–71]

The boat-shaped geometry of the homotropylium cation changes during the ring interconversion process via a planar homotropylium cation **10(TS)** (cf. Fig. 2); the inversion barrier was determined by low temperature NMR spectroscopy to be 22.3 kcal mol^{-1}.[48] Our calculations yielded a barrier to inversion of 37.74 kcal mol^{-1}, however, isolated molecules were studied but the transition state as the stronger polar state will be relatively stabilized by a polar solvent with respect to the ground states; thus, the difference between experiment and computation is not astonishing. Remarkable, on the other hand, is that the transition state, the planar homotropylium cation **10(TS)**, proves to be homoantiaromatic. In opposite to the diamagnetic ring current of the boat conformers in the ground states, the paramagnetic ring current of **10(TS)** is indicated by the reversed sign of the shielding/deshielding zones: above/below the ring system there is deshielding but the belt is shielding in this structure (cf. Fig. 2). The homoantiaromaticity of **10(TS)** is smaller than in cyclobutadiene as the prototype antiaromatic compound; employing the extension of the (now) lowfield shift ICSS=+0.1 ppm above/below the four-membered ring system as a quantitative measure of antiaromaticity,[21] the value in **10(TS)** proves to be 5.4 Å, in cyclobutadiene it is 6.2 Å (vide infra); on adequately declining antiaromaticity of **10(TS)** can be concluded. Alternatively, the different sizes of the two systems, cyclobutadiene and the transition state for inversion of **10**, will be of some impact (vide supra).[63]



10 10(TS) 10′

Figure 2. Ring interconversion process [ground states **10** and **10′** and transition state **10(TS)**] of the homotropylium cation **10** (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding).

The bishomoaromatic character, which has been assigned to **9**[59] is strikingly visualized by the TSNMRS; even if the molecule is not approximately planar[72] (actually it is a bicyclic skeleton of a folding angle of ca. 90°), the ICSS of different shielding visualize the homoaromatic delocalized 6π-electron system. The deshielding of the delocalized 6π-electron system shown by the various ICSS supports the bishomoaromaticity of the system. If the ICSS is used as a quantitative measure of aromaticity,[21–26] the homoaromaticity of **9** seems to be ca. the same as calculated for both benzene[21] and the homotropylium cation **10**.[26] Obviously, it can be concluded from the latter result that *planarity of the completely conjugated ring system seems to be not the fundamental postulate for the presence of at least homoaromaticity*; however, the distance between the two conjugated moieties (in case of **9** 1.94 Å, respectively) seems to be more important due to adequate π–π overlap for successful 6π electron delocalization in the seven-membered ring system (vide infra).

The reference, concerning spatial magnetic properties, for 2π-*electron homoaromaticity* in the cations **1**–**8** is the cyclopropenylium cation, which is included in Figure 3 together with these compounds (TSNMRS are again visualized as ICSS of shielding/deshielding in the same colors as above). The aromaticity of the cyclopropenylium cation is lower than in benzene [ICSS (−0.1 ppm)=7.2 and 5.9 Å, respectively, ICSS (−0.1 ppm)=8.9 and 7.2 Å, respectively][21] and is of about the size of homoaromaticity of cations **1**–**6**. Obviously, as is the 6π-*electron homoaromaticity*, the 2π-*electron homoaromaticity* is of about the same size in the different compounds as well and of comparable degree as usual aromaticity, e.g., as in the cyclopropenylium cation as the reference. Additionally, on basis of the spatial magnetic properties (TSNMRS) of **1**–**6**, few peculiarities of 2π-*electron homoaromaticity* must be reported: (i) Two preferred conformers, a *puckered* and a *planar* one (the structure of the more stable puckered conformer[56] is given in Fig. 3) have been obtained for **5** and both conformers are homoaromatic; actually, in terms of extension of the highfield ICSS=−0.1 ppm as a measure for aromaticity,[21] the homoaromaticity in the puckered structure [ICSS(−0.1 ppm)=5.2–5.8 Å] proves to be smaller than in the planar structure [ICSS(−0.1 ppm)=7.2 Å]. (ii) The puckered CH_2 moieties in **2** and **4** disturb the unrestricted spreading of TSNMRS in the cations subject to the present 2π-*electron homoaromaticity*; this effect is largest in **4**, the corresponding effect of the –CH_2–CH_2– group in **3** obviously in this sense proves to be negligible. However, all the cations **1**–**6** are homoaromatic, as reported previously,[2,3,45–49,53,67–69,73] and are of about same size as the cyclopropenylium cation as Ref. 21 (vide supra). (iii) The TSNMRS of the cyclobutenyl cation **4** draw a slightly different picture. The various ICSS, which visualize the ring current effect of this 2π-electron homoaromatic species, are tilted from being perpendicular to the planar three-membered moiety by ca. 45° and confirm a common ring current including the puckered CH_2 moiety (cf. Figs. 3 and 4). This result is rather surprising but fact and can be construed only as a special property of the four-membered ring in cyclobutenyl cation **4**. The puckered geometry of this homoaromatic cation changes during a ring interconversion process via a planar cyclobutenyl cation **4(TS)** (cf. Fig. 4); the inversion barrier was determined by low temperature NMR spectroscopy to be 8.4 kcal mol^{-1},[45,48] confirmed by a computational study.[49] Our calculations yielded a barrier to inversion of 11.39 kcal mol^{-1}. The transition state, the planar cyclobutenyl cation **4(TS)**, proved to be *not* homoantiaromatic as suggested.[3] Quite the contrary was

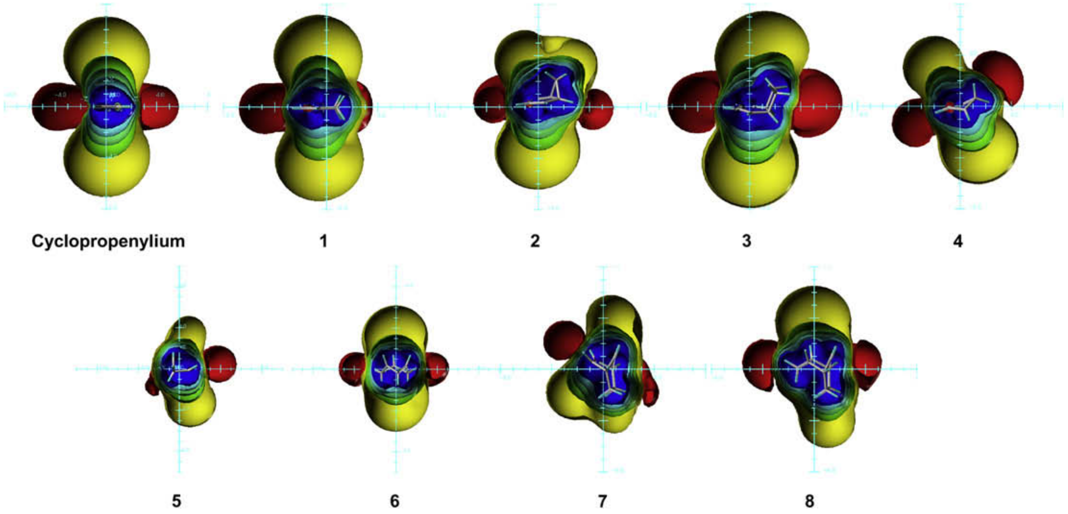


Figure 3. Structures and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of cyclopropenylium cation (as reference) and cations **1**–**8** as potential candidates of 2π-*electron homoaromaticity*.

obtained: identically to the ground states, TSNMRS proves the planar cyclobutenyl cation **4(TS)** to be still homoaromatic, however, of smaller size; employing the extension of the highfield shift ICSS=−0.1 ppm as a quantitative measure of aromaticity,[21] the value reduced from ca. 6.3 Å in the ground state to only 5.7 Å in the transition state. On adequately declining homoaromaticity can be concluded.

The bishomoheptafulvene cation **9** (cf. Fig. 1) proves to be heavily folded but homoaromatic as well. This is not an exception but is evidenced by the TSNMRS of the 7-norbornenyl cation **7** and the C_8 analogue **8**: similarly folded structures of the homoaromatic 1,2,3-C_3 moiety (cf. Scheme 1) were obtained with the usual shielding ICSS above/below these planes and the deshielding belt around these planes. Thus, these two cations are confirmed to be not only homoaromatic, as ascertained already previously,[56,58,62,66,67,73–76] but of about the same aromaticity as the cyclopropenylium cation.

3.2. Neutral homoaromaticity

While Minkin et al.,[2] in their book about the electronic and structural aspects of (*anti*)aromaticity, still in 1994 included an inquiring chapter ‘Can neutral molecules manifest homoaromaticity?’, the topic remains still controversial with few well-accepted examples of neutral homoaromatic molecules.[3] Cycloheptatriene **11** was assigned by Chen et al.[77] to be the prototype neutral homoaromatic system by employing geometric, energetic and magnetic criteria. In addition, the 2,8:4,6-bisethano- (**12**) and 2,8:4,6-bismethano-semibullvalene (**14**) and the transition state of the degenerate Cope rearrangement of semibullvalene (**13**) were found to be similarly homoaromatic by the same criteria[78] and enormeous synthetic efforts.[79] On the contrary, triquinacene **15** lacks homoaromaticity although the three double bonds might still interact in benzene-like mode.[80,81] The situation changes again when the three double bonds, which are too far apart in **15** to interact appropriately, are brought together, e.g., in tris(bis-methano)benzene **16**; beside acceptable distances between the C=C double bonds (1.79 Å), large negative NICS, the negative diamagnetic susceptibility and a high aromatic stabilization energy agree that **16** is one of the rare examples of a neutral homoaromatic hydrocarbon.[82–85]

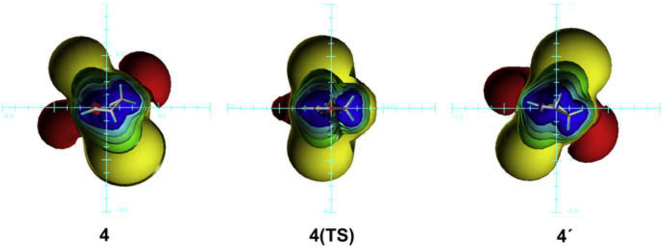


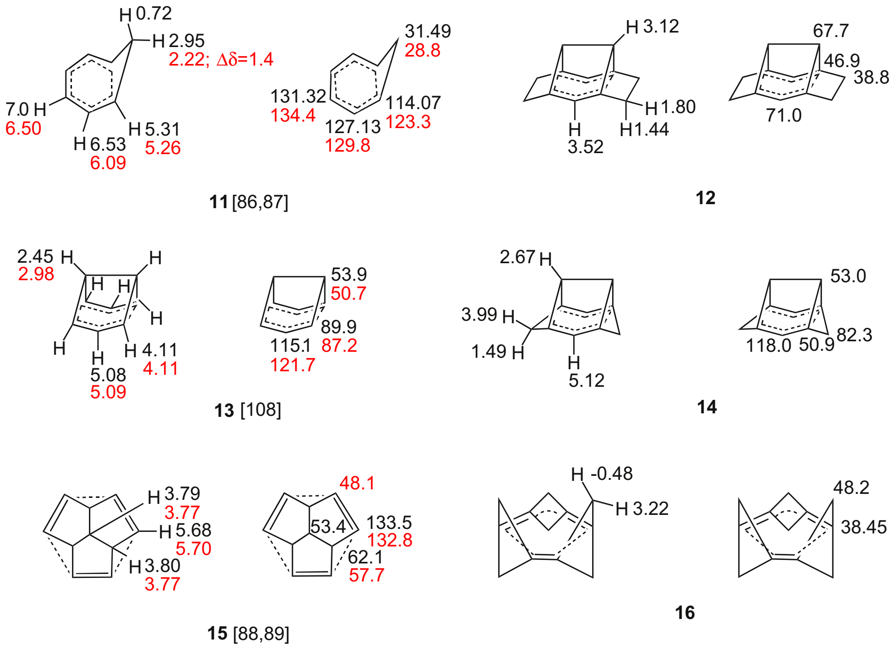
Figure 4. Ring interconversion process [ground states **4** and **4′** and transition state **4(TS)**] of the homoaromatic cyclobutenyl cation **4** (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding).

Thus, both structures and $^1H/^{13}C$ chemical shifts of the neutral compounds **11**–**16** (cf. Scheme 1) were ab intio MO calculated and the theoretical δ-values were compared with the experimental chemical shifts, as far as accessible (cf. Table 2). With the excellent agreement of experimental and computed chemical shifts of the known compounds **11**, **13**, and **15** in hand (and together with the results given in Table 1), it can be concluded that reasonable structures for **11**–**16** were obtained. The TSNMRS of **11**–**16** were calculated by our approach[4] and visualized as usual (vide supra); results are given in Figures 5–7 together with the TSNMRS of benzene as reference.

First, cycloheptatriene **11** was examined: TSNMRS are given in Figure 5 together with the corresponding values of benzene. In agreement with previous results,[77] a perfect ring current visualized by the various ICSS was obtained corroborating the homoaromaticity of cycloheptatriene, which is smaller than benzene aromaticity [ICSS(−0.1 ppm)=7.5 Å (benzene 8.8 Å); ICSS(+0.1 ppm)=7.2 Å (benzene 7.2 Å)]. The existence of the ring current is additionally corroborated by the ^1H chemical shift differences of the methylene protons ($\Delta\delta$=2.23 ppm; exp. 1.4 ppm).[83–85,90–92] The inside proton is shielded additionally due to the position in the shielding zone of the ring current effect of cycloheptatriene. Identical conclusions could be drawn from the ACID surfaces in Ref. 77 but TSNMRS visualized as ICSS seem to be more demonstrative in this respect. This latter statement is expressively supported by the ring inversion process of cycloheptatriene **11** (barrier to ring inversion ca. 6 kcal mol^{-1},[90–92] computed 11.34 kcal mol^{-1}) in terms of the spatial magnetic properties of the ground state and the planar transition state **11(TS)** of this dynamic process (given in Fig. 6). Chen et al.[77] could conclude from both the paramagnetic susceptibility and ACID calculated and visualized paramagnetic ring current, and from the positive NICS of

Table 2

Computed[a] and experimentally determined[b] ^{1}H and ^{13}C chemical shifts of the potentially homoaromatic neutral molecules **11**–**16**[86–89,108]



[a] This study.

[b] Reference given in brackets.

11(TS) that it is homoantiaromatic. This is impressively visualized by our TSNMRS (cf. Fig. 6). In opposite to the diamagnetic ring current of the boat conformers in the ground states, the paramagnetic ring current of **11(TS)** is indicated by the reversed sign of the shielding/deshielding zones: above/below the ring system there is deshielding but the *in-plane belt* is shielding in this structure. In Figure 6, in addition the TSNMRS of cyclobutadiene, the protoptype antiaromatic compound, is given for comparison and corroborating the generality of the results obtained. The antiaromaticity of **11(TS)**, seen also in **10(TS)**, is smaller than the homoantiaromaticity of cyclobutadiene. Using the (now) lowfield shift ICSS at +0.1 ppm (above/below the four-membered ring system) as a quantitative measure of antiaromaticity,[21] the value of 5.9 Å for **11(TS)** is similar to that in **10TS** and smaller than that of cyclobutadiene, 6.2 Å).[21] Additionally, similar antiaromaticity of the two transition states **10(TS)** and **11(TS)** can be concluded.

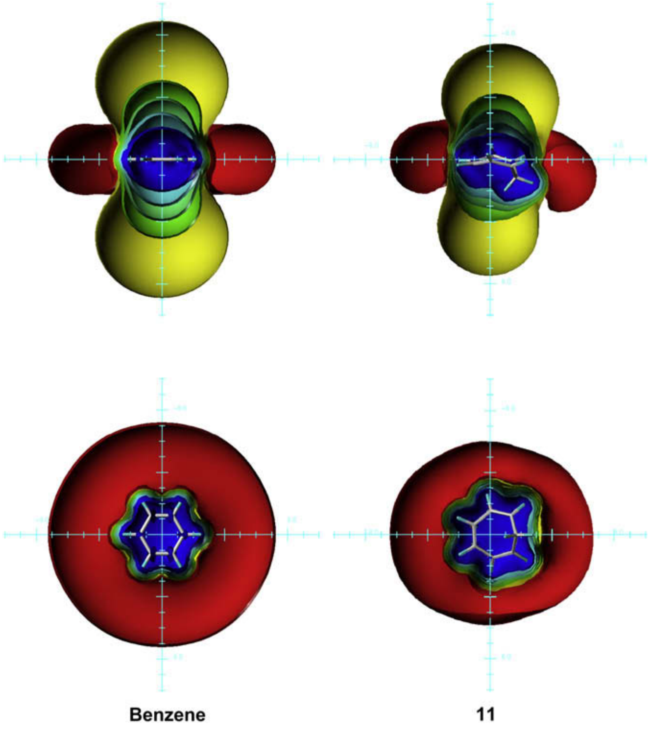
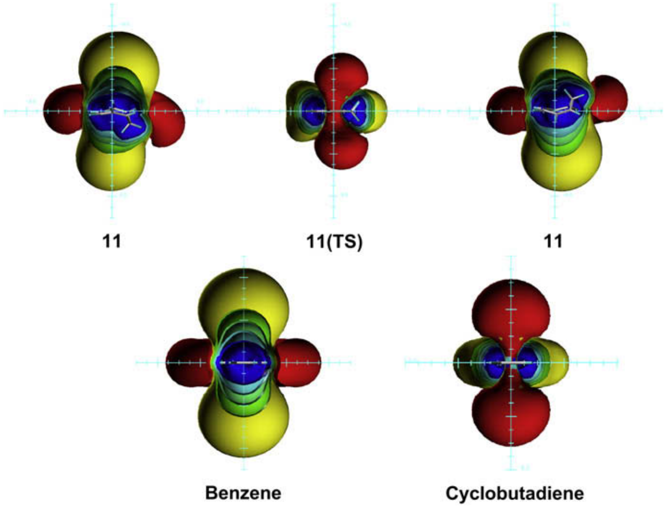

Benzene **11**

Figure 5. Structures and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of benzene (as reference) and cycloheptatriene **11**.


11 **11(TS)** **11**

Benzene **Cyclobutadiene**

Figure 6. Ring interconversion process [ground states **11** and **11′** and transition state **11(TS)**] of cycloheptatriene **10** (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) together with the TSNMRS of benzene and cyclobutadiene as prototype aromatic and antiaromatic compounds, respectively.

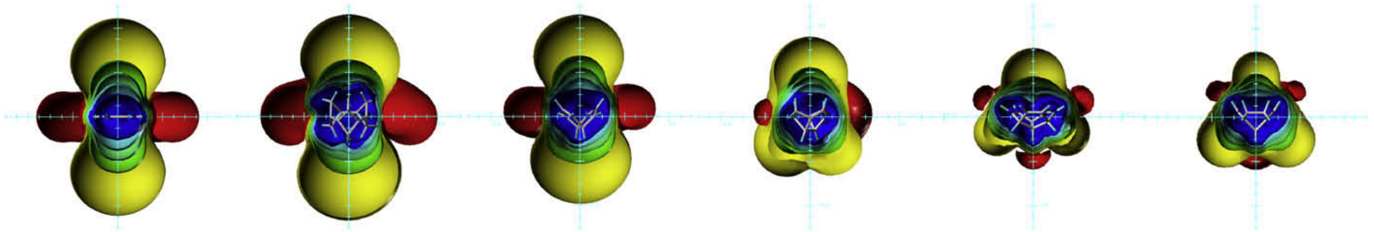

Benzene 16 13 14 12 15

Figure 7. Structures and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of benzene (as reference), the semibullvalene derivatives **12–14**, triquinacene **15** and tris(bismethano)benzene **16**.

The position of the ^{1}H chemical shifts of cycloheptatriene (δ 5.26–6.50 ppm) is another useful example for the fact that the chemical shifts of aromatic protons (benzene: δ 7.26 ppm) have proven to be due to reasons other than deshielding ring current effects and thus cannot be reliable indicators of aromaticity as well.[29,30,40,93]

The status of homoaromaticity in the semibullvalene derivatives **12**–**14**, as concluded from spatial magnetic properties of the compounds, is not so unequivocal. The homoaromaticity suggested for the transition state of the degenerate Cope rearrangement of semibullvalene (**13**) can be demonstrated (cf. Fig. 7): similar to the cations **7** and **8**, with 2π-electron homoaromaticity, and almost identical to the bishomoheptafulvene cation **9** with 6π-electron homoaromaticity, a uniform diamagnetic ring current was obtained; obviously, the common plane of the six sp^2 hybridized carbon atoms, constructing the 6π-electron homoaromatic moiety in **9** and **13** is not a postulate for establishing homoaromaticity. The diamagnetic ring current generates similar if not identical spatial magnetic properties as benzene (cf. Fig. 7) but the two five-membered ring moieties in **13**, however, are completely planar and folded by ca. 90° to each other.

This planarity of the two five-membered ring moieties is disturbed in the other two semibullvalene derivatives **12** and **14** and this more in 2,8:4,6-bisethano- (**12**) than in 2,8:4,6-bismethano-semibullvalene (**14**). Synchronously, **12** and **14** displace the former uniform diamagnetic ring current and hereby the TSNMRS to the increasingly distorted five-membered ring moieties and disconnect the former common ICSS above the ring system (at the side of the CH–CH bridge in **12** and **14**) into separated parts. Below the ring system the uniform ICSS remain unaffected but reduce strongly in size {from **13** [ICSS(+0.1 ppm)=9.2 Å] via **14** [ICSS(+0.1 ppm)=7.1 Å] to **12** [ICSS(+0.1 ppm)=5.9 Å]}.

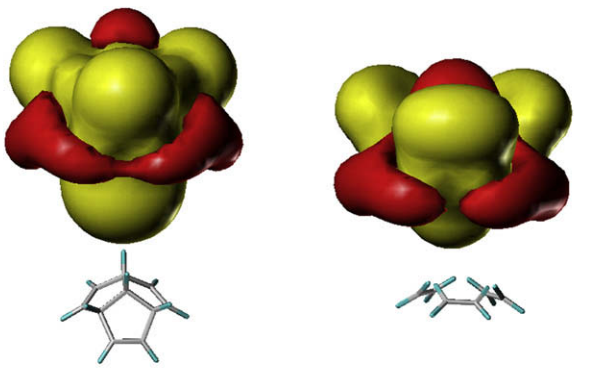

15 15a

Figure 8. Structures and TSNMRS (visualized as ICSSs: yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of triquinacene **15** and the combined anisotropic effects of three isolated C=C double bonds **15a**, identically positioned as the double bonds in **15**.

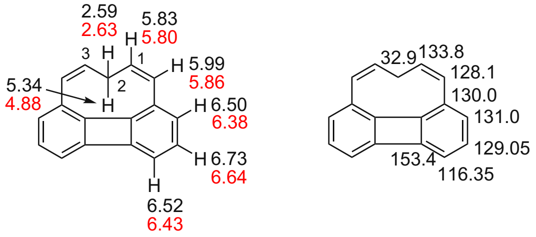
Finally, the spatial magnetic properties (TSNMRS) of triquinacene **15** are studied; triquinacene **15** lacks homoaromaticity due to the three double bonds, which are too far apart (2.52 Å) to get conjugated in a homoaromatic manner and can be the reference for non-existing homoaromaticity.[84] Examination of the corresponding ICSS result in uniform ICSS(+0.1 ppm)=6.1 Å below the ring system and completely separated ICSS above the five-membered ring moieties (cf. Fig. 7) as obtained for the semibullvalene derivatives **12** and **14**. The TSNMRS of triquinacene **15**, as reference for non-existing homoaromaticity, were simulated by the combined anisotropic effects of the three isolated C=C double bonds in **15a** at the same position as are the three C=C double bonds in **15** (cf. Fig. 8). The TSNMRS of both triquinacene **15** and the model **15a** are practically identical and prove the correctness of the homoaromaticity model proposed on the basis of TSNMRS values.

This means for the semibullvalene derivatives **12** and **14**, when consulting the uniform, almost identical ICSS below the ring system [**14** [ICSS(+0.1 ppm)=7.1 Å] and **12** [ICSS(+0.1 ppm)=5.9 Å], that they, as triquinacene **15**, are not homoaromatic [**15** ICSS (+0.1 ppm)=6.1 Å] and, when consulting the corresponding separated ICSS above the ring system in **12** and **14** (at the side of the CH–CH bridge), that the two five-membered ring moieties are isolated as the double bonds are in triquinacene **15**. The reason for the latter result could be the more diradical character of **12** and **14** compared with **13** due to the greater pyramidalization of the four identical terminal allylic carbons.[78] As a further support for this conclusion from TSNMRS can serve also the deshielding belt, which is characteristic for aromatic compounds and is still completed only in **13** but is interrupted in **12** and **14** and in the non-homoaromatic triquinacene **15**. Thus, non-existing homoaromaticity in the semibullvalene derivatives **12** and **14** is proposed by our approach[4] and this is in complete disagreement with previous theoretical calculations.[78]

Another conclusion from the semibullvalene results is that proximity between the two conjugated five-membered ring moieties proves to be, obviously, not the exclusive criterion for homoaromaticity in these compounds because distances in **12** and **14** are close to **13** and not to **15** (**13**, 2.06 Å; **14**, 1.82 Å; **12**, 2.04 Å; **15**, 2.52 Å). Steric strain due to the additional and twisted three- and four-membered ring units in **12** and **14** (unlike **13**) proves to be of great influence on the presence of homoaromaticity in these compounds as well.

In tris(bismethano)benzene **16**, on the other hand, which is homoaromatic,[75] the three C=C double bonds are sufficiently proximate (1.79 Å) to interact appropriately and the additional four-membered ring units are not sterically strained as in **12** and **14**. The TSNMRS of tris(bismethano)benzene **16** display a perfect 6π-electron ring current similar to benzene (cf. Fig. 7); the corresponding ICSS=−0.1 ppm (9.5 Å) and ICSS=+0.1 ppm (7.9 Å) of **16** prove to be even something larger than in the benzene reference (8.9 and 7.2 Å, respectively).

In order to look at neutral systems that would be expected to possess homoantiaromaticity, 3*H*-cyclonona[*def*]biphenylene **22**[94]



22 [94]

Scheme 2.

was investigated by our approach;[4] the structure and ^{1}H/^{13}C chemical shifts are given in Scheme 2, the TSNMRS are given in Figure 9. This hydrocarbon was synthesized and studied in detail by Wilcox et al.[94] Particularly the chemical shift difference of the methylene protons $\Delta\delta(CH_2)=2.25$ ppm, which was suggested to be due to a combination of the paratropic ring current and local anisotropies, but also PE and UV–vis spectroscopy point to significant neutral homoantiaromaticity in **22**.[94]

The spatial magnetic properties of 3*H*-cyclonona[*def*]biphenylene **22** are dominated by the ring currents of the two separated benzene moieties with usual shielding above/below the units and deshielding in-plane (cf. Fig. 9a). A completed paratropic ring current as in cyclobutadiene (cf. Fig. 6) for the nine-membered ring unit in **22** containing the 4 n (eight π electrons) is not generated. Instead, the four-membered ring unit between the two benzene moieties proves to be antiaromatic (cf. Fig. 9a,b), as in diphenylenecyclobutadiene,[21] and the two C═C double bonds in the nine-membered ring develop the corresponding anisotropic effect[4] only (cf. Fig. 9b). Obviously, the distance d_{1-3} with 2.48 Å is too wide, as in triquinacene **15** (vide supra), and the lacking four π electrons for developing noticeable 4*n* homoantiaromaticity in **22**, which should come from the two benzene moieties, are involved in the diatropic ring currents of these two aromatic ring units. Thus, as can be concluded from the spatial magnetic properties of *3H-cyclonona[def]biphenylene*, that this compound *is not homoantiaromatic* and the chemical shift difference of the methylene protons [$\Delta\delta(CH_2)=2.25$ ppm (computed 2.73 ppm)] is due to a combination of the paratropic ring current of the four-membered ring unit and the local anisotropic effects of the C═C double bonds of the nine-membered ring moiety and due to other effects because the latter two are not sufficient.

3.3. Homoaromatic anions

Both Williams and Kurtz[95] and Minkin et al.[2] in their reviews in the middle of the nineties of last century doubted serious evidence for the unequal assignment of homoaromaticity to anionic systems and asked 'Does homoaromaticity take place for anions?' Actually, there are three anionic hydrocarbons, which were studied in detail in this regard: homocyclopentadienide anion **18**,[96,97] homocyclooctatetraene dianion **21**[98] and bicyclo[3,2,1]octa-3,6-dien-2-yl anion **20**[99–106] (cf. Scheme 1). These three, together with homocyclobutadiene dianion (**17**) and cycloheptatrienyl dianion (**19**), which were suggested to be also potentially homoaromatic,[2] were computed in an analogous manner as achieved for **1**–**16**. ^{1}H and ^{13}C chemical shifts computed together with experimental δ values, as far as accessible, are given in Table 3, the global minima structures together with the TSNMRS obtained and visualized with the usual ICSS are displayed in Figure 10. Again, the agreement between computed and experimental chemical shifts is fairly good; on reasonable structures were concluded and, thus, the spatial magnetic properties obtained from the TSNMRS discussed subsequently.

For homocyclopentadienide anion **18** has been searched both experimentally and theoretically;[96,97] while Olah et al.[96] found that the species, generated experimentally, corresponding to the cyclohexadienyl anion, supported by other computations,[97] the latter authors found additionally a local minimum, which corresponds apparently to the homoaromatic structure of **18**. Along the present theoretical study, the puckered homoaromatic structure proved to be the global minimum; it is displayed in Figure 10 together with TSNMRS. The corresponding ICSS prove the structure to be homoaromatic. Compared with benzene as a reference and employing the two ICSS ±0.1 ppm as a quantitative indication,[21] homoaromaticity in **18** is found to be smaller than aromaticity of benzene, however, unequivocally present [ICSS(-0.1 ppm)=6.9 Å (benzene 8.8 Å); ICSS($+0.1$ ppm)=6.0 Å (benzene 7.2 Å)]. The same result was obtained for the homocyclooctatetraene dianion **21** in agreement with the literature.[98] Homoaromaticity, due to ten conjugated π-electrons, proves to be larger than benzene aromaticity [ICSS(-0.1 ppm)=9.6 Å (benzene 8.8 Å); ICSS($+0.1$ ppm)=7.9 Å (benzene 7.2 Å)]. In the latter two cases, the diamagnetic ring current effect, visualized by the ICSS, is tilted from being perpendicular to the unsaturated moiety by ca. 30° and visualize a common ring current including the puckered CH_2 moiety (cf. also Figs. 3 and 4). This behavior was observed already for the cyclobutenyl cation **4**, is hence

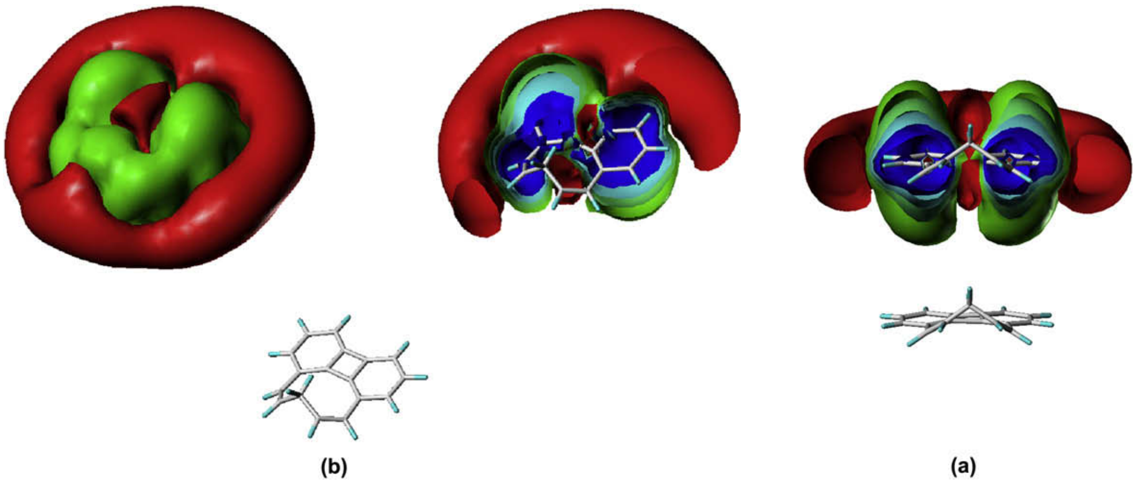
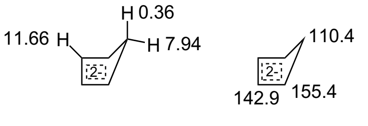


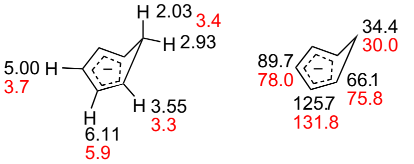
Figure 9. Structure and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding and red −0.1 ppm deshielding) of 3*H*-cyclonona[*def*]biphenylene **22**—different views.

Table 3

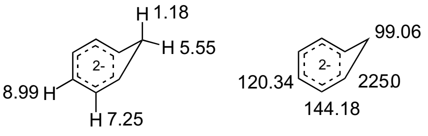
Computed[a] and experimentally determined[b] ^{1}H and ^{13}C chemical shifts of the potentially homoaromatic anions **17**–**21**[96,98–104]



17



18 [96]



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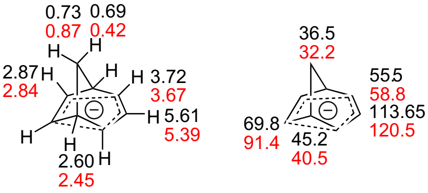
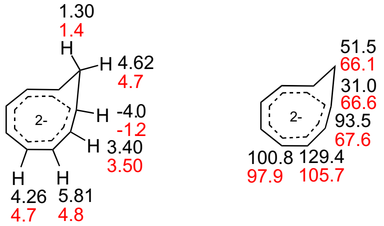


20 [99-104]



21 [98]

[a] This study.

[b] Reference given in brackets.

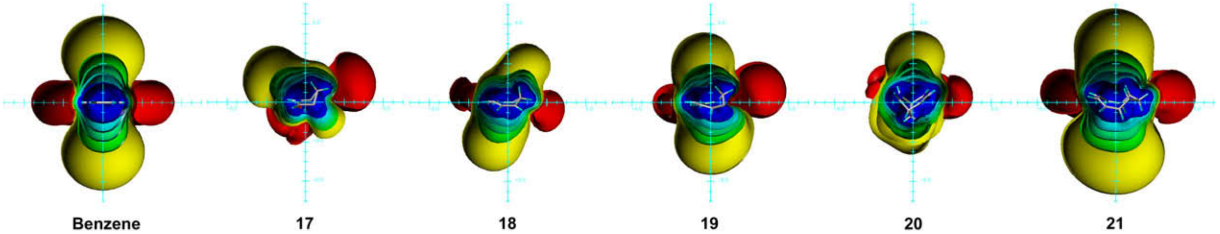


Figure 10. Structures and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm shielding, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red −0.1 ppm deshielding) of benzene (as reference) and anions/dianions **17**–**21** of potential homoaromaticity.

not a special property of the four-membered ring in **4**, and can serve as another certification for the matter of fact that the cyclopropane ring moiety (in cyclically delocalized systems) can extend but not transmit conjugation.[77,107]

The same is true for homocyclobutadiene dianion (**17**) and homocycloheptatrienyl dianion (**19**) (cf. Fig. 10); in **17**, obviously due to the carbene-like carbons in positions 1 and 3, the shielding zone below the ring system was not found. Only above the five-membered ring system, as usual, the shielding zone (of about the same size as in benzene) was affirmed [ICSS(−0.1 ppm)=7.5 Å (benzene 8.8 Å); ICSS(+0.1 ppm)=7.2 Å (benzene 7.2 Å)]. A fundamental study of homoaromaticity in singlet and triplet carbenes in terms of spatial magnetic properties is projected.

Finally, the spatial magnetic properties of bicyclo[3,2,1]octa-3,6-dien-2-yl anion **20**, the best studied molecule of potential anionic homoaromaticity,[99–106] were examined. As found in **7**–**9** and **12**–**16**, a uniform diamagnetic ring current was generated (cf. Fig. 10) and the distance between the two conjugated unsaturated moieties is with 2.36 Å obviously sufficiently short enough for the successful construction of the 6π-electron homoaromatic moiety. This diamagnetic ring current generates again similar spatial magnetic properties as benzene, the aromaticity, however, somewhat smaller [ICSS(−0.1 ppm) ca. 6.5 Å (benzene 8.8 Å); ICSS(+0.1 ppm) ca. 5.6 Å (benzene 7.2 Å)].

4. Conclusions

The physical organic term *homoaromaticity* was studied employing the spatial magnetic properties (Through Space NMR Shieldings—TSNMRS—as visualized by Iso-Chemical-Shielding Surfaces—ICSS—of different sign and size) of representative cationic, neutral and anionic molecules with potential homoaromaticity. Both structures and $^{1}H/^{13}C$ chemical shifts were computed at the MP2/6-311+G** level of theory and compared with experimental values; excellent agreement proves to be strong evidence for accurate calculated geometries of the potentially homoaromatic molecules. The following results were obtained:

(i) The homoaromaticity of the homotropylium cation **10**, when estimated with our approach,[21] proves to be even stronger than the aromaticity of benzene itself and ca. the same as computed for the tropylium cation.[26] In contrast, the transition state of the ring interconversion process, the planar homotropylium cation **10(TS)**, is homoantiaromatic, however, smaller in size than cyclobutadiene as the prototype antiaromatic compound. Similar conclusions from TSNMRS could be drawn concerning homoaromaticity of both ground and transition states of cycloheptatriene **11**.

(ii) As is the 6π-*electron homoaromaticity*, the 2π-*electron homoaromaticity* is of about the same size in the different cations **1**–**8** studied and of comparable degree as aromaticity in the cyclopropenylium cation as reference.

(iii) In the cyclobutenylium cation **4** the various ICSS are tilted from being perpendicular to the planar three-membered moiety by ca. 45° and confirm a common ring current including the puckered CH_2 moiety; in addition, the transition state of the four-membered ring inversion, the planar structure **4a**, is still homoaromatic but of smaller size than in the ground states.

(iv) Folded structures, as obtained for the bishomoheptafulvene cation **9**, were found for the 7-norbornyl cation **7** and the C_8 analog **8**. Again short distances of bonds 1–7 and 2–7 (in **8** also 1–2) prove to be required for being homoaromatic and this of about the same size as the cyclopropenylium cation.

(v) The influence of sufficient proximity of three $C{=}C$ double bonds to interact appropriately for establishing 6π-*electron homoaromaticity* was studied employing the neutral compounds **12**–**16**: While the tris(bismethano)benzene **16** and the transition state of the degenerate Cope rearrangement of semibullvalene **13** prove to be homoaromatic (due to short distances of 1.79 and 2.03 Å, respectively), there is no homoaromaticity in **12** and **14** [even if distances are comparable (2.04 and 1.83 Å, respectively) with **13**] and in triquinacene **15** (2.52 Å); in the latter compound, not homoaromaticity at all but the combined anisotropic effects of the three isolated $C{=}C$ double bonds were observed only. *Obviously, both the distance between conjugated homoaromatic moieties and the strain-free arrangement of these units ascertain the presence or absence of homoaromaticity*.

(vi) 3*H-Cyclonona[def]biphenylene* **22** proved to be *not homoantiaromatic* but the chemical shift difference of the methylene protons [$\Delta\delta(CH_2){=}2.25$ ppm (computed 2.73 ppm)] to be due to a combination of the paratropic ring current of the four-membered ring unit, the local anisotropies of the $C{=}C$ double bonds of the nine-membered ring moiety (and due to other effects).

(vii) Finally, the presence of homoaromaticity in the anionic molecules **17**–**21** was confirmed employing their spatial magnetic properties; in **20**, the bicyclo[3,2,1]octa-3,6-dien-2-yl anion and the best studied molecule of potential homoaromaticity of anions, the uniform ring current provided evidence of 6π-*electron homoaromaticity*, which is visualized by the various ICSS and estimated to be smaller than aromaticity in benzene as reference.

To summarize, *spatial NICS (TSNMRS)* are appropriate to visualize and quantify (*anti*)aromaticity but also homo(*anti*)aromaticity and the ring current effects as the basis of the two. They should be accepted as a measure of aromaticity[41] (even if not the average NICS index but only NICS(1)$_{zz}$ can be rigorously used to quantify aromativity)[39,40] because the anisotropic effect on proximate protons can be measured in ^{1}H NMR spectra and prove to be in excellent agreement with computed TSNMRS values at the respective position on the lattice around the molecule (vide supra).

Supplementary data

Absolute energies and Cartesian coordinates computed at the MP2/6-311G** level of theory for compounds **1**–**22** studied are given as supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.063

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36. The lattice points ('ghost atoms') should be sensor points only without energy contribution in the present calculations. Only if HF calculations are applied this is true; in case of electron correlation calculations, the 'ghost atoms' get their own electron density and show some influence on the energy of the studied molecule. In these cases the TSNMRS surfaces are heavily distorted.
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