ChemComm

Double aromaticity and anti-aromaticity in small carbon rings†

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Received (in Cambridge, UK) 12th April 2000, Accepted 4th July 2000
Published on the Web 19th July 2000

Calculated NICS indices for C_{10} and C_{14} indicate these species are doubly aromatic and that C_{12} is doubly anti-aromatic, with the π-aromaticity dominating the σ-contribution in systems such as triplet C_{10}, C_8N_2, $C_{10}B_2$ or C_{12}^{2+} all of which have opposing aromatic/anti-aromatic character.

Recent experimental studies[1] of the electronic absorption spectra of small carbon clusters have provided evidence for the first time that the fundamentally important C_{10}–C_{14} clusters are monocyclic polyalkynes or cumulenes rather than linear species.[2] Such rings were noted[1b] as being potentially doubly aromatic, *via* both conventional p_π–p_π overlaps, and *via* the novel in-plane conjugation of $4n + 2$ π-electrons described recently by Schleyer and co-workers.[3] The latter identified [10] and [14] trannulenes (all-*trans* annulenes) as having in-plane aromaticity, on the basis of calculated nucleus independent chemical shift values at the ring centroid (NICS[4] −14.0 and −17.2 ppm respectively, *cf.* benzene, −10 ppm) and the 4*n* electron [12] trannulene as being strongly anti-aromatic (NICS +35.7 ppm). We noted that the NICS aromaticities of the C_{10}–C_{14} carbon rings have not hitherto been reported. More importantly, we considered that these small carbon rings might be suitable systems for investigating the controversial suggestion[5] that the π-electrons in benzene have a distortive tendency towards bond localisation, and that the D_{6h} symmetry of benzene itself arises purely from the σ-framework. Adding or removing two electrons to the doubly aromatic C_{10} ring could give a 4*n* count for one set of p_π–p_π electrons, and a $4n + 2$ count for the orthogonal p_π–p_π set, resulting in molecules which would be simultaneously aromatic in one dimension and anti-aromatic in another. We also speculated whether the triplet[6] and higher excited states of these species might exhibit a similar effect. Finally, our recent studies[7] suggested to us that the two orthogonal $4n + 2$ sets of p_π–p_π electrons in C_{10} might be converted to a single 4*n* set by introducing a Möbius component into the ring. Here we report our theoretical findings on these various aspects.

Initial studies† of these species were at the AM1 semi-empirical level[8] followed by B3LYP/6-31G(d) geometry optimisation[9] with no symmetry constraints of the singlet states. All the rings were characterised as planar minima *via* inspection of the Hessian matrix. Of the four valence electrons available to carbon, two contribute to conventional C–C single bonds (*e.g.* sp hybridisation) and are not considered further here. The remaining two electrons occupy orthogonal p-orbitals which for C_{10} specifically, overlap cyclically to form a set of five doubly occupied in-plane σ-molecular orbitals and a set of five out of plane π-orbitals. Each set has a characteristic benzene-like double degeneracy (E) for the highest two pairs (*e.g.* the Hückel $4n + 2$, $n = 2$ electron rule, Table 1). The calculated NICS(0)-B3LYP/6-31G(d) value at the C_{10} ring centroid (D_{5h} symmetry) of −28.9 ppm implies the molecule is indeed doubly aromatic compared to benzene itself. The C_{14} homologue showed a similar pattern of orbital occupancy and even higher aromaticity (Table 1). C_{12} differs from C_{10} in having a pair of additional p_π electrons in both the σ- and π-planes, each of which occupies a single, now non-degenerate orbital. Such 4*n* occupancy ($n = 3$) results in doubly anti-aromatic character (NICS +50.0 ppm) and a Jahn–Teller distortion towards bond localisation of the geometry (Fig. 1). The degeneracy of the π HOMO can be recovered by promoting one π electron to the π LUMO to form a triplet state, calculated to be 6.7 kcal mol^{-1} higher than singlet C_{12}. This species can be described as out-of-plane π triplet aromatic[6] but remains an in-plane σ-anti-aromatic. The overall NICS value indicates the dominance of the π aromaticity over the in-plane σ-anti-aromaticity (Table 1). Further σ–σ* electron excitation to form the quintet state of C_{12} additionally removes the in-plane σ-anti-aromaticity, increasing the overall NICS aromaticity index to −31.5 ppm.

Although reliable calculations for small carbon clusters appears to require very high levels of theory,[2] we emphasize here the relative trends in the geometries and NICS values rather than the absolute values and energies. Thus the calculated B3LYP/6-31G(d) geometries of planar C_{10}, C_{12} and C_{14} differ markedly in the degree of calculated bond alternation (Fig. 1). The doubly aromatic singlet systems show no bond alternation, doubly-antiaromatic singlet C_{12} shows strong alternation (due as we note above to a Jahn–Teller distortion) but the bonds are

Table 1 Calculated energies [kcal mol^{-1} for AM1, Hartree for B3LYP/6-31G(d)] and NICS(0) values (ppm)

Species	AM1	B3LYP/6-31G(d)	NICS(0)	Orbital occupancy[a]
C_{10}	403.8	−380.6661	−28.9	π(E), σ(E), σ(E), π(E), π, σ
B_5N_5	−57.9	−398.2935	−2.5	π(E), σ(E), π(E), σ(E), π, σ
1,6-C_8N_2	358.7	−413.9714	−16.7	σ, σ, π, π, σ, σ, π, π, σ, π, σ
C_{12}^{2+}	954.2	−456.0285	+32.4	π, σ(E), π(E), σ(E), π(E), π, σ
1,7-$C_{10}B_2$	504.7	−430.3801	−11.0	σ, π, σ, σ, π, π, σ, σ, π, π, σ
C_{12}[b]		−456.7770	−8.7	
C_{12}[c]		−456.7452	−31.5	
C_{12}	438.5	−456.7878	+50.0	π, σ, σ(E), π(E), σ(E), π(E), π, σ
C_{14}	465.1	−533.0193	−35.6	σ(E), π(E), σ(E), π(E), σ(E), π(E), π, σ
$C_{11}H_2$	350.9	−419.9766	−13.4	
$C_{13}H_2$	387.3	−496.1407	+6.8	
C_{19}	664.5	−723.2905	−11.0	

[a] Doubly occupied singly or doubly (E) degenerate orbitals arising from parallel p_π–p_π (π) and in-plane p_π–p_π (σ) overlap. [b] Triplet state. [c] Quintet state.

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† Electronic supplementary information (ESI) available: computed 3D coordinates as PDB files. See http://www.rsc.org/suppdata/cc/b0/b002922j/

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again symmetrised when the π-system is aromatised *via* formation of triplet state C_{12}. The additional reversal of the σ-anti-aromaticity *via* the planar σ/π doubly aromatic quintet C_{12} reveals bond relocalisation (Fig. 1), the origins of which remain to be established. These various results contrast with the proposal that π-aromaticity in benzene is bond distortive and that the symmetry is due to the σ framework alone.[5]

B_5N_5 is isoelectronic with C_{10} and also has the characteristic cumulene structure (Fig. 1) with no bond alternation and a similar orbital ordering to the carbon analogue, but a surprisingly small NICS value (Table 1) corresponding to non-aromaticity. The anomalous behaviour of B_5N_5 in a different context has been previously noted.[10] Two valence electrons added to C_{10} in the form of C_8N_2 occupy an in-plane p_π–p_π orbital, resulting in an in-plane 4*n* (*n* = 3) rather than 4*n* + 2 occupancy. Overall, the NICS value suggests that the π 4*n* + 2 aromaticity is clearly dominant over the σ 4*n* anti-aromaticity (Table 1). The reverse effect is observed with C_{12}^{2+}. This is a 12-electron (4*n*) π-antiaromatic system (NICS +32.4) associated with bond alternation, dominating a 10-electron (4*n* + 2) in-plane σ-aromatic system. A third example of this π-dominance is the isoelectronic $C_{10}B_2$ which reveals 10-electron π-aromaticity and 12-electron in-plane p_π–p_π σ-anti-aromaticity, with overall NICS aromaticity (Table 1) and only mild bond alternation (Fig. 1).

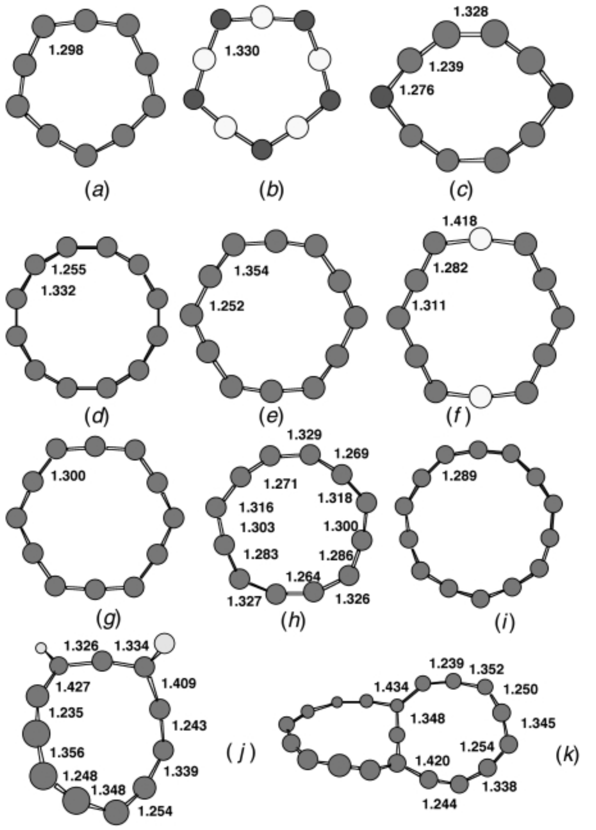

Fig. 1 B3LYP/6-31G(d) Calculated geometries (Å) for (*a*) C_{10}, (*b*) B_5N_5, (*c*) C_8N_2, (*d*) C_{12}^{2+}, (*e*) C_{12}, (*f*) $C_{10}B_2$, (*g*) triplet C_{12}, (*h*), quintet C_{12}, (*i*) C_{14}, (*j*) $C_{11}H_2$, (*k*) C_{19}.

We had previously suggested[7] that replacing a two electron C=C unit in a 4*n* + 2 electron annulene by a partially twisted four electron HC=C=CH unit can induce Möbius 4*n* aromaticity. Applying this analogy to replacing one four electron triple bond by this unit in C_{10} results in chiral $C_{11}H_2$, in which the in-plane p_π–p_π/σ and the out-of-plane p_π–p_π/π-systems interact to form a 20-electron Möbius 4*n* aromatic. Less effective orbital overlap reduces the NICS value compared to C_{10} and induces bond alternation (Fig. 1). Inserting the same HC=C=CH unit into the strongly anti-aromatic C_{12} to produce the 24 electron $C_{13}H_2$ reduces the anti-aromaticity substantially, but does not eliminate it (Table 1).[11] Finally, we note that two hydrogen atoms in $C_{11}H_2$ can be removed entirely by replacing them with a second carbon ring to give C_{19}, a novel form of chiral Möbius carbon (Fig. 1), again with mild NICS aromaticity indicated for each ring.

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