Distributed-Gauge Calculations of Current Density Maps, Magnetizabilities, and Shieldings for a Series of Neutral and Dianionic Fused Tetracycles: Pyracylene ($C_{14}H_8$), Acepleiadylene ($C_{16}H_{10}$), and Dipleiadiene ($C_{18}H_{12}$)

Patrick W. Fowler and Erich Steiner

Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK

Beniamino Cadioli and Riccardo Zanasi*

Dipartimento di Chimica, Università di Modena, via G. Campi 183, 41100 Modena, Italy

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Ab initio π-electron first-order current density maps and all-electron second-order magnetic properties, calculated at an uncorrelated level of theory by means of distributed-gauge methods, are presented for a series of neutral and dianionic fused tetracycles which can be regarded formally as perturbed annulenes. The reliability of the current density maps, which point to the naphthalene core rather than the annulene perimeter as the basic unit of current flow, is supported by the good agreement of the computed magnetic properties with the available experimental data. Unusually for a closed-shell system, the acepleiadylene dianion is predicted to be a paramagnetic molecule.

1. Introduction

Pyracylene and its relatives acepleiadylene and dipleiadiene were much discussed in the classical literature of the ring-current model as test systems for experimental verification of the predictions of the $4n/4n+2$ Hückel rule.[1−6] These fused tetracycles can be regarded, at least formally, as 12-, 14-, and 16-atom monocycles perturbed by a central C_2 unit that enforces planarity;[1,2] a different and, as it turns out, physically more realistic picture represents the three systems as bridged naphthalene cores.[7] These systems are also newly topical through their connection with fullerenes: the pyracylene skeleton forms a part of every well-characterized fullerene cage, and, at least in some ranges of nuclearity, nonclassical cages with heptagonal rings are predicted to be comparable in stability with the classical pentagon−hexagon cages.[8]

Semiempirical calculations on the neutral systems indicate paramagnetic circulations in the odd rings of pyracylene and dipleiadiene,[2,4−6] and in the case of pyracylene this qualitative picture is confirmed by more sophisticated ab initio calculations in implementations[7] based on Keith and Bader's distributed-gauge Ansatz[9] for calculation of current density, which was shown to give accurate displays of the induced current to the prediction and understanding of magnetic properties.[10] The aim of the present paper is to extend and place in context this result by plotting the magnetic-field induced current density and computing magnetizabilities and NMR shielding constants for neutral and 2^- charge states of pyracylene, acepleiadylene, and dipleiadiene.

2. Methods

All calculations of magnetic-field induced first-order current density and second-order magnetic properties were carried out at the uncorrelated SCF and CHF levels using the SYSMO package.[11] The magnetizability ξ and carbon and proton nuclear shieldings σ^C and σ^H were calculated by integration of current densities obtained by two different approaches that differ only in their treatment of the well-known problem of gauge dependence of computed magnetic properties. Both methods are based on the continuous transformation of origin of current density (CTOCD) approach,[9,12,13] which uses a different origin for each point at which the current density is to be computed. The two methods differ in the choice of the origin: in the CTOCD-DZ method the origin is coincident with the point itself, thereby making the diamagnetic contribution to the induced current density vanish; in the CTOCD-PZ method the origin is determined for each point in such a way that the transverse component of the paramagnetic induced current is annihilated. The details of CTOCD-DZ and CTOCD-PZ methods, which were also used in our calculations of ring current in C_{60},[14,15] their relation to the methods proposed by Keith and Bader[9] and Geertsen,[16] and their performance on test cases are described at length elsewhere.[17,18] A variant of each method, which greatly improves the results for the calculated nuclear magnetic shieldings, is obtained by shifting the origin of the current toward the nearest nucleus for points close to nuclei, as suggested originally by Keith and Bader with the CSDGT method.[9] These variants, indicated by the acronyms CTOCD-DZ2 and CTOCD-PZ2[7,18] have been adopted here.

All calculations of current density and magnetic properties were carried out with the 6-31G**[19] basis set. A larger basis set, as, for example, previously used for pyracylene,[7] was not used here owing to the larger size and lower symmetry of acepleiadylene and dipleiadiene molecules. However, it has been pointed out[20] that the quality of the current density plots obtained using the CTOCD approach is not significantly dependent on basis size, with the main features of the current flow being almost unaffected by basis set changes. Magnetizability and shielding constants usually require carefully tailored basis sets for their accurate prediction, and this turns out to be

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* Corresponding author. E-mail: zanasi@unimo.it.

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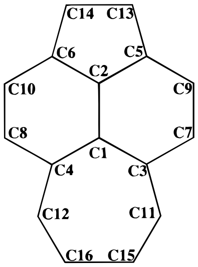

Figure 1. The diagram shows the scheme of atom numbering in acepleiadylene used in the present paper. Hydrogen atoms are given the same numbers as their carbon partners. An SCF optimization for the neutral molecule in the 6-31G** basis set gives a C_{2v} geometry with bond lengths (in Å) and angles: r(C1,C2) = 1.3846, r(C1,C3) = 1.4444, r(C2,C5) = 1.4146, r(C3,C7) = 1.3826, r(C5,C9) = 1.3610, r(C7,C9) = 1.4093, r(C3,C11) = 1.4606, r(C5,C13) = 1.4655, r(C11,C15) = 1.3334, r(C13,C14) = 1.3441, r(C15,C16) = 1.4495, r(C7,H7) = 1.0756, r(C9,H9) = 1.0765, r(C11,H11) = 1.0766, r(C13,H13) = 1.0735, r(C15,H15) = 1.0770, ∠(C2,C1,C3) = 115.3°, ∠(C1,C2,C5) = 125.6°, ∠(C3,C1,C4) = 129.4°, ∠(C5,C2,C6) = 108.8°, ∠(C1,C3,C7) = 118.5°, ∠(C2,C5,C9) = 118.2°, ∠(C1,C3,C11) = 125.6°, ∠(C2,C5,C13) = 106.5°, ∠(C3,C7,C9) = 124.2°, ∠(C5,C9,C7) = 118.2°, ∠(C3,C11,C15) = 130.6°, ∠(C5,C13,C14) = 109.1°, ∠(C11,C15,C16) = 129.1°. The structure of the dianion optimized in the same basis set and level of approximation has C_{2v} symmetry and the following geometrical parameters (changes from neutral in brackets): r(C1,C2) = 1.4030 (+0.0184), r(C1,C3) = 1.4454 (+0.0010), r(C2,C5) = 1.4340 (+0.0194), r(C3,C7) = 1.4302 (+0.0476), r(C5,C9) = 1.4456 (+0.0846), r(C7,C9) = 1.3588 (−0.0505), r(C3,C11) = 1.4546 (−0.0060), r(C5,C13) = 1.3849 (−0.0806), r(C11,C15) = 1.3398 (+0.0064), r(C13,C14) = 1.4400 (+0.0959), r(C15,C16) = 1.4788 (+0.0293), r(C7,H7) = 1.0856 (+0.0100), r(C9,H9) = 1.0822 (+0.0057), r(C11,H11) = 1.0857 (+0.0091), r(C13,H13) = 1.0818 (+0.0083), r(C15,H15) = 1.0836 (+0.0066), ∠(C2,C1,C3) = 115.7° (+0.4°), ∠(C1,C2,C5) = 125.7° (+0.1°), ∠(C3,C1,C4) = 128.6° (−0.8°), ∠(C5,C2,C6) = 108.5° (−0.3°), ∠(C1,C3,C7) = 118.0° (−0.5°), ∠(C2,C5,C9) = 117.0° (−1.2°), ∠(C1,C3,C11) = 125.5° (−0.1°), ∠(C2,C5,C13) = 107.0° (+0.5°), ∠(C3,C7,C9) = 125.9° (+1.7°), ∠(C5,C9,C7) = 117.6° (−0.6°), ∠(C3,C11,C15) = 133.1° (+2.5°), ∠(C5,C13,C14) = 108.7° (−0.4°), ∠(C11,C15,C16) = 127.2° (−1.9°).

an expensive restriction when the common origin (CO) method is employed. Adopting distributed-gauge methods, as here, reduces the importance of the choice of basis set, and with these methods a relatively modest basis set can be used to advantage, especially when combined with the CTOCD-PZ2 method.[18] On the basis of previous experience[7,14,15,17,18] the results presented in section 5 are likely to give good predictions of trends and useful semiquantitative conclusions.

3. Geometry

Complete geometrical optimizations were performed, with only one exception, at the Hartree−Fock level of accuracy, using the 6-31G** (6D) basis set and the default procedures and parameters of the Gaussian 94 system of programs.[21] This basis leads to molecular geometries close to the Hartree−Fock limit, though this may not always be in perfect agreement with the experimental data. To assess the quality of the geometrical parameters computed with this combination of method and basis set, a test calculation on the naphthalene molecule was performed. The test gives 1.358 and 1.420 Å for the shortest and longest C−C bond, respectively, to be compared with the X-ray values[22] of 1.364 and 1.421 Å, reinforcing our impression of the general reliability of the approach.

The results of the geometry optimizations are reported in Figures 1 and 2 for acepleiadylene and dipleiadiene, respectively, and those for pyracylene have already been given in ref 7. Planar C_{2v} structures were obtained for both neutral and 2$^-$ acepleiadylene, while for neutral dipleiadiene a nonplanar D_2 structure was found, stabilized by some 0.27 kcal mol^{-1} with respect to the planar D_{2h} geometry. These three structures were confirmed as minima on the potential energy hypersurface by calculating the second derivatives of the energy with respect to atomic positions: all vibrational modes were found to have real frequencies. For the dipleiadiene dianion a true minimum, characterized by $3N - 6 = 84$ real vibrational frequencies, was found for an unusual planar C_{2v} structure with the C_2 axis perpendicular to the central C1−C2 naphthalenic bond. This structure was found to be more stable by 4.06 kcal mol^{-1} than the planar D_{2h} configuration, the latter having two imaginary vibrational frequencies. This symmetry-breaking appears to be an artifact of the Hartree−Fock approximation, as it disappears when a method that implicitly includes electron correlation, such as the density functional theory (DFT), is adopted. Using Becke[23] and Lee, Yang, and Parr[24] recipes for local and nonlocal exchange and correlation functionals, respectively, we obtained a true minimum in D_{2h} symmetry for the structure of the dipleiadiene dianion. Figure 2 reports the optimized geometry at this latter level of approximation.

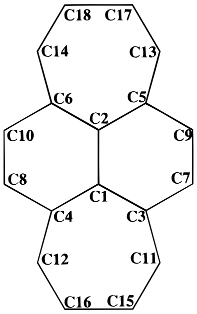

Figure 2. The diagram shows the scheme of atom numbering in dipleiadiene used in the present paper. Hydrogen atoms are given the same numbers as their carbon bonding partners. An SCF optimization for the neutral molecule in the 6-31G** basis set gives a D_2 geometry with bond lengths (in Å) and angles (experimental crystal structure in brackets,[26] averaged values): r(C1,C2) = 1.4387 (1.459), r(C1,C3) = 1.4463 (1.447), r(C3,C7) = 1.3650 (1.376), r(C7,C9) = 1.3915 (1.374), r(C3,C11) = 1.4785 (1.468), r(C11,C15) = 1.3244 (1.330), r(C15,C16) = 1.4529 (1.416), r(C7,H7) = 1.0748, r(C11,H11) = 1.0762, r(C15,H15) = 1.0767, ∠(C2,C1,C3) = 118.8°, ∠(C3,C1,C4) = 122.4°, ∠(C1,C3,C7) = 118.8°, ∠(C1,C3,C11) = 127.8°, ∠(C3,C7,C9) = 122.4°, ∠(C3,C11,C15) = 132.4°, ∠(C11,C15,C16) = 128.6°. The dihedral angles characterizing this helix-like structure are: ∠(C4,C1,C2,C3) = 180°, ∠(C3,C1,C2,C6) = −170.1°, ∠(C10,C6,C2,C1) = −6.2°, ∠(C14,C6,C2,C10) = +176.0°, ∠(C18,C14,C6,C2) = +17.3°, ∠(H10,C10,C6,C2) = −180.4°, ∠(H14,C14,C6,C18) = +178.7°, ∠(H18,C18,C14,C6) = +178.5°. The structure of the dianion optimized in the same basis set at DFT B3LYP level of theory is a planar (D_{2h}) geometry: r(C1,C2) = 1.4236, r(C1,C3) = 1.4965, r(C3,C7) = 1.4085, r(C7,C9) = 1.3775, r(C3,C11) = 1.4258, r(C11,C15) = 1.3957, r(C15,C16) = 1.3974, r(C7,H7) = 1.0923, r(C11,H11) = 1.0943, r(C15,H15) = 1.0941, ∠(C2,C1,C3) = 120.6°, ∠(C3,C1,C4) = 118.8°, ∠(C1,C3,C7) = 115.6°, ∠(C1,C3,C11) = 130.1°, ∠(C3,C7,C9) = 123.8°, ∠(C3,C11,C15) = 134.3°, ∠(C11,C15,C16) = 126.2°.

Direct comparison between the computed geometrical parameters for the isolated molecules and the experimental data available for neutral pyracylene[25] and dipleiadiene[26] in their crystalline phases is problematic for several well-known reasons. Nevertheless, reasonably good agreement is evident in the results reported in Figures 1 and 2. In particular, several chemical trends can be observed: e.g., (i) the central C1−C2 bond becomes much longer going from pyracylene (SCF 1.338, exptl 1.360 Å) to dipleiadiene (SCF 1.439, exptl 1.459 Å), and the calculated

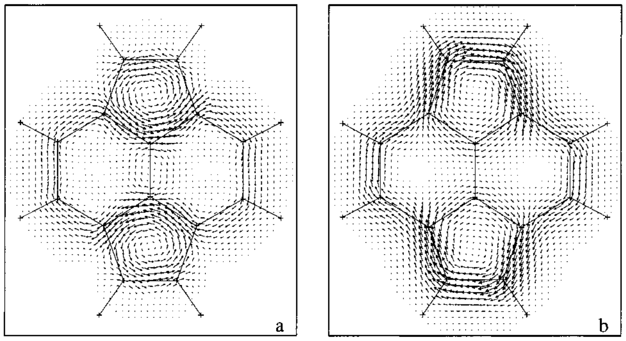

Figure 3. A comparison of induced current densities in pyracylene (a) and its dianion (b). Both diagrams show the direction and magnitude of the π-current at 1 bohr above the molecular plane induced by a perpendicular magnetic field of unit magnitude pointing out of the plane of the paper. Currents are calculated in the 6-31G** basis using the CTOCD-DZ2 approach at the optimal geometries for that basis. Maximum magnitude of the current is 0.10 au in (a) and 0.11 au in (b).

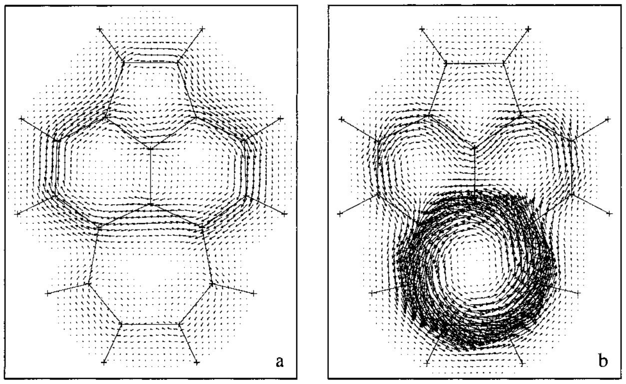

Figure 4. The same as in Figure 3 for acepleiadylene (a) and its dianion (b). Maximum magnitude of the current is 0.09 au in (a) and 0.32 au in (b).

value for acepleiadylene (SCF 1.385 Å) falls midway between them; (ii) the four bonds attached to the central C1−C2 unit are shorter in pyracylene (SCF 1.400, exptl 1.397 Å) than those in dipleiadiene (SCF 1.446, exptl 1.447 Å), whereas in acepleiadylene the bonds C1−C3 and C1−C4 are essentially the same length as in dipleiadiene, but the bonds C2−C5 and C2−C6 are slightly longer than in pyracylene; (iii) the odd-ring bonds attached to the naphthalene unit have an higher bond order in acepleiadylene than in pyracylene and dipleiadiene.

Experimental data are not available for the anionic forms, but it seems plausible that the theoretical geometries are of similar reliability to those obtained for the neutral species. Perhaps the most striking feature of the anion geometries is that the length of peripheral C−C bonds in pyracylene and dipleiadiene dianions is quite uniform, revealing strong conjugation of the corresponding π bonds. In the acepleiadylene dianion the picture is quite different, with a much clearer alternation of bonds around the perimeter.

4. Current Density Maps

Maps of the current density induced by an external, uniform magnetic field in the π-electron clouds of pyracylene, acepleiadylene, and dipleiadiene are presented in Figures 3, 4, and 5, respectively. Each figure shows magnitude and direction of the current flow computed for the neutral and charged species at a height of 1 bohr above the molecular plane, normalized to a perpendicular magnetic field of unit magnitude pointing out of the plane of the paper (so that diamagnetic circulation is clockwise). As noted earlier, the SCF/6-31G** model predicts dipleiadiene to be of D_2 rather than planar symmetry, and so Figure 5a treats a slice parallel to the average molecular plane and lacks mirror symmetries. In fact, the distortion from planarity is not very high. The arrow lengths in each plot are proportional to the current magnitude computed at the base of each arrow and all plots are on the same scale.

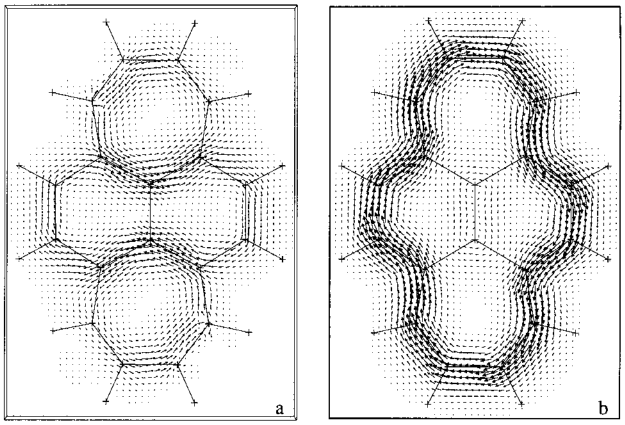

Figure 5. The same as in Figure 3 for dipleiadiene (a) and its dianion (b). For dipleiadiene in (a) current densities are at 1 bohr above the mean molecular plane. Maximum magnitude of the current is 0.11 au in (a) and 0.14 au in (b).

Considering first plots in Figures 3a to 5a, for the neutral molecules, one can observe in each case a diamagnetic ring current flowing above the central naphthalenic carbons, which is very similar to that calculated for the isolated naphthalene molecule.[20,27] For pyracylene (see also ref 7) and dipleiadiene, this diamagnetic circulation sits between two paramagnetic ring currents located on the odd-membered rings, whereas in acepleiadylene it is embedded in an extended diamagnetic current flowing above the outer circuit of carbon atoms. In the latter case the current does not flow with constant magnitude along the periphery, but is stronger on the acenaphthylene portion of the molecule and also shows local diamagnetic vortices on the bonds C11−C15 and C12−C16, which, therefore, exhibit some ethylenic character.

The regime of current found for all three molecules is consistent with the experimental and theoretical ^{13}C and proton NMR chemical shifts. As we will discuss in more detail in the next section, the paramagnetic ring currents located on the odd rings of pyracylene and dipleiadiene are sufficient to explain the observed upfield shift of the proton chemical shifts with respect to the naphthalenic protons, and the extended diamagnetic ring current in acepleiadylene accounts for the small downfield shift found for the acepleiadylene protons. Paramagnetic ring currents located on five-membered rings have also been proposed[28] and computed[14] in C_{60}, accounting for the experimental observation of downfield shifts in the proton NMR spectrum of some methanofullerenes and dihydrofulleroids.[29]

The set of plots in Figures 3b to 5b, for the dianionic species, shows a quite different pattern of circulation. The pyracylene and dipleiadiene dianions display an extended diamagnetic ring current flowing above the external carbon atoms and the diamagnetic ring current over the naphthalenic region disappears. In the ion of acepleiadylene a huge paramagnetic vortex is found on the seven-membered ring which includes also the naphthalenic portion of the molecule, with no significant dia- or paramagnetic ring current on the five-membered ring. As a result of the π-electron current displayed in Figure 4b, it turns out (see next section) that the acepleiadylene dianion is predicted

TABLE 1: Magnetic Properties of the Pyracylene Molecule, Computed at the Coupled Hartree−Fock Level with CTOCD (Continuous Transformations of Origin of the Current Density) Methods, Using the 6-31G Basis at the Optimal Geometry for That Basis[a]**

property	CTOCD-DZ2	CTOCD-PZ2	expt
ξ	−1128	−1388	
σ^{C_1}	57.8	50.3	53.1
σ^{C_3}	52.1	44.5	43.6
σ^{C_4}	68.2	61.0	60.7
$\sigma^{C_{13}}$	63.3	56.6	53.9
σ^{H_1}	22.8	24.7	24.8
σ^{H_4}	22.5	24.5	24.3

[a] Magnetizability in units of 10^{-30} J T^{-2} and absolute shieldings in ppm. Absolute experimental shieldings are derived from the shifts measured with respect to TMS[3,25] by assuming the usual value of 57.2 ppm for the absolute carbon shielding in benzene,[36] $\delta_C(C_6H_6) = 128.4$ and 23.57 ppm for the absolute proton shielding in benzene, the latter obtained from $\delta_H(CH_4) = 0.22$, $\delta_H(C_6H_6) = 7.26$ and $\sigma_H(CH_4) = 30.61$. The atom numbering is as in Figure 1 of ref 7.

to be a paramagnetic closed-shell molecule, one of few known examples (e.g., BH,[30] CH$^+$,[31], CrO_4^{2-}, MnO_4^{-}[32]).

Comparing now the two sets of figures it is clear that, apart from a few features on the central bridge, pyracylene and dipleiadiene share the same magnetic behavior, as they present the same kind of π-electron circulations in both neutral and charged species, and that acepleiadylene breaks the series. The latter fact is particularly intriguing. We believe that, in the light of the current density plots shown here, the explanation adopted in the earlier literature[1], based on the $4n/4n + 2$ Hückel rule, is not fully satisfactory for at least two reasons: (i) the main feature of the current flow of the three neutral molecules is a diamagnetic ring current flowing above the naphthalenic carbons; (ii) no paramagnetic currents flowing above the peripheral carbon atoms are found. We recall that the $4n/4n + 2$ Hückel rule is not a consequence of the particular approximations of the Hückel method, but derives solely from the symmetry and topology of [n]annulenes, and that therefore use of such a rule for polycyclic systems is an extension that may not always be justified.[33] The presence of the central C−C bond, even if fixed as a double bond in the Kekulé structure, is a strong perturbation of the [n]annulene picture. It is true that in the calculated maps for pyracylene and dipleiadiene dianions there is current flow above the peripheral carbons, which is also seen to some extent in the map for neutral acepleiadylene. There is, however, a strong correlation between bond lengths and current strength, which is not the simple, uniform ring current envisaged in a perturbed-annulene model. As noted in the previous section, alternation of bond lengths can be observed around the carbon perimeter for neutral pyracylene, dipleiadiene, and the dianion of acepleiadylene; this is connected with the presence of paramagnetic ring currents as shown in Figures 3a, 4b, and 5a. For neutral acepleiadylene the bond alternation is less evident, and the addition of two more π-electrons to pyracylene and dipleiadiene tends to equalize the bonds of the perimeter, with the formal double bonds of the main Kekulé structures of the neutrals becoming longer and single bonds shorter. This geometric evidence of increased electron delocalization around the perimeter is consistent with the ring current pattern shown in Figures 3b, 4a, and 5b.

TABLE 2: Magnetic Properties of the Acepleiadylene Molecule[a]

property	CTOCD-DZ2	CTOCD-PZ2	expt[b]	expt[c]
ξ	−1780	−2079		
σ^{C_1}	64.2	56.8	58.6	
σ^{C_2}	64.8	57.6	59.0	
σ^{C_3}	54.2	45.9	50.7	
σ^{C_5}	59.4	51.8	47.4	
σ^{C_7}	66.4	59.2	58.2	
σ^{C_9}	65.4	58.0	59.8	
$\sigma^{C_{11}}$	57.6	50.4	58.7	
$\sigma^{C_{13}}$	63.4	56.2	59.4	
$\sigma^{C_{15}}$	67.4	60.9	48.6	
σ^{H_7}	21.7	23.6	22.50	22.92
σ^{H_9}	21.3	23.2	22.88	22.51
$\sigma^{H_{11}}$	22.0	24.2	23.04	23.07
$\sigma^{H_{13}}$	21.6	23.6	23.00	23.00
$\sigma^{H_{15}}$	22.5	24.9	23.94	23.92

[a] The conventions, units, and basis are as in Table 1. Absolute experimental shieldings have been obtained from the shifts reported in ref 35 (see also ref 37), and ref 26. The atom numbering is as in Figure 1. The experimental assignments used are unchanged (but see text for discussion of how it might be modified). [b] See ref 35. [c] See ref 26.

TABLE 3: Magnetic Properties of the Dipleiadiene Molecule[a]

property	CTOCD-DZ2	CTOCD-PZ2	expt
ξ	−980	−1341	
σ^{C_1}	47.0	38.6	38.2
σ^{C_3}	54.1	46.4	44.9
σ^{C_7}	63.1	56.2	55.7
$\sigma^{C_{11}}$	55.7	48.8	45.0
$\sigma^{C_{15}}$	66.9	60.9	56.3
σ^{H_7}	23.3	25.4	25.52
$\sigma^{H_{11}}$	23.9	26.2	26.17
$\sigma^{H_{15}}$	24.1	26.4	26.39

[a] The conventions, units and basis are as in Table 1. Absolute experimental shieldings have been obtained from the shifts reported in ref 26. The atom numbering is as in Figure 2.

TABLE 4: Magnetic Properties of the Acepleiadylene Dianion Molecule[a]

property	CTOCD-DZ2	CTOCD-PZ2	expt
ξ	587	133	
σ^{C_1}	18.0	8.8	12.4
σ^{C_2}	59.0	52.4	39.5
σ^{C_3}	90.5	86.7	64.2
σ^{C_5}	65.9	59.3	53.5
σ^{C_7}	58.2	51.7	54.6
σ^{C_9}	97.4	93.2	87.0
$\sigma^{C_{11}}$	36.9	28.8	29.8
$\sigma^{C_{13}}$	101.8	98.2	98.8
$\sigma^{C_{15}}$	81.3	77.3	58.0
σ^{H_7}	28.0	30.6	31.16
σ^{H_9}	27.0	29.7	29.57
$\sigma^{H_{11}}$	29.8	32.1	32.88
$\sigma^{H_{13}}$	26.4	29.1	29.30
$\sigma^{H_{15}}$	30.5	33.8	32.88

[a] The conventions, units and basis are as in Table 1. Absolute experimental shieldings have been obtained from the shifts reported in ref 35. The atom numbering is as in Figure 1.

5. Magnetizabilities and Shielding Constants

Magnetizabilities and magnetic shielding constants, computed ab initio at the SCF plus CHF level of theory, in the 6-31G** basis set and using the CTOCD-DZ2 and -PZ2 methods, are reported in Tables 1−3 for the neutral molecules of pyracylene, acepleiadylene, and dipleiadiene, respectively. Table 4 collects the computed and measured magnetic properties of most interesting of the charged species, the acepleiadylene dianion.

An idea of the likely accuracy of the computed values is given by first recalling that the two methods adopted here would give the same results in the limit of a complete basis set calculation,[12,17] and then comparing the predictions relative to pyracylene with those previously obtained for the same molecule in a larger basis.[7] Inspection of Table 1 shows that the results of the two CTOCD methods are not as close as found previously,[7] but that the CTOCD-PZ2 approach gives the more stable results, which are also in better agreement with the experimental data. This matches our previous conclusions[7,18] about the superiority of CTOCD-PZ2 over CTOCD-DZ2 predictions.

Several points can be made about the magnetizabilities reported in the tables: (i) the CTOCD-PZ2 magnetizabilities of pyracylene and dipleiadiene are almost equal, namely, -1388 and -1341×10^{-30} J T^{-2}, respectively, and these values are higher than the naphthalene experimental data which range from -1507 to -1543×10^{-30} J T^{-2},[34] revealing the importance of the π-electronic paramagnetic ring current located in the odd rings (Figures 3a and 5a); (ii) acepleiadylene is significantly more diamagnetic than pyracylene, dipleiadiene, and naphthalene, and indeed in this case (Figure 4a), the π-electrons sustain a diamagnetic ring current located mainly in the acenaphthylene portion of the molecule, and paramagnetic ring currents are absent; (iii) the acepleiadylene dianion turns out to be a paramagnetic closed-shell molecule, with positive magnetizability predicted by both CTOCD methods, evidently as a result of the strong paramagnetic ring current in the heptagon (Figure 4b) overcoming the σ contributions. Unfortunately, there appear to be no experimental magnetizabilities for these molecules to compare with theory.

The physical origin of closed-shell paramagnetism can often be traced to low-energy, magnetic-dipole allowed transitions, and indeed the orbital energies in the 6-31G** basis show a small gap (~0.03 hartree) between the a_2 LUMO and b_2 LUMO + 1 levels of neutral acepleiadylene that would become the HOMO and LUMO levels of the dianion on addition of two electrons. This gap widens considerably in the SCF calculation on the anion itself. Precise ascription of the paramagnetism to particular $\pi \rightarrow \pi$ transition(s) would require explicit calculation of excited states, perhaps by an RPA (random-phase approximation) method.

However, experimental nuclear magnetic shielding constants are available for all three neutral molecules and for acepleiadylene dianion. These are collected with the computed values in the tables. As we have used without change the assignment for acepleiadylene made in the first experimental paper,[35] there is some disagreement for this system (Table 2). A modified assignment of the proton shifts has already been noted in the literature;[26] our calculations suggest exchanging C_3 with C_5, C_7 with C_9, permuting $C_{11} \rightarrow C_{13}$, $C_{13} \rightarrow C_{15}$, $C_{15} \rightarrow C_{11}$, and swapping the protons H_7 and H_9, the latter being the change proposed in ref 26. The overall level of agreement between the computed CTOCD-PZ2 values and experimental data is satisfying, particularly if the new assignment is accepted, considering the relatively modest size of the basis set. In particular, the comparison between computed proton shielding constants and experimental data is very close.

It is well known that proton shielding constants are sensitive to ring currents and this is fully confirmed by the results and current density maps presented here. The effect of the paramagnetic ring current located on the odd rings of pyracylene and dipleiadiene on the proton shielding constants is clearly documented by the values reported in Tables 1 and 3; upfield shifts can be observed for all protons, with the highest values for those attached to the five- and seven-membered rings. The strong paramagnetic current in acepleiadylene dianion has dramatic effects on the proton shielding constants which move so much upfield that, for example, the protons attached to the seven-membered ring appear at -2 ppm with respect to TMS (see Table 4). In contrast, the diamagnetic ring current in acepleiadylene pushes the proton shielding constants downfield, as shown in Table 2.

Although agreement of the chemical shifts is generally very good, there are some apparently much poorer comparisons between the calculated and experimental columns of Table 4; see, for instance, C2, C3, and C15 shieldings. Given the modest size of the basis set and neglect of electron correlation, both expected to be more troublesome for anionic than neutral systems, the problem may well be in the theoretical values. The general qualitative conclusions about the physical sign of the magnetism of the system are unaffected by these discrepancies.

6. Conclusions

We have presented ab initio π-electron first-order current density maps and second-order magnetic properties, calculated at the SCF/CHF level of approximation, for a series of neutral and dianionic fused tetracycles, which can be regarded, at least formally, as perturbed annulenes. Thanks to the use of a distributed-origin method, the computed magnetic properties are, despite the relatively modest basis set, in excellent agreement with the available experimental data, expecially the proton shielding constants. We conclude that the current density maps shown here can be taken as accurate indications of the π-electron flow induced by an external, uniform magnetic field in these and similar systems. The current maps do not support a perturbed-annulene model of these systems, but rather a bridged-naphthalene picture, where the naphthalene core plays a fundamental role in determining the current flow.

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