REGULAR ARTICLE

The ring current in cyclopropane

Patrick W. Fowler · Jon Baker · Mark Lillington

Abstract Mapping of induced current density using the coupled Hartree-Fock "ipsocentric" (CTOCD-*DZ*/6-31G**//RHF/6-31G**) method shows a ring current arising in the σ framework of cyclopropane that is intense, diatropic and annular, and hence is consistent with the numerous literature attributions of σ-aromaticity to this molecule. Localised orbital analysis shows that this current can be attributed to the set of three carbon–carbon bonds. In a similar analysis, the four carbon–carbon bonds of (planar constrained) cyclobutane are found to give rise to a central paratropic current. The maps are consistent with the view that cyclopropane is strongly σ-aromatic, cyclobutane is weakly σ-anti-aromatic, and the larger cycloalkane systems are essentially σ-non-aromatic.

1 Introduction

As a saturated system, cyclopropane may seem an unlikely candidate for an aromatic molecule, but there is a history of attribution of σ-aromaticity to this smallest of the cycloalkanes [1–6], though opinions on this point

P. W. Fowler (✉) · M. Lillington
Department of Chemistry,
University of Sheffield, Sheffield S3 7HF, UK
e-mail: P.W.Fowler@sheffield.ac.uk

J. Baker
Department of Chemistry, University of Arkansas,
Fayetteville, Arkansas 71701, USA

have not always been unanimous [7]. Two qualitative models of electronic structure have traditionally been used to account for the anomalous properties of cyclopropane. Walsh [8,9] proposed a description in terms of trigonal near-sp^2 CH$_2$ units, aligned perpendicular to the ring plane and each carrying a radial and a tangential hybrid. Coulson and Moffitt [10,11] described the strained carbon–carbon bonds of cyclopropane in terms of formation of bent bonds by overlap of local hybrids pointing away from the line of centres. Both descriptions are ultimately equivalent [11] and lead to useful predictions: the strain energy predicted on classical sp^3 bonding schemes is reduced; the doubly degenerate e' HOMO is seen to arise by overlap of tangential fragment orbitals; bending of the C–C bonds suggests an analogy with an in-plane π-system, invoked in the rationalisation of structures of hydrogen- and halogen-bonded complexes of cyclopropane [12]; enhanced s character leads to strengthening of the C–H bonds. This last effect is estimated [13] to contribute equally with σ-aromatic stabilisation to the low strain energy [1,2] of cyclopropane.

In parallel with the arguments based on energetics, the aromaticity of cyclopropane has been assessed using the magnetic criterion, according to which aromaticity is synonymous with ability to sustain a diatropic ring current induced by a perpendicular external magnetic field [14]. Cyclopropane shows exaltation of diamagnetisability [15,16], a large magnetisability anisotropy [17,18], and characteristic upfield ^{1}H NMR chemical shifts [19]. The cyclopropane ring is a source of intramolecular shielding effects [20]. Negative NICS(0) and NICS(1) [14] indices for cyclopropane (-42.8 and -8.9 ppm, respectively, [4]) are also interpreted as evidence for a ring current [4,13]. All of these data have

been interpreted as evidence for some form of ring current, but with some different opinions about its origin (see, e.g., footnote 29 in [2]). However, some authors have also asserted that cyclopropane does not sustain a ring current at all [7].

From the perspective of computational chemistry, a straightforward solution suggests itself: calculate the current density induced by an external magnetic field, and check to see if there is a global circulation, with the appropriate sense, strength and spatial distribution to merit its description as a ring current. An efficient and accurate approach to calculation and mapping of induced currents is available in the form of the ipsocentric method [21–23], which will be used here. A specific advantage of this method is that it allows partition of the total current into contributions from occupied orbitals (canonical [23], or localised [24]) and so can be used to provide a link to more qualitative theories. A discussion of the accuracy of the specific combination of method and basis set used here is given in [25], and comparisons of maps made with ipsocentric and allocentric variants of the method are made in [26]. Such variants differ in their representation of current density in regions (exponentially) close to the nuclei, but are qualitatively indistinguishable in the bonding regions that are of interest in the present paper.

2 Method

Current-density maps were calculated for cyclopropane and, for comparison, for the planar-constrained structures of cyclobutane and cyclopentane, using the coupled Hartree-Fock CTOCD-*DZ* (ipsocentric) approach. Molecular geometries for the C_nH_{2n} systems were optimised in D_{nh} symmetry at the RHF/6-31G** level, yielding a true minimum for cyclopropane, but for cyclobutane and cyclopentane stationary points with one (b_{2u}, $142i$ cm^{-1}) and two (e_2'', $215i$ cm^{-1}) imaginary-frequency modes, respectively. Geometry optimisation at this level shows a clear difference between cyclopropane—with short C–C bonds (1.497 Å), short C–H bonds (1.076 Å) and open HCH angles (114°)—and the larger systems—with longer C–C bonds (1.549 Å in C_4H_8, 1.546 Å in C_5H_{10}), longer C–H bonds (1.084 Å in both cases) and near-tetrahedral HCH angles (108° in C_4H_8, 106° in C_5H_{10}).

Calculations of the response to an external magnetic field directed along the C_n axis were carried out with the same 6–31G** basis, which has been shown in many studies to give well converged maps when used in conjunction with ipsocentric distributions of origin of vector potential [23,25]. Maps were constructed for current

density in the plane of the carbon nuclei and at a height 1 a_0 from this plane, applying the usual plotting conventions, where contours represent the magnitude of $\mathbf{j}^{(1)}$ in the plotting plane, and arrows its in-plane projection, where $\mathbf{j}^{(1)}$ is the first derivative of induced current density with respect to the applied field. A useful measure is j_{max}, the maximum magnitude in the plotting plane, which can be compared with the corresponding quantity for the archetypal benzene π ring current. (Using the present basis and level of theory, j_{max} for benzene is 0.080 a.u. in the 1 a_0 plane.) In addition to maps of the total induced current density (the response of *all* electrons to the magnetic field), maps of orbital contributions, individually and in combination, were also computed. For delocalised π systems, canonical orbital contributions have proved especially informative [27]. In the present case, an analysis in terms of localised orbitals is expected to be more appropriate, and this was made using the Pipek–Mezey criterion [28].

3 Results and discussion

Figure 1 shows the current density induced in cyclopropane by a perpendicular external magnetic field, plotted in the plane of the carbon nuclei. The main feature of the map is plain to see: a strong ($j_{max} = 0.121$ a.u.) diatropic circulation around the outside of the ring, one that reaches maximal intensity outside the line of carbon centres. Closer inspection also reveals a weaker paratropic
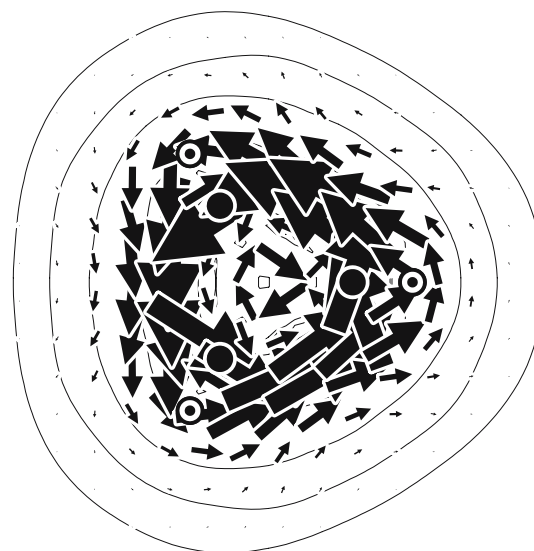

Fig. 1 Current density map for cyclopropane. The current induced in the plane of the carbon nuclei by a perpendicular external magnetic field is calculated at the (CTOCD-*DZ*/6-31G**//RHF/6-31G**) level and plotted in the plane of the carbon nuclei using the usual conventions (see the text)

Fig. 2 Schematic illustration of the transition from cyclic arrays of localised diatropic currents to concentric global currents as the inter-unit separation decreases

counter-circulation at the ring centre, and closed loops of circulation (vortices) in the core/C–H bond regions. This pattern is consistent with expectations based on the qualitative models of the electronic structure of cyclopropane. As Fig. 2 illustrates in a rough and schematic way, local diatropic current loops of cyclically arranged localised C–C bonds in close enough proximity can sum to concentric global diatropic and paratropic circulations, and in fact such paratropic central counter-rotation features are seen in maps of currents induced in the σ-framework of the π aromatic-hydrocarbons [29]. What is unusual about the map in Fig. 1 is the dominance of the diatropic current, its strength and continuity.

Inspection of maps of localised-orbital contributions (Fig. 3) confirms that the main diatropic current and its concomitant inner counter-circulation are both directly attributable to the summed contributions of the three C–C σ bonds. The map for an individual localised C–C bond orbital (Fig. 3a) gives an indication of how the overall pattern comes about: although the current loops in this map have the closed topology expected of any two-centre σ bond, the flow-lines adopt the banana shape consistent with a bent bond, bulging out from the line of centres to follow the overlap of the tangential atomic orbitals [11] and hence give a somewhat stronger current on the outside of the molecule. In the confined space of the three-membered ring, the superimposed inner arms of the bond contributions largely

cancel (Fig. 3b), to produce the pattern of a weak inner paratropic and strong outer diatropic current that is seen in the total map (Fig. 1).

The global current of cyclopropane therefore has the hallmarks of a (σ) ring current. It is diatropic, runs continuously around the ring of nuclei and is essentially annular in form. (Note that the counter-current on the central region is weaker than the main current, by a factor of at least 2.)

The localised-orbital picture, in this case, gives a much clearer account of the current than does the canonical-MO delocalised picture. A map of the contribution of the four HOMO electrons to the induced current density (Fig. 4a) shows a current that is strong and diatropic on the perimeter and also strong and paratropic at the molecular centre; only when contributions from all the other canonical valence σ orbitals (Fig. 4b) are added in, do we recover the annular pattern with decreased intensity at the molecular centre. (The sum of the maps in Fig. 4a and b is, by definition, equal to the map in Fig. 1.)

Unlike the classic π ring current of conventional aromatic systems, the current in cyclopropane is maximal in-plane, as σ symmetry dictates, and in fact the calculated j_{max} falls from 0.121 a.u. in the plane of the nuclei to 0.079 a.u. at a height of 1 a_0 when calculated from the sum of C–C-bond orbitals. There is no evidence of a π contribution to the ring current of cyclopropane: a map of the partial current density in the 1 a_0 plane arising from the three occupied canonical molecular orbitals of π symmetry ($a_2'' + e''$) (Fig. 5a), shows only localised current loops. The map derived from the sum of the six localised C–H bond orbitals ($a_1' + e' + a_2'' + e''$) (Fig. 5b) which includes both σ and π contributions from three orbitals also shows essentially localised current loops.

It has been proposed that the σ-aromaticity of cyclopropane places the molecule in an alternating

Fig. 3 Current density map for **a** a single localised C–C bond and **b** the set of three localised C–C bonds of cyclopropane, calculated at the (CTOCD-*DZ*/6-31G**//RHF/6-31G**) level with Pipek-Mezey localisation [28] and plotted in the plane of the carbon nuclei using the standard plotting conventions (see the text)
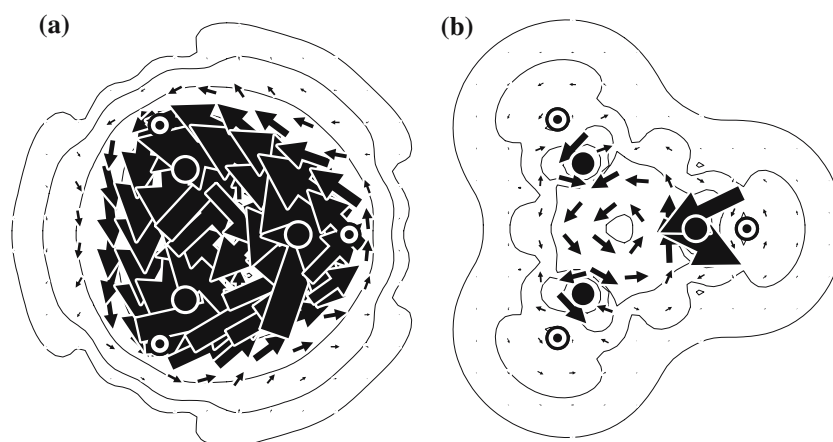
(a)

(b)

(a)   **(b)**
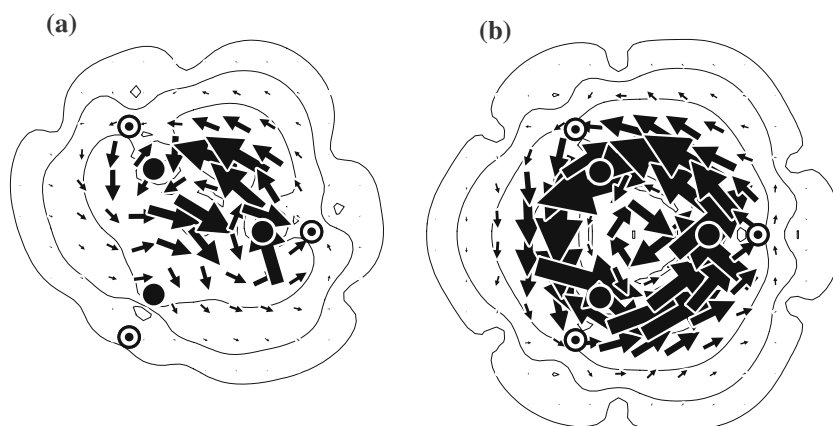
Fig. 4 Current density map for **a** the e′ HOMO and **b** the remaining ten occupied orbitals of cyclopropane, calculated at the (CTOCD-*DZ*/6-31G**//RHF/6-31G**) level with Pipek-Mezey localisation [28] and plotted in the plane of the carbon nuclei

using the standard plotting conventions (see the text). Apparent symmetry-breaking in **b** is purely an artefact of mismatch between the triangular molecule and the square plotting grid, and would disappear on use of a finer grid

Fig. 5 Current density maps for contributions of **a** sum of occupied π orbitals and **b** the sum of localised C–H bonds of the cyclopropane molecule, calculated at the (CTOCD-*DZ*/6-31G**//RHF/ 6-31G**) level with Pipek-Mezey localisation [28] and plotted at a height of 1 a_0 from plane of the carbon nuclei using the standard plotting conventions (see the text)

(a)   **(b)**
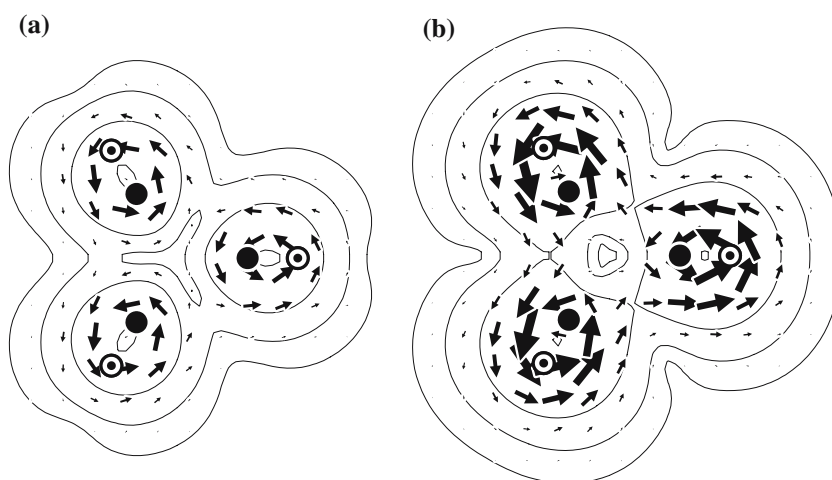
sequence of cycloalkane C_nH_{2n} aromatics and anti-aromatics. In particular, in planar conformations, cyclobutane/cyclopentane are found to have small positive/negative NICS(0) values [4]. For C_4H_8, the calculated NICS(0) is +2.6 ppm, for C_5H_{10} it is −5.2 ppm; these values change to NICS(1) = +1.1 and −2.8 ppm, respectively, evaluated at a height of 1 Å. Current-density mapping for these systems is complicated by the existence of intense but local circulations in the neighbourhoods of the tetrahedral carbon centres. Raising the plotting plane to 1 a_0 removes these local features and reveals any global circulations more clearly. Figure 6 compares the maps of current density produced from the set of C–C bond localised orbitals, for cyclopropane, (planar) cyclobutane and (planar) cyclopentane, respectively.

In cyclopropane, the C–C-bond contribution (Fig. 6a) shows an essentially diatropic circulation, with a weak

paratropic central vortex. In cyclobutane, the C–C-bond contribution (Fig. 6b) has reversed intensities, with a strong central paratropic current and a weaker outer diatropic part which is starting to break up into local and σ-bond circulations. For cyclopentane (Fig. 6c), the inner and outer circulations are of essentially equal intensity and now the map has the appearance of a superposition of five local σ-bond circulations consistent with the lack of angle strain in this structure.

The opposed senses of the main current in cyclopropane and cyclobutane are consistent with the signs of the NICS(0) and NICS(1) values, the much smaller integrated central shielding values for cyclobutane indicating a near complete cancellation of effects within the more complicated pattern of current density. A test calculation on the D_{2d}-symmetric fully optimised structure of cyclobutane shows no major change in the current density map.

Fig. 6 Comparison of current density maps for localised C–C orbital frameworks of **a** cyclopropane, **b** cyclobutane, **c** cyclopentane plotted at a height of 1 a_0 from the planar (or planarised) carbon framework at the (CTOCD-*DZ*/6-31G**//RHF/6-31G**) level with Pipek-Mezey localisation [28] and plotted using the standard plotting conventions (see the text)
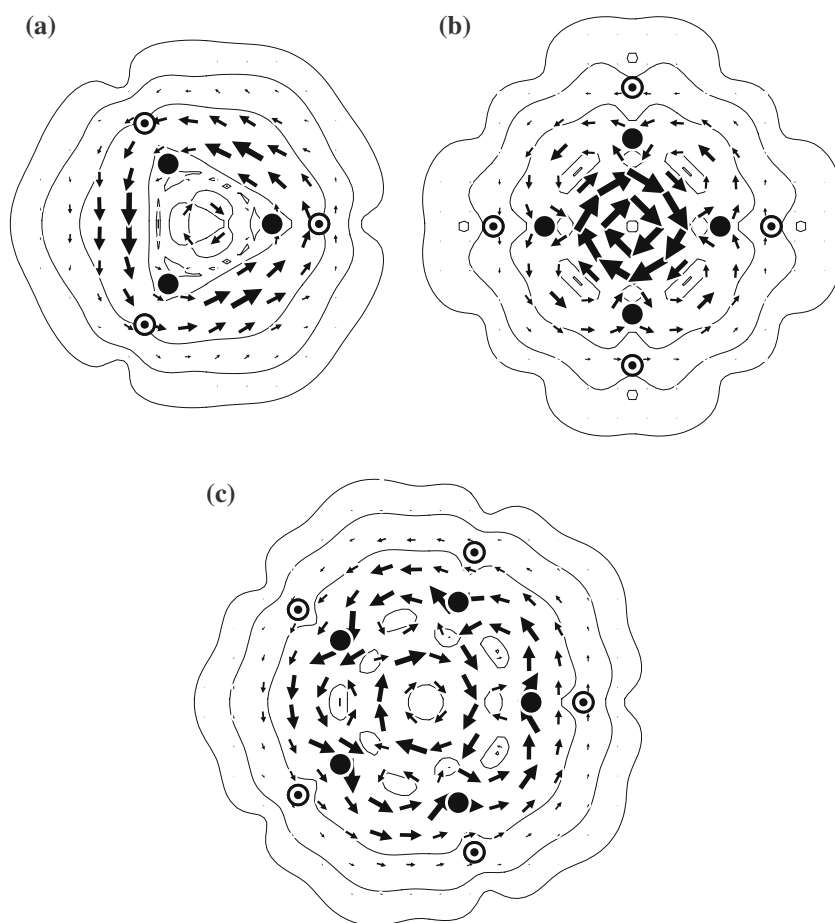
In summary, the maps are consistent with the assignment of an exceptional status of cyclopropane as strongly σ-aromatic and an attribution of weakly σ-antiaromatic character to cyclobutane, with non-aromatic character prevailing for cyclopentane and (presumably) the larger systems.

References

1. Dewar MJS, McKee ML (1980) Pure Appl Chem 52:1431
2. Dewar MJS (1984) J Am Chem Soc 106:669
3. Minkin VI, Glukhovtsev MN, Simkin BY (1994) Aromaticity and antiaromaticity. Wiley, New York
4. Moran D, Manoharan M, Heine T, Schleyer PvR (2003) Org Let 5:23
5. Cremer D, Kraka E (1985) J Am Chem Soc 107:3800
6. Cremer D, Gauss J (1986) J Am Chem Soc 108:7467
7. Lazzeretti P, Rossi E, Zanasi R (1983) J Am Chem Soc 105:12
8. Walsh AD (1947) Nature 159:712
9. Walsh AD (1949) Trans Faraday Soc 45:79
10. Coulson CA, Moffitt WE (1947) J Chem Phys 151
11. Coulson CA, Moffitt WE (1948) Phil Mag 40:1
12. Legon AC (1998) Chem Eur J 4:1890
13. Exner K, Schleyer PvR (2001) J Phys Chem A 105:3407
14. Schleyer PvR, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes NJR (1996) J Am Chem Soc 118:6317
15. Lacher JR, Pollack JW, Park JD (1951) J Chem Phys 20:1047
16. Dauben HJ, Wilson JD, Laity JL (1971) Snyder JP (ed) Non-benzenoid aromatics, vol 2. Academic, New York
17. Aldrich PD, Kukolich SG, Campbell EJ, Read WG (1983) J Am Chem Soc 103:5569
18. Lukins PB, Laver DR, Buckingham AD, Ritchie GLD (1985) J Phys Chem 89:1309
19. Burke JJ, Lauterbur PC (1964) J Am Chem Soc 86:1870
20. Sauers RR (1998) Tetrahedron 54:337
21. Keith TA, Bader RFW (1993) J Chem Phys 99:3669
22. Coriani S, Lazzeretti P, Malagoli M, Zanasi R (1994) Theor Chim Acta 89:181
23. Steiner E, Fowler PW (2001) J Phys Chem A 105:9553
24. Steiner E, Fowler PW, Havenith RWA (2002) J Phys Chem A 106:7048
25. Steiner E, Fowler PW (2001) Chem Comm 2220
26. Fowler PW, Steiner E, Zanasi R, Cadioli B (1999) Mol Phys 96:1099
27. Soncini A, Fowler PW (2004) Chem Phys Lett 396:174
28. Pipek J, Mezey PG (1989) J Chem Phys 90:4916
29. Steiner E, Fowler PW (1996) Int J Quant Chem 60:609