orthogonal to columns of **B**. In particular, **P** satisfies the equation

$$\mathbf{PB} = \mathbf{O} \tag{A2}$$

Let **U** be a unitary matrix which diagonalizes the Hermitian matrix **PSP** where S is defined in eq 12.

$$(\mathbf{PSP})\mathbf{U} = \mathbf{U}\lambda \tag{A3}$$

Let **Q** be a rectangular matrix with elements

$$Q_{ij} = U_{ij}\lambda_{jj}^{-1/2} \tag{A4}$$

where columns of **Q** are simply omitted if the corresponding eigenvalue λ_{jj} is below some tolerance, e.g., $\lambda_{jj} > 10^{-6}$. It follows that **Q** satisfies eq 14 and 15.

Registry No. NH_4, 14798-03-9; ND_4, 83682-14-8; Na, 7440-23-5.

Nuclear Magnetic Shielding in Cyclopropane and Cyclopropenyl Cation

P. Lazzeretti,* E. Rossi, and R. Zanasi

Contribution from the Istituto di Chimica Organica e Centro di Calcolo Elettronico dell'Università di Modena, I-41100 Modena, Italy. *Received March 8, 1982*

Abstract: The magnetic shielding tensors of the proton and carbon nuclei have been rationalized by coupled Hartree–Fock theoretical studies. Orbital contributions are systematically analyzed and electron current density maps are shown, indicating the typical paramagnetic axial vortex of cyclic molecules. Satisfactory agreement with experimental carbon chemical shift data has been found for cyclopropane. The results show that any ring current hypothesis in either of these molecules is misleading.

Introduction

In previous papers we attempted to rationalize the characteristic magnetic properties of cyclopropenyl cation[1] and benzene[2,3] by visualizing the stationary flow of electron density induced by a uniform magnetic field.

The main features emerging from these studies[1-3] are the following. (i) As a mere consequence of symmetry, all planar cyclic molecules are endowed with a paramagnetic axial vortex[4,5] due to σ electrons flowing around the highest symmetry axis. (ii) In aromatic rings the intensity of such a vortex is high enough to overcome the diamagnetic "ring current" of π electrons. (iii) Quasi-toroidal vortices are found near each of the skeletal carbon atoms, perpendicular to the molecular plane. (iv) In benzene[2,3] the electron circulation in the neighborhood of each carbon deviates significantly from the shape of a perfect geometrical torus in such a way that the perpendicular component of carbon magnetic shielding is unusually upfield ($\sigma_{33}(\mathrm{C}) \approx 190$ ppm in benzene[2].

There is recent experimental evidence[6] that nonaromatic rings, such as cyclopropane, are also characterized by an anomalous high-field value of $\sigma_{33}(\mathrm{C})$. This paper sets out to explain this behavior in cyclopropenyl cation and cyclopropane through an analysis of theoretical nuclear shielding and electron density maps.

Results and Discussion

The theoretical approach and the computational scheme employed in this study have been previously outlined in detail.[1-3] The Gaussian basis sets used in the calculation for the ion are the same as in a previous study,[1] e.g., (11s7p2d/5s1p) contracted to [6s5p$_x$5p$_y$7p$_z$1d/3s1p]. The same primitive basis is used for cyclopropane, contracted to [6s5p1d/3s1p] (117 contracted functions). The geometry assumed in the calculation is that adopted in ref 1. For cyclopropane we retained the geometry of ref 10, as specified in Table I here.

Since the polarization functions have exponents optimized for the magnetic properties, our self-consistent field (SCF) energy for C_3H_6, which is −117.089055 hartree, is ≈5 mhartree higher than the best previous value[7], −117.0945. However, a number of results indicate the near-Hartree–Fock (HF) character of our wave function for cyclopropane. In particular, for the Arrighini–Maestro–Moccia (AMM) tensors,[8] denoting the components parallel to the C_3 axis by $\parallel$, we found $(P_\parallel,P_\parallel) = 22.893$; $(P_\perp,P_\perp) = 22.601$, i.e., ≈95% of the exact value of 24. Adopting a slightly different definition with respect to our previous paper[9] for the magnetic perturbation, e.g., explicitly including the imaginary unit i, we introduce

$$h^{H_\alpha} = -(i/2c)\epsilon_{\alpha\beta\gamma}r_\beta\nabla_\gamma \tag{1}$$

$$h^{(dxH)_\alpha} = -(i/2c)\nabla_\gamma \tag{2}$$

$$h^{\mu_\alpha}(N) = -(i/c)|\mathrm{r} - \mathbf{R}_\mathrm{N}|^{-3}\epsilon_{\alpha\beta\gamma}(r - R_\mathrm{N})_\beta\nabla_\gamma \tag{3}$$

possessing representations on the LCAO basis

$$\mathbf{H}^{H_\alpha} \tag{1'}$$

$$\mathbf{H}^{(dxH)_\alpha} \tag{2'}$$

$$\mathbf{H}^{\mu_\alpha}(N) \equiv \mathbf{H}^{\mu_\alpha} \tag{3'}$$

The (P,P) tensor is defined as

$$(P_\alpha,P_\beta) = -8c^2\mathrm{Tr}\mathbf{H}^{(dxH)_\alpha}\mathbf{R}^{(dxH)_\beta} \tag{4}$$

and satisfies the sum rule (5), valid for exact HF functions

$$(P_\alpha,P_\beta) = N\delta_{\alpha\beta} \tag{5}$$

Owing to the form of the exact coupled Hartree–Fock (CHF) perturbed orbitals, it can be easily shown that (5) is a direct

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Table I. Quantities Necessary for Evaluating the Shielding Tensor in Any Gauge (in au)[a]

$\langle x/r^3\rangle_C$	$(L_z/r^3,P_y)_C$	$(L_y/r^3,P_z)_C$	$\langle x/r^3\rangle_H$	$(L_z/r^3,P_y)_H$	$(L_y/r^3,P_z)_H$	$\langle z/r^3\rangle_H$	$(L_y/r^3,P_x)_H$	$(L_x/r^3,P_y)_H$
−1.17388	−1.05208	0.99786	−1.44430	−1.35062	1.34773	−1.61447	−1.50214	1.52261
−1.35496	−0.95626	1.12047	−2.01819	−1.89138	1.88426	0.0	0.0	0.0

[a] Coordinates of the nuclei (the molecules lie in the *xy* plane with the *z* axis as threefold axis. C≡(1.651825, 0, 0), H≡(2.732315, 0, 1.735879) in cyclopropane, from ref 10; C≡(1.502354, 0, 0), H≡(3.571604, 0, 0) in cyclopropenyl cation, from ref 1.

Table II. Magnetic Susceptibility in Cyclopropane in ppm au[a]

$\chi_\perp{}^\alpha$	$\chi_\perp{}^p$	$\chi_\perp$	$\chi_\parallel{}^d$	$\chi_\parallel{}^p$	$\chi_\parallel$	$\chi_{av}{}^d$	$\chi_{av}{}^p$	χ_{av}	$\Delta\chi$
−1254.70	781.34	−473.36	−1669.08	1030.44	−638.64	−1392.83	864.37	−528.46	−165.28

[a] The conversion factor to irrational cgs emu is 8.92394×10^{-2} cm^3 mol^{-1}. Experimental values for the average susceptibility: −439 ± 9 (gas, ref 13); −426 (liquid, ref 14); −447 (liquid, ref 15). Experimental anisotropy from the Cotton–Mouton molar constant, $\Delta\chi = \chi_\parallel - \chi_\perp = -216$; estimated anisotropy in ref 19 and 20: −112.

Table III. Orbital Contributions to H Nuclear Magnetic Shielding in $C_3H_3^+$ in ppm[a]

orbital	σ_{xx}	σ_{yy}	σ_{zz}
$1a_1'$	0.16	−0.07	−0.38
$1e_x'$	0.27	−0.59	−2.17
$1e_y'$	0.09	−0.02	0.54
$2a_1'$	1.80	−0.12	0.07
$2e_x'$	13.21	4.79	4.14
$2e_y'$	2.88	−0.36	0.86
$3a_1'$	7.92	7.16	6.15
$3e_x'$	4.43	6.11	3.54
$3e_y'$	−13.28	0.15	5.19
$1a_2''$ (π)	1.85	2.94	−0.73
total	19.33	19.98	17.23

[a] The origin of the gauge is assumed in the center of mass.

Table IV. Orbital Contributions to H Nuclear Magnetic Shielding in C_3H_6 in ppm[a]

orbital	σ_{xx}	σ_{yy}	σ_{zz}
$1a_1'$	0.13	−0.38	−0.01
$1e_x'$	0.05	−1.01	−0.89
$1e_y'$	0.22	0.25	0.62
$2a_1'$	2.10	0.20	1.16
$2e_x'$	6.60	2.99	8.41
$2e_y'$	2.52	0.69	1.82
$1a_2''$	3.84	4.40	4.02
$3a_1'$	4.29	3.03	1.27
$1e_x''$	−2.61	−1.63	−0.80
$1e_y''$	8.83	13.41	11.35
$3e_x'$	2.79	1.38	0.77
$3e_y'$	3.83	0.12	8.08
total	32.60	23.46	35.78

[a] The origin of the gauge is assumed in the center of mass, c.m.

Table V. Orbital Contribution to Carbon Magnetic Shielding in $C_3H_3^+$ in ppm

orbital	σ_{xx}	σ_{yy}	σ_{zz}
$1a_1'$	67.02	66.92	67.28
$1e_x'$	134.01	134.29	134.27
$1e_y'$	0.47	−0.03	1.82
$2a_1'$	14.05	−32.26	−25.86
$2e_x'$	14.71	40.81	53.89
$2e_y'$	20.08	2.48	−5.68
$3a_1'$	3.70	−115.15	−57.46
$3e_x'$	−5.19	−191.51	−18.30
$3e_y'$	−286.23	7.18	54.68
$1a_2''$ (π)	−11.31	−35.52	7.75
total	−48.70	−122.80	212.36

Table VI. Orbital Contributions to Carbon Magnetic Shielding in C_3H_6 in ppm

orbital	σ_{xx}	σ_{yy}	σ_{zz}
$1a_1'$	67.41	67.26	67.26
$1e_x'$	134.18	134.06	134.20
$1e_y'$	0.72	0.57	1.52
$2a_1'$	13.35	−10.23	−9.11
$2e_x'$	16.54	61.71	50.81
$2e_y'$	6.46	2.67	−3.29
$1a_2''$	−4.06	−46.44	6.78
$3a_1'$	8.34	24.57	−88.15
$1e_x''$	−5.82	−1.27	−1.30
$1e_y''$	−35.84	−73.52	6.18
$3e_x'$	4.38	16.74	4.33
$3e_y'$	−33.33	10.39	64.08
total	172.32	186.53	233.29

consequence of the basic commutation rule $i[P_\alpha,r_\alpha] = 3$. It can also be proven that (5) is nothing but a restatement of the Thomas–Reiche–Kuhn sum rule[11] written in dipole velocity formalism. Other useful quantities such as

$$(L_\alpha/r^3,P_\gamma)_N = -4c^2\mathrm{Tr}\mathbf{H}^{\mu_\alpha}(N)\mathbf{R}^{(d\times H)_\gamma} \quad (6)$$

are reported in Table I. These must obey the sum rules

$$(L_\alpha/r^3,P_\gamma)_N = \langle r_\beta/r^3\rangle_N = -(L_\gamma/r^3,P_\alpha)_N \quad (7)$$

It can be shown that (7), valid for exact CHF functions, is directly related to the commutation rule $i[r^{-3}L_\alpha,r_\beta] = r^{-3}\epsilon_{\alpha\beta\gamma}r_\gamma$. In addition, (5) and (7) can be obtained from a hypervirial theorem, as an immediate consequence of Epstein's sufficient condition for gauge invariance.[12]

The results in Table I indicate that (7) is satisfactorily fulfilled for both the proton and the carbon. The theoretical susceptibility obtained in this way for the cyclopropenyl cation has been already reported.[1]

Data relative to cyclopropane are displayed in Table II. A significant difference emerges between the theoretical average susceptibility and corresponding experimental results,[13-20] as well as other theoretical predictions.[16] The origin of this pattern is unclear to us. Either a coupled self-consistent-field (CSCF) wave function expanded over a basis set of higher quality might yield a sensibly different result—which, however, does not seem sufficient to explain the discrepancy, owing to the near HF character of our calculation, as shown by the sum rules (5), (7)—or the

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Table VII. Inner Orbital Contributions to Carbon Shielding in Benzene in ppm[a]

orbital	σ_{xx}	σ_{yy}	σ_{zz}
$1a_{1g}$	34.44	33.52	33.84
$1e_{1u}$-x	67.15	67.05	67.42
$1e_{1u}$-y	1.12	−0.01	0.52
$1e_{2g}$-1	67.46	67.21	67.57
$1e_{2g}$-2	0.86	−0.12	1.50
$1b_{1u}$	33.85	33.54	34.82

[a] The source of CHF wave function is ref 2.

experimental data need some revision. As a matter of fact, it is well known that measurements on small strained cyclic molecules are difficult.[16]

The orbital contributions to the proton and carbon nuclear shielding tensors are reported in Tables III to VI. These should be defined

$$\sigma^{p}{}_{\alpha\beta,i} = [\langle \phi_i^{(0)} | h^{\mu_\alpha} \phi_i^{H_\beta} \rangle + \text{C.C.}] + [\langle \phi_i^{(0)} | h^{H_\beta} \phi_i^{\mu_\alpha} \rangle + \text{C.C.}] \tag{8}$$

$$\sigma^{d}{}_{\alpha\beta,i} = 2\langle \phi_i | h^{\mu_\alpha H_\beta} \phi_i^{(0)} \rangle \tag{9}$$

$$\sum_i^{\text{occ}} \sigma^{p}{}_{\alpha\beta,i} = \sigma^{p}{}_{\alpha\beta} = \text{Tr}\mathbf{H}^{\mu_\alpha}\mathbf{R}^{H_\beta} + \text{Tr}\mathbf{R}^{\mu_\alpha}\mathbf{H}^{H_\beta} = 2\text{Tr}\mathbf{H}^{\mu_\alpha}\mathbf{R}^{H_\beta} \tag{10}$$

in the notation of previous papers.[8,9] The interchange theorem embodied in (10) is currently exploited in computing total CSCF nuclear magnetic shielding, but an analogous theorem for the orbital contributions

$$\langle \phi_i^{(0)} | h^{\mu_\alpha} \phi_i^{H_\beta} \rangle + \text{C.C.} = \langle \phi_i^{(0)} | h^{H_\beta} \phi_i^{\mu_\alpha} \rangle + \text{C.C.} \tag{11}$$

is only valid in the limit of complete basis sets, e.g., for exact CHF orbitals[17] and the simplified form of (8)

$$\sigma^{p}{}_{\alpha\beta,i} = 2\ [\langle \phi_i^{(0)} | h^{\mu_\alpha} \phi_i^{H_\beta} \rangle + \text{C.C.}] \tag{8'}$$

is therefore ambiguous to a certain extent when limited basis sets are employed.[17] Since, however, use of (8) would imply other expensive CSCF calculations to evaluate the perturbed orbitals ϕ^{μ}, the practical definition (8′), which has been customarily used in previous searches,[2,3,17] has been retained here also, relying on the good quality of our basis set.

The orbital contributions to the diagonal components of the proton shielding are shown in Tables III and IV, respectively, for cyclopropenylcation and cyclopropane. It is interesting to see that, in the ion, the largest deshielding effect (−13.28 ppm for σ_{xx}) is caused by electron circulations induced in the $3e'_2$ orbital, whereas the diamagnetic flow of $1a''_2$ (π) electrons contributes a rather small downfield shift, −0.73 ppm, to σ_{zz}; this leads to criticism of the ring current model.[1]

Also, in the case of cyclopropane, the calculations reveal that the proton σ_{yy} is somewhat deshielded with respect to σ_{xx} and σ_{zz}, which in turn, are the same as, or slightly higher than, those of other aliphatic protons (the typical value in methane is σ_{av} = 30.72).[1]

The results displayed in Table IV clearly demonstrate that any hypothesis of "ring current" in cyclopropane[18,19] is misleading: the $1a''_2$ orbital contribution to σ_{zz} is positive and small deshieldings are provided by the e'_x, e''_x orbitals. The maps of electron current density in Figure 1 confirm these points unequivocally.

It can be seen by inspection of Tables V and VI that the largest contributions to carbon shielding are provided by electronic circulations induced in the inner molecular orbitals $1a'_1$ and, expecially, $1e'_x$. This is the most interesting feature peculiar to all planar cyclic molecules. The isotropic contribution provided by $1e'_x$ orbitals amounts to ≈135 ppm for both the molecules (i.e., it is transferable), to be matched with the same value determined in benzene as a sum of $1e_{1u}$ − 1, $1e_{2g}$ − 1. The contribution of $1a'_1$, ≈67 ppm, in the three-membered rings corresponds in benzene to the sum of the $1a_{1g}$ and $1b_{1u}$ contributions. Inspection of Table VII, relative to the first occupied orbitals in benzene,[2,3] seems to suggest that in this molecule as well, the upfield σ_{zz} or carbon is due to inner orbitals of similar symmetry. This seems to suggest that a unified model for the comprehension of carbon shielding in all planar cyclic molecules, aromatic and saturated molecules as well, is probably possible. Of course, our analysis is only a first step and other investigations are necessary to confirm these findings. On the other hand, the in-plane xx and yy components are sensibly smaller—they are actually negative in the

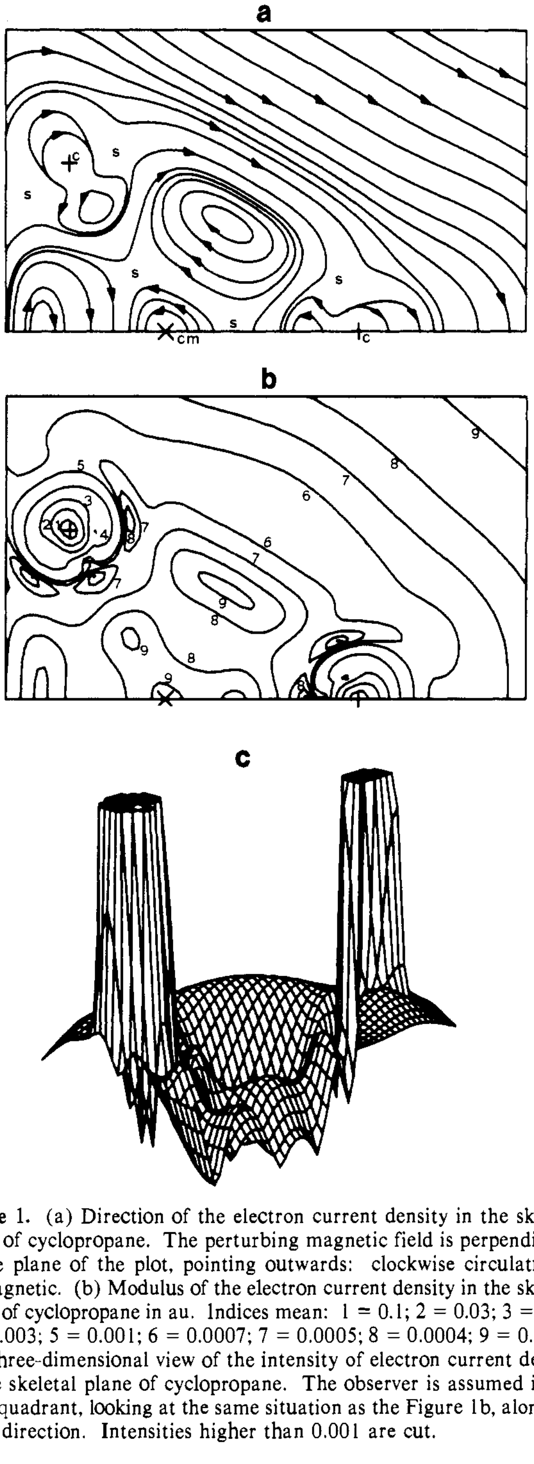

Figure 1. (a) Direction of the electron current density in the skeletal plane of cyclopropane. The perturbing magnetic field is perpendicular to the plane of the plot, pointing outwards: clockwise circulation is diamagnetic. (b) Modulus of the electron current density in the skeletal plane of cyclopropane in au. Indices mean: 1 = 0.1; 2 = 0.03; 3 = 0.01; 4 = 0.003; 5 = 0.001; 6 = 0.0007; 7 = 0.0005; 8 = 0.0004; 9 = 0.0001. (c) Three-dimensional view of the intensity of electron current density in the skeletal plane of cyclopropane. The observer is assumed in the third quadrant, looking at the same situation as the Figure 1b, along the $5\pi/4$ direction. Intensities higher than 0.001 are cut.

Table VIII. Nuclear Magnetic Shielding Tensor of Proton in Cyclopropane[a]

gauge at c.m.			gauge at H		
32.60	0.0	14.15	37.79	0.0	5.98
0.0	23.46	0.0	0.0	34.52	0.0
5.29	0.0	35.78	0.83	0.0	42.80

[a] For the definition of the components, see eq 5. The coordinates of the proton are specified in Table I.

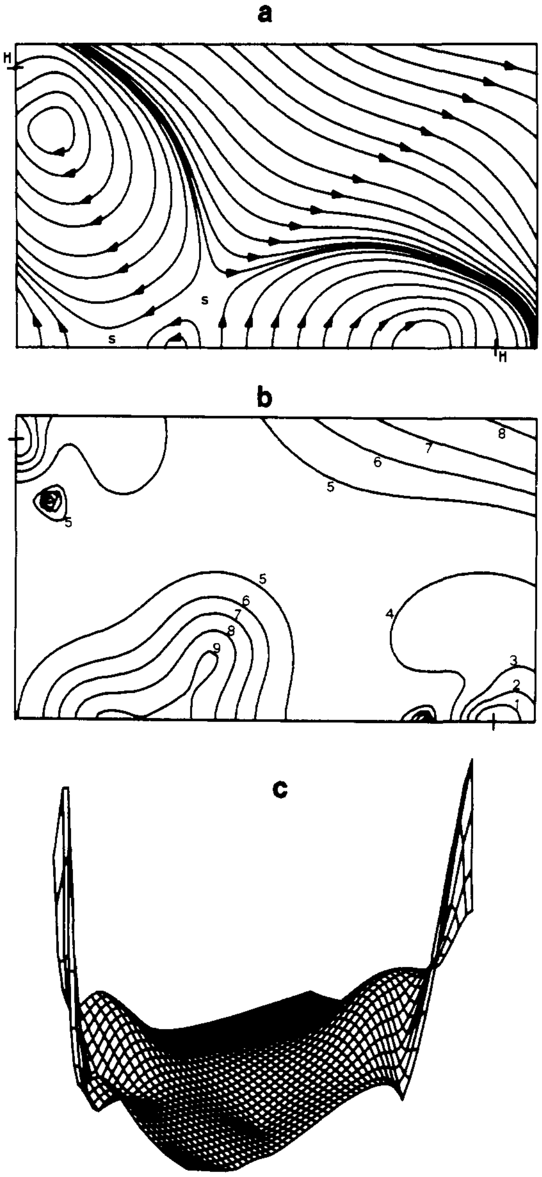

Figure 2. (a) Direction of the electron current density in the plane of hydrogens in cyclopropane. (b) Modulus of the electron current density in the plane of hydrogens in cyclopropane in au. Indices mean: 1 = 0.001; 2 = 0.0007; 3 = 0.0005; 4 = 0.0003; 5 = 0.0001; 6 = 0.00007; 7 = 0.00005; 8 = 0.00003; 9 = 0.00001. (c) Three-dimensional view of the intensity of the current density in the plane of hydrogens in cyclopropane. The conventions are the same as in Figure 1c applied to the situation of Figure 2b.

ion—so that the upfield shift of carbon is uniquely due to the large *zz* component.

With regard to σ_{xx}, deshielding effects seem to be determined by electron circulations in the e'_y and e''_y orbitals; cf. the contribution of −286 ppm to σ_{xx} in the ion from the $3e'_y$ orbital. Other deshielding contributions to σ_{yy} can be seen in Tables V and VI.

Table IX. Comparison between Experimental and Theoretical Chemical Shifts in C_3H_6 in ppm[a]

	δ_{11}	δ_{22}	δ_{33}
gauge at c.m.	14.21	0.0	−46.76
gauge at C	19.57	0.0	−49.14
experimental[b]	20 ± 2.5	0.0	−38 ± 2.5

[a] The chemical shift tensor is defined as $\delta_{ii} = -(\sigma_{ii} - \sigma_{22})$, assuming as reference zero the shielding component σ_{22}. [b] See ref 6b.

A comparison with the recent experimental data reported by Zilm et al.[6b] for cyclopropane is satisfactory: our theoretical results support the same orientation of the principal axes of the C nuclear shielding tensor. From the quantitative point of view, slight discrepancies have been found concerning the value of the chemical shifts, evaluated assuming σ_{zz} as reference zero, see Table IX. These differences might be imputed to some insufficiencies of the Gaussian basis set employed in our study.

Maps showing the electron circulation in cyclopropane are given in Figures 1 and 2. Figure 1a shows the direction of induced electron flow in the molecular plane. The general features are virtually the same as those previously reported for cyclopropenylcation.[1] In particular, the central paramagnetic axial vortex is expected as a consequence of the nodal topology of the wavefunction.[3] Similar circulations localized around C–C bonds are found and delocalized streamlines due to electrons are observed in the outer reaches of the molecular plane. A complicated pattern in the region of the carbon atoms is observed, which is a common characteristic of planar cyclic molecules.[1-3] The toroidal vortex is evident in the plot. In addition, a couple of singular points, a source and a sink, symmetrically placed with respect to carbon, are found; this is an unpleasant drawback originating from the lack of gauge invariance of the theoretical CSCF current. In fact, gauge invariance is a necessary condition for current conservation.[3] Several stagnation (s) points, i.e., points where the electron flow is zero due to destructive interference, are seen in the plot.

The magnitude of the vector field is shown in different ways in Figure 1b and 1c. The modulus map, Figure 1b, clearly shows the enhancement of circulation in the region closely surrounding the carbon nucleus, where the intensity is several times higher than anywhere else. A less quantitative, but somewhat more impressive, description is given by inspection of Figure 1c, where a prospective view of intensities is given.

The analysis of the direction and magnitude of the electron current shown in Figure 1 provides an explanation for the high value of σ_{zz} for the carbon nucleus. The general pattern for the currents flowing in the plane passing through the hydrogen nuclei and parallel to the plane of the carbons is shown in Figure 2. Diamagnetic circulations of higher intensity occur around H nuclei, and the central axial vortex is still evident. The diamagnetic streams are responsible for the value of the proton σ_{zz}, which is ≈5 ppm higher than the average shielding in methane.[1] Stagnation points appears in the boundary regions between the central vortex and the diamagnetic circulations.

Registry No. Cyclopropenyl cation, 26810-74-2; cyclopropane, 75-19-4.