Ring Currents in Icosahedral C_{60}

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A new formulation of the current within the London approximation allows the calculation of ring currents in topologically complex molecules. Application of this theory to C_{60} demonstrates the existence of remarkable π electron ring currents. Paramagnetic currents, in size comparable to the ones in benzene, flow within the pentagons, whereas weaker diamagnetic currents flow all around the C_{60} molecule. The overall vanishing ring-current magnetic susceptibility results from a cancellation of diamagnetic and paramagnetic contributions. The presence of ring currents significantly affects chemical shifts as measured in nuclear magnetic resonance experiments. In contrast to the magnetic susceptibility, which is a property of the molecule as a whole, chemical shifts are sensitive to the local magnetic field and the effect of ring currents does not vanish.

The initial suggestion by Kroto and coworkers (*1*) that the sea of π electrons on the inner and outer surface of C_{60} could give rise to remarkable ring currents has stimulated extensive theoretical and experimental work (*2–7*). It was first predicted that the ring-current magnetic susceptibility was vanishingly small (*2*), and this prediction was then confirmed experimentally (*6, 7*). The conclusion was drawn that ring currents were absent in C_{60} (*6*). We report that, although the ring-current magnetic susceptibility is vanishingly small in C_{60}, there nevertheless exist remarkable ring currents.

Because of the complex pattern of bonding in C_{60} (*8*), it was generally believed that a direct evaluation of the ring currents was not possible. However, within the London theory (*9*), spanning trees are not required and the current $\mathbf{J}_{ij}$ from site $\mathbf{R}_i$ to the nearest-neighbor site $\mathbf{R}_j$ can be expressed with the eigenvectors C_i^n of the Hamiltonian matrix:

$$\mathbf{J}_{ij} = \left[\sum_n (C_i^n)^* C_j^n\right] \exp\left\{\frac{ie}{2\hbar c}\left[\mathbf{A}(\mathbf{R}_i) - \mathbf{A}(\mathbf{R}_j)\right]\cdot(\mathbf{R}_i + \mathbf{R}_j)\right\} \mathbf{j}_{ij}$$

where the sum is over the occupied orbitals, $\mathbf{A}(\mathbf{r})$ is the vector potential, $\mathbf{j}_{ij}$ is a vector directed along the bond and of constant modulus, which can be related to the bond strength, $\hbar$ is Planck's constant divided by 2π, and c is the speed of light. The total current in the ij bond is given by $\mathbf{J}_{ij} + \mathbf{J}_{ji}$ and is real. For simplicity, we adopt an idealized geometry for C_{60}, with a common bond length of 1.4 Å, including only π orbitals in our calculation, and with a resonance integral $\beta = 2.66$ eV (*10*).

In Fig. 1, A and B, the ring currents in the upper cap of C_{60} are drawn for a magnetic field oriented perpendicular to the plane containing the central pentagon and hexagon, respectively. From Fig. 1 we can see that, for both directions of the field, the currents flowing in the bonds within the same pentagon are as strong as in benzene although opposite in direction (paramagnetic), whereas the currents in the bonds that connect different pentagons are overall much weaker. We note that this result is not in contradiction with the vanishingly small magnetic ring-current susceptibility found with the same theory (*2*). The ring-current susceptibility can be directly related to the magnetic field generated by the currents at the center of the fullerene. The ring currents can be thought of as a sum of two main contributions: (i) paramagnetic currents in every pentagon; and (ii) diamagnetic currents flowing all around the molecule. Because the fields generated at the center by these two contributions are opposite, the vanishingly small susceptibility has to be interpreted as a cancellation effect. It has been previously shown that the paramagnetic contributions increase when the bond strength of bonds connecting different pentagons are weakened, suggesting that paramagnetic pentagon currents might be present (*3*). The present result shows that this is indeed the case even when the bond strengths are all equal.

Ring currents generate magnetic fields that shield (or deshield) the external field H at a position in which an ideal probe-

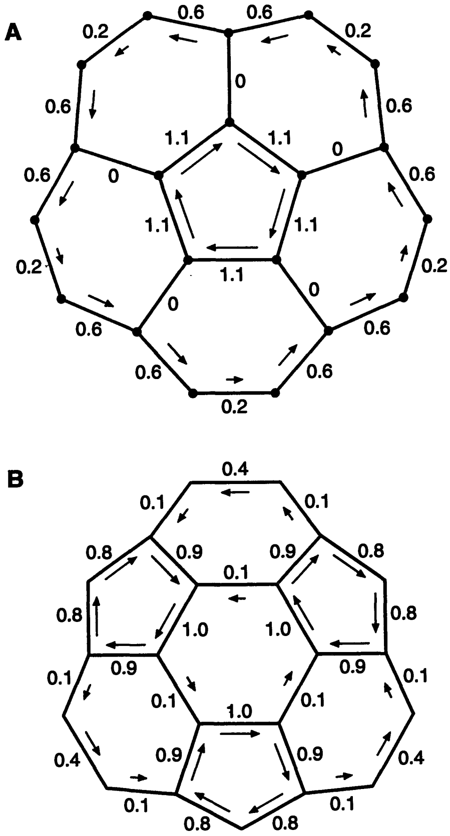

Fig. 1. Electron ring current in C_{60} for a magnetic field oriented perpendicular to a plane containing (**A**) a pentagon and (**B**) a hexagon, respectively. The currents in the pentagons are paramagnetic. The current strength is given with respect to that in benzene.

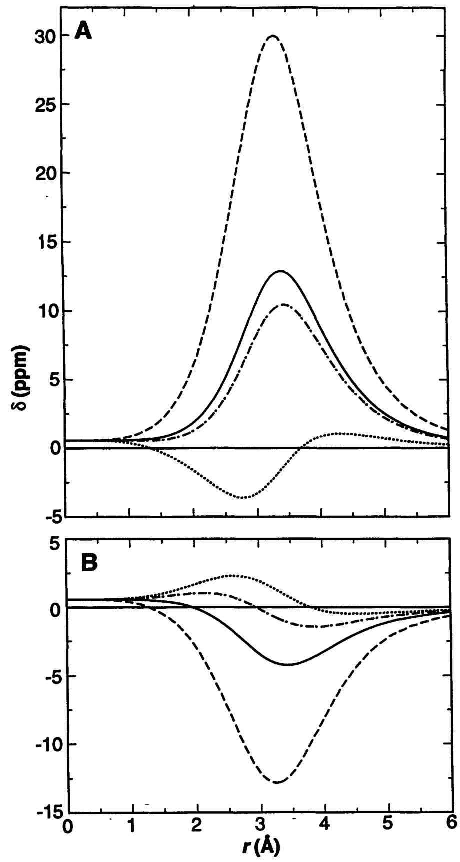

Fig. 2. Calculated ring-current chemical shifts plotted along radial lines through the centers of (**A**) pentagons and (**B**) hexagons. The different curves correspond to inequivalent pentagon and hexagon lines for a magnetic field direction pointing to the middle of a bond separating two hexagons. Solid curves are spherical averages. In (B), the average coincides with the curve for one of the hexagon lines. The radius of C_{60} is ~3.5 Å.

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dipole μ is located, giving rise to a chemical shift $\delta = \Delta H/H$. Ideally this shift can be detected experimentally as a contribution to the chemical shift in the nuclear magnetic resonance (NMR) of a proton located at that position. Paramagnetic and diamagnetic currents give rise to positive and negative chemical shifts of inner protons, respectively. These shifts for protons at arbitrary positions can be obtained either from the ring currents or from the total energy (*3*). Here, we follow the second procedure. The total energy is calculated in the presence of an external magnetic field and of the field generated by a probe-dipole at a given position (*3*). By evaluating the energy difference ΔE between the cases in which the dipole is oriented parallel and antiparallel to the external field, it is possible to extract the chemical shift $\delta = \Delta E/(2\mu H)$.

We have oriented the external magnetic field through the middle of a bond separating two hexagons. We then calculate the ring-current chemical shift along every radial line going through the center of a hexagon or pentagon. In Fig. 2, A and B, we report ring-current chemical shifts for all of the three nonequivalent pentagon directions and the four nonequivalent hexagon directions together with their spherical averages, respectively. Note that the chemical shift at the origin δ_0 is directly related to the ring-current susceptibility χ, $\delta_0 = 2\chi/l^3$ (*2, 3*), where l is the radius of C_{60}. As can be seen from Fig. 2, the chemical shifts are enhanced by at least an order of magnitude in the vicinity of the surface because of the remarkable ring currents. In the pentagon directions, the external magnetic field is generally deshielded by the ring-currents, whereas it is shielded in the hexagon directions. In Fig. 2, A and B, the largest absolute values are obtained for the cases in which the external field is nearly perpendicular to the plane containing the pentagon or hexagon, respectively. The values in Fig. 2 should be compared to the value of −41.4 parts per million (ppm), which is the ring-current chemical shift obtained at the center of the benzene ring with the external field oriented perpendicular to the plane.

The ring currents in C_{60} are found to be very sensitive to the electronic structure. In fact, a different occupation of the electronic levels completely modifies the current patterns. For instance, in the case of C_{60}^{6-} (that is, the T_{1u} level occupied), all of the currents are found to be diamagnetic and flow around the fullerene. The paramagnetic pentagon ring current is thus peculiar to C_{60}.

Very recently, NMR measurements on fullerenes have been performed that are affected by the presence of ring currents (*11, 12*). Suzuki *et al.* (*11*) synthesized the dihydrofulleroid H_2C_{61} molecule and measured its proton chemical shifts. In this molecule, the additional carbon atom bridges a bond separating a pentagon and a hexagon. The two inequivalent protons, which are directly above a pentagon and a hexagon, show shifts of 2.87 and 6.35 ppm (*11*). Although the presence of the bridge is expected to modify the local electronic structure (*13*) and thus the ring-current pattern with respect to pure C_{60}, the results in Fig. 2 suggest that the observed difference in the NMR shifts could be related to ring currents in H_2C_{61}.

In another experiment, Diederich and Whetten have measured carbon NMR shifts in C_{60} and higher fullerenes (*12*). In C_{60}, all C atoms are equivalent by symmetry and only one resonance line is observed. In C_{70}, however, there are five inequivalent carbon atoms that give five different NMR lines in a range of 20 ppm. Preliminary calculations for C_{70} show that the ring-current pattern is similar to the one in C_{60}. Again, paramagnetic ring currents are found in the pentagons and diamagnetic ring currents are found to flow around the equatorial region. The latter are stronger in C_{70} than in C_{60}, explaining the diamagnetic susceptibility of C_{70} (*6*). The presence of this complicated pattern of ring currents in C_{70} affects the magnetic fields on the carbon atoms and could be one of the underlying reasons for the spread of observed chemical shifts (*12*).

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Uranium Stabilization of C_{28}: A Tetravalent Fullerene

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Laser vaporization experiments with graphite in a supersonic cluster beam apparatus indicate that the smallest fullerene to form in substantial abundance is C_{28}. Although ab initio quantum chemical calculations predict that this cluster will favor a tetrahedral cage structure, it is electronically open shell. Further calculations reveal that C_{28} in this structure should behave as a sort of hollow superatom with an effective valence of 4. This tetravalence should be exhibited toward chemical bonding both on the outside and on the inside of the cage. Thus, stable closed-shell derivatives of C_{28} with large highest occupied molecular orbital–lowest unoccupied molecular orbital gaps should be attainable either by reacting at the four tetrahedral vertices on the outside of the C_{28} cage to make, for example, $C_{28}H_4$, or by trapping a tetravalent atom inside the cage to make endothedral fullerenes such as Ti@C_{28}. An example of this second, inside route to C_{28} stabilization is reported here: the laser and carbon-arc production of U@C_{28}.

Buckminsterfullerene, C_{60}, is the most symmetrical and least chemically reactive member yet discovered of a potentially huge class of closed carbon cage molecules composed of 12 five-membered rings and any number (except 1) of six-membered rings (*1*). The smallest of these, C_{20}, has only one possible structure, the dodecahedron. Each carbon in such a C_{20} cage is bonded to three others with a bond angle of 108°, which is so close to the tetrahedral bond angle of 109.5° that the bare C_{20} molecule would be expected to be extremely reactive, with each carbon striving to passify its fourth "dangling" bond. In fact, despite some theoretical evidence to the contrary (*2*), no indication has ever been found in carbon cluster beams for a particularly abundant bare C_{20} cluster, whereas the fully hydrogenated $C_{20}H_{20}$ molecule, dodecahe-

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