Magnetizabilities of Ring-Structured Molecules, [8]-Cyclacene, [8]-BN-Cyclacene and [8]-Collarene, and their Effect on [3]He Nuclear Shielding Tensor

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The magnetizabilities of three ring-structured molecules, [8]-cyclacene, [8]-BN-cyclacene, and [8]-collarene, were subsequently calculated at the B3LYP/6-31G* level with the CSGT gauge-origin treatment. The magnetizability of [8]-cyclacene shows a large diamagnetic nature in the direction parallel to the ring cylindrical axis, while the value of [8]-BN-cyclacene is nearly isotropic, and that of [8]-collarene is slightly more diamagnetic in the perpendicular direction than in the parallel direction. A large diamagnetic magnetizability in the parallel direction of [8]-cyclacene arises from the current flow around the ring circumference. The magnetic environment in the ring channel of these three molecules was investigated by calculating the nuclear shielding tensor of the [3]He atom when the atom moves through the ring channel. The GIAO nuclear shielding tensor changes significantly toward a prolate shape in [8]-cyclacene, but becomes a slightly oblate shape in [8]-BN-cyclacene and [8]-collarene. The changes correlate well with the magnetizabilities of the ring-structured molecules.

Cyclacenes are ring-structured molecules which consist of several benzene units forming a closed loop. It can sometimes be thought of as basic cylindrical carbon units of a zigzag nanotube.[1–4] Although a successful synthetic attempt of monomeric cyclacene has not yet been reported, there are a number of theoretical investigations of these molecules, particularly a study of the relationship between the electronic structure and the aromaticity as a function of its ring size.[1–4] Türker calculated the HOMO–LUMO energy gap of a series of Hückel and Möbius cyclacene with various ring sizes at the semiempirical MNDO level.[1] As the ring size increases, the author found a decrease in the energy gap of the Möbius type while it is nearly constant in the Hückel type. Choi and Kim calculated the isotropic magnetic susceptibilities, the proton chemical shifts, and the energy gaps of the cyclacene ring as a function of the number of fused benzene rings.[2] The authors observed an odd-even effect in most properties considered; this was discussed in terms of the aromaticity of two trannulene units.[3] Houk et al. re-investigated the singlet–triplet energy gap and the structural parameters of cyclacene.[4]

It is well known that the benzene ring has a large degree of electron delocalization.[5] It is, therefore, interesting to investigate the electron delocalization in a system constructed from benzene subunits, such as cyclacene. In cyclacene (see Fig. 1), there are two distinguished directions for the electron delocalization: around the ring circumference and in the perpendicular direction. A difference in the degree of electron delocalization between two directions implies a large anisotropic

magnetizability, hence yielding an interesting anisotropic magnetic environment inside the ring channel.

In this work, we calculated the magnetizability of cyclacene and investigated its effect on a nuclear shielding tensor of a [3]He atom when the atom moves through the ring channel. The [3]He atom is used as a probe atom to study the magnetic field along the ring channel of cyclacene since it interacts weakly with cyclacene. Therefore, it does not significantly perturb the investigated molecule. Bühl et al. calculated the chemical shifts of an encapsulated [3]He atom in fullerene and fullerene derivatives.[6] The authors deduced the degree of aromaticity of C_{60} and C_{70} fullerenes from this shielding information. Schleyer et al. later generalized the method of using an inert atom to probe the magnetic environment of a small ring system: the nucleus-independent chemical shift (NICS) is defined as the negative of the absolute magnetic shielding at some selected point in space, for example, at the ring center.[7,8] The NICS was used by Schleyer and co-workers as an aromaticity/antiaromaticity indicator.[7,9] It was pointed out, however, by Aihara that the NICS is the measurement of the diatropicity/paratropicity character which correlates with aromaticity/antiaromaticity only in certain case.[8]

In addition to cyclacene, BN-cyclacene, and collarene were also included in our studies. BN-cyclacene is isoelectronic to cyclacene with B–N bonds replacing all C–C bonds (see Fig. 1). Collarene is a ring structure consisting of benzene ring units connected together by CH_2-linkages (see Fig. 1). Because of the limitation in computational resources, only com-
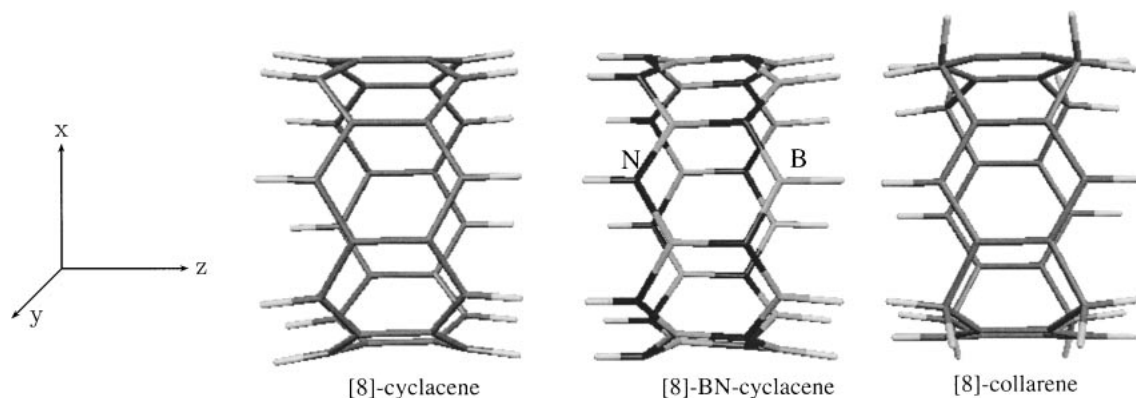
Fig. 1.   The ring-structured molecules considered in this work: [8]-cyclacene, [8]-BN-cyclacene, and [8]-collarene. For [8]-BN-cyclacene, the nitrogen end is pointed toward the negative *z* direction. The distances between the hydrogen atoms at both ends are 9.41, 9.40, and 9.47 bohr for [8]-cyclacene, [8]-BN-cyclacene, and [8]-collarene respectively.

pounds with eight six-membered ring units ($n = 8$), which are large enough to accommodate ^{3}He atom inside their channels, were considered.

Computational Methods

The structures of [8]-cyclacene, [8]-BN-cyclacene, and [8]-collarene were optimized at the semiempirical AM1 level using the GAMESS program.[10] The structure of [8]-cyclacene obtained at this level agrees favorably with the literature values calculated using the Density Functional Theory (DFT).[2,4] Thus, the AM1 optimized structures are adequately sufficient for our investigations and were used throughout this study. The vertical energy gaps between the lowest singlet and triplet states were calculated within the unrestricted Hartree–Fock (UHF) and DFT/6-31G* with the B3LYP functional (B3LYP/6-31G*) frameworks. The magnetizabilities of all molecules were computed at the B3LYP/6-31G* level with the continuous set of gauge transformation (CSGT) method to overcome the gauge-origin dependent problem. The CSGT was chosen because it is the best method for the magnetizability currently implemented in the Gaussian 98 program.

The ^{3}He atom was then positioned along the ring cylindrical axis (*z* axis in Fig. 1). The interaction energy (ΔE), the nuclear shielding constant ($\bar{\sigma} = (\sigma_\parallel + 2\sigma_\perp)/3$), and the nuclear shielding anisotropy ($\Delta \sigma = \sigma_\parallel - \sigma_\perp$), where the parallel direction is along the ring cylindrical axis, were then calculated as a function of the distance R between the ^{3}He atom and the center of mass of a ring-structured molecule. The B3LYP/6-31G* with the gauge-independent atomic orbitals (GIAO) method was used for the shielding tensor calculations. We note that although the DFT is the most economical way to include the electron correlation, the functionals currently used such as the B3LYP functional are not the current-density functional and, hence, do not necessarily yield the magnetic properties better than those obtained from conventional ab initio correlated methods, such as the GIAO/MP2 method.[11] However, the DFT is the method of choice in our case due to the large system size considered. All ab initio calculations were performed using the Gaussian 98 program.[12]

Results and Discussion

The vertical singlet–triplet energy gaps of all compounds

Table 1.   The Vertical Energy Gaps between the Lowest Singlet and Triplet States of [8]-Cyclacene, [8]-BN-Cyclacene, and [8]-Collarene at the AM1 Optimized Structure. The 6-31G* Basis Set is Used in the Calculations

	UHF/kJ mol^{-1}	UB3LYP/kJ mol^{-1}
[8]-Cyclacene	−224.5	9.3
[8]-BN-cyclacene	923.3	562.7
[8]-Collarene	553.0	388.0

Table 2.   The Magnetizabilities of [8]-Cyclacene, [8]-BN-Cyclacene, and [8]-Collarene. For the Purpose of Comparison, the Magnetic Anisotropy is Defined as $\Delta \chi = \chi_\parallel - \chi_\perp$ where the Parallel Direction is along the Ring Cylindrical Axis. The Method of Calculation is the B3LYP/6-31G* with the CSGT Gauge-origin Treatment

	$\chi_\perp$/cgs	$\chi_\parallel$/cgs	$\bar{\chi}$/cgs	$\Delta \chi$/cgs
[8]-Cyclacene	−274	−837	−462	−563
[8]-BN-cyclacene	−197	−174	−189	23
[8]-Collarene	−274	−145	−231	129

are tabulated in Table 1. The UHF energy gap of [8]-cyclacene (−224.5 kJ/mol) indicates that at a given structure the triplet state is more stable than the singlet state. However, the UB3LYP result (9.3 kJ/mol) leads to an inverse conclusion, i.e. the singlet state is slightly more stable than the triplet state. Our result re-emphasizes the importance of the electron correlation in this type of molecule.[3] Interesting magnetic properties of the cyclacene molecule are thought to originate from this low-lying triplet state.[2] For [8]-BN-cyclacene and [8]-collarene, both UHF and UB3LYP predict a singlet ground state with a lesser energy gap from the UB3LYP than from the UHF.

Considering the magnetizabilities of these three molecules (see Table 2), it is clear that [8]-cyclacene has a large negative magnetizability in the parallel direction to the cylindrical axis ($\chi_\parallel$). As will be shown later, this is due to an electron delocalization around the ring circumference. The magnetizability in the perpendicular direction ($\chi_\perp$) is, however, equal to that of [8]-collarene. Our $\bar{\chi}$ of [8]-cyclacene (−462 cgs) compares well with the value of −469 cgs reported previously by Choi

and Kim;[2] the difference is most likely due to the use of a slightly different geometry used.

The perpendicular component of the magnetizability of [8]-collarene is more negative than the parallel component, which is in an opposite trend to [8]-cyclacene. In other words, [8]-collarene is more diamagnetic in the perpendicular direction than in the parallel direction. The magnetizabilities in the perpendicular component of [8]-collarene and [8]-cyclacene should be attributed to the π electron delocalization in benzene subunits; this is supported by the fact that they have the same numerical value in our calculation. Since the [8]-collarene consists of four benzene units linked together by CH_2 linkages, one would expect that π electrons do not delocalize easily between each benzene unit, hence leading to a less negative $\chi_\parallel$ of [8]-collarene. The difference between $\chi_\parallel$ of [8]-cyclacene and [8]-collarene should provide an indication of an enhanced magnetizability due to an electron delocalization around the ring circumference in the [8]-cyclacene. The [8]-BN-cyclacene, in contrast, shows a small and rather isotropic magnetizability with $\Delta\chi$ of only 23 cgs. This seems to imply that there

is no favorable delocalization in both directions. In other words, the electron is more localized in the [8]-BN-cyclacene system than in the other two systems. This agrees with the fact that the triplet–singlet energy gap is largest in the [8]-BN-cyclacene.

An enhanced diamagnetic magnetizability in the parallel direction of [8]-cyclacene in comparison to those of other two molecules can be confirmed by examining the current density plot in the plane passing through the middle of the ring perpendicular to the axis direction (the *xy* plane in Fig. 1). Figures 2(a)–2(c) show the current density of [8]-cyclacene, [8]-BN-cyclacene, and [8]-collarene, respectively. The current flow in this plane leads to a magnetic field in the axis direction, which is anti-parallel to the applied external magnetic field. A large diamagnetic magnetizability in the parallel direction of [8]-cyclacene should have an origin from the complete current flow around the ring circumference, which can be observed in Fig. 2(a). This feature is missing in the cases of [8]-BN-cyclacene and [8]-collarene, which have a much less $\chi_\parallel$ (see Figs. 2(b), 2(c)); both plots show only a localized cur-

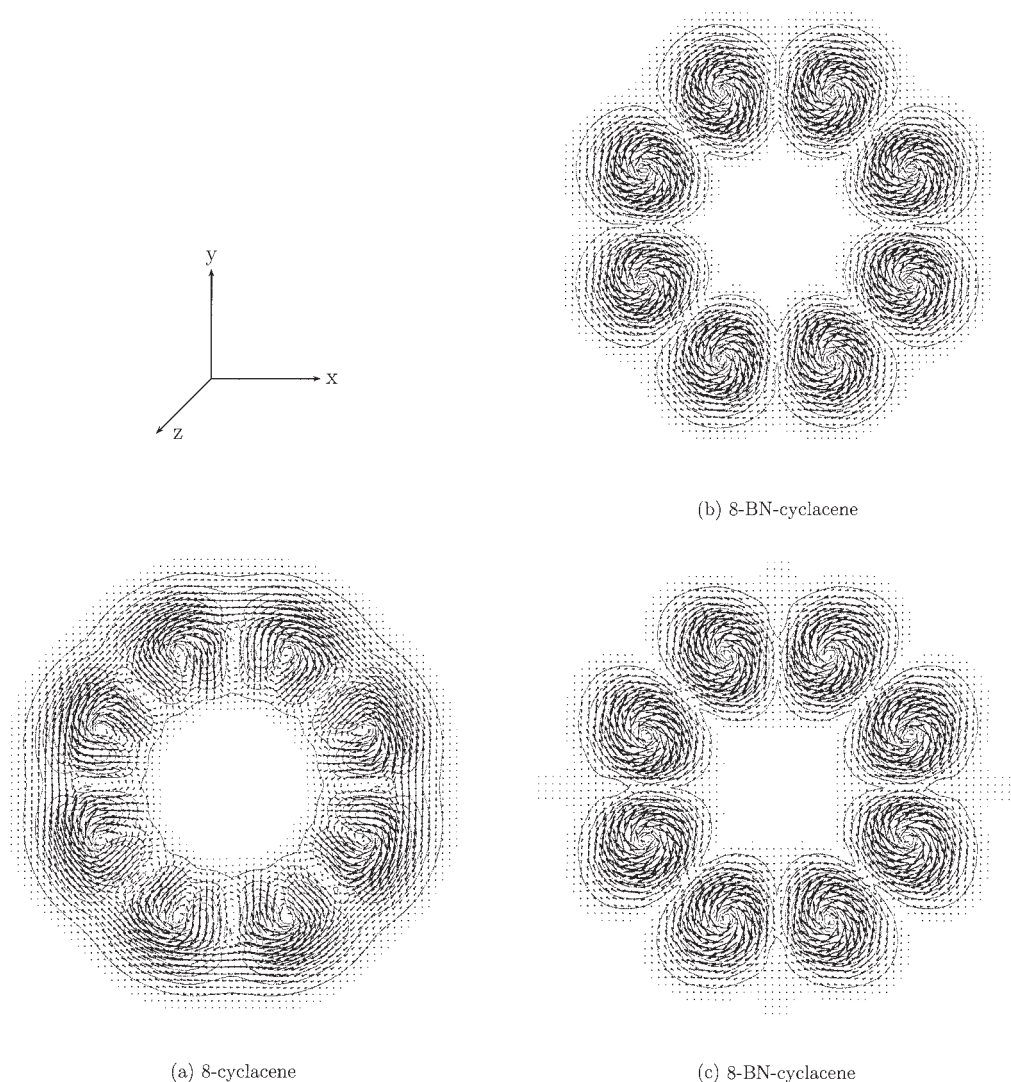(b) 8-BN-cyclacene

(a) 8-cyclacene

(c) 8-BN-cyclacene

Fig. 2.   The current density plots in the plane perpendicular to the cylindrical axis at the middle of the ring-structured molecule. The current density is represented by an arrow at a given point. The contour plot of the current density magnitude is also shown.
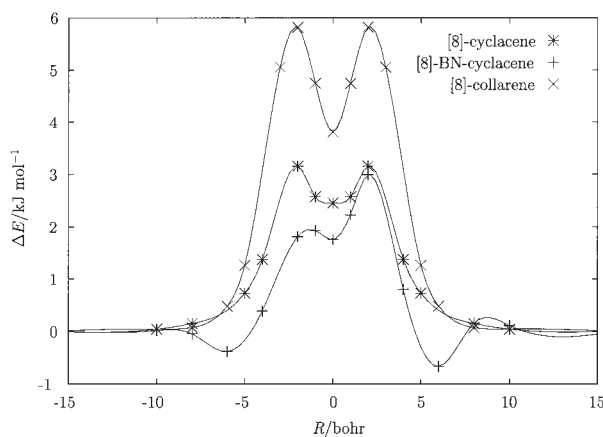
Fig. 3.   The interaction energy ΔE between the ^{3}He atom and the ring-structured molecule as the ^{3}He atom moves through the ring channel along the ring cylindrical axis. The intermolecular distance R is measured from the ^{3}He atom to the center of mass of the ring-structured molecule. All lines joining calculated values were interpolated using the cubic spline method. The B3LYP/6-31G* method was used in the calculations.

rent flow in the subunits.

Considering the insertion of ^{3}He into a ring-structured molecule, the interaction energies (ΔE) between ^{3}He and each three ring-structured molecules as a function of intermolecular distance (R) are displayed in Fig. 3. We considered this term qualitatively, since it is known that the DFT method with the B3LYP functional does not describe the van der Waals interaction well.[13] The interaction energy is positive but small, less than 6 kJ/mol, in all cases. There is a local minimum at the center of the ring channel for all systems considered. Although the interaction energy is positive, it is so small that the thermal energy would overcome the positive potential barrier making it possible for the ^{3}He atom to move through the channel. The interaction energy curve of the ^{3}He···[8]-BN-cyclacene complex is not symmetrical; the barrier is smaller if the ^{3}He atom enters the ring channel through the nitrogen end (negative R). The insertion process becomes much more favorable when a neutral ^{3}He atom is replaced by a small-sized cation, such as Li$^+$.[14]

The ^{3}He nuclear shielding constant and the shielding anisotropy as a function of the intermolecular distance in all complexes are represented in Fig. 4. The shielding constant of ^{3}He (see Fig. 4(a)) increases when a ^{3}He atom moves inside the ring channel; the ^{3}He···[8]-cyclacene complex has the largest change, approximately 50%, while the ^{3}He···[8]-BN-cyclacene complex has the smallest change. The ^{3}He shielding constant is maximum at the center of the ring channel ($R = 0$) in the [8]-cyclacene and [8]-collarene systems, whereas the maximum is shifted toward the boron-end in the [8]-BN-cyclacene. The shielding anisotropy, $\Delta\sigma = \sigma_\parallel - \sigma_\perp$, (see Fig. 4(b)) increases when ^{3}He enters the ring channel of [8]-cyclacene, but decreases in the other two cases. In other words, the shielding tensor of ^{3}He becomes prolate when the atom moves inside the [8]-cyclacene channel, while it becomes oblate when the atom moves inside the channel of the other two ring-structured molecules. The shielding tensor changes inside three
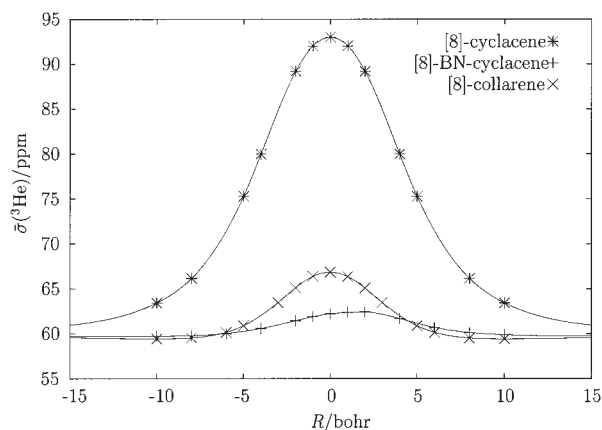
(a)
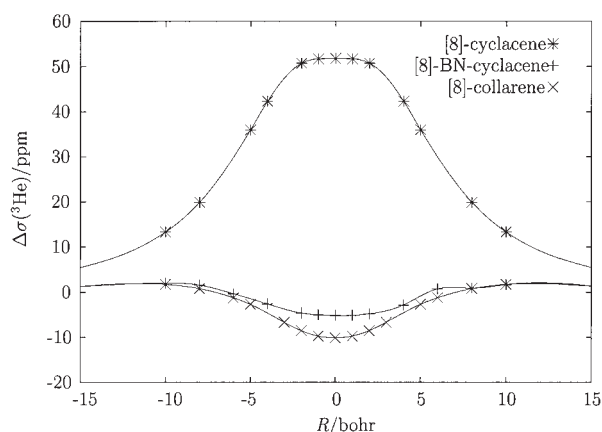
(b)

Fig. 4.   The ^{3}He shielding constant ($\bar{\sigma} = (\sigma_\parallel + 2\sigma_\perp)/3$) and the ^{3}He nuclear shielding anisotropy ($\Delta\sigma = \sigma_\parallel - \sigma_\perp$), where the parallel direction is along the ring cylindrical axis, as the atom moves through the ring channel along the ring cylindrical axis. For a free atom, $\bar{\sigma}(^3$He) is 59.8 ppm. The B3LYP/6-31G* with the GIAO gauge-origin treatment was used in the calculation.

ring-channels correlate well with the magnetizability tensor of the ring-structured molecules (see Table 2). Inside the channel of [8]-cyclacene, the shielding anisotropy varies slowly with the distance. Both the shielding constant and the shielding anisotropy return to the free-atom value when ^{3}He moves further out of the ring channel.

Conclusion

The magnetizabilities of [8]-cyclacene, [8]-BN-cyclacene and [8]-collarene are reported. A large difference in the parallel component of the magnetizability of [8]-cyclacene and of [8]-collarene indicates an enhanced electron delocalization around the ring circumference. This is evidently supported by the current density plot in the plane perpendicular to the ring cylindrical axis. The perpendicular component of the magnetizability of [8]-collarene is more negative than the parallel component; this should arise mainly from the π-electron delocalization within the benzene subunits. The [8]-BN-cyclacene has a small and nearly isotropic magnetizability, suggesting an electron localization in this system. The different nature

of the magnetizabilities of the three ring-structured molecules leads to different behaviors of the magnetic field in the ring channel, as probed by the [3]He atom. A large increase in the isotropic and anisotropic parts of the [3]He shielding tensor, when the atom moves through the ring channel of [8]-cyclacene, indicates a anisotropic magnetic environment due to current flow around the ring circumference of the [8]-cyclacene system. The changes of the [3]He shielding tensor in the three complexes correlate well with the magnetizabilities of the corresponding ring-structured molecules.

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