Nuclear magnetic shielding and chirality. II. The shielding tensor of a naked spin in Ne helices

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We continue our investigation of the nuclear magnetic shielding tensors of Xe@Ne_n helix complexes (I). Here we replace Xe by a naked spin. The full shielding tensor of Ne_8 helix diastereomers is calculated and compared with the equivalent Xe@Ne_8 diastereomers. [DOI: 10.1063/1.1586699]

INTRODUCTION

We consider the shielding of a naked spin in a chiral environment. In Paper I we considered the shielding response of a Xe atom to a chiral environment.[1] The overlap and exchange of the Xe electrons with those of the chiral system provides a shielding response that is large enough to observe. Indeed the chiral shifts calculated for diastereomeric pairs are the same order of magnitude as those observed for Xe in chiral cages electronically coupled to chiral tethers.[2] Now we wish to examine the molecular shielding of the chiral system itself. This is the shielding that can be mapped by placing a magnetic moment anywhere around (or in) the molecule.[3] We expect the large deshielding that is usual for the Xe atom closely interacting with any neighbors to be dominated by paramagnetic deshielding arising from overlap and exchange and also electron correlation contributions.[4] Without this large deshielding arising from the response of the Xe electron to its environment, to what extent does the shielding tensor (at a particular location) of the molecule by itself reflect its chiral character? Is the sign of the chiral shift between diastereomers related to the same or opposite handedness of the two chiral systems that make the diastereomeric pair? If so, assignment of chiral structures in the NMR spectrum would be possible. In this paper, we use a naked spin to calculate the molecular shielding at the center of helical systems to find the answers to these questions.

METHOD AND RESULTS

To model the chiral environment we choose the most symmetric Ne helix in Paper I. That is, a helix (R or L) of eight neon atoms with a radius of 3.260 Å and a pitch of 3.5 Å. The Ne atoms are in the range 3.27–3.70 Å from the center. A second helix with a radius of 6.3706 Å, co-axial with the helix of Ne atoms, made up of a partial charge array of 15 equally spaced positive charges (magnitude $+0.061\,953e$), (r_+ or ℓ_+) is coupled to the first helix to produce diastereomeric pairs ($L\ \ell_+$), ($R\ r_+$), ($L\ r_+$), and ($R\ \ell_+$). The Ne atoms and the positive charges are equally spaced on the inner and outer helices. For each Ne atom we use 77 basis functions, uncontracted ($18s\ 13p$) plus four d polarization functions.[5] Distributed gauge origins are implemented through the use of gauge-including atomic orbitals (GIAO) and the GAUSSIAN 98 program package was used for all calculations,[6] using density-functional theory, in particular using the popular hybrid functional B3LYP. In addition to the chiral systems used for Xe in Paper I, we use negative charges for the outer helix to see whether the sign of the chiral shift would be different than that for the Ne_8 helix coupled to 15 positive point charges. We shall refer to these diastereomeric pairs as: ($L\ \ell_-$), ($R\ r_-$), ($L\ r_-$), ($R\ \ell_-$). In all cases the naked spin is located at the center of the helix (the origin); the helical axis is along the Z axis, and the X axis is chosen along the C_2 axis. The shielding tensor reflects the symmetry at the site of the naked spin. The coordinate axes have been chosen so as to reflect the minimum number of unique nonvanishing components dictated by this symmetry in the laboratory axes. By rotation of the laboratory axes, mixing of elements of the full tensor can lead to apparently larger number of nonvanishing tensor elements. The proper choice leads to a tensor that has elements that cannot be reduced further in number.

The results are shown in Tables I and II, where the full tensor, the symmetric part, and the antisymmetric part are separately shown. The shielding tensor has a nonvanishing antisymmetric part in a chiral environment. Since the helical axis is chosen along the Z direction in the laboratory frame, the signs of the antisymmetric tensor elements are reversed for the components involving Z, when the handedness of the Ne helix is changed from L to R. We show only the components for the L enantiomer. In the presence of the charges the antisymmetric elements increased in magnitude, just as they did for Xe located at the same site. We show only one each of the diastereomeric pairs since the components of the mirror image enantiomer are the same except for a change in sign of certain of the off-diagonal elements. As discussed earlier, these are not measures of chirality since one may be reached from the other via a rotation.[1]

The results for the perturbation by an external helix of negative charges are shown in Table III. The sign of the

TABLE I. Shielding tensor of a naked spin at the center of the $(L)Ne_8$ helix, ppm.

Full tensor		
1.1267	0	0
0	0.6934	0.9742
0	0.9748	−1.8249
Symmetric tensor		
1.1267	0	0
0	0.6934	0.9745
0	0.9745	−1.8249
Antisymmetric tensor		
0	0	0
0	0	−0.0003
0	+0.0003	0

antisymmetric part is opposite to that of the corresponding diastereomeric helices with positive charges.

A summary of the isotropic shielding values for the various chiral systems studied here is given in Table IV. The isotropic shielding at the center of the Ne_8 helix is a small negative value (deshielding). In the diastereomeric pairs having the external helix of positive point charges, it is positive shielding of around 0.9 ppm, whereas in the diastereomeric pairs having the external helix of negative point charges, it is negative shielding, around −0.9 ppm. The coupling of the Ne_8 helix to the chiral field of positive point charges leads to a net withdrawal of electron density from the center of the Ne_8 helix where the naked spin is located, whereas the negative point charges leads to a net increase of electron density. The chiral shift is −0.0191 ppm for $\sigma_{iso}(L\ \ell_+) - \sigma_{iso}(L\ r_+)$. We found this sign for Xe in the same diastereomeric helices. On the other hand, $\sigma_{iso}(L\ \ell_-) - \sigma_{iso}(L\ r_-) = +0.0258$ ppm. Both the sign and the magnitude of the chiral shift changed. Thus the sign of the chiral shift between diastereomers of the co-axial helices is not uniquely related to the handedness of the diastereomeric pairs.

TABLE II. Shielding of a naked spin at the center of co-axial helices $Ne_8 \cdot (+q)_{15}$.

$n@Ne_8 \cdot (+q)_{15}(L\ell_+)$		
Full tensor		
1.4034	0	0
0	1.0482	0.5330
0	0.6439	0.3138
Symmetric tensor		
1.4034	0	0
0	1.0482	0.5885
0	0.5885	0.3138
Antisymmetric tensor		
0	0	0
0	0	−0.0555
0	+0.0555	0
$n@Ne_8 \cdot (+q)_{15}(\mathrm{Lr}_+)$		
Full tensor		
1.4094	0	0
0	1.0535	0.5170
0	0.6282	0.3597
Symmetric tensor		
1.4094	0	0
0	1.0535	0.5726
0	0.5726	0.3597
Antisymmetric tensor		
0	0	0
0	0	−0.0556
0	+0.0556	0

TABLE III. Shielding of a naked spin at the center of co-axial helices $Ne_8 \cdot (-q)_{15}$.

$n@Ne_8 \cdot (-q)_{15}(L\ell_-)$		
Full tensor		
0.8487	0	0
0	0.3425	1.4182
0	1.3082	−3.9742
Symmetric tensor		
0.8487	0	0
0	0.3425	1.3632
0	1.3632	−3.9742
Antisymmetric tensor		
0	0	0
0	0	+0.0555
0	−0.0555	0
$n@Ne_8 \cdot (-q)_{15}(Lr_-)$		
Full tensor		
0.8387	0	0
0	0.3366	1.4371
0	1.3193	−4.0358
Symmetric tensor		
0.8387	0	0
0	0.3366	1.3782
0	1.3782	−4.0358
Antisymmetric tensor		
0	0	0
0	0	+0.0589
0	−0.0589	0

DISCUSSION

We note the parallel behavior of the Xe shielding (in *I*) and the naked spin shielding. In particular, we compare the chiral shift −0.0191 ppm with the chiral shift induced by the same system in Xe atom: −0.9324 ppm.[1] The response of the electrons of Xe is 46 times as large. Although we did not do the Xe calculations in the Ne_8 helix coupled to a helix of negative point charges, it is expected that the Xe chiral shift too will change in sign.

TABLE IV. Isotropic shielding of a naked spin in chiral systems.

System	Mirror image system	σ_{iso}, ppm
$n@Ne_8\ (L)$	$n@Ne_8\ (R)$	−0.0016
$[n@Ne_8 \cdot (+q)_{15}]\ (L\ell)$	$[n@Ne_8 \cdot (+q)_{15}]\ (Rr)$	+0.9218
$[n@Ne_8 \cdot (+q)_{15}]\ (R\ell)$	$[n@Ne_8 \cdot (+q)_{15}]\ (Lr)$	+0.9409
$[n@Ne_8 \cdot (-q)_{15}]\ (L\ell)$	$[n@Ne_8 \cdot (-q)_{15}]\ (Rr)$	−0.9277
$[n@Ne_8 \cdot (-q)_{15}]\ (R\ell)$	$[n@Ne_8 \cdot (-q)_{15}]\ (Lr)$	−0.9535

The shielding tensor of a naked spin in the center of the Ne_8 helix has a nonvanishing antisymmetric part, just as was found for a Xe atom located at the same position. The 54 electrons of Xe located at the same position amplified the effect. The antisymmetry elements are purely paramagnetic since the diamagnetic part of the shielding is a symmetric tensor. The chiral shift, on the other hand, may include both diamagnetic and paramagnetic terms for a spin at the origin. With the origin defined at the naked spin, how much of the chiral shift is due to differences in diamagnetic and paramagnetic contributions cannot be easily determined due to the use of gauge-including atomic orbitals in the calculations. We could have used a common origin method of calculation, but it is well known that unless distributed origins are used, the imbalance between the accuracy of calculating the (first order) diamagnetic term and the (second order) paramagnetic term leads to poor results except in the limit of complete basis sets.[7] Therefore it would not be possible to find out whether the chiral shift here found to be 0.0191 ppm is dominated by the paramagnetic or the diamagnetic term. We leave that question to be answered in Paper III, where the knowledge of all excited states is complete and both the diamagnetic and the paramagnetic term can be calculated to the desired precision.[8]

CONCLUSION

The molecular shielding of the system of Ne_8 and point charge helices is sampled by the naked spin at the center, revealing the diastereomerism in the scalar property, the chiral shift. Replacing Xe by a naked spin gives a clear indication of the induced diastereomerism of the Xe electrons: the chiral shift is 0.9342 ppm for Xe compared to 0.0191 ppm for the naked spin. The same or opposite handedness of the enantiomers that make the diastereomeric pairs do not intrinsically determine the sign of the chiral shift. In other words, it is not possible to assign the individual peaks which would be observed in an NMR spectrum unequivocally to (*Ll*, *Rr*) or (*Lr*, *Rl*). We have shown that the sign of the chiral potential affects whether the same-handed diastereomers appear more shielded or less.

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