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^{199}Hg Shielding Tensor in Methylmercury Halides: NMR Experiments and ZORA DFT Calculations

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The isotropic average, $\sigma_{\mathrm{Hg}}^{\mathrm{iso}}$, and the anisotropy, $\Delta\sigma_{\mathrm{Hg}}$, of the ^{199}Hg shielding tensor in methylmercury halides, CH_3HgX (X = Cl, Br, I), were determined by studying the ^{199}Hg NMR of these molecules dissolved in liquid crystals. Furthermore, density functional calculations were performed using the zeroth order regular approximation, inluding also dimethylmercury. Detailed comparison of the experimental and calculated results is problematic because of the sensitivity of the ^{199}Hg shielding to environmental effects. It is, however, clear that calculations with spin−orbit interaction taken into account lead to the $\sigma_{\mathrm{Hg}}^{\mathrm{iso}}$ and $\Delta\sigma_{\mathrm{Hg}}$ values that predict the same trend as the experiments; the chemical shift relative to dimethylmercury, $\sigma_{\mathrm{Hg}}^{\mathrm{iso}}((CH_3)_2Hg) - \sigma_{\mathrm{Hg}}^{\mathrm{iso}}(CH_3HgX)$, increases while the shielding anisotropy decreases along the series $(CH_3)_2Hg$ to CH_3HgI.

Introduction

The nuclear shielding and spin−spin coupling are tensor quantities. However, NMR experiments carried out in conventional liquid solutions, that is in isotropic liquids, yield exclusively scalar quantities, nuclear shielding constant (σ_K) and spin−spin coupling constant (J_{KL}), which are isotropic parts (1/3 of the sum of the diagonal elements) of the respective tensors. Consequently, theoretical calculations often concentrate on these quantities. However, much more information about the electronic structure of a molecule and about the functionality of computational methods can be gained if the complete tensor or at least its diagonal elements are available.

NMR spectroscopy of solute molecules in liquid crystals (LCNMR), that is in anisotropic liquids, is a method very applicable to investigate nuclear shielding and spin−spin coupling tensors.[1−3] The experimentally detected chemical shift (chemical shift increases to high frequency) can be represented as

$$\delta^{\mathrm{exp}} = \delta^{\mathrm{iso}} - \frac{2}{3}\left(\sum_{\alpha\beta} S_{\alpha\beta}\sigma_{\alpha\beta}\right)P_2(\cos\theta_{Bn}) \tag{1}$$

where $S_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ in the latter term, which is due to the anisotropic liquid-crystalline environment, are the elements of the Saupe orientational order tensor[4] and the nuclear shielding tensor, respectively, in the molecule fixed coordinate frame. Further, $P_2(\cos\theta_{Bn}) = (1/2)(3\cos\theta_{Bn} - 1)$ is the second-order Legendre polynomial, with θ_{Bn} being the angle between the external magnetic field, $\mathbf{B}_o$, and the LC director, $\mathbf{n}$. In the cases, as the ones here, where the LC director orients parallel with the external field $P_2 = 1$. For linear molecules, such as the methylmercury halides, eq 1 transforms into the simple form

$$\delta^{\mathrm{exp}} = \delta^{\mathrm{iso}} - \frac{2}{3}\Delta\sigma S_{xx} P_2(\cos\theta_{Bn}) \tag{2}$$

where $\Delta\sigma = \sigma_{xx} - (1/2)(\sigma_{yy} + \sigma_{zz}) = \sigma_{\parallel} - \sigma_{\perp}$ is the anisotropy of the shielding tensor with respect to the *x*-axis (which is chosen to be along the molecular symmetry axis) of the molecule fixed frame, and S_{xx} is the orientational order parameter of the *x*-axis. The terms $\sigma_{\parallel}$ and $\sigma_{\perp}$ in turn are the shielding tensor elements in the direction of the molecular symmetry axis and perpendicular to it, respectively.

Equation 2 indicates that the isotropic average (or the chemical shift δ^{iso}) and the anisotropy of the shielding tensor can be determined provided that the orientational order parameter S_{xx} or the P_2 factor can somehow be changed. There exist various possibilities to do this.[1,2] We chose in the present case the method in which the sample temperature is varied. The details of the method will be discussed below.

In this work we have experimentally determined the chemical shifts, $\delta_{\mathrm{Hg}}^{\mathrm{iso}}$, with respect to an external dimethylmercury reference as well as the anisotropy of the mercury-199 shielding tensor for the methylmercury halides, CH_3HgX (X = Cl, Br, I). The tensor anisotropies were studied earlier by Kennedy and McFarlane[5] applying LCNMR but a different method and without correcting the dipolar couplings for vibrational motions. This study led to practically the same $\Delta\sigma_{\mathrm{Hg}}$ value for each halide, ca. 5500 ppm, contrary to the monotonic decrease along the series CH_3HgCl to CH_3HgI observed in the present work. Apart from the experiments, also zeroth-order regular approximation (ZORA) density functional theory (DFT) calculations were carried out. Wolff et al. earlier reported ZORA DFT results for the mercury-199 shielding constants and chemical shift (relative to dimethylmercury) in the same compounds[6] but with a

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somewhat different gradient-corrected (GGA, generalized gradient approximation) functional as the one used in this work. This is the first time that the full ^{199}Hg shielding tensors are reported both experimentally and computationally.

Experimental and Theoretical

NMR Experiments. The spin−lattice and spin−spin relaxations of the ^{199}Hg isotope in mercury compounds are known to be dominated by the chemical shielding anisotropy (CSA) mechanism.[7] For example, for methylmercury bromide T_1 (measured in the course of the present study) decreases from ca. 450 ms to ca. 90 ms when changing the magnetic field from 4.7 to 11.7 T at 300 K.[8] Therefore, to achieve a reasonable line width, the ^{199}Hg NMR spectra were recorded at the lowest magnetic field available in our laboratory in Oulu, i.e., a 200 MHz spectrometer Bruker Avance DPX200 was used. All the methylmercury halides and dimethylmercury were dissolved in the Merck Phase 4 liquid crystal (eutectic mixture of *p*-methoxy-*p*′-*n*-butylazoxybenzenes) and MeHgCl also in the Merck ZLI 1982 liquid crystal (mixture of alkylphenylcyclohexanes, alkylcyclohexanebiphenyls, and bicyclohexanebiphenyls). The concentration of the solute varied from 2.7 to 4.4 mol %. The samples were degassed carefully. In each case the spectra were recorded using a broad band 10-mm probehead at variable temperatures in order to change the degree of order of the liquid crystal solvent and the solute molecules. As the knowledge of real sample temperature is not essential in the present case, no temperature calibration was performed. A pulse width of 20 μs and spectral width of 21600 Hz were applied in each experiment. The number of scans varied from 32k to 400k, the experiment time being from 30 minutes to 5 hours, respectively.

ZORA DFT Calculations. The computations of the ^{199}Hg shielding tensors were carried out by applying the program code described in ref 6, employing the popular BP86 density functional.[9] This functional is a well-established and reliable GGA that has been successfully applied in many NMR computations involving heavy elements.[10] Our results in this work in comparison to the ones obtained in ref 6 confirm that the NMR chemical shifts are not critically dependent on which particular flavor of GGA is used in the calculations (that is, out of the available “standard” nonhybrid GGA functionals). The NMR code is part of the Amsterdam Density Functional (ADF) program system.[11] The two-component relativistic “zeroth order regular approximation” (ZORA)[12] density functional (DFT) method including spin−orbit (SO) coupling has been employed for the computations. We have used two different all-electron Slater-type basis sets in order to assess the dependence of the results on the quality of the basis. One basis set is the triple-ζ polarized ADF basis set “V”[11] that has also been used in ref 6. It includes one steep 1s function with an exponent of ∼10^3 for Hg in order to account for the strong relativistic increase of electron density at the nucleus (which is treated as a point nucleus here). This type of basis has been confirmed to yield reliable relativistic binding energies for a number of heavy metal compounds. However, we have previously found that a proper treatment of heavy nuclear spin−spin coupling constants needs a more flexible basis with 1s exponents at least up to ∼10^4 in the very vicinity of the heavy nucleus.[13−15] Similar basis set requirements have been reported for the ZORA computation of the hyperfine tensors of electron spin resonance.[16] Therefore, it is reasonable to expect that an accurate estimate of the SO Fermi-contact contribution to the shielding tensor requires a similarly flexible basis set. By “Fermi-contact” term we mean here the contribution from the operators that yield the well-known Fermi-contact term in the nonrelativistic limit. In the ZORA case, there is no actual contact term (i.e., a contribution from an operator with a δ function) but from an operator that weights the very vicinity of the nuclei instead (see refs 6, 13 for details). Therefore, the ZORA “Fermi-contact” term is heavily influenced by the relativistic increase of electron density around the nuclei, and an appropriately flexible basis needs to be employed. A newly developed ADF basis[17] offers an improved flexibility as compared to basis V in the near-nuclear region. It is of quadruple-ζ quality in the valence shell, with three 6p, one 6d, and two 5f polarization functions for Hg. Additionally, scalar relativistic ZORA calculations with basis set “V” have been carried out in order to determine the magnitude of the SO contributions. We will label these scalar relativistic calculations by “Method A”, spin−orbit calculations with the new quadruple-ζ basis by “Method B”, and spin−orbit calculations with basis set V by “Method C” in the following for simplicity. The computations of the shielding tensors are based on gauge-independent or gauge-including atomic orbitals (GIAOs).[18−20] However, because of the quality of the basis sets employed here the gauge dependence of the shielding tensor is rather small.

Due to recent improvements of the numerical integration grid generator of the ADF program, the use of a higher integration accuracy in this work, and the use of a somewhat different density functional as compared to ref 6, the isotropic shielding contributions reported in ref 6 are not exactly (but very closely) reproduced here (Method C). The changes are insignificant, however, with respect to the accuracy of the results as compared to experimental data. The same molecular geometries as used in ref 6 based on experimental bond lengths have been employed in the computations of this work.

Results

LCNMR Results. The dipolar coupling between the nuclei K and L is defined by eq 3:[2,3]

$$D_{\mathrm{KL}} = -\frac{\mu_o \hbar \gamma_K \gamma_L}{8\pi^2}\left\langle \frac{s_{\mathrm{KL}}}{R_{\mathrm{KL}}^3} \right\rangle = D_{\mathrm{KL}}^{\mathrm{eq}} + D_{\mathrm{KL}}^{\mathrm{ah}} + D_{\mathrm{KL}}^{\mathrm{h}} + D_{\mathrm{KL}}^{\mathrm{d}} \quad (3)$$

where μ_o is the permeability in vacuo, γ_K and γ_L are the gyromagnetic ratios of the nuclei K and L, respectively, R_{KL} is the internuclear distance, the ⟨ ⟩ brackets indicate rovibrational averaging, and

$$s_{\mathrm{KL}} = \frac{1}{2}(3\cos^2\theta_{z',\mathbf{R}_{\mathrm{KL}}} - 1) \quad (4)$$

where $\theta_{z',\mathbf{R}_{\mathrm{KL}}}$ is the angle between the external magnetic field (which coincides with the z'-axis of the laboratory frame) and the $\mathbf{R}_{\mathrm{KL}}$ vector. The terms after the second equality in eq 3 possess the following meaning: $D_{\mathrm{KL}}^{\mathrm{eq}}$ is the dipolar coupling corresponding to the equilibrium structure, $D_{\mathrm{KL}}^{\mathrm{ah}}$ and $D_{\mathrm{KL}}^{\mathrm{h}}$ are contributions arising from the anharmonic and harmonic vibrations, respectively, and $D_{\mathrm{KL}}^{\mathrm{d}}$ (the deformation contribution) is due to the correlation between the vibrational and reorientational motions. In addition, the experimentally determined anisotropic coupling, $D_{\mathrm{KL}}^{\mathrm{exp}}$, may include a contribution from the respective indirect spin−spin coupling tensor, $(1/2)\,J_{\mathrm{KL}}^{\mathrm{aniso}} = D_{\mathrm{KL}}^{\mathrm{ind}}$, whence

$$D_{\mathrm{KL}}^{\mathrm{exp}} = D_{\mathrm{KL}} + \frac{1}{2}J_{\mathrm{KL}}^{\mathrm{aniso}} \quad (5)$$

TABLE 1: Structure Parameters, Harmonic Correction Factors, and the J_{HgH} Spin−Spin Coupling Constants Used in the Determination of the Orientational Order Parameter S_{xx} for the Methylmercury Halides[a]

parameter	MeHgCl	MeHgBr	MeHgI
$R_{\mathrm{HgH}}{}^{b}$ (Å)	2.623	2.634	2.644
$R_{\mathrm{HgC}}{}^{c}$ (Å)	2.061	2.074	2.087
β^{d} (deg.)	23.56	23.45	23.50
α^{e} (deg.)	110.61	110.67	110.83
$p^{\mathrm{h}}_{\mathrm{HgH}}{}^{f}$	0.039	0.053	0.057
J_{HgH} (Hz)^{g}	−203.47 −202.59	−200.11	−187.58

[a] Data are taken from ref 22 if not otherwise indicated. [b] R_{CH} was assumed to be 1.10 Å. [c] From refs 23 and 24. [d] HHgC angle. [e] HCH angle. [f] $p^{\mathrm{h}}_{\mathrm{HgH}} = D^{\mathrm{h}}_{\mathrm{HgH}}/D^{\mathrm{exp}}_{\mathrm{HgH}}$. [g] The values were determined in the isotropic phase of the Phase 4 LC at 358 K. The lower value for MeHgCl is determined in the ZLI 1982 LC at 358 K.

The experimental $\delta^{\mathrm{iso}}_{\mathrm{Hg}}$ and $\Delta\sigma_{\mathrm{Hg}}$ values were derived applying eq 2. The orientational order parameter, S_{xx}, of the molecular symmetry axis was obtained from the dipolar Hg−H coupling constant, neglecting the deformation and indirect contributions. The latter are generally found to be negligible for couplings to protons, and in the present case the upper limit for $D^{\mathrm{ind}}_{\mathrm{Hg}}/D^{\mathrm{exp}}_{\mathrm{Hg}} \simeq 0.8\%$.[21] With these approximations, the experimental Hg−H dipolar coupling can be represented in the form

$$D^{\mathrm{exp}}_{\mathrm{HgH}} = -\frac{\mu_{\mathrm{o}}\hbar\gamma_{\mathrm{Hg}}\gamma_{\mathrm{H}}}{8\pi^2}\left\langle\frac{1}{R^3_{\mathrm{HgH}}}\right\rangle S_{xx}P_2(\cos\beta) \qquad (6)$$

where

$$S_{xx} = \frac{1}{2}\langle 3\cos^2\theta_{z',x} - 1\rangle \qquad (7)$$

Here, $S_{xx}P_2(\cos\beta)$ is the order parameter of the $\mathbf{R}_{\mathrm{HgH}}$ vector with respect to the external magnetic field, and β is the angle between this vector and the x-axis of the molecule fixed coordinate frame. The Hg−H distance and the angle β were adopted from ref 22 and assumed to be independent of temperature.

The orientational order parameter, S_{xx}, was thus calculated from eq 6 using $D^{\mathrm{exp}}_{\mathrm{HgH}}$ corrected for harmonic vibrations:

$$S_{xx} = -\frac{8\pi^2}{\mu_o\hbar\gamma_{\mathrm{Hg}}\gamma_{\mathrm{H}}}\frac{(1+p^{\mathrm{h}}_{\mathrm{HgH}})D^{\mathrm{exp}}_{\mathrm{HgH}}}{\langle R^{-3}_{\mathrm{HgH}}\rangle P_2(\cos\beta)} \qquad (8)$$

where $p^{\mathrm{h}}_{\mathrm{HgH}} = D^{\mathrm{h}}_{\mathrm{HgH}}/D^{\mathrm{exp}}_{\mathrm{HgH}}$ is the correction factor that takes into account the effect of harmonic vibrations. The relative harmonic vibrational correction is independent of molecular orientation for molecules possessing a 3-fold symmetry axis, and consequently, the correction factor could be taken from an earlier study.[22] One should notice that the molecular structure determined with the aid of dipolar couplings corrected for harmonic vibrations is the so-called r_α structure in which the internuclear distances are distances between the average positions of the nuclei, i.e., they differ from the equilibrium values because of the anharmonicity of the vibrational potential. The structure parameters (determined by LCNMR in the Phase 4 LC,[22] the same LC as used in this work) needed in the calculation of the S_{xx} values are listed in Table 1.

The proton-coupled ^{199}Hg NMR spectrum of methylmercury halides is a quartet where the separation between two successive peaks equals $|2D^{\mathrm{exp}}_{\mathrm{HgH}} + J_{\mathrm{HgH}}|$. This means that the spin−spin coupling constants, J_{HgH}, must be known in order to be able to resolve the experimental dipolar coupling. The J_{HgH} values were obtained from the ^{199}Hg NMR experiments performed in the isotropic phases of the LCs (at ca. 358 K); then $D_{\mathrm{HgH}} = 0$ and the observable spectral splitting equals $|J_{\mathrm{HgH}}|$. The J_{HgH} values are also shown in Table 1.

As mentioned in the Introduction section, there exist various means to solve the properties of a shielding tensor from eq 2. Which method is chosen depends on the system and shielding tensor studied. Generally, the experimentally detected shielding constant includes contributions from various sources

$$\sigma^{\mathrm{exp}} = \sigma^{\mathrm{mol}} + \sigma^{\mathrm{a}} + \sigma^{\mathrm{b}} \qquad (9)$$

where σ^{mol} arises from the electron distribution in the molecule and is the property looked for, σ^{a} is a local contribution that is caused by the nearest neighbor molecules (this contribution is furthermore anisotropic), and σ^{b} is a bulk effect that stems from the other parts of the sample. Due to the large anisotropy of the ^{199}Hg shielding tensor, the first term, σ^{mol}, is dominant, and consequently almost anyone of the available LCNMR methods should lead to fairly reliable results. We have chosen to use the so-called gradient method in which the molecular degree of order, S_{xx}, is changed by changing the sample temperature[1,2] and which renders possible the utilization of the large chemical shift range of mercury when also the point $S_{xx} = 0$ is included in the analysis. This means that both $\sigma^{\mathrm{iso}}_{\mathrm{Hg}}$ and $\Delta\sigma_{\mathrm{Hg}}$ are assumed to be *independent* of temperature and the phase of the LC solvent. Then the experimental ^{199}Hg NMR chemical shift is a linear function of the order parameter S_{xx}. In other words, the $\Delta\sigma_{\mathrm{Hg}}$ is obtained from the slope and the $\delta^{\mathrm{iso}}_{\mathrm{Hg}}$ from the intercept of the straight line resulting from the linear least-squares fit of the experimental data to the function in eq 2. The chemical shifts were measured with respect to an external dimethylmercury reference, i.e., dimethylmercury was dissolved in the Phase 4 LC and the sample was heated to the isotropic state at 358 K. The $\delta^{\mathrm{iso}}_{\mathrm{Hg}}$ and $\Delta\sigma_{\mathrm{Hg}}$ values are shown collected in Table 2. These parameters were determined for MeHgCl in two LC solutions—Phase 4 and ZLI 1982. As the table shows, the values derived in these two environments are the same within experimental uncertainty.

ZORA DFT Results. The ZORA ^{199}Hg shielding tensor can be represented as a sum of three contributions[6]

$$\sigma_{\alpha\beta} = \sigma^{\mathrm{d}}_{\alpha\beta} + \sigma^{\mathrm{p}}_{\alpha\beta} + \sigma^{\mathrm{SO}}_{\alpha\beta} \qquad (10)$$

where $\sigma^{\mathrm{d}}_{\alpha\beta}$ is the diamagnetic contribution, $\sigma^{\mathrm{p}}_{\alpha\beta}$ the paramagnetic contribution, and $\sigma^{\mathrm{SO}}_{\alpha\beta}$ the spin−orbit contribution. The latter arises from the fact that, in systems with a significant amount of electronic spin−orbit coupling present, the external magnetic field induces an electronic spin density. This spin density then causes nonvanishing shielding contributions by magnetic interaction with the nuclear spin (Fermi-contact and spin-dipole term, see also the Experimental and Theoretical sections). Of the two contributions, the one due to the Fermi-contact term has been shown to be the dominant one in most cases investigated so far.[10] This is in close analogy to the Fermi-contact contribution to nuclear spin−spin coupling tensors, except that in the latter case the electronic spin density is induced by the presence of the other nuclear spin instead of the external field. The analogy between spin−spin coupling constants and spin−orbit contributions to nuclear shieldings has been proposed in the literature several decades ago,[27] and has been investigated in detail by DFT computations in ref 28.

The computational results are collected together with the corresponding experimental data in Tables 2 and 3. In accor-

TABLE 2: ^{199}Hg Chemical Shifts (relative to dimethylmercury) and Shielding Tensor Anisotropies of Methylmercury Halides (All values are given in ppm)

molecule	basis [a]	calculated $\delta^{\mathrm{iso}\ b,c}$	experimental $\delta^{\mathrm{iso}\ b}$	calculated $\Delta\sigma$	experimental $\Delta\sigma^{c}$
MeHgMe	A	0	0	5975	
	B	0	0	8868	7260(90)[d]
	C	0	0	7857	7355(55)[e]
MeHgCl	A	−898		4750	
	B	−1080	−771(18)	6967	5330(110)
	C	−921	−771(5)[f]	6319	5430(40)[f]
MeHgBr	A	−818		4878	
	B	−1206		6831	
	C	−1050	−884(15)	6168	5140(90)
MeHgI	A	−590		5226	
	B	−1279		6697	
	C	−1103	−1080(10)	6071	4840(70)

[a] A = scalar relativistic calculation with the same basis as C, B = Slater quadruple ζ basis with 1s exponents up to 10^4, and C = Slater triple ζ basis with 1s exponents up to $\sim 10^3$. [b] $\delta^{\mathrm{iso}} = \delta^{\mathrm{iso}}(\mathrm{MeHgX}) - \delta^{\mathrm{iso}}(\mathrm{Me_2Hg}) = \sigma^{\mathrm{iso}}(\mathrm{Me_2Hg}) - \sigma^{\mathrm{iso}}(\mathrm{MeHgX})$. The figures in parentheses indicate the standard error in units of the last digit. Calculations were performed for the eclipsed conformation of dimethylmercury. [c] Experiments were carried out in the Phase 4 LC if not otherwise indicated. The figures in parentheses indicate the standard error in units of the last digit. [d] Ref 25. Experiments were carried out in the mixtures of Phase 4 and ZLI 1167 (mixture of 4-*n*-alkyl-*trans*,*trans*-bicyclohexyl-4′-carbonitriles) LCs. [e] Ref 26. Experiments were carried out in the smectic phase of the HAB (*p*,*p*′-di-*n*-heptylazoxybenzene) LC. [f] The value was derived in the ZLI 1982 solution.

dance with results obtained previously by other authors for the same or similar compounds,[6,29] the spin−orbit contributions to the isotropic Hg shielding are far from being negligible. The situation is similar for the anisotropy of the shielding tensor. As compared to the isotropic shielding, though, the magnitudes of the spin−orbit contributions represent a smaller fraction of the respective paramagnetic terms. Still, for both the Hg chemical shifts and for the shielding anisotropy, the scalar ZORA computations predict a different trend along the series HgMeX (*X* = Me, Cl, Br, I) as it is observed experimentally. As in many other cases (such as hydrogen halides, methyl halides), the spin−orbit contributions are largely responsible for the trend that is observed experimentally, even though their relative importance is smaller here as, e.g., in the hydrogen halides.

For the spin−orbit results for the different basis sets (Methods B and C), we observe a systematic overestimation of the results in comparison with the experimental data, in particular for Method B (larger basis) and somewhat less pronounced for Method C (basis V). The additional presence of steep 1s functions in Method B cause the Fermi-contact matrix elements to be larger in magnitude, therefore in particular the $\sigma^{\mathrm{SO}}_{\alpha\beta}$ contributions in Table 3 are significantly larger for Method B than for Method C. However, the computations do not account for the surrounding liquid crystal environment used for the experiments. Therefore, we cannot yet conclude that Method C yields "better" results than Method B, because inclusion of environmental effects can have a substantial effect on the results.[6] Previous experience with the computation of nuclear spin−spin coupling constants for the same series of molecules[14,15] suggests that the trends that are observed experimentally in the NMR spectrum can be reproduced and correctly interpreted on the basis of calculations of isolated molecules. Inclusion of steep 1s basis functions are necessary in order to obtain the correct magnitude for the Fermi-contact contributions to the spin−spin couplings. We can expect a similar behavior with respect to the basis set flexibility for nuclear shieldings. At the same time, one needs to consider the presence of surrounding solvent molecules in order to achieve quantitative agreement with experimental data. In that respect, the data of Method B might well prove to lead to much better agreement with experiment once the computations can take the liquid crystal environment explicitly into account.

TABLE 3: ^{199}Hg Shielding Tensor Elements, Tensor Anisotropy, and Isotropic Average As Obtained by ZORA DFT Calculations for Dimethylmercury and Methylmercury Halides (All values are given in ppm)

molecule	basis [a]	contribution	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma^{b}$	$\sigma^{\mathrm{iso}\ c}$
MeHgMe[d]	A	paramagnetic	188	−5766	5954	−3781
		diamagnetic	9602	9581	21	9588
		total	9790	3815	5975	5807
	B	paramagnetic	361	−6691	7052	−4340
		diamagnetic	9635	9613	22	9620
		SO	4301	2507	1794	3105
		total	14297	5429	8868	8385
	C	paramagnetic	246	−6207	6453	−4056
		diamagnetic	9620	9611	9	9614
		SO	3392	1997	1395	2462
		total	13258	5401	7857	8020
MeHgCl	A	paramagnetic	268	−4456	4724	−2881
		diamagnetic	9604	9578	26	9586
		total	9872	5122	4750	6705
	B	paramagnetic	362	−5171	5533	−3326
		diamagnetic	9636	9611	25	9619
		SO	4111	2702	1409	3172
		total	14109	7142	6967	9465
	C	paramagnetic	283	−4885	5168	−3163
		diamagnetic	9623	9611	12	9615
		SO	3249	2109	1140	2489
		total	13154	6835	6319	8941
MeHgBr	A	paramagnetic	272	−4580	4852	−2963
		diamagnetic	9605	9580	25	9588
		total	9877	5000	4877	6625
	B	paramagnetic	380	−5364	5744	−3450
		diamagnetic	9637	9612	25	9621
		SO	4128	3066	1062	3420
		total	14145	7314	6831	9591
	C	paramagnetic	298	−5008	5306	−3239
		diamagnetic	9624	9608	16	9613
		SO	3260	2414	846	2696
		total	13182	7014	6168	9070
MeHgI	A	paramagnetic	275	−4926	5201	−3193
		diamagnetic	9607	9582	25	9590
		total	9882	4656	5226	6397
	B	paramagnetic	411	−5833	6244	−3751
		diamagnetic	9639	9614	25	9623
		SO	4079	3651	428	3794
		total	14129	7432	6697	9664
	C	paramagnetic	324	−5422	5748	−3506
		diamagnetic	9626	9609	17	9615
		SO	3220	2912	308	3014
		total	13171	7100	6071	9123

[a] See footnote *a* in Table 2. [b] $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. [c] $\sigma^{\mathrm{iso}} = (1/3)\,(\sigma_{\parallel} + 2\sigma_{\perp})$. [d] Calculations were performed for the eclipsed conformation.

Discussion

As already mentioned, the comparison of the experimental and computed chemical shifts and shielding anisotropies is complicated by the fact that the calculations are performed for isolated molecules whereas experiments are carried out in solutions. The ^{199}Hg chemical shift is extremely sensitive to medium effects;[30,31] the shift for each methylmercury halide as well as for dimethylmercury changes tens of ppm when the solvent is changed. Anyway, although the ZORA DFT calculations overestimate the chemical shift, the experimentally observed increasing trend along the series from MeHgCl to

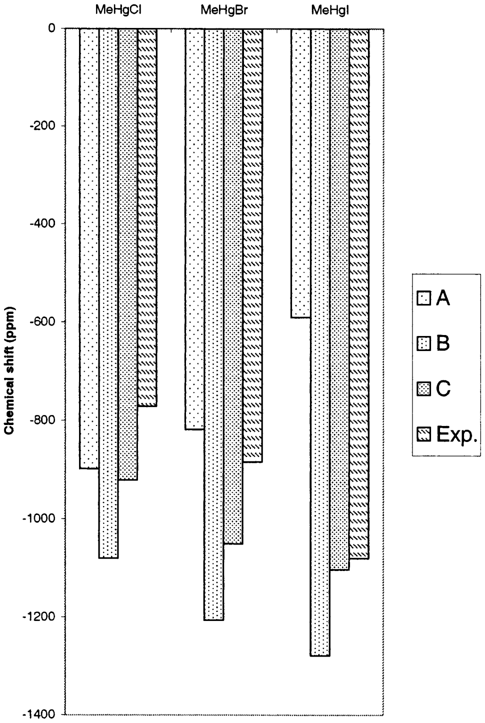

Figure 1. Comparison of the ^{199}Hg chemical shifts of methylmercury halides as determined by ZORA DFT calculations and LCNMR experiments. Shifts are relative to the external dimethylmercury reference. A = scalar relativistic calculation, B = Slater quadruple ζ basis with steep core functions, C = Slater triple ζ with one steep core function, and Exp = present LCNMR result.

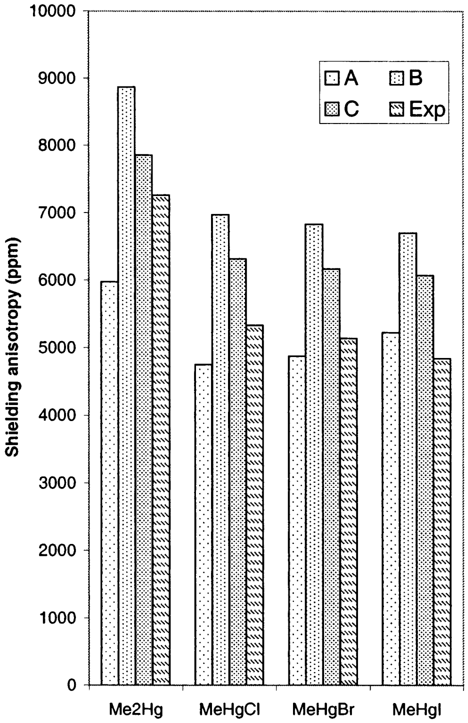

Figure 2. Comparison of the ^{199}Hg shielding tensor anisotropies in methylmercury halides and dimethylmercury as determined by ZORA DFT calculations and LCNMR experiments. A = scalar relativistic calculation, B = Slater quadruple ζ basis with steep core functions, C = Slater triple ζ with one steep core function, and Exp = present LCNMR result.

MeHgI is clearly predicted provided that the spin−orbit coupling is taken into account. The scalar relativistic calculations lead to an opposite behavior. The graphical comparison of the chemical shifts is made in Figure 1.

The shielding anisotropy was earlier determined with the aid of LCNMR by Kennedy and McFarlane.[5] They applied an indirect method in which the ^{1}H NMR spectra of the halides were detected with simultaneous decoupling of ^{199}Hg. The spectra were taken in the isotropic phase and in the nematic phase of the DHOAB (4,4′-dihexyloxyazoxybenzene) LC, and the vibrational contributions to the dipolar couplings were not taken into account. When harmonic vibrations are considered, their results approach those of the present work. Comparison of the present calculated and experimental values is made graphically in Figure 2.

Regarding the computational results it is found that the Hg nuclear shieldings in comparison to the ones previously reported in ref 6 become larger and therefore lead to less good agreement of the chemical shifts with experimental data when additional steep basis functions are used for Hg (compare the results for Method B and Method C). This is mainly due to an increasing spin−orbit contribution resulting from a better description of the Fermi-contact matrix elements. At the same time, the results of ref 6 indicate that a large compensating effect is likely to occur in case the surrounding environment of liquid crystal molecules would be considered in the computations. Furthermore, the program evaluates a contribution to the shielding tensor that is caused by the induced spin density in the molecule in an “uncoupled” manner. The corresponding first-order exchange potential can be determined in a self-consistent procedure similar to the one already available in a related ZORA DFT code to determine nuclear spin−spin couplings.[13,14] At present, however, it is not possible to predict the magnitude of these correction terms in comparison to the main contributions $\sigma^{d}_{\alpha\beta}$, $\sigma^{p}_{\alpha\beta}$, and $\sigma^{SO}_{\alpha\beta}$. The overall agreement with experiment that has been achieved for the determination of the Hg shielding anisotropy is already quite satisfactory and allows an interpretation of the experimentally observed trend in terms of an increasing magnitude of the spin−orbit contributions to $\Delta\sigma$ along the series MeHgX (X = Cl, Br, I).

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