

surface we have been able to stimulate the formation of benzene from an acetylene adlayer. It is possible that through further examination of this model system we might be able to discover which of platinum's properties normally prohibit the formation of benzene from acetylene, and how the presence of Sn in the surface alloy alters the Pt surface so that the reaction can take place. In a separate experiment we have found that carbon, which usually acts as a site blocker, cannot promote benzene formation.³⁰

Therefore, an electronic effect of Sn must be important in the production of benzene.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

(30) Peck, J. W.; Xu, C.; Koel, B. E., to be submitted for publication.

Comments Concerning the Computation of ¹¹³Cd Chemical Shifts

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Abstract: We have examined the ¹¹³Cd chemical shift difference between dimethyl- and diethylcadmium from both an experimental and a theoretical perspective. Further, we have determined the chemical shift difference in the gas phase, in which diethylcadmium is more shielded than dimethylcadmium by 142.6 ppm. In contrast to other reported calculations, we demonstrate that these chemical shifts cannot be calculated quantitatively. The reasons for this lack of quantitation are discussed.

In the past several years, we¹ and others² have developed and utilized Cd²⁺ via ¹¹³Cd NMR spectroscopy as a "spin-spy" to study Zn²⁺ and Ca²⁺ sites in metal-dependent proteins and metalloproteins. The reasoning behind this strategy is the fact that Zn²⁺ and Ca²⁺ have such poor spectroscopic properties. Both have closed shell electron configurations; hence, ESR spectroscopy is unavailable. Further, both have d¹⁰ electron configurations; therefore, their UV/vis spectroscopy lacks "color" and distinction. As a consequence of these "boring" spectroscopic properties, other alternatives have been pursued, i.e., the surrogate probe strategy as a means to study these metals in this important class of biological systems. In every case studied to date, the surrogate strategy has been successful, i.e., it has provided results which are consistent with the known chemistry of the system of interest. ¹¹³Cd NMR spectroscopy is recognized as one of the best (if not the best) spectroscopic methods with which to understand the ligand chemistry and dynamics associated with Zn²⁺ or Ca²⁺ sites in metalloproteins.² Parallel to these efforts are fundamental experiments directed toward the understanding of the structural and electronic basis for these metal ion magnetic resonance parameters, e.g., chemical shifts and shielding tensors. Single crystal NMR experiments^{1d-f} have been utilized to correlate X-ray data with these tensor quantities. With such correlations, empirical models^{1b} have been developed that can be utilized to predict the orientation of shielding tensors of metal ions. Similar models can be developed for electric field gradient tensors. These models form the basis for the understanding of the protein-metal ion shielding data.^{1c} These models also have the advantage that they can be tested by ab initio MO methods for calculating shielding tensors.

We have been interested in the calculation of shielding tensors³ for several years. However, only recently have we begun to

perform calculations of ¹¹³Cd shielding tensors via ab initio MO methods. The reason for this delay has been 2-fold. First, we believe that these shielding tensors have significant relativistic contributions from L-S terms, and second, the importance of the contribution that electron correlation makes to these shielding tensors is unknown. The spin-orbit terms arise from the uncoupling of the angular momentum and spin by the applied magnetic field. The basis for this hypothesis is the position of cadmium in the periodic table. As is well known from atomic spectroscopy, *l* and *m_l* are no longer good quantum numbers for elements with atomic number greater than approximately 35 (Br) to 40 (Zr).⁴ Further, for electron velocities Hartree⁵ states, "For an atom of atomic number *N*, velocities (in atomic units) are on the order of *N*²; so relativistic effects are of order (*N*/137).^{2"} For cadmium, *N* is 48 and (*N*/137)² is 0.123. For other metal ions of biological interest, e.g., Zn, Mo, and Hg, (*N*/137)² is 0.048, 0.094, and 0.341, respectively. Relativistic effects should be noticeable for cadmium and especially mercury. Cadmium and mercury are known⁶ to have parallel trends in shielding, with an increased sensitivity for mercury.

Given this perspective, we were surprised to read a paper by Nakatsuji and co-workers⁷ which stated that ¹¹³Cd chemical shifts could be calculated quantitatively by ab initio coupled Hartree-Fock (CHF) methods. The experimental systems treated were organocadmium compounds, i.e., dimethylcadmium, diethylcadmium, and ethylmethylcadmium. The chemical shift difference for dimethyl- and diethylcadmium, 99.7 ppm for the neat liquids, was difficult for us to explain in our original determination.^{1a} We noted in that work that a chemical shift difference may result from self-association in the neat liquids.

The results of Nakatsuji and co-workers⁷ looked excellent; however, on closer examination some puzzling questions arose.

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Table I. ^{113}Cd Isotropic Chemical Shifts for Dimethyl- and Diethylcadmium in the Liquid and Gas Phases

sample	chemical shift ^a
$\text{Cd}(\text{C}_2\text{H}_5)_2$, neat	-99.7 ^b
$\text{Cd}(\text{C}_2\text{H}_5)_2$, 1% solution ^c	-85.23
$\text{Cd}(\text{C}_2\text{H}_5)_2$, gas ^d	-80.52
$\text{Cd}(\text{CH}_3)_2$, neat	0.0
$\text{Cd}(\text{CH}_3)_2$, 1% solution ^c	35.32
$\text{Cd}(\text{CH}_3)_2$, gas ^d	62.09

^a All chemical shifts are expressed in ppm with respect to neat $\text{Cd}(\text{CH}_3)_2$. The chemical shift of neat $\text{Cd}(\text{CH}_3)_2$ with respect to 0.1 M CdClO_4 is 642.93 ppm. ^b A positive chemical shift denotes resonance to lower shielding. ^c Reference 1a. ^d Approximate concentration in cyclohexane. See the text for experimental details. ^e The temperature was 97 °C.

The approximate geometry used was based upon Pauling's tetrahedral covalent radii,⁸ with C–Cd distance of 2.25 Å and CH bond distances chosen to be 1.094 Å with a CdCH angle of 109.5°. The experimental C–Cd distance and HCCd angle are known⁹ for dimethylcadmium and are 2.112 Å and 108.4°, respectively. How sensitive are the results to this choice of geometry? The basis set they used,¹⁰ MIDI-1, needed to be augmented. Two p-polarization functions¹¹ were added with ζ_p of 0.16 and 0.04094. Further, no d-polarization functions on the Cd were utilized except the splitting in the occupied 4d functions, i.e., (...|3) to (...|21). A potential problem with the calculation was the nonuniform utilization of the basis set, i.e., MIDI-1 on the cadmium and contiguous atoms and MINI-1 on the remaining atoms. With this basis set, one of Nakatsuji's⁷ conclusions was that d–p metal–ligand interactions are *not* important for ^{113}Cd chemical shifts. It is interesting to note that the basis set utilized did not allow (except as noted above) such interactions to be fully explored. A natural question at this point is, how sensitive are the calculated results to the choice of basis sets?

With these questions in mind we initiated the following investigation. We will present an experimental redetermination of the ^{113}Cd chemical shift difference between dimethyl- and diethylcadmium. This was accomplished in two ways. First, liquid-state methods were used at moderate concentrations in a noninteracting solvent (cyclohexane) to minimize the self-association present in the neat liquids. Second, the shift difference was determined in the gas phase. Further, we present results of calculations of ^{113}Cd chemical shifts that demonstrate that even with careful selection of the basis sets and geometry these shifts cannot be calculated quantitatively.

Experimental Methods

Synthetic Methods. The organocadmium compounds dimethyl- and diethylcadmium were prepared by standard Grignard methods in ether solutions.¹² The solvents diethyl ether and cyclohexane were freshly distilled under N_2 and freeze–thaw degassed prior to their use. The purification of the compounds was accomplished by high-vacuum trap-to-trap fractionation and variable-temperature cold column separation.¹³ The purity (>99%) was confirmed by ^1H and ^{13}C NMR spectroscopy on a Bruker AM-300 instrument.

The liquid-state NMR samples were prepared by vacuum condensation of the compound and the solvent into a 10-mm NMR tube. Each sample was freeze–thaw degassed before being flame sealed under dynamic vacuum. The concentration of the $\text{Cd}(\text{CH}_3)_2$ sample was calculated to be 0.088 M, and that for the $\text{Cd}(\text{C}_2\text{H}_5)_2$ sample was 0.176 M. For the gas-phase NMR samples, the appropriate amount of material

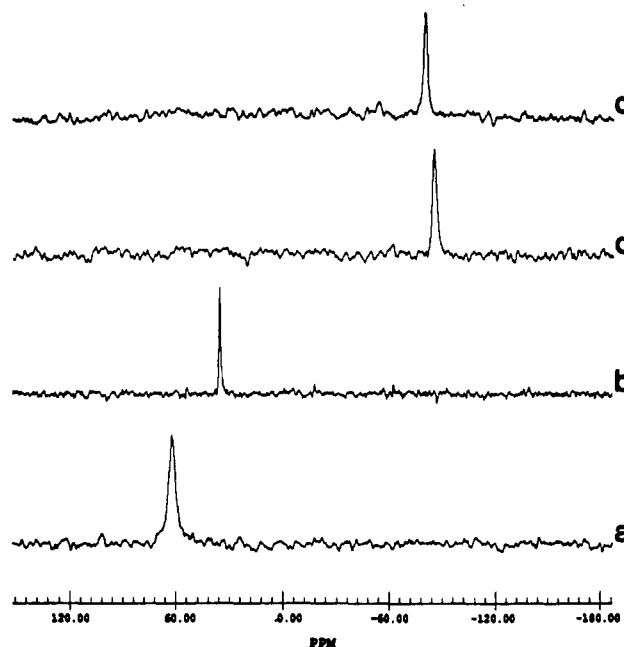


Figure 1. Bloch decay spectra run at 88.7 MHz with a spectral width of 30030 Hz and zero-filled to 8K complex pairs. For the gas samples a $\pi/2$ pulse was 29 μs , and a $\pi/2$ pulse for the liquid samples was 25 μs . (a) 10000 transients using a 10-ms delay and a $\pi/2$ pulse for $\text{Cd}(\text{CH}_3)_2$ in the gas phase; (b) 512 transients with a 2-s delay and a $\pi/2$ pulse for 1% $\text{Cd}(\text{CH}_3)_2$ in cyclohexane; (c) 1% $\text{Cd}(\text{C}_2\text{H}_5)_2$ in cyclohexane with 2048 transients using a 1-s delay and a $\pi/4$ pulse; (d) $\text{Cd}(\text{C}_2\text{H}_5)_2$ in the gas phase after 120000 transients with a 30-ms delay and a $\pi/2$ pulse.

Table II. Basis Set Descriptions

atom	basis set descriptor ^a	number of basis functions ^b
H	(31)	2
	(31 1)	5
	(43 4)	5
C	(421 31)	9
	(43333 433 43)	26
	(433321 4321 421)	36
	(433321 43311 4311)	45
Cd	(433321 43311 4311 11)	65

^a The notation (...|.j...|k...) denotes that there are i , j , and k primitives used in the expansion of the s-orbitals, p-orbitals, and d-orbitals, respectively. The ordering is always (s|p|d|f|...). ^b Six d-orbitals and ten f-orbitals were used in the calculation of the total number of basis functions.

was condensed under vacuum into an 8-mm (7-mm i.d. and approximately 5 cm in length) insert and then flame sealed under dynamic vacuum. The 8-mm sample was placed into a 10-mm tube with $\text{DMSO}-d_6$ as a lock solvent. A vortex plug was utilized to keep the 8-mm insert from "floating" in the lock solvent.

NMR Spectroscopy. The NMR measurements were made on a Varian XL-400 spectrometer operating at 9.4 T, 88.7 MHz for ^{113}Cd . The probe used was a broad-band, tunable 10-mm liquids probe from Varian Associates. The spectra of neat $\text{Cd}(\text{CH}_3)_2$ and the 1% solutions in cyclohexane were all obtained under unlocked conditions. All chemical shifts reported are relative to external neat dimethylcadmium. In order to ensure total vaporization of both dimethyl- and diethylcadmium, the gas-phase shifts were measured at 97 °C. The chemical shifts of the gas-phase sample of dimethylcadmium were independent of temperature, i.e., any variation was within the line width, which was typically 3 ppm. Figure 1 summarizes the ^{113}Cd liquid- and gas-phase NMR spectra. Presented in Table I is a summary of the resulting chemical shifts.

Computational Details. The shielding calculations were performed with the Gaussian 90¹⁴ systems of programs, including an updated version

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Table III. Exponents for Polarization Functions^a

atom	MIDI-4p2		MIDI-4p2d2f2					
	ζ_{p1}	ζ_{p2}	ζ_{p1}	ζ_{p2}	ζ_{d1}	ζ_{d2}	ζ_{f1}	ζ_{f2}
Cd ^b	0.9405	0.0755	0.9446	0.0779	0.4113	0.0990	0.9731	0.1193
Cd ^c	0.5138	0.0706	0.4754	0.0733	0.3498	0.1392	0.9594	0.1252

^a Basis sets used were p2 and p2d2f2 as described in the text. ^b Exponents optimized for the MINI-4 basis set. In the optimization the number of d- and f-functions was limited to 5 and 7, respectively. ^c Exponents optimized for the basis set of Friedlander, Howell, and Synder.²⁰

Table IV. MP2 Optimized Geometries^a

		r_{CdC}	r_{CC}	r_{CH}	θ_{CdCH}	θ_{CdCC}	θ_{CCH}
Cd(CH ₃) ₂	MIDI-4p2d2f2 ^b	2.149 66		1.101 08	110.103 48		
	MIDI-4p2d2f2 ^c	2.142 00		1.106 99	110.346 88		
	fhs-p2d2f2 ^d	2.131 07		1.106 99	110.441 72		
Cd(C ₂ H ₅) ₂	MIDI-4p2d2f2 ^b	2.158 16	1.585 00	1.100 83	107.805 97	113.252 32	110.742 21
	MIDI-4p2d2f2 ^c	2.149 42	1.601 44	1.106 10	108.421 18	112.792 17	110.267 82
	fhs-p2d2f2 ^d	2.138 08	1.600 86	1.106 06	108.606 64	112.252 92	110.404 81

^a All distances are in angstroms, and the angles are in degrees. ^b See footnote b, Table VI for details. ^c See footnote c, Table VI for details. ^d See footnote d, Table VI for details.

of the RPAC¹⁵ program of Bouman and Hansen capable of utilizing f-orbitals. The shielding constants were computed on a VAX-Station 3540. Geometry optimizations were also performed on the VAX-Station. However, some of these optimizations were also performed on an IBM RISC-6000/550 computer. The shielding calculations were performed two ways: The localized orbital/local origin method (LORG) of Hansen and Bouman^{15,16} and the coupled Hartree-Fock (CHF) method.¹⁷ The origin dependence of the former and the sensitivity of the latter to the quality of the basis set are well known^{16,18,19} and will not be discussed here. We simply present both methods for comparison purposes.

The basis sets employed were of the MIDI-*N*¹⁰ variety (where *N* ranged from 1 to 5) and those of Friedlander, Howell, and Synder.²⁰ Both basis sets were used in conjunction with the basis set of Dunning and Hay²¹ for carbon and hydrogen. The details of the basis set nomenclature can be found in Table II. For example, the basis sets MINI-1, MIDI-4, and MIDI-4p2d2f2 for Cd would be designated as (33333|333|33), (433321|4321|421), and (433321|43311|4311|11), respectively. The Dunning and Hay²¹ basis for hydrogen and carbon would be denoted as (31) and (6111|41), respectively. As in the previous work,⁷ it proved necessary to augment the basis functions for Cd. However, in the present calculations the exponents for the polarization functions were determined with the Gaussian¹⁴ utility program g90opt. The energy-optimized exponents are summarized in Table III. When d- or f-orbital exponents were being optimized the number of d- or f-Gaussian-type orbitals was 5 and 7, respectively. However, in subsequent calculations using d- or f-orbitals, the number of orbitals was 6 and 10, respectively. For cadmium, the exponents were optimized in the triplet state. This was done to simulate the "valence" nature of the added functions.

The first two columns of Table III denote exponents for p-orbital polarization functions when no other polarization functions are to be added to the basis set, i.e., MIDI-4p2. The remaining entries correspond to the case when multiple polarization functions are being added to the basis set, i.e., MIDI-4p2d2 or MIDI-4p2d2f2. The exponents for the p- and d-orbital polarization functions did not change upon adding the f-orbital polarization functions.

Geometries do not play an essential role in the computation of the shielding tensors for dimethyl- and diethylcadmium. However, we have chosen to use theoretical geometries for the simple reason that an experimental geometry for diethylcadmium has not been determined. Hence, a balanced comparison of predicted shielding differences can only be made with optimized theoretical geometries. Figure 2 summarizes the framework geometry utilized in the present study. For dimethylcadmium, three parameters were optimized: r_{CdC} , r_{CH} , and θ_{CdCH} . If one hydrogen from each methyl group, the carbons, and the cadmium lie in

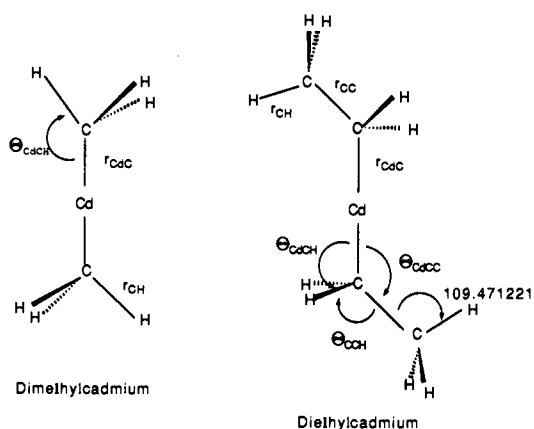


Figure 2. Framework geometries utilized in the MO calculations.

a plane, then the angle made by the "out-of-plane" hydrogens to this plane is constrained to be 60°. The framework of diethylcadmium is more complicated, and as a result only six parameters were optimized: r_{CdC} , r_{CC} , r_{CH} , θ_{CdCC} , θ_{CdCH} , and θ_{CCH} . The basic framework was kept in a "trans-like" geometry, and the value of the CCH bond angle for the methyl group was kept at its tetrahedral value of $2 \cos^{-1}(3^{-1/2})$.

The geometries used for these calculations were optimized at the MP2^{14,22} level of approximation for each of the basis sets. From a comparison of the resulting geometries of an MP2 optimization with and without f-orbitals, we determined that the f-orbitals made a significant difference to the predicted geometries. The experimental Cd-C bond distance⁹ is 2.112 Å. The predicted bond distance for dimethylcadmium using MP2 methods with p2d2 or p2d2f2 basis sets was 2.2006 and 2.1495 Å, respectively. That is, the inclusion of f-orbitals led to an improvement in the predicted bond length by 5.11×10^{-2} Å. Hence, all of the MP2^{14,22} optimizations were performed with a basis augmented by a pair of p-, d-, and f-, functions, e.g., the so-called p2d2f2 basis set. The results are summarized in Table IV using the framework depicted in Figure 2. These geometries were optimized using all of the electrons instead of using the so-called "frozen-core" approximation.²³ Using frozen-core methods in the correlation calculation results in a bond length for the Cd-C bond of 2.1544 Å, i.e., a bond lengthening of 4.9×10^{-3} Å. Since this trend is in the wrong direction, we chose to use all of the electrons in the correlation.²⁴

Results and Discussion

There are two points that we would like to cover in the present investigation: (1) the question of using chemical shifts from neat liquids as reference points for essentially gas-phase calculations

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(24) The computational speed of the all-electron methods is much faster than the frozen-core approach as well. This is due to the nongradient methods employed in the frozen-core calculations.¹⁴

and (2) the sensitivity of the calculated shielding tensor to the choice of basis set and geometry. We will address each of these points in turn.

In our original paper on ^{113}Cd NMR spectroscopy,^{1a} which dealt in part with the determination of the isotropic chemical shift difference between dimethyl- and diethylcadmium, we noted that the chemical shift of neat dimethylcadmium was due to an associated species. This was clear from the 101.12-ppm chemical shift range observed for 1.0 M solutions of dimethylcadmium in a variety of solvents. The most telling data point was the shift of 34.67 ppm to lower shielding for the dimethylcadmium in going from the neat liquid to a 1.0 M solution in cyclohexane. Hence, it was clear that the observed shift difference of 99.73 ppm for dimethyl- and diethylcadmium was not representative of the isolated molecules. As mentioned above, we have redetermined the shift difference in two ways. First, we have used a solvent which should minimize the apparent self-association in the neat liquids. We chose cyclohexane with concentrations of 0.088 and 0.176 M for dimethyl- and diethylcadmium, respectively. These concentrations correspond to approximately 1% (v/v) solutions. The chemical shift difference in this solvent resulted in diethylcadmium being more shielded than dimethylcadmium by 120.6 ppm. Second, we have determined the shift difference in the gas phase. The spectra are presented in Figure 1, and the shifts are summarized in Table I. The gas-phase chemical shift measured for dimethylcadmium, 62 ppm to lower shielding with respect to neat dimethylcadmium, is larger than the corresponding difference obtained for diethylcadmium, i.e., 19.2 ppm to lower shielding with respect to neat dimethylcadmium. These chemical shifts with respect to the corresponding neat liquids are significant. However, one can only speculate at this point as to their origin. We suspect that these shifts arise from van der Waals-type association rather than the specific formation of a dimer structure involving bridging methyl groups. However, more experimental work is required to test such speculation.

The chemical shift difference in the gas phase was determined to be 142.6 ppm. To put this chemical shift difference into perspective, the normal range of ^{13}C chemical shifts is typically 200 ppm. The 200-ppm range of chemical shifts for carbon relative to the 900-ppm shift range for cadmium² is principally related to the smaller value of $\langle r^{-3} \rangle_{\text{val}}$ for carbon relative to $\langle r^{-3} \rangle_{\text{val}}$ for cadmium.²⁵ Hence, the "simple" replacement of both methyl groups by ethyl groups has led to a gas-phase ^{113}Cd chemical shift difference of 142.6 ppm or $\sim 71\%$ of the common ^{13}C chemical shift range! Therefore, the dimethyl- and diethylcadmium gas-phase chemical shift represents about 16% of the range of ^{113}Cd chemical shifts. The origin of this chemical shift can be addressed only by calculations of the ^{113}Cd chemical shifts.

Our original data^{1a} undoubtedly represented a partial motivation for the pioneering computations of Nakatsuji and co-workers.^{7,11} However, as we have pointed out in the introduction, these computations raise some interesting questions. Of particular interest here is the basis set used in the calculation, i.e., a mixture of MIDI-1 and MINI-1 (see Table II). That is, the MIDI-1 basis was used for cadmium and its contiguous atoms, whereas the remaining atoms used a MINI-1 basis. This type of uneven basis is an example of what has been termed by Chesnut and Moore²⁶ as a "locally dense" basis set. With such a basis the predicted chemical shift difference was 97 ppm. This result would be considered by anyone to be in excellent agreement with our results for neat liquids, 99.7 ppm, and in modest agreement for the results for the gas phase, i.e., 142.6 ppm. To examine the sensitivity of the previously computed shift difference to changes in basis set (for a fixed geometry⁷), we made a subtle change, i.e., the use of MIDI-1 for all of the atoms. The results are outlined in Table V. The results for dimethylcadmium are nearly the same as those reported previously. This near equivalence arises from the subtle differences between MIDI-1 and MINI-1 for hydrogens. However, this is not the case for the diethylcadmium calculation. That

Table V. Effect of Mixed versus Uniform Basis Sets on the Calculation of the Chemical Shift Difference of Dimethyl- and Diethylcadmium

	mixed MIDI and MINI ^a	uniform MIDI basis ^b
$\text{Cd}(\text{CH}_3)_2$	$\sigma^{\text{dia}} = 4851$ ppm	$\sigma^{\text{dia}} = 4851$ ppm
	$\sigma^{\text{para}} = -1090$ ppm	$\sigma^{\text{para}} = -1092$ ppm
	$\sigma^{\text{tot}} = 3761$ ppm	$\sigma^{\text{tot}} = 3759$ ppm
$\text{Cd}(\text{C}_2\text{H}_5)_2$	$\sigma^{\text{dia}} = 4896$ ppm	$\sigma^{\text{dia}} = 4897$ ppm
	$\sigma^{\text{para}} = -1038$ ppm	$\sigma^{\text{para}} = -1094$ ppm
	$\sigma^{\text{tot}} = 3858$ ppm	$\sigma^{\text{tot}} = 3803$ ppm
	$\delta = 97$ ppm	$\delta = 44$ ppm

^a See ref 7. ^b The present work.

is, making a "small" change in the basis set for noncontiguous atoms, i.e., going from MINI-1 to MIDI-1, results in a change in the predicted chemical shift difference of 53 ppm! If we use the energy-optimized exponents for a pair of p-functions (see Table III) instead of those employed by Nakatsuji and co-workers,^{7,11} the results are equally disappointing. One has to suspect that the quantitative agreement between theory and experiment reported by Nakatsuji and co-workers^{7,11} may be fortuitous.

A reasonable question at this point is whether any basis set can work for these systems. We have addressed this question by performing calculations of the shielding constants with three basis sets, i.e., an augmented MIDI-4 basis on the cadmium and MIDI-4 basis functions on carbon and hydrogen, the same augmented MIDI-4 basis set that was used on the cadmium with the basis set of Dunning and Hay²¹ on carbon and hydrogen, and an augmented version of Friedlander, Howell, and Synder's²⁰ basis function used for cadmium in conjunction with the Dunning and Hay²¹ basis for carbon and hydrogen. These results are summarized in Table VI. The augmented basis sets' exponents are presented in Table III.

The first point to make concerning the results summarized in Table VI is a comparison between calculations performed with MIDI-4p2, MIDI-4p2d2, and MIDI-4p2d2f2 basis set with a geometry optimized at the MIDI-4p2d2f2 level (the first three entries for $\text{Cd}(\text{CH}_3)_2$ and $\text{Cd}(\text{C}_2\text{H}_5)_2$ in Table VI). There is a strong dependence of the computed shielding upon the quality of the basis set. Further, there is *no* hint that the dependence is converging. That is, the basis sets are not saturated with respect to their ability to predict the observed shielding. This trend is also reflected in the predicted chemical shifts. The inclusion of f-orbitals is important in describing the chemical shift difference between dimethyl- and diethylcadmium. This is not to say that f-orbitals are essential in describing cadmium chemistry. However, it does say that the calculation must have a better description of the "low-lying" virtual orbitals which play such an important role in the coordination chemistry of cadmium.

Clearly the "so-called" paramagnetic term is dominant in describing the shielding of cadmium. However, comparison of the computed shielding by the LORG and CHF methods represents a reminder that only the *sum* of the diamagnetic and the paramagnetic terms are gauge invariant.^{3,16,17} That is, comparing the CHF results for the chemical shift difference using the fns-p2d2f2 basis set would predict that of the -110.84-ppm shift computed, -45.4 ppm of that shift would arise from the diamagnetic term while -65.4 ppm arises from the paramagnetic term. Comparing the results for the same basis set and geometry but computed via the LORG approach, one obtains -10.2 and -77.1 ppm, respectively, for the diamagnetic and paramagnetic contributions to the computed shift difference.

The overall quality of the calculation is reminiscent of the phrase "beauty is in the eyes of the beholder". A worst-case comparison would be the -93.52-ppm LORG prediction of the chemical shift difference (i.e. 65.6% of the experimental shift difference). The best-case predicted shift difference would correspond to the MIDI-4p2d2f2/D95 CHF results of -115.26 ppm (or 80.8% of the experimental result). However, the results could never be described as quantitative. There are potentially simple reasons for this, and they were spelled out in the introduction. That is, there are excellent reasons to believe that relativistic terms, via

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Table VI. ^{113}Cd Shieldings with MP2 Optimized Geometries^a

		LORG			δ_{LORG}	CHF			δ_{CHF}
		σ^{dia}	σ^{para}	σ^{tot}		σ^{dia}	σ^{para}	σ^{tot}	
$\text{Cd}(\text{CH}_3)_2$	MIDI-4p2 ^b	4774.61	-903.72	3870.90		4872.16	-944.76	3927.37	
	MIDI-4p2d2 ^b	4771.03	-959.61	3811.42		4871.97	-1004.45	3867.52	
	MIDI-4p2d2f2 ^b	4765.82	-1252.54	3513.28		4872.43	-1335.76	3536.68	
	MIDI-4p2d2 ^c	4771.89	-931.88	3840.01		4872.12	-979.62	3892.50	
	MIDI-4p2d2f2 ^c	4765.31	-1266.08	3499.23		4872.61	-1346.20	3526.41	
	fhs-p2d2 ^d	4762.54	-1143.60	3618.95		4875.78	-1226.13	3649.65	
	fhs-p2d2f2 ^d	4767.07	-1205.44	3561.63		4875.59	-1284.43	3591.15	
	$\text{Cd}(\text{C}_2\text{H}_5)_2$	MIDI-4p2 ^b	4782.58	-863.33	3919.25	-48.35	4917.22	-923.42	3993.80
MIDI-4p2d2 ^b		4780.25	-904.52	3875.73	-64.31	4917.04	-967.52	3949.51	-81.99
MIDI-4p2d2f2 ^b		4776.43	-1181.53	3594.91	-81.63	4917.46	-1279.09	3638.37	-101.69
MIDI-4p2d2 ^c		4780.52	-868.49	3912.02	-72.01	4917.24	-928.57	3988.67	-96.17
MIDI-4p2d2f2 ^c		4775.86	-1183.11	3592.75	-93.52	4917.70	-1276.03	3641.67	-115.26
fhs-p2d2 ^d		4773.02	-1077.69	3695.33	-76.38	4921.20	-1171.02	3750.19	-100.54
fhs-p2d2f2 ^d		4777.32	-1128.34	3648.98	-87.35	4921.01	-1219.02	3701.99	-110.84

^a Optimized at the MIDI-4p2d2f2 level of basis set. All tensor elements and chemical shifts are expressed in ppm. A negative sign of the *chemical shift* denotes resonances to higher shielding. ^b Geometry optimized with the MIDI-4p2d2f2 basis set on cadmium with a MIDI-4 basis set for carbon and hydrogen. The optimized orbital exponents are given in Table III. ^c Geometry optimized as described in footnote a, except that the basis set of Dunning and Hay¹² was used for carbon and hydrogen. ^d Geometry optimized with the basis set of Friedlander, Howell, and Synder²⁰ (fhs) of the cadmium augmented with a pair of p-, d-, or f-orbitals with a Dunning and Hay²¹ basis for the carbon and hydrogens. The values of the orbital exponents used for the fhs basis are given in Table III.

L-S interactions, and/or two-electron contributions (electron-correlation)^{18,19} to the shielding should make significant contributions to the observed shielding for heavy atoms such as cadmium. However, before these points can be addressed the basis set dependence of the shielding must be examined. The *chemical shifts* in Table VI are strongly dependent upon the choice of basis.

A partial rationalization of this basis set dependence is the potential lack of balance in the basis set. That is, the valence region is probably described reasonably well by the augmented p-, d-, and f-functions. However, it is not clear whether the details (shape and amplitude) of the inner shell orbitals are correct. Clearly, more work is needed, and we are pursuing these points. The basis set is the probable reason as to why the CHF results are closer to experiment than the results predicted by the LORG approach.

Within the scope of the present calculation, can an explanation be put forth for this exceptional chemical shift difference observed for dimethyl- and diethylcadmium? To address this point one generally examines differences in structure. However, examination of the results summarized in Table IV does not lead one to believe that there are significant structural differences between dimethyl- and diethylcadmium. The exception is molecular symmetry, and this point is important but *not causal*. The shift difference between dimethyl- and diethylcadmium is analogous to that of a β -effect in ^{13}C shieldings. A clear physical picture of the origin of the β -effect in ^{13}C shieldings has not been delineated. Given the overall level of agreement between predicted shielding and experiment and the strong basis set dependence manifested in Table VI, it should be concluded that questions relating to the origin of the chemical shift difference between dimethyl- and diethylcadmium are premature at this point. Further, conclusions concerning the importance of ligand orbitals to the observed ^{113}Cd shielding difference are likewise considered premature. Similar arguments can be made concerning the importance of the geometry utilized in calculations such as are reported here. However, until the level of agreement between theory and experiment improves, such a

discussion would seem premature as well.

Summary and Conclusions

In the present paper we have illustrated several facets of the maturing area of the computation of heavy atom magnetic resonance parameters. We have demonstrated that even with care in geometry and basis set selection, one cannot obtain quantitative results for the calculation of ^{113}Cd chemical shifts. However, the overall trends are apparent from the calculations. In this same vein, care should be exercised in making comments as to what type of orbital interactions will be important in determining ^{113}Cd chemical shifts. It is suspected that the reasons for the observed lack of quantitative results are 2-fold: basis sets and failure to incorporate all of the applicable physics into the calculations. Basis sets are clearly important, but they are not the whole story. Before this area of computational chemistry can advance significantly, the computational theorists must address the unknown importance of spin-orbit terms and electron correlation on the chemical shieldings. Finally, we do not suggest that the results reported here be used in some fashion to illustrate which method of calculating the shielding tensor is better, i.e., distributed origin methods, e.g., LORG^{15,16}, or CHF¹⁷ approaches. Such conclusions would be clearly premature.

Acknowledgment. The authors would like to acknowledge the National Institutes of Health for award GM-26295 (P.D.E.) and GM-42907 (J.D.O.) for partial support of this research. Further, we would also like to thank Ms. Dorothy Tudor and Ms. Sibyl Hare of the Computer Services Division at USC for their efforts with regard to the IBM RISC 6000/550 Gaussian calculations. It is a pleasure to acknowledge several stimulating and informative conversations with Tom Bouman as well as his donation of the functional portions of the f-orbital version of the RPAC¹⁵ program to P.D.E. Sadly, shortly after this work was submitted for publication Tom Bouman died. He will be missed. Finally, P.D.E. would like to acknowledge discussions with Tom Dunning concerning strategies for polarization function development.