approach for structure–spectra correlations and as a conceptual tool for designing further spectroscopic studies.

Acknowledgment. We with to thank Professor R. H. Holm for his interest in this project and Ruth Records for her assistance with the measurements. Y.-C.L. was a visiting scholar from the Beijing Institute of Chemical Reagents. A.M.S. was a predoctoral fellow of the Fannie and John Hertz Foundation. Financial support for this research was provided by grants from the National Science Foundation (CHE-77-04397 and CHE-80-09240) and the National Institutes of Health (GM-20276 and HL-16833).

Registry No. P^{2-}, 30882-36-1; PH_2, 101-60-0; PH_4^{2+}, 20910-09-2; ZnP, 14052-02-9; TPP^{2-}, 32796-32-0; $TPPH_2$, 917-23-7; $TPPH_4^{2+}$, 50849-35-9; ZnTPP, 14074-80-7; OEP^{2-}, 52985-81-6; $OEPH_2$, 2683-82-1; $OEPH_4^{2+}$, 24804-25-9; ZnOEP, 17632-18-7; CH_2, 2683-84-3; CH_4^{2+}, 82135-15-7; ZnC, 77124-66-4; ZnC·pyr, 82135-40-8; $OECH_2$, 991-74-2; $OECH_4^{2+}$, 82135-16-8; ZnOEC, 28375-45-3; ZnOEC·Pyr, 82149-91-5; $TPCH_2$, 2669-65-0; $TPCH_4^{2+}$, 50849-36-0; ZnTPC, 14839-32-8; BCH_2, 2683-78-5; BCH_4^{2+}, 82135-17-9; ZnBC, 78802-04-7; $TPBCH_2$, 5143-18-0; $TPBCH_4^{2+}$, 82113-35-7; ZnTBC, 50795-70-5; $OEPBCH_2$, 23016-64-0; $OEBCH_4^{2+}$, 82113-34-6; ZnOEBC, 82135-39-5; iBC^{2-}, 82113-48-2; $iBCH_2$, 67883-10-7; $iBCH_4^{2+}$, 82113-49-3; ZniBC, 79008-66-5; $TPiBC^{2-}$, 82113-50-6; $TPiBCH_2$, 25440-13-5; $TPiBCH_4^{2+}$, 82113-37-9; ZnTPiBC, 14705-64-7; $OEiBC^{2-}$, 82113-51-7; $OEiBCH_2$, 72260-12-9; $OEiBCH_4^{2+}$, 82113-36-8; ZnOEiBC, 39001-89-3; zinc bonellin, 82135-38-4; zinc bonellin·pyr, 82149-92-6.

Thermochemistry of Group 4A Isobutene Analogues by Pulsed Ion Cyclotron Double Resonance Spectroscopy

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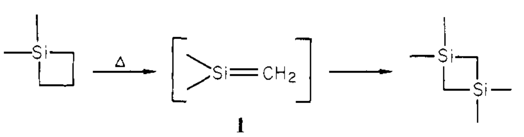
Abstract: Pulsed ion cyclotron double resonance spectroscopy has been employed to obtain heats of formation of 1,1-dimethylsilaethylene (7 kcal mol^{-1}), 1,1-dimethylgermaethylene (6 kcal mol^{-1}), 1,1-dimethylstannaethylene (31 kcal mol^{-1}), and 1,1-dimethylplumbaethylene (59 kcal mol^{-1}), neutral products derived from proton abstraction from the corresponding trimethylsilyl, trimethylgermyl, trimethylstannyl, and trimethylplumbyl cations in the gas phase. These data, combined with estimates for the heats of formation of the corresponding biradical forms (obtained from the heats of formation of the tetramethyl compounds, $M(CH_3)_4$, and estimates of CH and MC bond dissociation energies), yield π-bond energies of 38, 43, 45, and 30 kcal mol^{-1} for the four olefin analogues, respectively.

The apparent absence of multiple bonding in the higher group 4A elements is a well-known and intriguing phenomenon. Compounds incorporating multiple bonds between carbon and other first-row elements are commonplace, while stable, isolable congeners involving silicon are rare[1] and (as yet) nonexistent for germanium, tin, and lead. Olefin analogues of higher group 4A elements have, however, been proposed as transient species or short-lived intermediates in many reactions.[2] For example, the observation that pyrolysis of 1,1-dimethylsilacyclobutane results in the formation of the corresponding tetramethyl-1,3-disilacyclobutane may best be rationalized in terms of the intermediacy of 1,1-dimethylsilaethylene (**1**).[3] Further support for such a mechanism may be found in the work of Grinberg,[4] who reported that pyrolysis of a mixture of 1,1-dimethylsilacyclobutane and the bis(deuteriomethyl-d_3) derivative led to all three possible dimerization products. The silaethylene intermediate has also been chemically trapped by carrying out the pyrolysis in the presence of ammonia, water, and alcohols.[5] Other agents (e.g., phenols, amines, and nitriles) have also been employed as chemical traps.[6] The proposed silaethylene intermediate has also been made to undergo [2 + 2] and [2 + 4] cycloaddition upon pyrolysis in the presence of olefins and dienes.[7] [2 + 2] cycloaddition products have also been detected when ketones, thioketones, and imines were used in place of olefins.[6a,8] By rapidly immobilizing the very-low pressure pyrolysis products of 1,1,3-trimethyl-1-silacyclobutane on a frozen argon matrix, Maltsev and co-workers,[9] among others, have obtained infrared spectra of **1**. Koenig and McKenna[10] have recorded the photoelectron spectrum of 1,1-dimethylsilaethylene, and Montgomery and co-workers[11] have determined its structure by electron diffraction.



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Numerous reports have appeared that strongly implicate the existence of other short-lived intermediates containing formally unsaturated silicon.[2] Among the most interesting are molecules related to silabenzene.[12]

Pyrolysis of 1,1-dimethylgermacyclobutane does not, as might be expected, result in cyclodimerization products of intermediate

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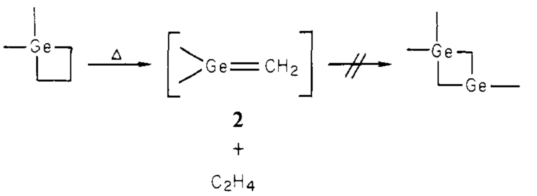
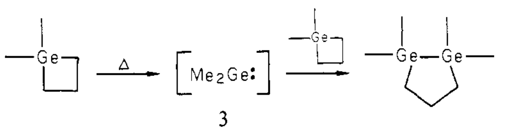
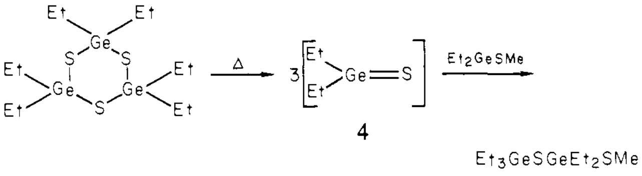
1,1-dimethylgermaethylene (**2**).[13] Rather, pyrolysis gives rise



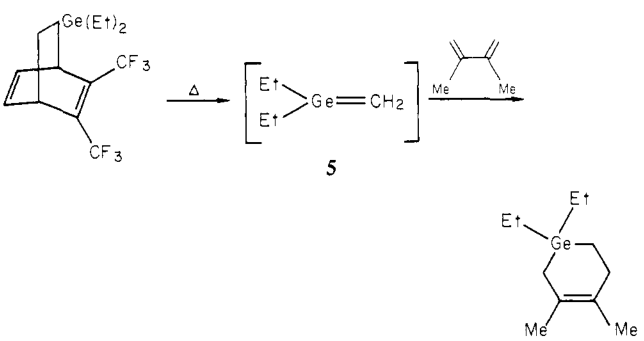
to addition products attributable to dimethylgermylene (**3**).



Intermediacy of either **2** or **3** would explain the production of ethylene during the reaction. Lavoyssiere[14] has reported evidence for a germathianone intermediate, **4**, formed in the pyrolysis of $(Et_2GeS)_3$. He has also postulated the intermediacy of transient



germanones ($R_2Ge{=}O$) formed upon thermolysis of a number of heterocyclic germanium compounds.[15] Barton and co-workers[16] have reported the product of [4 + 2] cycloaddition of 1,1-diethylgermaethylene (**5**), formed upon pyrolysis of a germanorbornadiene derivative, to 2,3-dimethylbutadiene.



Far less attention has been given to the possibility of species containing multiple bonds to tin or lead. We are aware of only a single report describing the intermediacy of a species with a tin–carbon double bond,[17] and none on lead-containing systems.

Despite the considerable efforts that have already been expended, little is known experimentally about the thermochemical stabilities of group 4A olefin analogues or about the π-bond strengths in these compounds. Systems containing silicon are the best characterized. Kinetic studies by Gusel'nikov and co-workers,[18] as analyzed by Walsh,[19,20] on the pyrolysis of 1,1-dimethylsilacyclobutane have yielded a heat of formation of 7 ± 5 kcal mol^{-1} for 1,1-dimethylsilaethylene; the heat of formation derived in an analogous manner for 1-methylsilaethylene is 23 ± 5 kcal mol^{-1}.[20] These data suggest that the silicon–carbon π-bond strengths in these systems range between 34 and 44 kcal mol^{-1}. For comparison, the π-bond energy in ethylene is 65 kcal mol^{-1}.[21] The best theoretical estimate of the π-bond energy in parent silaethylene appears to be 46 kcal mol^{-1}, due to the work of Ahlrichs and Heinzmann.[22] No quantitative thermochemical data on the heats of formation or π-bond strengths in the analogous germanium, tin, or lead systems have as yet appeared in the literature. Theoretical work is also lacking.

Table I. Proton Affinities of $Me_2M{=}CH_2$ by ICR Spectroscopy

M	proton affinity, kcal mol^{-1} rel to NH_3^{a}	absolute^b
Si	−22.7	−227.7
Ge	−0.9	−205.9
Sn	−11.8	−216.8
Pb	−20.8	−225.8

^{a} Proton affinities (rel. to NH_3) of all reference bases used were taken from R. W. Taft in "Proton Transfer Equilibria", E. F. Caldin and V. Gold, Eds., Wiley-Halstead, N.Y., 1975, p 31, or from R. W. Taft, unpublished results, and have been slightly modified to account for higher ambient temperatures. ^{b} Absolute proton affinities are based on a proton affinity for NH_3 of 205 kcal mol^{-1}.[33]

Table II. Heats of Formation of Me_3M^+ from Appearance Potentials

M	appearance potential,^{a} eV	$\Delta H_f(Me_4M)$, kcal mol^{-1}	$\Delta H_f(Me_3M^+)$ kcal mol^{-1}
Si	10.25^b	−55^c	146
Ge	10.05	−30^d	167
Sn	9.58	−5^e	181
Pb	8.77	33^f	200

^{a} Unless otherwise noted, appearance potentials are from ref 34b. ^{b} Reference 34a. ^{c} Reference 20. ^{d} See text. ^{e} Reference 39. ^{f} Reference 40.

In recent years, we and others[23] have successfully applied ion cyclotron double resonance spectroscopy to the determination of the thermochemical stabilities of a variety of short-lived or otherwise highly reactive molecules. Among the systems studied to date in our laboratory are *o*-benzyne,[24] *o*- and *p*-xylylene,[25] methanimine,[26] hydrogen isocyanide,[27] and hydroxymethylene.[28] In addition, we have applied the technique to the determination of the heat of formation of 1,1-dimethylsilaethylene.[29] We report here the results of our efforts to obtain experimental heats of formation for the heavier group 4A isobutene analogues (i.e., 1,1-dimethylgermaethylene, 1,1-dimethylstannaethylene, and 1,1-dimethylplumbaethylene) and to assign π-bond energies in these compounds.

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Table III. Heats of Formation and π-Bond Energies of Groups 4A Isobutylene Analogues (kcal mol^{-1})

M	$\Delta H_f(\mathrm{Me_3M}\cdot)^a$	$D_e(\mathrm{MC})^b$	$\Delta H_f(\mathrm{Me_2M\cdot{-}CH_2\cdot})^c$	$\Delta H_f(\mathrm{Me_2M{=}CH_2})^d$	E_π
Si	−1	89	45	7^e	38
Ge	3	68^f	49	6	43
Sn	30	70	76	31	45
Pb	43	45	89	59	30

[a] See text. [b] Defined as ΔH for $\mathrm{Me_4M \rightarrow Me_3M\cdot + Me\cdot}$; $\Delta H_f(\mathrm{CH_3\cdot})$ taken as 35 kcal mol^{-1} (ref 37). [c] $D_e(\mathrm{CH})$, i.e., ΔH for $\mathrm{CH_3{-}M(Me)_3 \rightarrow CH_2\cdot{-}M(Me)_3 + H\cdot}$, estimated to be 98 kcal mol^{-1} for all biradicals on the basis of a bond dissociation energy of 99 kcal mol^{-1} for ethane, corrected by 1 kcal mol^{-1} for the calculated (3-21G level; J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980)) energy for the reaction $\mathrm{SiH_3CH_2\cdot + CH_3CH_3 \rightarrow SiH_3CH_3 + CH_3CH_2\cdot}$ $\Delta H_f(\mathrm{H\cdot})$ taken as 52 kcal mol^{-1} (ref 37). [d] Based on proton affinities from this work. $\Delta H_f(\mathrm{H^+})$ taken as 367 kcal mol^{-1} (ref 37). [e] Our assignment of the heat of formation of 1,1-dimethylsilaethylene has decreased by 13 kcal mol^{-1} since our initial publication,[29] a change not due at all to our measurements but ultimately to a reassessment of the preferred value for the heat of formation of tetramethylsilane (ref 38b). [f] A value for $D_e(\mathrm{Me_3Ge{-}CH_2})$ of 76 kcal mol^{-1} may be determined from the measured $D_e(\mathrm{Me_3Ge{-}H})$ (A. M. Doncaster and R. Walsh, *J. Phys. Chem.*, **83**, 578 (1979), and R. Walsh, private communication). The calculated E_π is then 51 kcal mol^{-1}, which appears to be somewhat too large. The situation reflects the high degree of uncertainty associated with the thermochemistry of germanium compounds.

Experimental Section

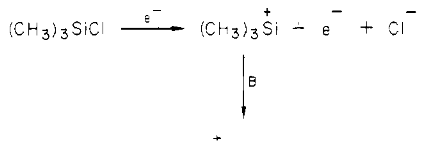
Chlorotrimethylsilane was purchased from Aldrich (reagent grade) and used without further purification. Chlorotrimethylgermane and tetramethyltin were purchased from Alfa Ventron and distilled under an inert atmosphere prior to use. Tetramethyllead was purchased from Nalco and used without further purification.

Chlorotrimethylsilane or chlorotrimethylgermane was admitted into a pulsed ion cyclotron resonance spectrometer[30] along with a base in a 3:1 ratio. The pressure was then increased 50–100 times with an inert buffer gas (argon or krypton). The total pressure in the spectrometer was typically (1–2) × 10^{-5} torr. $\mathrm{Me_3M^+}$ (M = Si, Ge) ions were produced by 20-eV electron impact on the chlorinated compound. Signals corresponding to the protonated base were observed at 400 ms, and standard double resonance techniques[30,31] were used to determine whether its presence was a consequence of reaction with $\mathrm{Me_3M^+}$.

Trimethyltin and trimethyllead cations were studied in a similar manner with the exception that they were created by 16-eV impact on tetramethyltin or tetramethyllead, respectively.

Results and Discussion

Electron impact ionization of trimethylsilyl chloride in an ICR spectrometer resulted in the formation of the trimethylsilyl cation, which could be detected for as long as 800 ms. Proton abstraction from trimethylsilyl cation, resulting in the production of $\mathrm{BH^+}$, which can be detected, as well as the formation of the neutral product, 1,1-dimethylsilaethylene, were observed when compounds of sufficient base strength were also present in the spectrometer. The reaction sequence is outlined as follows:



$$\mathrm{(CH_3)_3SiCl \xrightarrow{e^-} (CH_3)_3\overset{+}{Si} - \overset{-}{e} + \overset{-}{Cl}}$$
$$\mathrm{\downarrow B}$$
$$\mathrm{B\overset{+}{H} + (CH_3)_2Si{=}CH_2}$$

The proton affinity (PA) of 1,1-dimethylsilaethylene was determined by admitting bases into the spectrometer of gradually increasing base strength and monitoring the onset of proton transfer.[32] In a similar manner, the proton affinities of $\mathrm{Me_2M{=}CH_2}$, M = Ge, Sn, Pb, were also determined. The data are presented in Table I. Heats of formation of the corresponding cations, $\mathrm{M(CH_3)_3{}^+}$, as determined from literature appearance potentials from the tetramethyl derivatives, are given in Table II. For our calculations we used the data of Potzinger and Lampe[34a] for trimethylsilyl cation and those of Lappert, Pedley, Simpson, and Spalding[34b] for the analogous germanium-, tin-, and lead-containing molecules. These constitute the lowest appearance potential thresholds available for this set of compounds. Many other measurements closely agree with these appearance potentials,[35] although a few are substantially different.[36] These data, together with the proton affinities of the olefin analogues and the heat of formation of $\mathrm{H^+}$,[37] yield heats of formation of the latter species, i.e., eq 1. They are displayed in Table III.

$$\Delta H_f(\mathrm{Me_2M{=}CH_2}) = \Delta H_f(\mathrm{Me_3M^+}) - \Delta H_f(\mathrm{H^+}) - \mathrm{PA(Me_2M{=}CH_2)} \quad (1)$$

π-bond energies of the olefin analogues, also displayed in Table III, may now be defined as the difference between heats of formation of the olefin analogues and the heats of formation of the corresponding biradicals. The latter quantities are not known experimentally but may be estimated by combining the heats of formation of the corresponding tetramethyl compounds, $\mathrm{Me_4M}$, and of H· and $\mathrm{CH_3\cdot}$[37] with M–C and C–H bond dissociation energies, i.e., eq 2. The M–C bond dissociation energies were calculated according to eq 3. The heat of formation of $\mathrm{Me_3Si\cdot}$ has been taken from the work of Doncaster and Walsh.[38] Heats of formation for the remaining $\mathrm{Me_3M\cdot}$ radicals (M = Ge, Sn, Pb) have been obtained by a least-squares fit to the appearance potential data of Potzinger and Lampe[34a] for $\mathrm{Me_3Si^+}$ from $\mathrm{Me_4Si}$ and of Lappert et al. for $\mathrm{Me_3M^+}$ (M = Ge, Sn, Pb) from $\mathrm{Me_4M}$ and $\mathrm{Me_3M{-}M'Me_3}$ (M, M′ = C, Si, Ge, Sn, Pb). Also assumed were heats of formation of $\mathrm{Me_4Si}$ (−55 kcal mol^{-1} [20]), $\mathrm{Me_4Sn}$ (−5

$$\Delta H_f(\mathrm{Me_2\dot{M}{-}CH_2\cdot}) = D_e(\mathrm{MC}) + D_e(\mathrm{CH}) + \Delta H_f(\mathrm{Me_4M}) - H_f(\mathrm{H\cdot}) - \Delta H_f(\mathrm{CH_3\cdot}) \quad (2)$$

$$D_e(\mathrm{M{-}C}) = \Delta H_f(\mathrm{Me_3M\cdot}) + \Delta H_f(\mathrm{CH_3\cdot}) - \Delta H_f(\mathrm{Me_4M}) \quad (3)$$

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(33) The original value of 202.3 kcal mol^{-1} for the proton affinity of the ammonia standard as derived for ICR spectroscopy ((a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977)) has been revised upward to 205 kcal mol^{-1} due to recent work. (b) 203.6 kcal mol^{-1}: S. T. Ceyer, P. W. Tiedmann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **70**, 14 (1979). (c) 207 kcal mol^{-1}: F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4067 (1979). (d) 209.2 kcal mol^{-1}: R. G. McLoughlin and J. C. Traeger, *ibid.*, **101**, 5791 (1979).

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kcal mol^{-1}[39]), Me$_4$Pb (33 kcal mol^{-1}[40]), Me$_3$C· (10 kcal mol^{-1}[41]), Me$_3$Si· (−1 kcal mol^{-1}[38]), and Me$_3$C$^+$ (165 kcal mol^{-1}[42]). We are aware of a measured value of −21 kcal mol^{-1} for the heat of formation of tetramethylgermane.[43] However, we and others[44] feel that this is subject to considerable uncertainty, as it leads to a Ge–C bond energy that is conspicuously low.

It should be stressed that the π-bond energies in Table III are subject to considerable uncertainty. While they are independent of the heats of formation of the tetramethyl compounds, they are sensitive to the measured appearance potentials. Our estimates are based on what we believe are the best data currently available. An interesting picture of the bonding in these compounds arises. While the π-bond energy of the silaolefin is considerably less than that in the hydrocarbon, in agreement other experimental. work[18,19] and with the best available theoretical calculations,[22] no further decrease in π-bond strengths in the corresponding germanium and tin compounds is noted. In fact, small increases are suggested. The lead–carbon double bond is indicated to be weaker but only by about 10 kcal mol^{-1}. Further experimental and theoretical work is desirable and is under way in our laboratory. In particular, we are attempting to define π-bond strengths in these and related compounds with reference to as little external stabilities of olefin- and carbene-like isomers. A preliminary report on the silicon system will appear shortly.[45]

Registry No. Me$_2$Si=CH$_2$, 4112-23-6; Me$_2$Ge=CH$_2$, 82064-99-1; Me$_2$Sn=CH$_2$, 82065-00-7; Me$_2$Pb=CH$_2$, 82065-01-8; Me$_3$Si$^+$, 28927-31-3; Me$_3$Ge$^+$, 76568-90-6; Me$_3$Sn$^+$, 5089-96-3; Me$_3$Pb$^+$, 14570-16-2.

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NMR Spectra of Porphyrins. 18. A Ring-Current Model for Chlorophyll Derivatives[1]

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Abstract: A double dipole model of the macrocyclic ring current in the dihydroporphyrin ring of chlorophyll derivatives is presented and parameterized. The model includes a close-range approximation that has both first-order and second-order continuity at all points in space, except through the current loop itself. The model is tested by comparison of the proton chemical shifts of methyl pyropheophorbide *a* (**1**) with the corresponding porphyrin, 2-vinylphylloerythrin methyl ester (**2**). Aggregation effects were eliminated by use of the zinc(II) complexes bearing an apical pyrrolidine ligand, and substitution effects were isolated by use of the corresponding chlorin and porphyrin 9-ketals (**3** and **4**, respectively). The exocyclic ring E has no appreciable effect on the macrocyclic ring current, but the C$_9$ keto function and the reduction in ring D in the chlorin both reduce the ring current by about 6 and 10%, respectively. The resulting model gives a good account of the chemical shift differences of all the protons in methyl pyropheophorbide *a* and 2-vinylphylloerythrin methyl ester. Owing to very low yields encountered in the preparation of 2-vinylphylloerythrin methyl ester from methyl pyropheophorbide *a*, a new route involving DDQ oxidation of the chlorin 9-ketal (**3**) is described.

The nature of the molecular organization of chlorophylls in green plants and photosynthetic bacteria is of fundamental importance in the understanding of the photoreaction processes,[3] and the extent and structures of the chlorophyll aggregates formed have been the subject of many investigations.[4] Application of NMR spectroscopy to the study of the aggregation process in solutions of chlorophyll derivatives has been highlighted by the extensive investigations of Katz and co-workers[5–7] and also by Fong.[8] Synthetic approaches to models of the special pair photosynthetic reaction center have also been investigated by several groups,[9,10] and structures of the derived complexes in solution have been studied by NMR and other spectroscopic techniques. In these investigations, the interpretation of the NMR shifts is usually given in terms of the ring-current shifts experienced by nuclei situated near to the chlorophyll ring; thus, the ring current serves as a geometric probe of the structure of the complexes. Obviously, the more accurate the ring-current model used, the better the structural information obtained from it. However, in the absence of a refined ring-current model for the chlorophyll (7,8-dihydroporphyrin) ring, previous investigations have either made use of relatively crude models, such as the single-current loop (which does not reflect the asymmetry of the chlorin ring), or discussed the observed shifts in an entirely qualitative manner. Such qualitative discussions, e.g., into the different postulated structures of the aggregates,[10] would benefit greatly from a more

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