Cluster Analysis of ^{13}C Chemical Shift Tensor Principal Values in Polycyclic Aromatic Hydrocarbons

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This paper presents a hierarchical cluster analysis of the principal values of the ^{13}C chemical shift tensors encountered in polycyclic aromatic hydrocarbons (PAHs). Because of the limited set of experimental data presently available, the analysis was performed using chemical shifts tensors calculated using the DFT (B3PW91) GIAO method with a D95 basis set on optimized molecular geometries obtained using the CVFF force field and the DISCOVER routine in MSI's InsightII package. The good correlation observed between the calculated and the available experimental values supports the use of calculated values in the analysis. The hierarchical cluster analysis was performed for two data sets of increasing size and the classification was found independent of the size of the sample, leading to the conclusion that the results presented here are valid for the types of PAHs reported. The classification of the tensors using hierarchical cluster analysis produces classes of chemical shift principal values that can be associated with intuitive chemical types of carbons present in PAHs.

Introduction

NMR spectroscopy has a long tradition of being used to gain structural information from complex materials, such as coals, soots, tars, chars, and so forth.[1] One common characteristic of all these materials is that they are not pure substances or even well-defined mixtures of pure substances in the chemical sense. Therefore, the analysis of the solid-state NMR (SSNMR) spectra of these substances is hindered by the lack of information on how many distinct spectral signatures should be encountered. For a pure substance, even in the presence of accidental degeneracy or lack of resolution, the number of peaks or tensor components in a spectrum is a known quantity. In complex substances, the concept of the number of peaks or of individual signatures is undefined, and therefore, it is more appropriate to cast the problem in terms of a distribution of spectral signatures.

The task at hand is to infer the distribution of chemical environments of resonant nuclei in the sample from the measured spectrum. The resultant information on the types of chemical environments present and their relative amounts can be used to derive realistic models or to formulate surrogate formulations of the material under consideration.[2] These models or surrogate ensembles can then be used for modeling the behavior of the material under different physical conditions or chemical processes. It is important to realize that the task of finding the distribution of chemical environments is an inverse problem; therefore, any useful analysis tool should provide statistical estimates of the number of different spectral signatures that can be extracted with confidence from the spectrum as well as information on the uniqueness of the solution.

The isotropic chemical shift has traditionally been relied on to provide details of structural elements in complex hydrocarbon materials.[3] Using modern SSNMR experiments, such as the ^{13}C CP/MAS spectral editing techniques pioneered by the Zilm group[4] and recently refined and adapted to principal value measurements by Hu,[5−7] it is possible to extract the more detailed information provided by the principal values of the chemical shift tensor in these materials. A good account of the state of the art in the measurement of chemical shift tensor components and using this information to gain structural information in coals, etc. has been published recently by Hu et al.[7] However, even using these modern spectral editing techniques, significant problems remain in extracting structural information in these substances due to the overall spectral broadening observed in the samples.[8] This broadening of the NMR signals can be classified as homogeneous and inhomogeneous. The first originates from interactions with the lattice and/or incomplete decoupling, whereas the second originates in the diversity of chemical or magnetic environments of closely resonant nuclei. Separation of these two effects is necessary when trying to find the number of statistically different chemical shift tensors contributing to the spectrum of a complex material.

The labor-intensive experimental methods used to measure chemical shift tensors or their principal values have restricted the analysis and classification of the chemical shift tensor values in PAHs. By using modern computational chemistry techniques to calculate molecular geometries and NMR chemical shift tensors,[9] it is possible to enlarge the number of compounds and type of structures that can be included in the analysis. To accomplish this at a reasonable computational cost, the choice was made to do the geometry optimizations using the molecular mechanics approach followed by the calculation of the chemical shift tensors at the GIAO/D95 level of theory. These choices reflect a compromise between accuracy and computational cost. Although most of these individual molecules could be treated at more refined levels of theory, the computational cost associated with applying these methods to the entire set of molecules studied here is prohibitive. The choice of the levels of theory adopted can be justified by the comparison of the results obtained with existing experimental data and by literature

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precedence.[9] For the subset of compounds for which experimental data is available, the calculated shifts agree with the experimental ones almost within the experimental errors. Therefore, we believe that the use of calculated values, at the chosen level of theory, does not degrade the analysis in any significant way.

This paper presents a classification scheme of the principal components of the ^{13}C chemical shift tensors of PAHs using hierarchical cluster analysis techniques.[10] This classification can be used to determine the number of possible distinct aromatic signatures expected in the SSNMR spectrum of highly aromatic systems. This method has been used to classify the principal values of the ^{13}C chemical shift tensors of 25 PAHs, which have 150 different sets of the three principal values of the shift tensor. The results of this analysis lead to the determination of the number of statistically different sets of chemical shifts tensors (characterized by their three principal values) that can be used to fit an experimental spectrum dominated by resonance signals of aromatic carbons belonging to PAH structures. The dispersion of values within each class can be used as an indication of the amount of inhomogeneous broadening for each class of tensor. The chemical shift classes correlate well with the intuitive chemical classification of carbon types.

Althouhg this paper looks at the application of these classification concepts to SSNMR, the concepts developed here are also applicable to other spectroscopic techniques used to analyze complex materials that do not have a well-defined chemical formula.

Computational Procedures

Chemical shift calculations were performed with the GAUSSIAN98[11] suite of programs. The calculations were done for most of the PAHs for which the Utah lab has collected experimental data, along with PAHs from which experimental data has been reported by Duncan[12] and a number of “interesting” PAHs for which the experimental chemical shift tensors have not yet been reported. The additional “interesting” compounds are a selection of nonplanar PAHs, including the canastanes[13] and the so-called buckybowl compounds,[14] which are thought to be present in young soots, nanotubes, and fullerenes.[15] A list of all the compounds included in this study and their calculated chemical shift tensor principal values is given as Supporting Information along with the experimental principal values, when available. The geometries were fully optimized prior to the calculation of the chemical shieldings using the molecular mechanics procedures and the consistent-valence force field (CVFF) available in the MSI suite of programs.[16]

The chemical shift calculations employed the method proposed by Cheeseman et al.[17] with the B3PW91 exchange-correlation functional,[18−19] as implemented in the GAUSSIAN98 program using a D95 basis set.[20] This method makes use of an efficient implementation[21] of the gauge including atomic orbitals (GIAO) methods.[22−23]

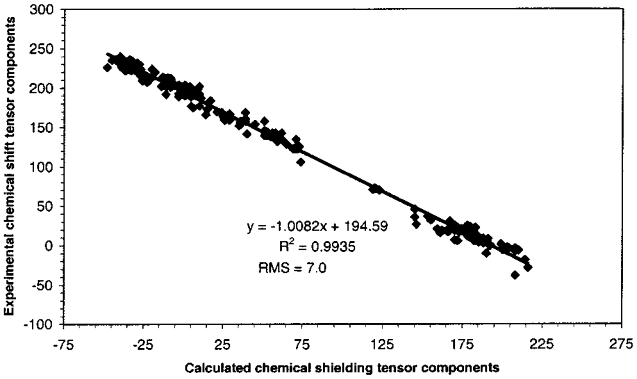

Figure 1. Linear relationship between experimental (shifts) and calculated (shieldings) ^{13}C chemical shift principal values in PAHs. All values are in ppm; the values included in the correlation are given in the Supporting Information.

It is well-known that the agreement between experimental and calculated NMR chemical shift values can be improved by adjusting the calculated values by linear regression.[24] This procedure tends to correct systematic errors in the inclusion of correlation effects, which are observed as slopes different than unity in the correlation, and in the inaccuracies in the referencing procedures, seen as small differences in the intercept from the shielding value of TMS. Using all the PAHs for which experimental values of the principal values of the chemical shift tensors are known (see Supporting Information), the experimental (shift) values correlate with the calculated (shielding) values with a slope of −1.0082 and an intercept of 194.6 ppm. This value for the intercept compares well with the estimated value of 185.4 ppm, which can be obtained from the calculated shielding in methane minus the 7 ppm reported as the difference between liquid TMS and gas-phase methane.[25] The RMS for the fit, given in Figure 1, for 51 sets of three chemical shift principal values is 7.0 ppm.

The excellent agreement between the calculated and the experimental principal values of the ^{13}C chemical shifts tensors in this set of compounds validates the use of computational methods to secure a larger set of representative values for chemical compounds and to include moieties for which experimental chemical shift values are not available. Calculations provide a very expeditious way to increase the variety of carbon structures that can be included in the analysis of SSNMR spectra as well as a method to test the different hypothesis on the carbon structure of soots or other materials inferred from kinetic models of their formation.[26]

The hierarchical cluster analysis[27−30] of 150 different sets of three principal values of chemical shift tensors was performed using the Clustan Graphics (version 3.16) program.[10] The following parameters were used in the cluster analysis: proximities were calculated using the squared Euclidian distance, the increase in the sum of squares was the classification criteria, and the upper tail criteria was chosen to obtain the “best cut”, i.e., the maximum number of statistically significant clusters.[31−32] Analysis of the variance in the identified clusters was performed using the standard statistical tools available in the Excel program.[33] This analysis of variance was used to provide quantitative estimation of the distance among the clusters as well as their specificity, information that was not available from the classification using cluster analysis tools.

Classification of ^{13}C Chemical Shift Tensors in PAHs. Figure 2 presents the results of the hierarchical cluster analysis of all the ^{13}C chemical shift principal values included in the first data set (150 different sets of chemical shift principal values, see Supporting Information). The figure presents the results for classifications including one to seven clusters, which is the maximum allowable number of clusters using the “best cut” method. In Table 1, the distances between all the centers of the clusters given in Figure 2 are presented. The members of each class, using the notation given in Figure 2 are given in the Supporting Information.

The cluster analysis of the ^{13}C chemical shift tensor principal values is a purely mathematical formulation and was performed without any consideration of the chemical environment of the carbon nuclei that gives the tensor. The relationship between

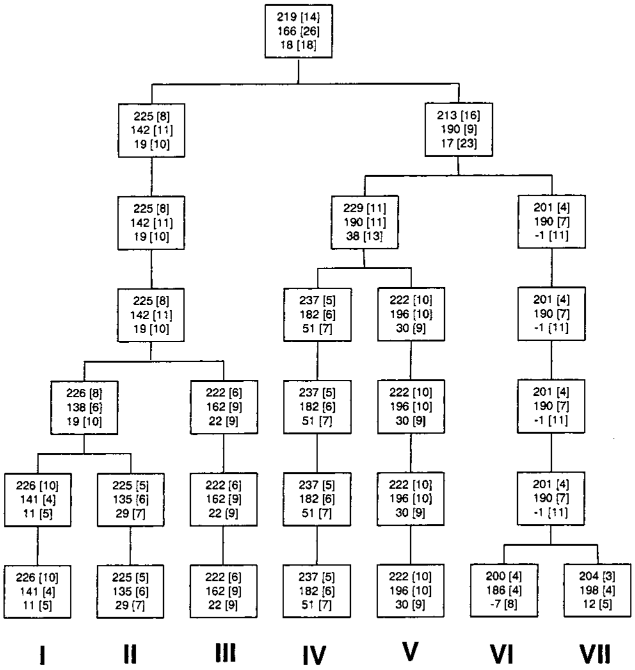

Figure 2. Hierarchical cluster analysis of the ^{13}C chemical shift tensor principal values of the PAHs studied. The hierarchy includes classifications of from one to seven clusters. The number in square brackets after the principal values is the standard deviation. Seven is the number of significant clusters given by the "best cut" procedure. The seven classes can be associated with the following types of carbons: I: C$-$H aromatic carbons. **II**: C$-$H aromatic carbons that are subject to steric strain. **III**: C$-$C$_a$ aromatic carbons where C$_a$ is an aliphatic carbon in a planar configuration. **IV**: C$-$C$_a$ aromatic carbons where C$_a$ is an aliphatic carbon in a nonplanar configuration. **V**: Bridgehead aromatic carbons attached to two six membered rings and one five membered ring. This is always a nonplanar configuration. **VI**: Bridgehead aromatic carbons attached to three six membered rings in a planar configuration. **VII**: Bridgehead aromatic carbons attached to three six membered rings in a nonplanar configuration.

the classes obtained by the cluster analysis and the chemical environment of the nuclei given in the caption of Figure 2, which is the ultimate information desired, was established by judicious inspection of the different classes. Note that there is no a priori reason for which the mathematical classification has to map onto the intuitive chemical classification by carbon type (see below for the case of the isotropic values). The existence of such a relationship is proof of the sensitivity of the data to the property, in this case the sensitivity of the principal values of the ^{13}C chemical shift tensors to the molecular structure. Fortunately, for this case there is a very strong correlation between the mathematical classification and the chemical environment. In fact, careful analysis of the classes obtained by cluster analysis reveals only a few misclassifications.

Following the progeny of the final seven classes, it is interesting to note how the separation into classes emerges during the classification process. Note that in many cases, the way in which the classifications emerge is not intuitive. For instance, although the first classification ($m = 2$) is quite natural, separating bridgehead carbons and aromatic carbons attached to an aliphatic bond, the split at $m = 3$ separates different classes of bridgehead carbons while the split between substituted carbons and protonated carbons does not occur until $m = 5$.

In addition to the set of average principal values for each class, Figure 2 gives the standard deviations of these values. As the level of classification increases, these standard deviations decrease, as does the distances between clusters. Comparing the standard deviations in Figure 2 with the distances between the centers of the clusters given in Table 1, it becomes apparent that when the distances between clusters reach a value close to twice the standard deviation of the principal values, the mathematical basis for further separation no longer exists; i.e., the "the best cut" cluster classification is reached. For the PAH chemical shift data, this point is reached at $m = 7$. Further classification will lead to clusters with substantial overlap for which the classification scheme is not statistically significant.

The level of classification useful for the interpretation of experimental data depends on the intrinsic resolution of the data. In the case of the chemical shifts studied here, it is clear that we can use the highest level of classification given by the "best cut" analysis, $m = 7$. At this level of classification, the standard deviations in the principal values of the shift tensors ranges from 3 to 10 ppm which is comparable to the uncertainties of ~5 ppm achievable by the SSNMR.[34] Note that if experiments with lower resolution are used, the classification level should be reduced accordingly. For instance, the results in Figure 2 indicate that at the level of ~20 ppm error in the SSNMR measurements, the resolution of the classes of carbon is totally lost.

A serious concern associated with the analysis presented above is to understand how the classification scheme depends on the data set used in its determination. To address this issue, 11 compounds with an additional 132 sets of three principal values was added to the data set. These compounds and their calculated principal values are also included in the Supporting Information. The hierarchical cluster analysis of this new extended set of data did not change from the original classification scheme presented above in any significant way. Both the average values and standard deviations for the new set are within the deviations observed in the original set. This is an indication of the robustness of the classification scheme.

The results discussed above show that the hierarchical cluster analysis produce quite satisfactory results for the analysis of the sets of three principal values. Unfortunately, when the same analysis is applied to the average or isotropic values the results are much less satisfactory. The hierarchical cluster classification of the isotropic chemical shifts of the 150 carbons included in the original analysis leads to only five different classes. The average isotropic chemical shift values for these classes of carbons are given in Table 2. It is apparent from Table 2 that the classification of isotropic values is less representative of the chemical environment of carbons in PAHs. First, the number of classes is smaller (five vs seven) than when using the principal values of the chemical shift tensors. Second, the results in Table 2 show that there is very poor correspondence between the isotropic classes and the type of carbons. For instance, the isotropic class labeled **A**, with an isotropic value of 126 ppm includes 44 C$-$H carbons and 25 bridgehead carbons and within the C$-$H carbons there is no discrimination between those with and without steric interaction. Similar problems are apparent for the other isotropic classes, indicating that the use of isotropic shifts alone to obtain structural information in PAHs is problematic.

Conclusions

This paper demonstrates that it is possible to augment existent experimental data of principal values of the ^{13}C chemical shielding tensors with calculated values using modern computational techniques. The computational methods used here can produce a large collection of principal values in a reasonably short time with accuracy close to that obtained from experimental methods. It should be pointed out that this method appears to be invalid for those cases in which force field used

TABLE 1: Distance between the Centers of the Clusters Given in Figure 2[a]

	1.1	1.2	2.2	1.3	2.3	3.3	1.4	2.4	3.4	4.4	1.5	2.5	3.5	4.5	5.5	1.6	2.6	3.6	4.6	5.6	6.6	1.7	2.7	3.7	4.7	5.7	6.7	7.7
1.1	**0**																											
1.2	25	**0**																										
2.2	25	**50**	**0**																									
1.3	25	0	50	**0**																								
2.3	33	52	26	**52**	**0**																							
3.3	36	57	22	**57**	**48**	**0**																						
1.4	25	0	50	0	52	57	**0**																					
2.4	41	53	42	53	17	64	**53**	**0**																				
3.4	32	55	17	55	12	38	**55**	**29**	**0**																			
4.4	36	57	22	57	48	0	**57**	**64**	**38**	**0**																		
1.5	29	4	54	4	55	61	4	56	59	61	**0**																	
2.5	6	20	30	20	33	42	20	38	35	42	**25**	**0**																
3.5	41	53	42	53	17	64	53	0	29	64	**56**	**38**	**0**															
4.5	32	55	17	55	12	38	55	29	0	38	**59**	**35**	**29**	**0**														
5.5	36	57	22	57	48	0	57	64	38	0	**61**	**42**	**64**	**38**	**0**													
1.6	27	8	51	8	56	56	8	58	58	56	9	24	58	58	56	**0**												
2.6	33	12	58	12	56	67	12	53	61	67	10	28	53	61	67	**19**	**0**											
3.6	6	20	30	20	33	42	20	38	35	42	25	0	38	35	42	**24**	**28**	**0**										
4.6	41	53	42	53	17	64	53	0	29	64	56	38	0	29	64	**58**	**53**	**38**	**0**									
5.6	32	55	17	55	12	38	55	29	0	38	59	35	29	0	38	**58**	**61**	**35**	**29**	**0**								
6.6	36	57	22	57	48	0	57	64	38	0	61	42	64	38	0	**56**	**67**	**42**	**64**	**38**	**0**							
1.7	27	8	51	8	56	56	8	58	58	56	9	24	58	58	56	0	19	24	58	58	56	**0**						
2.7	33	12	58	12	56	67	12	53	61	67	10	28	53	61	67	19	0	28	53	61	67	**19**	**0**					
3.7	6	20	30	20	33	42	20	38	35	42	25	0	38	35	42	24	28	0	38	35	42	**24**	**28**	**0**				
4.7	41	53	42	53	17	64	53	0	29	64	56	38	0	29	64	58	53	38	0	29	64	**58**	**53**	**38**	**0**			
5.7	32	55	17	55	12	38	55	29	0	38	59	35	29	0	38	58	61	35	29	0	38	**58**	**61**	**35**	**29**	**0**		
6.7	37	57	28	57	54	7	57	69	44	7	60	44	69	44	7	55	67	44	69	44	7	**55**	**67**	**44**	**69**	**44**	**0**	
7.7	36	60	13	60	37	16	60	54	26	16	64	41	54	26	16	61	69	41	54	26	16	**61**	**69**	**41**	**54**	**26**	**23**	**0**

[a] The notation *n.m* indicates the cluster *n* in the classification using *m* clusters. The distances between clusters in the same classification scheme are given in bold in the diagonal blocks of the matrix. All values are in ppm.

TABLE 2: Classification of Isotropic Chemical Shifts

isotropic class	average isotropic chemical shift[a]	no. of carbons in the principal values classes[b]						
		I	II	III	IV	V	VI	VII
A	126	30	14				25	
B	132	3	14	6			4	
C	139			7	8			13
D	150				3	6		
E	158				11	6		

[a] All values in ppm, referenced to TMS. [b] The classes refer to the classes described in Figure 2. These classes correspond to the classification done using the same 150 sets of three principal values included in the classification of the isotropic values.

for the geometry optimizations does not reproduce the molecular structure. Such a case has been found in biphenylene, which has not been included here.[35]

Using hierarchical cluster analysis techniques, it is possible to analyze a large collection of principal values of the ^{13}C chemical shift tensors of PAHs. This analysis leads to a classification of the principal values that correlates well with the intuitive classification of the carbon atoms according to the common chemical criteria of hybridization and steric effects. This classification method allows for a precise determination of the characteristic sets of principal values for each type of carbon. The classification scheme also provides standard deviations within each class; these can be used as a measure of the inhomogeneous broadening expected for each characteristic NMR signal in complex mixtures of PAHs.

The comparison of the classification schemes obtained using isotropic chemical shift values with the one using the full sets of principal values shows clearly the advantages of using tensor information when available. Although this claim has been made many times based on qualitative arguments, the hierarchical cluster analysis provides quantitative verification for the first time.

The hierarchical cluster analysis method for classification and its application to provide insight in the inhomogeneous broadening of ^{13}C NMR signals can be extended to the analysis of other types of carbons atoms, other NMR nuclei and even other spectroscopic techniques without significant changes. This method provides a systematic way to resolve problems encountered when trying to differentiate between homogeneous and inhomogeneous broadening of spectroscopic signatures from complex materials.

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Supporting Information Available: A list of all the compounds included in this study and their calculated chemical shift tensor principal values. This material is available free of charge via the Internet at http://pubs.acs.org.

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