assignments of the principal components in the molecular frame. The orientation of the chemical shift tensor on the molecule may be related to theoretical electron distributions using standard quantum mechanical methods. Moreover, the current ab initio results agree sufficiently well with the previous calculations using a semiempirical model[17] that these later methods may be used, especially for certain orientational information, for very large systems in which ab initio calculations may not be feasible.

Acknowledgment. This work was funded by General Medical Sciences, National Institutes of Health under Grant GM 08521-30 and by a grant from the Basic Molecular Sciences in Department of Energy under DE-FG02-86ER13510. A grant of computer time from the Utah Supercomputing Institute, which is funded by the State of Utah and the IBM Corporation, is gratefully acknowledged.

Registry No. 1, 27650-58-4; **2**, 138722-63-1; **3**, 138722-64-2; **5**, 56179-82-9; **6**, 138722-65-3; **7**, 27650-86-8; **8**, 138722-66-4; **9**, 87683-04-3; **10**, 573-22-8; **11**, 7508-20-5; **12**, 118018-28-3; **13**, 947-84-2; **14**, 16605-99-5; **15**, 2928-43-0; **16**, 19853-09-9; **17**, 138722-67-5; **18**, 138722-68-6; **19**, 138722-69-7; **20**, 138722-70-0; 3-(2-naphthyl)-1-propanol, 27650-98-2; phenanthrene, 85-01-8; triphenylene, 217-59-4.

Carbon-13 Chemical Shift Tensors in Aromatic Compounds. 4. Substituted Naphthalenes

Anita M. Orendt, Naresh K. Sethi,[†] Julio C. Facelli,[§] W. James Horton, Ronald J. Pugmire,[‡] and David M. Grant*

Contribution from the Departments of Chemistry and Fuels Engineering and the Utah Supercomputing Institute, University of Utah, Salt Lake City, Utah 84112.

Received June 21, 1991

Abstract: The principal values of the ^{13}C chemical shift tensor were measured for the aromatic carbons of 1,4,5,8-tetramethylnaphthalene, 1,2,3,6,7,8-hexahydropyrene, and pyracene using the variable angle spinning technique. Ab initio calculations of the complete shielding tensors are also reported and provided the orientation of the principal values in the molecular frame. Good agreement between theory and experiment is obtained. The chemical shift principal values and orientations of these substituted naphthalenes correspond to those found in naphthalene; the observed differences can be rationalized in terms of the strain introduced by the alkyl substituent. In the naphthalenic derivatives studied, the bridgehead carbons exhibit relatively extensive π-electron delocalization not found in some bridgeheads in more highly condensed aromatic systems.

Introduction

Although polycyclic aromatic hydrocarbons (PAHs) are of great interest in many areas of chemistry, there still exists only a limited amount of chemical shift tensor information on this class of molecules. The lack of tensor data on PAHs is in part due to the newness of the field, but also to the experimental difficulties some of these compounds exhibit. The extremely long relaxation times of many PAHs has proved a serious hurdle for their study. The majority of data available for aromatic carbons is on substituted benzene compounds, i.e., molecules with only one aromatic ring.[1] The only polycyclic aromatic compounds for which the ^{13}C chemical shift tensor or its principal components have been measured are naphthalene,[2] pyrene,[3] coronene,[4] and most recently buckminsterfullerene (C_{60}).[5] In addition, phenanthrene and triphenylene have also been recently studied in our laboratory, and these results are reported in the preceding paper in this series.[6]

PAHs are important as substructures in the aromatic clusters found in coal. Both coal and coal liquids are currently being widely studied by NMR, and much information is being gained on the composition of various coals in terms of structural features.[7] However, the majority of the current solid state NMR studies of coal are only concerned with the isotropic chemical shifts. The anisotropic information, due to its three-dimensional nature, can be used to differentiate carbons that may have similar isotropic chemical shifts but very different tensor components. However, before this type of information on the coals themselves will be useful, more tensorial information must be obtained in representative "model" compounds of known structure which exhibit structural features, such as the substituted PAHs, believed to be found in coals. Aromatic carbons in these compounds can be divided into four groups: protonated, alkyl substituted, oxygen substituted, and bridgehead or condensed, with each of these carbon types having a distinctive line-shape reflective of its local electronic environment. Our primary goal is to establish a data base of chemical shift values for each of these classes of carbons in order to explore the structural factors that influence the individual tensor components and to possibly obtain structure–tensor component relationships similar to the correlations that were observed years ago for the average chemical shifts observed in liquids. The set of chemical shift tensor components presented in this paper is for the following substituted naphthalenes: 1,4,5,8-tetramethylnaphthalene, 1,2,3,6,7,8-hexahydropyrene, and pyracene.

Experimentally, there are a number of methods available that can be used to obtain the shielding tensor components.[8] In this

---

[†] Present Address: Amoco Corporation, P.O. Box 400, Naperville, IL 60566.

[§] Utah Supercomputing Institute.

[‡] Department of Fuels Engineering.

(1) Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; The Farragut Press: Chicago, 1990; pp C28–C33.

(2) Sherwood, M. H.; Facelli, J. C.; Alderman, D. W.; Grant, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 750.

(3) Carter, C. M.; Alderman, D. W.; Facelli, J. C.; Grant, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2639.

(4) Resing, H. A.; VanderHart, D. L. *Z. Phys. Chem.* **1987**, *151*, 137.

(5) Yannonci, C. S.; Johnson, R. D.; Meijer, G.; Bethune, D. S.; Salem, J. R. *J. Phys. Chem.* **1991**, *95*, 9.

(6) Soderquist, A.; Hughes, C. D.; Horton, W. J.; Facelli, J. C.; Grant, D. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(7) Orendt, A. M.; Solum, M. S.; Sethi, N. K.; Pugmire, R. J.; Grant, D. M. In *Advances in Coal Spectroscopy*; Meuzelaar, H. L. C., Ed.; Plenum Press: New York, 1992; pp 215–254 and references within.

(8) Orendt, A. M.; Solum, M. S.; Sethi, N. K.; Hughes, C. D.; Pugmire, R. J.; Grant, D. M. In *Advances in Chemistry Series* No. 229; Botto, R. E., Sanada, Y., Eds.; American Chemical Society: Washington, DC, in press, and references within.

0002-7863/92/1514-2832$03.00/0

work the tensor components are measured using the technique of variable angle spinning (VAS).[9,10] By obtaining multiple spectra at several nonmagic angles and simultaneously fitting them while locking the average shift values to those obtained from a magic angle spectrum, one can extract the tensor components of four or possibly five shielding tensors with similar isotropic chemical shifts. This is an improvement over the two or three distinct patterns that can be extracted from a static powder pattern, making VAS the preferred method for many compounds. In the compounds studied here, VAS removes the overlap observed in static powder patterns between the σ_{33} component of the aromatic shielding tensor and any aliphatic signals, improving the accuracy of the σ_{33} determination.

In addition to the experimental determination of the principal values, ab initio calculations of the complete shielding tensor for the three naphthalene derivatives are also presented in this paper. Calculations were also performed on naphthalene, a related PAH for which the complete chemical shift tensor has been determined experimentally,[2] as well as on fluorene, biphenylene, and dicyclobuta[*de*,*ij*]naphthalene. Previously, the combination of the calculated and experimental shielding results has led to valuable insights into structure-shielding relationships.[11] The calculations are also used to provide the information on the orientation of the chemical shift tensor components in the molecular frame, information not available from the powder experiment.

In the case of aromatic carbons, some information about the orientation of the chemical shift tensor has been obtained from the NMR study of single crystals.[2,3,12] From these studies it is known that σ_{33} is always perpendicular to the plane of the aromatic ring, and its value in the aliphatic chemical shift region reflects the fact that it is dependent on the σ-electron structure and highly independent of the π-system. This forces the remaining two components to be oriented in the plane of the aromatic system. Semiempirical calculations performed on a number of aromatic systems[13] indicated that the σ_{11} component tends to be perpendicular to the bond with the largest π-bonding character; this requires that σ_{11} lie nearly along the C–H or aliphatic C–C bond for protonated and alkyl-substituted aromatic carbons, respectively. For condensed carbons, with all three bonds having similar π characters, the expected orientation is not easily rationalized. However, for the naphthalenic compounds studied in this paper, molecular symmetry requires that one of the in-plane components lie perpendicular to the central C–C bond. Only small, long-range intermolecular effects or actual deformations of the *mmm* naphthalenic symmetry will moderate this requirement.

Experimental and Computational Methods

Materials. 1,2,3,6,7,8-Hexahydropyrene was prepared by the reported procedure.[14] Pyracene was prepared as described in the literature,[15,16] mp 206–220 °C, lit.[15] 214–217 °C. Purity of both compounds was confirmed by solid state CP/MAS spectra. 1,4,5,8-Tetramethylnaphthalene was prepared by the following procedure.

1,4,5,8-Tetramethyl-3,4-dihydronaphthalene. A solution of 3.60 g of 1,4,5,8-tetramethyl-1-tetralol[17] was refluxed with 20 mg of toluenesulfonic acid in 500 mL of benzene with the separation of water using a Dean–Stark separator for 4 h.[18] The reported workup gave 2.42 g (73.9%) of a colorless liquid, bp 74–85 °C/(0.10 mm), lit.[17] 85–90 °C/(0.05 mm).

Table I. Experimental and Calculated Tensor Components[a]

carbon type	σ_{11}	σ_{22}	σ_{33}	σ_{avg}
Naphthalene[b]				
protonated (α)	225 (245)	140 (144)	23 (20)	129 (136)
protonated (β)	228 (245)	139 (147)	11 (5)	126 (132)
condensed	209 (201)	202 (222)	−6 (−3)	135 (140)
1,4,5,8-Tetramethylnaphthalene				
protonated	235 (248)	123 (131)	32 (31)	130 (137)
substituted	231 (245)	161 (155)	14 (18)	135 (139)
condensed	204 (213)	202 (201)	1 (17)	136 (144)
1,2,3,6,7,8-Hexahydropyrene				
protonated	221 (240)	129 (137)	24 (19)	124 (132)
substituted	230 (239)	167 (160)	11 (7)	136 (135)
condensed	202 (213)	197 (192)	−5 (1)	131 (135)
Pyracene				
protonated	209 (223)	142 (143)	19 (15)	124 (127)
substituted	226 (236)	166 (163)	36 (33)	142 (144)
condensed	202 (205)	192 (200)	24 (23)	139 (143)
Dicyclobuta[*de*,*ij*]naphthalene[c]				
protonated	(210)	(155)	(19)	(128)
substituted	(254)	(174)	(11)	(146)
condensed	(219)	(197)	(7)	(141)
Fluorene				
protonated (C_1)	(235)	(154)	(13)	(134)
protonated (C_2)	(241)	(144)	(7)	(131)
protonated (C_3)	(244)	(149)	(6)	(133)
protonated (C_4)	(241)	(145)	(11)	(132)
substituted (C_{4a})	(251)	(169)	(39)	(153)
substituted (C_{9a})	(256)	(173)	(25)	(151)
Biphenylene				
protonated (C_1)	(222)	(157)	(10)	(128)
protonated (C_2)	(242)	(154)	(5)	(134)
substituted	(271)	(165)	(56)	(164)

[a] Values given are experimental results with calculated results in parentheses. Experimental results are referenced externally to $(CH_3)_4Si$. Calculated values are referenced to CH_4, with the CH_4 absolute shielding being 221 ppm at the 4-31G basis set level. [b] Protonated values are averages of single crystal values. α chemical shifts are averages of C_1 and C_4 and β chemical shifts are averages of C_2 and C_3. The single crystal values exhibit inversion symmetry such that $C_1 = C_5$, $C_2 = C_6$, etc. [c] Unknown compound.

1,4,5,8-Tetramethylnaphthalene. Dehydrogenation of 6.61 g of the above dihydronaphthalene over 1.2 g of 10% Pd/C at 275–300 °C gave 3.44 g (52.7%) of oily light yellow crystals. This, combined with 4.28 g of picric acid and crystallized from 95% ethanol, gave 2.56 g of red picrate, mp 155–158 °C, lit.[16] 154.6–155.4 °C; 1.07 g of colorless material was recovered from the picrate in the usual manner, mp 124–130 °C, lit.[17] 132–133 °C. Purity was greater than 95% by ^{13}C NMR.

NMR Measurements. All spectra were recorded at room temperature on a Bruker CXP-100 spectrometer with a home-built doubly tuned MAS probe[19] using variable angle spinning[9,10] and standard cross-polarization techniques with high power decoupling.[20] A proton 90° pulse width of 5.5 μs, 3 ms contact times, and a recycle time of 3 s were generally used; 256 data points were collected and the FID was zero filled to 1K points before the FT. The spinning angle was determined from the position of $\sigma_{\perp}$ of the aromatic carbon powder pattern in hexamethylbenzene (HMB) recorded under the same conditions. All spectra were referenced externally to a MAS spectrum of HMB, with the aliphatic peak being 17.6 ppm relative to $(CH_3)_4Si$. For each sample a total of five spectra were recorded: two at angles larger than the magic angle, one at the magic angle, and two at angles less than the magic angle.

The spectral analysis was completed using a POWDER routine based on the SIMPLEX method that has been previously described.[21] The four non-MAS spectra were fit simultaneously, with the fit locked to the isotropic chemical shift values obtained from the MAS spectrum.

Calculations. Calculations of the chemical shielding tensor were performed on an IBM 3090-600S using the LORG program[22,23] with a

---

(9) Stejskal, E. O.; Schaefer, J.; McKay, R. A. *J. Magn. Reson.* **1977**, *25*, 569.

(10) Sethi, N. K.; Grant, D. M.; Pugmire, R. J. *J. Magn. Reson.* **1987**, *71*, 476.

(11) Facelli, J. C.; Grant, D. M. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; John Wiley: New York, 1989; Vol. 19, pp 1–61, and references within.

(12) (a) Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338. (b) Torman, J. V.; Veeman, W. S. *J. Chem. Phys.* **1978**, *68*, 3233. (c) Pausak, S.; Pines, A.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 591.

(13) Facelli, J. C.; Grant, D. M. *Theor. Chim. Acta* **1987**, *71*, 277.

(14) Cook, J. W.; Hewett, C. L. *J. Chem. Soc.* **1933**, 398.

(15) Trost, B. M.; Bright, G. M.; Frihart, C.; Britelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737.

(16) Carpino, L. A.; Gowecke, S. *J. Org. Chem.* **1964**, *29*, 2824.

(17) Mosby, W. L. *J. Am. Chem. Soc.* **1952**, *74*, 2564.

(18) Konieczny, M.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 2158.

(19) Jiang, Y. J.; Woolfenden, W. R.; Alderman, D. W.; Mayne, C. L.; Pugmire, R. J.; Grant, D. M. *Rev. Sci. Instrum.* **1987**, *58*, 755.

(20) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

(21) Alderman, D. W.; Solum, M. S.; Grant, D. M. *J. Chem. Phys.* **1986**, *84*, 3717.

(22) Hansen, Aa. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035.

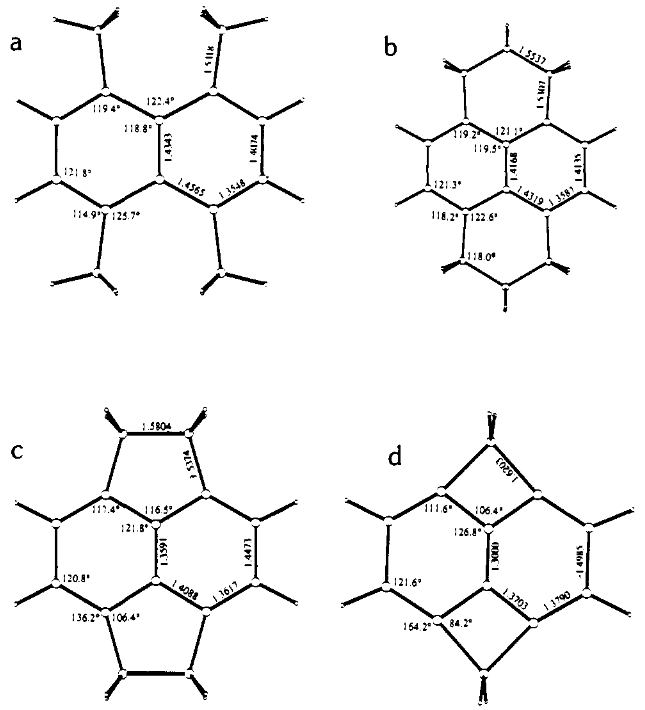

Figure 1. The 4-31G optimized heavy atom bond lengths and angles in (a) 1,4,5,8-tetramethylnaphthalene, (b) 1,2,3,6,7,8-hexahydropyrene, (c) pyracene, and (d) bicyclobuta[*de*,*ij*]naphthalene.

4-31G basis set.[24] The calculated results are referenced to calculated results of CH_4 with the same basis set (221 ppm) being 0 ppm. It should be noted that these calculations are among the largest calculations of this type, with 176 basis set functions used for 1,2,3,6,7,8-hexahydropyrene. For naphthalene,[25] fluorene,[26] and biphenylene,[27] the experimental geometries were used; for the remaining molecules, the geometries were optimized using the routines in the GAUSSIAN86 package[28] at a 4-31G basis set level as no experimental geometries have been reported. The optimized heavy atom bond lengths and angles are shown in Figure 1.

Results and Discussion

Both the experimental and calculated principal values for naphthalene, 1,4,5,8-tetramethylnaphthalene, 1,2,3,6,7,8-hexahydropyrene, and pyracene are listed in Table I. The experimental results for naphthalene are from a single crystal study.[2] Experimentally, the symmetry of the isolated naphthalene molecule is not maintained in the crystal, and, therefore, slightly different chemical shift tensor components were obtained for carbons that are considered equivalent in the isolated molecule (C_2 symmetry); however, for the purposes of this work the average of these similar components is used. Calculated results on fluorene, biphenylene, and bicyclobuta[*de*,*ij*]naphthalene are also included in Table I.

Several observations can be made from the experimental results. For the condensed or bridgehead carbons, σ_{11} and σ_{22} are nearly equivalent, with the largest difference, 10 ppm, observed in pyracene. As discussed in the preceding paper in this series,[6] this is an indication that the three adjoining π-bonds to the bridgehead carbon in the compounds studied here have similar electronic densities suggesting that a delocalized π-electronic structure is realized. Furthermore, the data indicate that the alkyl substituents do not significantly change the π-electronic structure of the parent compound, naphthalene. In addition, σ_{33} of the condensed or bridgehead carbons are also further upfield than σ_{33} of the protonated or alkyl substituted aromatic carbons. This trend is also observed in pyrene,[3] triphenylene,[6] and coronene.[4] The downfield isotropic chemical shift arising from alkyl substitution of the aromatic carbon is primarily concentrated in σ_{22}; however, σ_{11} is also shifted slightly downfield while σ_{33} tends to shift upfield in going from a protonated to a substituted carbon. Again, pyracene is unique with σ_{33} shifted downfield along with σ_{11} and σ_{22}. The large downfield shifts observed in σ_{33} for both the substituted and condensed carbons in pyracene are the reasons for the isotropic chemical shifts of these carbons appearing several ppm downfield relative to the other compounds in this study. Similar downfield shifts in σ_{33} are found in the theoretical calculations for fluorene and biphenylene, making it reasonable to attribute this trend to the presence of strain in the attached C–C σ-bonds. However, calculations on the unknown compound of bicyclobuta[*de*,*ij*]-naphthalene do not show the isolation of the large downfield shift calculated for the isotropic shift in σ_{33}. These results clearly indicate that the substituent effects are highly dependent on the nature and symmetry of the alkyl substituent. Efforts are underway to obtain experimental data on the chemical shift tensor components of aromatic carbons in fluorene and biphenylene as well as in other compounds containing four- or five-membered rings.

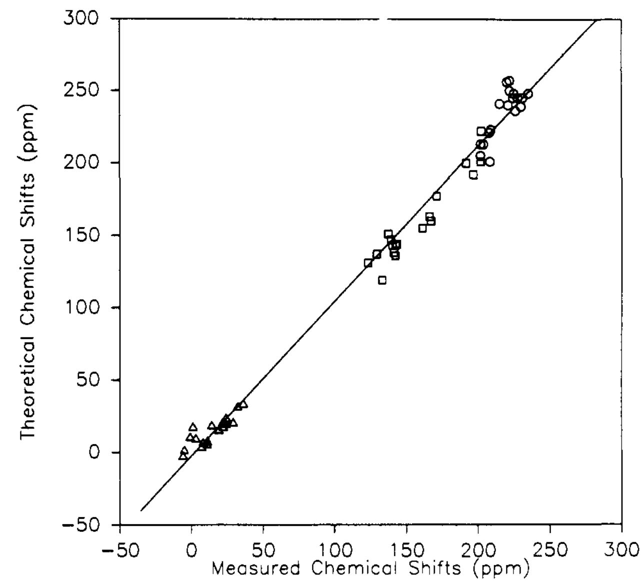

Figure 2. Least squares fit of calculated versus experimental chemical shielding tensor components for the substituted naphthalenes, triphenylene, and phenanthrene. The triphenylene and phenanthrene data are reported elsewhere.[6] Circles are σ_{11} values, squares σ_{22}, and triangles σ_{33}.

The excellent agreement between the experimental and calculated results noted in Table I may be seen in Figure 2. A least squares fit to the line in Figure 2 has a slope of 1.07, an intercept of −2.5 ppm, and a correlation coefficient of 0.990. The only major differences between experiment and theory are observed in σ_{11}, with the calculated values nearly always 10 to 20 ppm further downfield than the observed values. This is reflected in the effect of the 1.07 correlation slope as the σ_{33} values cluster in the region of CH_4 (0 ppm) where the experimental and theoretical values are put into correspondence with each other. This trend has been previously observed for unsaturated carbon[29] and nitrogen[30] chemical shieldings and is believed to reflect an inadequacy of the theory and the possible need for electron correlation in the calculations.

The calculated orientations of the principal axis system for all the compounds are shown in Figure 3. For all carbons σ_{33} is found

---

(23) Bouman, T. D.; Hansen, Aa. E. *Chem. Phys. Lett.* **1988**, *149*, 510.

(24) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(25) Pawley, G. S.; Yeats, E. A. *Acta Crystallogr.* **1969**, *B25*, 2009.

(26) Burns, D. M.; Iball, J. *Proc. R. Soc. London* **1955**, *A227*, 200.

(27) Fawcett, J. K.; Trotter, J. *Acta Crystallogr.* **1966**, *20*, 87.

(28) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, D. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

(29) Orendt, A. M.; Facelli, J. C.; Beeler, A. J.; Reuter, K.; Horton, W. J.; Cutts, P.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 3386.

(30) Schindler, M. *Magn. Reson. Chem.* **1988**, *26*, 394.

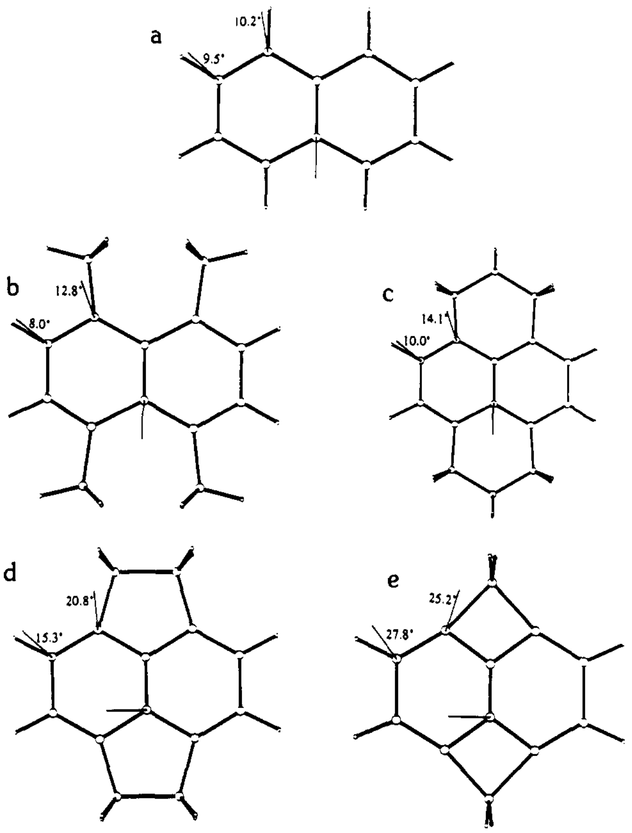

Figure 3. Orientation of calculated principal axis system of the chemical shielding tensor in (a) naphthalene, (b) 1,4,5,8-tetramethylnaphthalene, (c) 1,2,3,6,7,8-hexahydropyrene, (d) pyracene, and (e) bicyclobuta[*de*,*ij*]naphthalene. For clarity of presentation only σ_{11} is shown; σ_{22} is also in the aromatic plane and perpendicular to σ_{11} while σ_{33} is always calculated to be perpendicular to the aromatic plane.

to be perpendicular to the aromatic plane. For clarity only the orientation of σ_{11} is shown in the figure; σ_{22} is in the aromatic plane and perpendicular to σ_{11}. In all of these molecules, molecular symmetry dictates that for the bridgehead carbons σ_{11} must lie either along or perpendicular to the central C–C bond; however, because of the similarity of σ_{11} and σ_{22} the determination of which one of these two directions the σ_{11} component should lie along lacks reliability at the present level of theoretical development. Early theoretical predictions[13] at the MNDO level for naphthalene essentially agreed with the single crystal results, but more recent ab initio calculations presented here disagree with these simpler calculations. Because σ_{11} and σ_{22} are nearly identical in the naphthalenic derivatives, there remains no theoretical basis for dealing with this minor discrepancy at this time.

Before considering the trends observed in the calculated orientations, a comparison between theory and experiment can be made for naphthalene, where the orientations have also been determined experimentally.[2] For the bridgehead carbon of naphthalene the calculations place σ_{11} along and σ_{22} perpendicular to the central bond, in disagreement with the experimental results. Experimentally, a deviation of 10° from the symmetrical orientations is observed with σ_{22} being nearly along the central bond. This 10° rotation, with sizable relative errors, was attributed to either the effects of intermolecular interactions in the crystal and/or to deformations from *mmm* symmetry.[2] The calculation on an isolated molecule with *mmm* symmetry has no basis to reproduce these minor deviations from the symmetry directions. The theory and experiment also differ in the magnitude of the component that is associated with the direction along the bond. This disagreement is probably related to a greater theoretical break from trigonal symmetry at the bridgehead carbon than reflected by the small experimental difference, 7 ppm, between σ_{11} and σ_{22}. This small difference, coupled with limits in the accuracy of the calculated values of σ_{11} and σ_{22}, could easily lead to the observed reversal in orientations. Therefore, for the bridgehead carbons in the three substituted naphthalene compounds, no discussion about the relative directions of the σ_{11} and σ_{22} axes is now possible.

For the protonated aromatic carbons of naphthalene, σ_{11} is always approximately along the C–H bond, rotated slightly away such that σ_{11} is closer to being perpendicular to the C–C bond with the highest π-bond order.[2,13] For both protonated carbons the calculated orientation of σ_{11} and σ_{22} shows the rotation in the same direction as the experimental results, and the calculated angle is within 4° of the experimentally determined angle. For the protonated carbons in the substituted naphthalene compounds studied, the σ_{11} component is also always calculated to lie nearly along the C–H bond. The angle of rotation from the C–H bond is always in the same direction as observed for the same carbon (C_2) of naphthalene, but as the substituent on C_1 becomes more strained the angle between the σ_{11} axis and the C–H bond increases. This suggests that it is the π-electron system in the associated ring which dominates the σ_{11} direction. Unlike pyrene, phenanthrene, and triphenylene,[6] the naphthalenic fused ring system allows for all the π-bonds to be reasonably highly populated. An appreciation of this feature is readily obtained from a consideration of the regular Kekulé structures possible for these various condensed aromatics and the corresponding π-bond population distributions. For highly fused systems, a given π-bond often may be populated only in a single Kekulé structure.

While experimentally determined chemical shift orientations are not available for any of the aliphatically substituted aromatic carbons studied in this paper, there is no reason to believe that the calculated orientations will not be as accurate as those for the protonated carbons. In addition, single crystal results of 1,2,4,5-tetramethylbenzene (durene)[12c] place σ_{11} nearly along the substituent C–C bond. In the three alkyl-substituted carbons, σ_{11} is always rotated away from the saturated C–C bond such that it approaches the perpendicular to the same aromatic bond as the σ_{11} of the corresponding protonated compound. This is expected owing to the alternation of π-bond order characteristic of aromatic systems, as σ_{11} tends to be perpendicular to the bond with the highest π-bond order in both the substituted carbon (C_1) as well as in the protonated C_2 carbon. As the strain in the alkyl substituent increases, the angle of rotation away from the aliphatic C–C bond also increases. Calculations completed on dicyclobuta[*de*,*ij*]naphthalene, an unknown compound in which the alkyl substituent is a four-membered ring, continue to support this general rule.

Conclusions

The valuable technique of variable angle spinning has been used to extract the principal values of the chemical shift tensor from molecules with three highly overlapping powder patterns as well as a strong aliphatic signal, a task that could not easily be accomplished by a measurement on a static sample without resorting to isotopic enrichment. The chemical shift tensor components obtained for 1,4,5,8-tetramethylnaphthalene, 1,2,3,6,7,8-hexahydropyrene, and pyracene indicate that the aromatic structure, which dominates the value of σ_{11} and σ_{22} as well as their orientation in the molecular frame, does not vary much from unsubstituted naphthalene. The effects of the substitution on the components as well as their orientations in the molecular frame can be rationalized in terms of substituent effects and the strain associated with four- and five-membered rings.

While good general agreement is obtained between experimental and theoretical chemical shift components, a problem still exists with orientational information in cases where two of the components are within about 10 ppm. Therefore, at the current level of theory no differences between the chemical shielding tensors of the bridgehead carbons of the compounds studied in this paper can be discussed. However, in cases where the separation of components is larger, as in the protonated and substituted carbons of these compounds, greater confidence in the calculated orientational information is warranted.

Acknowledgment. This work was supported by the Department of Energy Office of Basic Science (Grant No. DE-FG02-

86ER13510), by the Pittsburgh Energy Technology Center through the Consortium for Fossil Fuel Liquefaction Science (Contract No. DE-FC22-89PC89852), and by the National Science Foundation through the Advanced Combustion Engineering Research Center (Cooperative Agreement No. CDR8522618). Computer time on the IBM 3090-600S of the Utah Supercomputing Institute, funded by the State of Utah and the IBM Corporation, is also gratefully acknowledged.

Catalysis by Heteropoly Compounds. 20.[†] An NMR Study of Ethanol Dehydration in the Pseudoliquid Phase of 12-Tungstophosphoric Acid

Kwan Young Lee,[‡] Takeo Arai,[‡,‖] Shin-ichi Nakata,[§] Sachio Asaoka,[§] Toshio Okuhara,[‡] and Makoto Misono*[,‡]

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan, and R&D Center, Chiyoda Corporation, Kanagawa-ku, Yokohama 221, Japan. *Received August 14, 1991*

Abstract: Dehydration of ethanol in the pseudoliquid phase of 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, was studied by means of solid-state NMR combined with IR, thermal desorption, and transient-response methods. It was confirmed by the transient-response method using isotopically labeled ethanol that a large amount of ethanol was absorbed in the lattice of the catalyst bulk (pseudoliquid phase) under the reaction conditions, and the reaction proceeded in the bulk phase. Probable reaction intermediates of the ethanol dehydration such as protonated ethanol dimer ($(C_2H_5OH)_2H^+$) and monomer ($C_2H_5OH_2^+$) were directly identified in this phase by solid-state NMR spectroscopy. The assignments were supported by IR spectroscopy and stoichiometry of ethanol absorption. By comparison of the NMR data with the results of thermal desorption of ethanol, the dimer and monomer species are very likely the intermediates for diethyl ether and ethylene formation, respectively. The unusual pressure dependence observed for the dehydration of ethanol was reasonably explained by the changes in the concentration of these intermediates in the pseudoliquid phase.

Introduction

Heteropoly acids are good cluster models of mixed oxide catalysts, and their catalyses can be described at the molecular level.[1-5] At the same time, they are good starting materials for catalyst design based on their acid and redox properties.[5] In fact, heteropoly compounds are used as catalysts for several industrial processes[6] such as oxidation of methacrolein, hydrations of propene, *n*-butene, and 2-methylpropene, and polymerization of tetrahydrofuran.

A very remarkable property of the heteropoly acids when they are used as solid catalysts is the formation of a "pseudoliquid phase" that we reported earlier.[7] Higher activities of $H_3PW_{12}O_{40}$ at low temperatures for dehydration of alcohols,[8-10] etheration,[11] esterification,[12] alkylation,[13] and decomposition of ester[14] than of SiO_2–Al_2O_3 and other solid acids are closely related to this property. Polar molecules like H_2O, alcohols, and ethers readily move into or out of the three-dimensional bulk phase, sometimes expanding or shrinking the distance between the anions.[7,15,16] This behavior is due to the flexible nature of the secondary structure (or the three-dimensional arrangement of polyanions, counter cations, etc.) of the heteropoly acid in the solid state.[5] This is not the adsorption in the micropores of the heteropoly acids (there are no micropores in the crystal structure[17]). A large number of alcohols were readily absorbed during the dehydration,[18,19] as revealed by the transient-response analysis using isotopically labeled alcohols. This pseudoliquid phase behavior brought about high catalytic activities for a variety of reactions as cited above.[8-14,20,21] Besides the activities, unique selectivities for dehydration of ethanol[22] and conversion of dimethyl ether to hydrocarbons[23] have been reported.

(1) (a) Pope, M. T.; Muller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34–48. (b) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer: Berlin, 1983.

(2) Tsigdinos, G. A. *Top. Curr. Chem.* **1978**, *76*, 1–64.

(3) (a) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030–6044. (b) Day, V. W.; Fredric, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491–492.

(4) (a) Lyon, D. K.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1787–1789. (b) Mizuno, N.; Lyon, D. K.; Finke, R. G. *J. Catal.* **1991**, *128*, 84–91.

(5) (a) Misono, M. *Catal. Rev. Rel. Subj.* **1987**, *29*, 269–321; **1988**, *30*, 339–340. (b) Misono, M. *Mater. Chem. Phys.* **1987**, *17*, 103–120.

(6) Misono, M.; Nojiri, N. *Appl. Catal.* **1990**, *64*, 1–30.

(7) (a) Misono, M., et al. CSJ/ACS Chemical Congress, Honolulu, 1979: 1st Japan-France Seminar on Catalysis, Lyon, 1979. (b) Misono, M.; Sakata, K.; Yoneda, Y.; Lee, W. Y. *Proceedings of the 7th International Congress on Catalysis, 1980*; Kodansha(Tokyo)–Elsevier(Amsterdam), 1981; pp 1047–1059.

(8) Okuhara, T.; Mizuno, N.; Lee, K. Y.; Misono, M. *Acid-Base Catalysis*; Tanabe, K., Hattori, H., Yamaguchi, T., Tanaka, T., Eds.; Kodansha: Tokyo, 1989; pp 421–438.

(9) Saito, Y.; Cook, P. N.; Niiyama, H.; Echigoya, E. *J. Catal.* **1985**, *95*, 49–56.

(10) Highfield, J. G.; Moffat, J. B. *J. Catal.* **1985**, *95*, 108–119; **1986**, *98*, 245–258.

(11) Igarashi, S.; Matsuda, T.; Ogino, Y. J. *Jpn. Petrol. Inst.* **1979**, *22*, 331–335.

(12) Izumi, Y.; Hasebe, R.; Urabe, K. *J. Catal.* **1983**, *84*, 402–409.

(13) Okuhara, T.; Kasai, A.; Hayakawa, N.; Yoneda, Y.; Misono, M. *Shokubai (Catalyst)* **1980**, *22*, 226–228.

(14) Okuhara, T.; Nishimura, T.; Ohashi, K.; Misono, M. *Chem. Lett.* **1990**, 1201–1202.

(15) Misono, M.; Mizuno, N.; Katamura, K.; Kasai, A.; Konishi, Y.; Sakata, K.; Okuhara, T.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 400–406.

(16) Okuhara, T.; Tatematsu, S.; Lee, K. Y.; Misono, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 717–723.

(17) Mizuno, N.; Misono, M. *Chem. Lett.* **1987**, 967–970.

(18) Okuhara, T.; Hashimoto, T.; Misono, M.; Yoneda, Y.; Niiyama, H.; Saito, Y.; Echigoya, E. *Chem. Lett.* **1983**, 573–576.

[†] Part 19: Mizuno, N., et al. *Nippon Kagaku Kaishi* **1991**, 1066–1072. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

[‡] Department of Synthetic Chemistry, The University of Tokyo.

[§] Chiyoda Corporation.

[‖] Present address: Konica Co. Inc., Japan.