perfine structure indicative of an exchange-coupled manganese center in signals near $g = 4$ in ammonia-treated PS II preparations. In addition, Baumgarten et al.[34] measured light-induced changes in the magnetic susceptibility of fluoride-treated PS II preparations, which exhibit an altered EPR signal at $g = 4.2$ in the S_2 state,[7,35] that they interpreted as evidence of a magnetically coupled site. These chemically inhibited preparations, although giving rise to altered EPR properties, have been considered as possible analogues for the native $g = 4.1$ species, with the suggestion that both this signal and the multiline signal may originate from the same multinuclear cluster. However, we note that addition of exogenous ligands has been seen to significantly alter exchange couplings and bridging structure within multisite metalloprotein complexes, either by disrupting existing bridges or by leading to the formation of new bridging interactions,[36] suggesting that these chemically inhibited preparations may have exchange interactions different from those of the native enzyme.

In conclusion, the detection of the parallel polarization EPR signal in the S_1 state of the oxygen-evolving complex demonstrates the presence of a paramagnetic intermediate in the resting state of the enzyme and provides an additional spectroscopic probe for understanding the structure and mechanism of this complex. The behavior of the signal in the S_1 to S_2 transition suggests that the S_1-state signal arises from the reduced form of the species that produces the multiline signal in the S_2 state, and the properties of the S_1-state intermediate provide additional insight into the electronic structure of the manganese ions.

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Registry No. Mn, 7439-96-5.

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Carbon-13 Chemical Shift Tensors in Aromatic Compounds. 3. Phenanthrene and Triphenylene

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Abstract: Measurements of the principal values of the ^{13}C chemical shift tensor are presented for the three carbons in triphenylene and for three different α-carbons in phenanthrene. The measurements in triphenylene were made in natural abundance samples at room temperature, while the phenanthrene tensors were obtained from selectively labeled compounds (99% ^{13}C) at low temperatures (~25 K). The principal values of the shift tensors were oriented in the molecular frame using ab initio LORG calculations. The steric compression at C_4 in phenanthrene and in corresponding positions in triphenylene is manifested in a sizable upfield shift in the σ_{33} component relative to the corresponding σ_{33} values at C_1 and C_9 in phenanthrene. The upfield shift in σ_{33} is mainly responsible for the well-known upfield shift of the isotropic chemical shifts of such sterically perturbed carbons. In phenanthrene C_9 exhibits a unique σ_{22} value reflecting the greater localization of π-electrons in the C_9–C_{10} bond. This localization of the π-electrons at the C_9–C_{10} bond in the central ring of phenanthrene also corresponds with the most likely ordering of electrons described by the various Kekulé structures in phenanthrene. The analysis of the ^{13}C chemical shieldings of the bridgehead carbons in triphenylene provides significant experimental information on bonding between rings in polycyclic aromatic compounds. The results confirm that the electronic structure of triphenylene is best described by three fairly isolated benzene rings linked by C–C bonds of essentially single bond character. Similarly in phenanthrene, the bonding structure which correlates the shielding information may be characterized by the dominance of two benzene rings comprising the biphenyl moiety. A strong C_9–C_{10} π-bond with only limited π-electron character in the C_{8a}–C_9 and C_{10}–C_{10a} bonds is indicated by both the experimental and theoretical results.

I. Introduction

Important information on carbon-13 chemical shift tensors may be obtained from solid state NMR spectra of either powders or single crystals. Single crystal data are required to determine completely all six elements of an experimental carbon-13 chemical shift tensor, but principal tensor values may be obtained from powdered solids whenever the spectral bands can be individually identified and assigned to a specific nucleus. The need for the powerful but more demanding single crystal methods is reduced in powders when molecular symmetry features and/or theoretical information are available to assist in specifying some or all of the principal axes associated with the measured principal shifts. The use of low-temperature NMR methods in powdered solids for measuring the principal components of the chemical shift tensor in small and medium size molecules is now well established,[1-9]

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and has been used routinely to investigate the electronic structure of organic molecules.

The principal values of the chemical shift tensors and their orientations provide valuable information on the electronic structure of molecules such as variations in the bonding environment. Isotropic ^{13}C shifts have long been known to be very sensitive to steric effects,[10–13] but the effect of steric compression on the ^{13}C shift tensor elements has largely been neglected. To the authors knowledge, steric effects on the principal components of the ^{13}C chemical shift have been reported only in *cis*-butene.[8] One of the closest approaches between intramolecular hydrogens known in organic compounds is found in phenanthrene and triphenylene, and this structural feature provided one of the main motivations for this study.

Limited data exist on ^{13}C shift tensors in polycyclic planar aromatic ring systems with only experimental results for coronene,[14] pyrene,[15] and naphthalene[16] now appearing in the literature. Single crystal studies for the latter two molecules have provided a number of basic rules for interpreting aromatic chemical shift tensor values and their orientational features. The planarity of aromatic molecules dominates the orientation of the shift tensor with the highest field component, σ_{33}, always appearing perpendicular to the aromatic rings. Orientations of the two in-plane components, σ_{11} and σ_{22}, are determined by the relative magnitude of π-bond orders between the carbon under study and the adjacent aromatic carbons.[17] The σ_{11} component tends to orient perpendicular to the π-bond with greatest double bond character. For protonated or substituted aromatic carbons, the σ_{11} direction therefore lies either along or close to the proton or substituent single bond. The presence of three multiple bonds for bridgehead carbons requires that a compromise be struck for the orientation of the σ_{11} and σ_{22} components relative to the three aromatic bonds of the resonating carbon. Because of a general similarity of bridgehead π-bonds, the corresponding σ_{11} and σ_{22} components tend to have rather similar magnitudes. It is often their orientational features which contain the more interesting information.

The naturally abundant ^{13}C powder spectrum of phenanthrene cannot be properly analyzed because of a superposition of seven overlapping shift patterns of similar but chemically nonequivalent carbons. To compare the three C_α positions in phenanthrene, it is necessary to selectively introduce labels at each position to obtain the corresponding ^{13}C shift principal values. Free of overlapping bands, these results provide an unambiguous identification and assignment of the principal values. The greater effective symmetry[18] of triphenylene relative to phenanthrene reduces the number of chemically different carbons to only three general types from the seven chemically unique carbons in phenanthrene. The naturally abundant ^{13}C powder spectrum of triphenylene therefore is more amenable to spectral analysis.

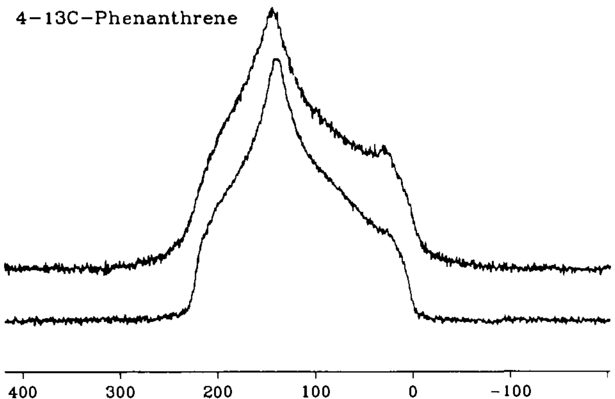

Figure 1. Effect of the H_1 decoupling field on the powder spectrum of phenanthrene. The top spectrum employs a decoupling field of about 36 kHz and the bottom spectrum is at 70 kHz.

Full ab initio calculations are required to calculate the σ_{33} components that cannot be predicted with the much less demanding semiempirical methods described before[17] for the two in-plane components, σ_{11} and σ_{22}.

II. Experimental and Computational Details

A. NMR Measurements. It has been shown previously[15,16] that it is necessary to use strong decoupling fields in order to obtain fully ^1H decoupled ^{13}C solid state spectra of aromatic compounds; therefore, a special high power double-tuned probe was constructed for the phenanthrene experiments. The probe was built to accommodate a cryogenic apparatus in the detection coil and to allow the placement of the probe into the gap of an electromagnet. This probe gives in excess of 70 kHz proton decoupling field and the respective Hartman–Hahn matching carbon field in a coil volume of ~ 3.7 cm^3. The design and construction of the probe is described in detail elsewhere.[19]

The importance of using large decoupling fields is exhibited in Figure 1 where two different spectra for [4-^{13}C]phenanthrene are shown. The top spectrum is the powder pattern obtained at a proton decoupling field of ~ 36 kHz, while the bottom spectrum was obtained at a proton decoupling field of ~ 70 kHz. Two important features are noted; first, there is an overall, decrease in the inhomogeneous line width as the decoupler field strength is increased. Second, owing to incomplete ^1H decoupling, the top spectrum is complicated further by the presence of differential broadening across the spectrum producing a measurable distortion in the normal asymmetric shift patterns. For example, the interpretation of the spectrum is complicated by greater line broadening in the vicinity of the σ_{11} breakpoint which lacks definition in the top spectrum. The lower spectrum exhibits a typical response, and it is concluded that the larger decoupling field is essential to obtain a suitable aromatic powder pattern. The lower asymmetric band shape can be fit using the well-known POWDER technique,[20] whereas the fit of the upper spectrum is seriously degraded, and the corresponding accuracy of the principal shift values is decreased below acceptable limits.

The cross-polarization phenanthrene spectra were obtained on a home-built spectrometer operating a 1.9 T with the frequency for ^1H at 80.0 MHz and for ^{13}C at 20.12 MHz. The sample is at a temperature of about 20–25 K, and the cryogenic apparatus has been described previously.[2] To minimize probe ringdown, it was necessary to use a spin-echo sequence to acquire the FID data on this probe. Sufficient transients were collected to provide adequate signal to noise. A recycle delay of 20 s was used between successive acquisitions.

The triphenylene powder spectrum was recorded on a Bruker CXP-200 spectrometer in a 4.7 T magnetic field operating at 200.04 MHz for ^1H and 50.30 MHz for ^{13}C. A home-built, large sample volume probe was used. The spectrum was acquired at ambient temperature (ca. 25 °C) using a cross-polarization, spin–echo pulse sequence. Because of the relatively long ^1H T_1 of triphenylene, a flip back 90° ^1H pulse[21] was

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(18) In a powder sample of triphenylene, the local D_{3h} symmetry renders the spectrum interpretable with only three tensor patterns (α, β, and bridgehead carbons). This effective symmetry is not, of course, totally precise as intermolecular crystal effects can produce small differences in the otherwise chemically similar sets of carbons.

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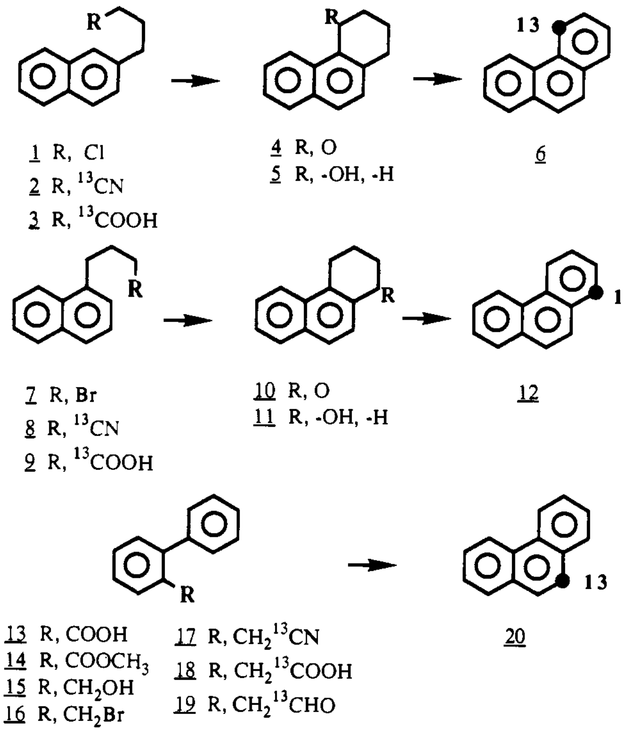
Scheme I



employed after the acquisition period to restore the ^{1}H magnetization along the external field. The proton decoupling field was 42 kHz, and 2808 transients were acquired using a delay time between acquisitions of 30 s. All powder spectra, referenced to external TMS, were fit with the POWDER routine.[20]

The CP/MAS spectrum of triphenylene was recorded on the same Bruker CXP-200 spectrometer using a Doty Magic Angle Spinning, double resonance probe. The spinning speed was 4.386 kHz, and the ^{1}H decoupling field was 68 kHz. There was a 15-s delay time between 512 acquisitions using the same pulse sequence as was used to acquire the powder spectrum.

B. Computational Procedures. Computer calculations of the shift tensors of phenanthrene and triphenylene have been performed using the LORG method.[22,23] The geometry used in this calculation was taken from X-ray[24] and neutron[25] diffraction studies. In all cases the planar structures of the compounds were used because of the minor deviations of the carbon skeleton of these molecules from planarity. The calculations[26] utilized the D95 basis set calculations for phenanthrene and the 4-31G basis set for triphenylene and were done using an IBM 3090/600S under the MVS/ESA operating system. The phenanthrene calculation uses 160 basis sets while 186 basis sets were used for triphenylene. Files containing the two electron integrals in the AO and MO basis sets were kept in extended storage, when possible, to decrease the elapsed time of the computations which can become I/O limited; each calculation requires auxiliary storage well in excess of 2 GB.

C. Compounds. The ^{13}C-labeled phenanthrenes synthesized in this work included the three positions α to bridgeheads: 1, 4, and 9; they were prepared as follows (see Scheme I).

2-(3-Chloropropyl)naphthalene (1). The addition of 1.5 mL of pyridine and 1.6 mL of thionyl chloride to 2.70 g of 3-(2-naphthyl-)-1-propanol below 30 °C, stirring overnight at room temperature and 3 h at 50–60°, gave after the usual workup 2.68 g (93.6%), bp 104–108 °C (0.08 mm). This solidified on standing, mp 32–35 °, lit.[27] bp 120 °C (0.5 mm).

4-(2-Naphthyl)butanoic Acid-*1*-^{13}C (3). A solution of 0.68 g of 99% ^{13}C sodium cyanide (Cambridge Isotope Labs) in DMSO[28] with 2.68 g of the above chloro compound gave 2.53 g of nitrile (2) (98.5%), mp 64–70 °C. This (2.53 g) gave, after 20 h refluxing in 1.34 mL of water, 1.34 g of KOH and 5 mL of diethylene glycol, 2.76 g (99.2%) of the acid (3), mp 92–99 °C, lit.[29] 94–95 °C.

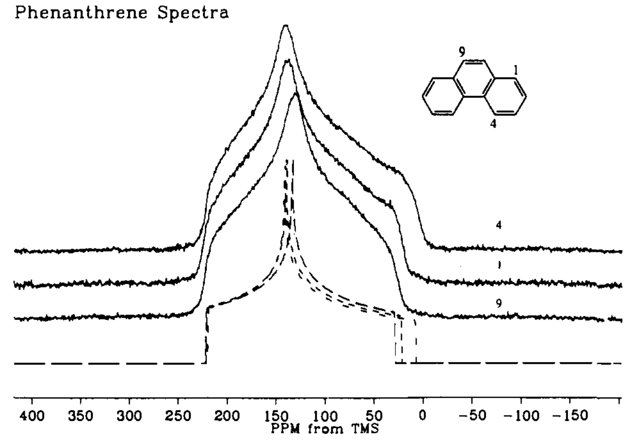


Figure 2. Carbon-13 powder spectra for singly labeled C-4, C-1, and C-9 phenanthrenes (top to bottom, respectively). The similarity of these spectra preclude their determination from a composite natural abundance spectrum, but systematic labeling provides a clear delineation of the modest but measurable differences.

Phenanthrene-*4*-^{13}C (6). The acid above (2.76 g) was converted to the acid chloride and cyclized with stannic chloride.[30] Reduction of the resultant 4-phenanthrone (4) with LAH in THF gave 1.94 g (76.4% from the acid) of 4-hydroxy-1,2,3,4-tetrahydrophenanthrene-*4*-^{13}C (5), mp 124–130 °C, which gave 0.94 g (53.3%) of colorless phenanthrene-*4*-^{13}C (6) when heated under argon with 30% Pd/C to 280 °C. The identity and purity were confirmed by the ^{13}C NMR spectrum.

4-(1-Naphthyl)butanoic Acid-*1*-^{13}C (9). Treatment of 1-(3-bromopropyl)naphthalene (7)[31] with 0.76 g of 99% ^{13}C sodium cyanide (Merck Isotopes) in DMSO[28] gave 2.55 g (100%) of the ^{13}C nitrile (8), bp 125–128 °C (0.05 mm), shown to have the expected structure by its ^{13}C NMR spectrum. This (2.44 g), hydrolyzed as described for the above isomer, gave 2.82 g (100%) of snow-white solid (9), mp 108–112 °C, lit.[32] mp 107.5–108.5 °C. A ^{13}C spectrum showed no compounds present other than the acid.

Phenanthrene-*1*-^{13}C (12). The butyric acid above (2.82 g) was cyclized, as described for the isomer to give 1.70 g (69.3% based on the nitrile) of sublimed snow-white keto compound (10), mp 87–92 °C. This was reduced with LAH/THF to the carbinol (11) (1.73 g), mp 87–92 °C (quantitative); the carbinol was converted to phenanthrene-*1*-^{13}C (12) (1.32 g, 84.5% from the ketone), mp 93–96 °C. The purity and identity were confirmed by ^{13}C NMR.

2-Biphenylacetic Acid-*1*-^{13}C (18). 2-Biphenylcarboxylic acid (13) (Fluka) was converted to the methyl ester (14) (97.5%) and reduced to the carbinol (15) (LAH/ether), bp 110–112 °C (0.25 mm) (98.7%). The carbinol was converted to the bromide (16) (96.6%) by refluxing for 21 h in 48% HBr. The material boiled at 114–118 °C (0.40 mm), lit.[33] 166 °C (12 mm). Treatment of 2.48 g of the 2-biphenylmethyl bromide with 0.56 g of 99% ^{13}C NaCN (Merck Isotopes) in DMSO[28] gave 1.92 g (98.8%) of 2-biphenylacetonitrile-*1*-^{13}C (17) which was hydrolyzed to 2.01 g (95.4%) of the acid (18) by refluxing in diethylene glycol/KOH/H$_2$O. The light yellow solid was shown to be pure and have the correct structure by ^{13}C NMR.

Phenanthrene-*9*-^{13}C (20). To a suspension of 1.33 g of LAH in 80 mL of THF (held below 0 °C), 3.12 g of *N*-methylpiperazine dihydrochloride[34] was added in portions followed by 5.36 g of *N*-methylpiperazine. The solution was allowed to come to room temperature and stirred for 9 h, then chilled in ice water; 2.01 g of the labeled acid (18) in 45 mL of THF was added dropwise. The mixture was refluxed for 6.5 h and chilled in ice water; 50 mL of ether was added to the solution. The reaction was quenched by the addition of 65 mL of saturated sodium chloride. Then 127 ml of 2 N HCl was added followed by extraction with

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Table I. Principal Values of the ^{13}C Chemical Shifts in Phenanthrene[a]

	σ_{11}		σ_{22}		σ_{33}		σ_{ave}		σ_{liq}[b]
position	calc	exp	calc	exp	calc	exp	calc	exp	exp
α-carbons									
C_1	250	222	138	141	17	22	135	128	128.5
C_4	256	220	136	142	3	7	132	123	122.6
C_9	257	222	119	133	20	29	132	128	126.9
β-carbons									
C_2	250		135		3		129		126.5
C_3	262		135		9		135		126.5
bridgehead carbons									
C_{4a}	227		189		−3		138		130.3
C_{10a}	230		196		−6		140		132.0

[a] All values in ppm. Experimental values referenced to external TMS and calculated values to CH_4 (CH_4 absolute shielding using the D95 basis set is 192 ppm.) [b] Liquid isotropic chemical shifts were referenced to internal TMS and the solvent was $CDCl_3$ (see refs 37 and 38).

Table II. Principal Values of the ^{13}C Chemical Shifts in Triphenylene[a,b]

	σ_{11}		σ_{22}		σ_{33}		σ_{ave}			σ_{liq}[c]
positions	calc	exp	calc	exp	calc	exp	calc	exp	MAS	exp
α-carbons										
C_1	241	215	143	140	9	2.8	131	119	121	123.2
β-carbons										
C_2	248	225	151	137	6	8.2	135	123	124	127.1
bridgehead carbons										
C_{4a}	221	208	177	171	10	−1	136	126	128	129.7

[a] All values in ppm. Experimental values referenced to external TMS; calculated values are relative to CH_4. (CH_4 absolute shielding using the 4-31G basis set is 221 ppm.) [b] The α- and β-carbons assignments are presently tentative for solids. They were based on the liquid shifts. [c] The shifts are referenced to internal TMS; the solvent was $CDCl_3$, from ref 38.

ether. The ether solution was washed twice with 2 N NaOH, twice with 2 N HCl, and once with saturated NaCl. Evaporation of the ether after drying gave 1.42 g (76.4%) of yellow oily liquid. This 2-biphenylacetaldehyde-*1*-^{13}*C* (**19**) was cyclized according to Bradsher[35] in 28 mL of refluxing acetic acid by the dropwise addition of 14.2 mL of 48% HBr (7 min) and further refluxing for 5 min. After chilling in ice water, filtration, and washing with water, the solid, combined with solid which separated in the water washes, was sublimed. The 0.50 g obtained (30%) (**20**) melted at 94–97 °C, lit.[35] 97.5–99 °C. It was shown to be pure and have the correct structure by ^{13}C NMR.

Triphenylene was purchased from Aldrich and used without further purification.

III. Results

The single spin anisotropic shift bands for C_1, C_4, and C_9 are presented together in Figure 2. Marked differences may be noted in the location of the breakpoints between the three different shift patterns for the two upfield components, while one obvious feature of Figure 2 is the similarity of the σ_{11} shifts in all three α-carbons. The unique σ_{22} upfield shift for C_9 and the diversity of σ_{33} shifts provide interesting information on phenanthrene. The prominent upfield shift for σ_{33} in C_4 is one of the most distinguishing features in this set of spectra.

The measured ^{13}C shift principal values taken from Figure 2 for the α-carbons at positions 1, 4, and 9 are given in Table I along with the LORG calculated principal values for all seven magnetically nonequivalent carbons in phenanthrene.

At this point in time there is no experimental information on the orientation of the principal axes of the experimental ^{13}C chemical shifts in phenanthrene as this information is unavailable from powders except in cases of high symmetry or in instances where dipolar NMR spectroscopy[36] is used.

Figure 3 shows the CP/MAS spectrum of triphenylene. The three isotropic chemical shifts taken from this spectrum are 127.9, 124.4, and 121.1 ppm from TMS. This spectrum confirms that there are at least three ^{13}C chemical shift tensors in triphenylene. The unusual shapes of these CP/MAS peaks in triphenylene are replicated in the spinning sidebands (not shown in the figure) but not present in the corresponding HMB reference spectrum. It is concluded, therefore, that the asymmetrically broadened lines in this spectrum represent small dispersions in the isotropic chemical shifts from chemically equivalent but crystallographically inequivalent sites in the unit cell of the crystal. As individual tensor elements tend to exhibit larger crystallographic effects than do isotropic shifts,[16] these intermolecular crystallographic shifts in triphenylene make this compound an excellent candidate for a single crystal study of the effect of the intermolecular interaction on ^{13}C chemical shielding tensors.

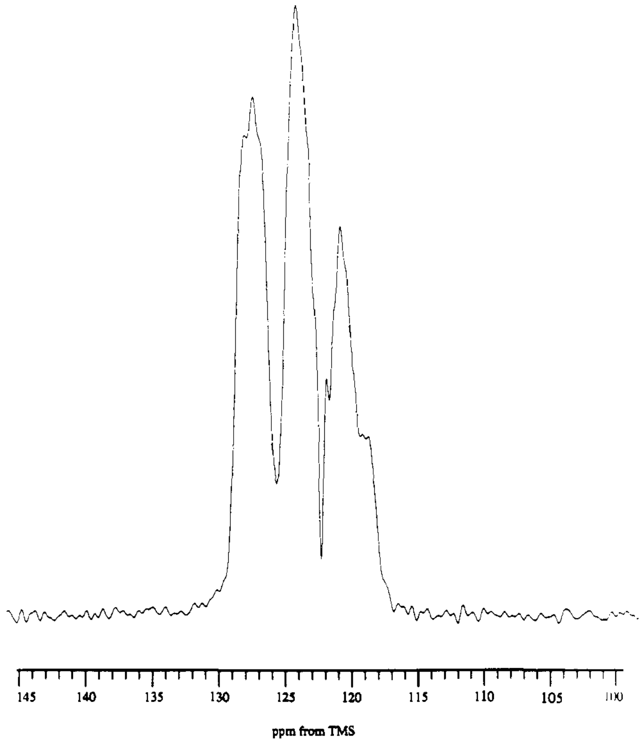

Figure 3. Carbon-13 CP/MAS NMR spectrum of triphenylene. The spinning speed was 4.39 kHz, and the chemical shifts were referenced to external TMS. The unusual line shapes are reproducible and also observed in the spinning sidebands (see text).

The experimental powder spectrum of triphenylene is presented in Figure 4, and the experimental chemical shift values were obtained from a three tensor fit of the powder pattern. The

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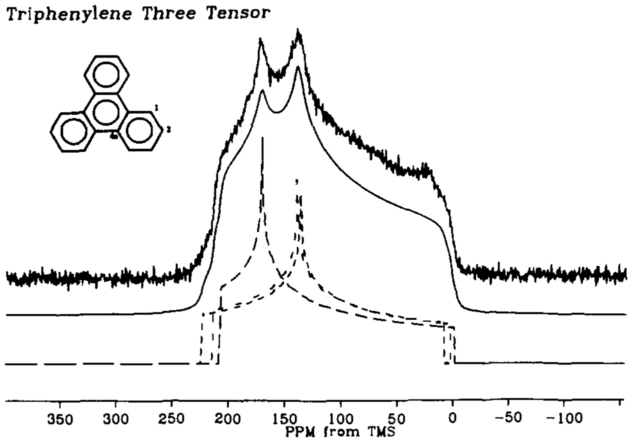

Figure 4. Carbon-13 NMR powder spectrum of triphenylene: (a) experimental trace acquired at 50.3 MHz in a 4.7-T magnetic field (the chemical shifts are referenced to external TMS); (b) the "best fit" composite simulation of the three ^{13}C chemical shift tensors in triphenylene (solid line) with line broadening; (c) the three unbroadened individual ^{13}C chemical shift tensors (dashed lines) comprising the composite "best fit" simulations.

assignments were made by comparing the known ^{13}C liquid isotropic chemical shifts of triphenylene[37,38] with both the solid state CP/MAS isotropic shifts and the isotropic shifts calculated from the three tensor fit of the powder spectrum. These results are reported in Table II. There are small (2–3 ppm) differences between the liquid, CP/MAS, and powder pattern isotropic chemical shifts in keeping with typical referencing errors for solids. However, the ordering of and the differences between the isotropic shifts remains relatively constant between liquids and solids. This tentative assignment discounts the possibility that isotropic chemical shifts exchange positions between the liquid and solid states. Furthermore, the α-carbon of triphenylene exhibits shift principal values in this assignment which are similar to those of C_4 in phenanthrene. Note the similarities in the σ_{33} components for these two structurally similar carbons. As in phenanthrene this upfield σ_{33} shift for the α carbon of phenanthrene is attributed to the proximity effect of the two hydrogens in the C_4–C_5 bay region of both phenanthrene and triphenylene.

The β-carbons in triphenylene show principal values which are similar to corresponding carbons in naphthalene, but the σ_{11} and σ_{22} principal shift values of the bridgehead carbon in triphenylene fail to exhibit the almost degenerate values observed in the corresponding naphthalene shifts. These distinctive bridgehead features are discussed below in terms of the π-bond orders and their variations in triphenylene, phenanthrene, and appropriate related molecules.

IV. Discussion

The overall agreement between measured and calculated principal values is reasonable for σ_{22} and σ_{33}, but the σ_{11} component is systematically overestimated by the calculations. This problem also has been noted in other compounds[9] with sp^2 carbons, and the larger spread between σ_{11} and σ_{33} may be attributed to the neglect of the electronic correlation effects in the theoretical calculations. As both experimental and theoretical values are referenced to TMS, this problem is not apparent for the σ_{33} values which fall in the vicinity of TMS, but the discrepancy is maximized for σ_{11} which lies farthest from TMS. An overall agreement of experimental and theoretical results is found in Figure 5 where it may be observed that major experimental shifts can be correlated with the theory. Minor shifts of a few ppm still cannot be reproduced in the theoretical calculations for relatively large molecules.

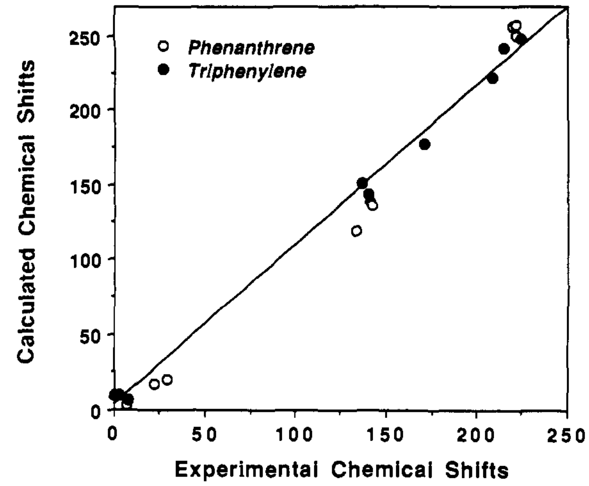

Figure 5. Calculated versus experimental chemical shifts for phenanthrene and triphenylene indicated that the correlation between theory and experiment is largely monotonic. Modest scatter about the best correlation line and an approximately 6% greater spread in the theoretical values reflect present limitations in the theoretical methods.

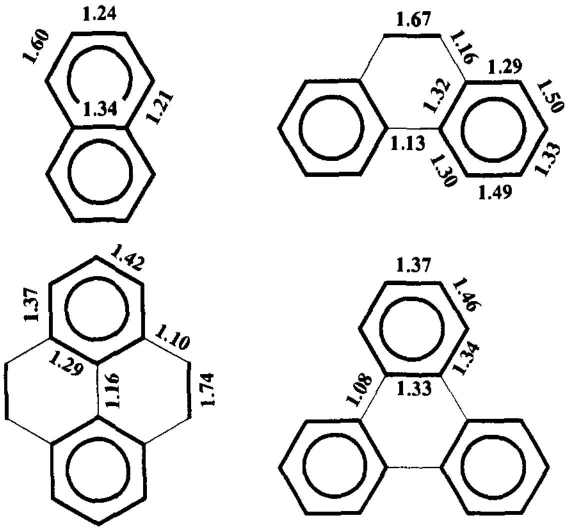

Figure 6. The MNDO calculated bond orders in naphthalene, pyrene, phenanthrene, and triphenylene indicate a diversity of π-electron delocalization.[17] Weighting of lines indicates the dominant π-bonds and the variations in π-electron localization.

In phenanthrene all the experimental α-carbons shift tensors show very similar σ_{11} components, and this trend is reproduced by the ab initio calculations. Carbons C_1 and C_4 show very similar σ_{22} components, but σ_{22} is 8–9 ppm upfield for C_9. While the theory overestimates the upfield σ_{22} shift at C_9, it nonetheless follows the trend observed in experimental data. The upfield shift in σ_{22} probably is associated with the localization of double bond character in the C_9–C_{10} bond and the corresponding decrease in the C_8–C_9 (or C_{10}–C_1) bond order (see Figure 6) as indicated by the MNDO calculated bond orders. Note, the value of σ_{22} in C_9 is closer to the values observed in olefinic carbons,[37] in agreement with the larger π-bond character for C_9–C_{10} compared with either C_1–C_2 or C_3–C_4. Similar effects were found at the $C_{4,5,9,10}$ positions in pyrene which also exhibits large π-bond orders for C_4–C_5 and C_9–C_{10} comparable to the C_9–C_{10} in phenanthrene (see Figure 6).

The most relevant feature observed in the ^{13}C shifts of the α-carbons is perhaps the large upfield shift in the σ_{33} component of C_4 in phenanthrene relative to C_1. It is observed that this σ_{33} shift, 15 ppm upfield from C_1, is primarily responsible for the significant upfield shift of the corresponding C_4 isotropic chemical shift.[37,38] This result agrees with previous results which show that steric shifts are observed along directions which are perpendicular

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Table III. Principal Values[a] of 13C Chemical Shieldings of the Bridgehead Carbons in Naphthalene, Pyrene, and Triphenylene

compound	σ_{11}	σ_{22}	σ_{33}	$(\sigma_{22}-\sigma_{11})$
naphthalene[b]	209	202	−6	7
pyrene[c]				
C_{3a}	213	187	−7	26
C_{10b}	197	191	−18	6
triphenylene[d]	208	171	−1	37

[a] Values in ppm from TMS. [b] Values taken from ref 16. [c] Values taken from ref 15. [d] This work.

to the planes in which the interaction forces operate.[8,39] A similar upfield shift is observed for the α-carbons in triphenylene.

In Table III the ^{13}C chemical shift principal values of the bridgehead carbons of triphenylene are compared with those of pyrene and naphthalene. It is apparent from the values presented in Table III that two different patterns of ^{13}C chemical shifts exist for bridgehead carbons. The bridgehead tensors in naphthalene and at C_{10b} in pyrene show small anisotropy (7 ppm and 6 ppm, respectively) for the two in-plane components. The other bridgehead shift tensors in the table exhibit in-plane anisotropies of 26 ppm and 37 ppm for C_{3a} in pyrene and C_{4a} in triphenylene, respectively. From Figure 6 it is apparent that the shieldings in the first group are characteristic of those carbons in which the bond orders for the bonds directly attached to the bridgehead carbon under consideration are of similar value, while those in the second group have one bond order significantly smaller than the others. This classification of bridgehead carbons by the anisotropy of their in-plane components discriminates between those systems in which the fused benzene rings form a single delocalized structure (e.g., naphthalene) from those in which the benzene rings are connected by C–C bonds with mostly single bond characteristics, as in triphenylene. The longer C–C bond distances observed by diffraction techniques[24,25] for these bonds with low π-bond order is a corresponding manifestation of this feature. The weights of lines in Figure 6 correspond to the bond order magnitudes. A simple view in these molecular representations is given by an assemblage of three loosely bonded benzenes for triphenylene, while pyrene and phenanthrene both reflect two dominant benzenes as part of a biphenyl moiety embeded within the fused aromatic systems. The anisotropy of σ_{11} and σ_{22} at bridgeheads reflects the varying degree of localization of π-electrons.

The calculated orientations of the ^{13}C principal shielding axes are presented in Figure 7. It has been well established that the upfield components, σ_{33}, are perpendicular to the molecular plane,[15,16] and this is reproduced by the ab initio calculations presented here. The upfield position of σ_{33} falls in the aliphatic spectral region and reflects the importance of the σ-electron structure which dominates the σ_{33} component.

The calculated ab initio orientations of σ_{11} for C–H carbons agree with those calculated using a simplified semiempirical model presented previously.[17] For all of the C–H carbons in Figure 7, the orientation of the σ_{11} and σ_{22} principal components is dictated by the local electronic symmetry and, with the exception of C_9 in phenanthrene, lies within a few degrees of the C–H bonds. The σ_{11} component of C_9 in phenanthrene lies 17.4° from the C–H bond and therefore the σ_{22} direction is only 12.6° from the C_9–C_{10} bond direction. These orientations resemble that (15°) found for $C_{4,5,9,10}$ in pyrene[15] and corresponds to the calculated orientation of similar components in olefinic carbons.[39] The σ_{11} orientation of $C_{9,10}$ in phenanthrene and of $C_{4,5,9,10}$ in pyrene[15] can be rationalized by noting that the C_9–C_{10} bond order is considerably larger than either the C_{10}–C_{10a} bond or, for that matter, any other π-bond in the molecule.

The orientations of the principal axis of the remaining CH shift tensors in both phenanthrene and triphenylene are also given in Figure 7 and follow similar trends. Note the very minor deviations of the σ_{11} axes from the CH bond directions, except for C_9 in phenanthrene already discussed. These deviations, which are generally much less than those observed in naphthalene (6° to 12°) for α- and β-carbons, further support the *isolated* benzene concept proposed for phenanthrene and triphenylene. This CH tensor orientation feature, which appears to be relatively easy to predict even at approximate levels of theory, provides interesting insights into the electronic structure of fused aromatic systems.

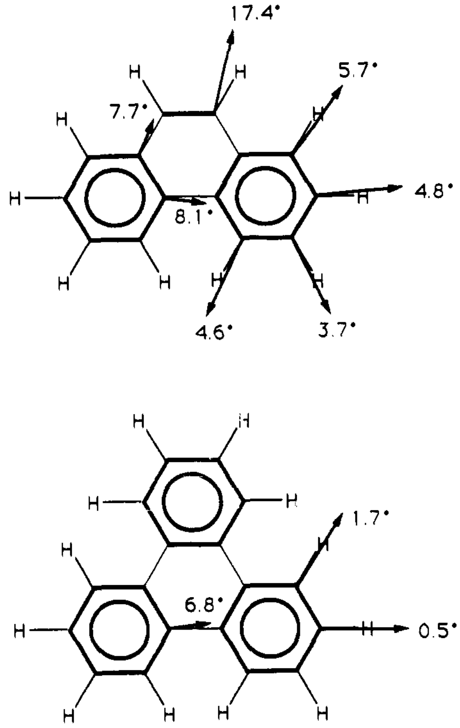

Figure 7. Orientation of the σ_{11} in-plane principal components of the ^{13}C chemical shift tensors in phenanthrene and triphenylene. The σ_{22} axis lies in the molecular plane perpendicular to σ_{11}, and σ_{33} is perpendicular to the molecular plane. When σ_{11} lies close to a given C–H or C–C substituent bond, it indicates that the two adjoining π-bonds are equivalent. Conversely, preferential localization of the π-electrons in one of the two adjoining π-bonds will reorient the σ_{11} axis toward the perpendicular to this higher electron density bond.

In both compounds the σ_{11} component of the shielding tensor for the bridgehead carbons lies close to the bonds that bridge between the emphasized benzene rings in Figure 6. As discussed above, this is another indication that the π-electrons in these molecules do not form completely delocalized systems. However, it should be noted that the errors in these angles for the bridgehead carbons are also relatively larger (e.g., estimated to approach 10°) than the corresponding errors in the C–H orientational angles. These greater inaccuracies in bridgehead shift tensor orientations follow from the considerably reduced σ_{11} and σ_{22} anisotropies. Tensor orientations in CH carbons with a much larger σ_{11} and σ_{22} anisotropy give orientation angles with errors less than 2°.

V. Conclusions

Using low-temperature solid state NMR and selective enrichment it was possible to measure the principal values of the ^{13}C chemical shift tensors of the α-carbons in phenanthrene. The well-known upfield shift on C_4 largely originates in the shift principal component perpendicular to the molecular plane, reinforcing the principle that interaction forces affect the shift components perpendicular to the plane containing the interacting forces. The use of ^{13}C chemical shift information also provides valuable information on the π-bonding characteristics of polycyclic compounds. The theoretical correlation of tensor orientations and the variations in π-bond orders portend interesting consequences as complete shift tensors become available for greater numbers of aromatic systems.

Quantum mechanical calculations of the chemical shift correlate with the experimental values and provide a way to make the

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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.

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

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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

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