Solid-State ^{13}C NMR Measurements in Methoxynaphthalenes: Determination of the Substituent Chemical Shift Effects in the Principal Values

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The principal values of the ^{13}C chemical shift tensor are measured in 1-methoxy-, 2-methoxy-, 1,4-dimethoxy-, 2,6-dimethoxy-, and 2,7-dimethoxynaphthalene using the triple echo version of the 2D magic angle turning (MAT) experiment. In the case of 1-methoxynaphthalene, a room-temperature liquid, the experiment was performed at low temperature. Assignments of the measured principal values of the chemical shift tensors to the individual carbons are made by both comparison of the solid-state isotropic chemical shift to the known solution values and comparison of the experimental principal values to the results of ab initio calculations of the chemical shielding tensor. The methoxy group substituent chemical shift parameters for each of the three components is determined relative to the parent unsubstituted naphthalene for the protonated and *ipso* carbons. The substituent parameters are very similar to those previously observed for methoxy substituted benzenes. The bond populations, determined using ab initio methods, are used to show how sensitive the orientation of the in-plane components of the chemical shift tensor is to the electronic distribution in aromatic systems.

Introduction

Substituent chemical shift parameters have long played an important role in the prediction of isotropic ^{13}C chemical shifts, and there are numerous examples in the literature of the measurement of substituent chemical shift parameters for a variety of basic molecular systems.[1,2] Aromatic systems have been widely studied in this manner, and the substituent effects in the isotropic chemical shift have been related to the electron density and the relative change in the electron distribution in the aromatic system upon substitution.[3−5] In addition, it has been shown in the absence of steric interactions that substituent chemical shifts parameters in aromatic systems are additive in nature.[6] This additivity has played an important role in assigning the numerous ^{13}C resonances in fairly complex spectra of substituted aromatics. The isotropic shift is, however, an average of the three principal values of the chemical shift tensor, and hence, the isotropic chemical shift discards the three-dimensional information.

Unfortunately, the paucity of chemical shift tensor data for many related compounds has prohibited the exploration of the additivity relationships in the individual tensor components. Owing to overlap of shift tensor powder patterns, much of the earlier work on the measurement of the principal values of magnetically inequivalent carbons was completed on relatively small systems, typically those with three or fewer magnetically distinct carbons. A limited amount of data exist on more complex molecules, mainly from single-crystal studies or from compounds that have been selectively enriched with ^{13}C at specific positions. The ^{13}C NMR literature contains two examples, a single-crystal NMR study[7] along with a more recent powder study[8] in which substituent effects were determined for the individual tensor components in methoxy substituted benzenes. In both cases, the substituent chemical shift parameters in all three of the shift tensor principal values are shown to be additive, and in the single-crystal work the substituent parameters are discussed in terms of the σ-acceptor and π-donor nature of the methoxy group.

With the recent development of a variety of 2D solid-state NMR experiments,[9] e.g., the 2D magic angle turning (MAT) experiment[10] and its derivative forms,[11,12] it has now become practical to obtain the chemical shift tensor components for fairly complex molecules without resorting to single crystals or ^{13}C labeled samples. In the 2D MAT experiment the powder patterns for each of the inequivalent carbons in the molecule are separated in the evolution dimension by their isotropic chemical shift. Although there have been a variety of 2D methods proposed in the literature over the past 10−15 years that accomplish this type of spectral separation, the MAT technique accomplishes the task with a minimum of special equipment, elaborate pulse sequences, and/or extensive data processing. The experiment can be run on a standard MAS probe, although probes optimized for slow spinning are often used, and unscaled, undistorted powder patterns are obtained directly from slices through the 2D spectra.

The precision of the principal shift values obtained from a powder is generally on the order of 1−2 ppm, and some of the smaller effects may, at times, be lost in this uncertainty. However, substituents with large effects, such as the methoxy group, can be characterized using powder data. In this paper the principal values are obtained for most of the carbons in 1-methoxy- (**I**), 2-methoxy- (**II**), 1,4-dimethoxy- (**III**), 2,6-dimethoxy- (**IV**), and 2,7-dimethoxynaphthalene (**V**). Theoretical geometry optimizations and calculations of the chemical shielding tensor are also completed on these compounds in order to obtain the orientation of the shift tensor in the molecular

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frame, information not provided by the experiment. The substituent chemical shift parameters due to the methoxy substitution are reported for the individual principal components of the protonated and *ipso* carbons. These parameters are compared with and contrasted to those previously obtained for methoxybenzenes and are rationalized using the concept of "polar bond−polarizable bond" (PB−PzB) interaction recently introduced[13] to rationalize the conformational preference of methoxy and ethoxy side chains in aromatic systems.

Experimental Details

NMR Spectroscopy. 1-Methoxy-, 2-methoxy-, 2,6-dimethoxy-, and 2,7-dimethoxynaphthalene were obtained from Aldrich, and 1,4-dimethoxynaphthalene was obtained from Lancaster. Samples were used as received after purity was confirmed by either ^{13}C solution or CP/MAS spectra. Solid-state NMR experiments were performed on a Varian VXR-200 spectrometer, operating at a carbon frequency of 50.3185 MHz. The CP/MAS spectra were recorded using a 7 mm high-speed probe from Doty Scientific.

The 2D MAT experiment was performed on **II**, **IV**, and **V** using the triple echo MAT sequence[11] on a home-built probe designed specifically to perform the MAT experiment. Details on the construction of the probe have been given elsewhere.[11] A pulse sequence with two levels of proton power was used: 300 W during the cross polarization period (about a 7.5 μs 90° pulse) and 600 W during decoupling, corresponding to a B_2 field strength of approximately 48 kHz. Other spectral parameters of interest are 4 ms contact time, 8−10 s recycle time, 44 Hz spin rate, 32 kHz spectral width in the acquisition dimension, and spectral width in the evolution dimension of one-third of the acquisition dimension spectral width. The spectra of **I** and **III** were obtained on a second home-built MAT probe capable of low-temperature operation.[14] This probe has a volume of 1.5 cm^3 and achieves a Hartmann−Hahn match at a proton 90° pulse of about 5.2 μs. The same ^{1}H power level was used for both cross polarization and decoupling. Other acquisition parameters of interest are 4 ms contact time, 2.5 s recycle time with a flipback proton pulse, 16 Hz spin rate, 25 kHz spectral width in the acquisition dimension, and spectral width in the evolution dimension of one-third that in the acquisition dimension. The spectra of **I** was acquired at a temperature of −120 °C.

Spectra were transferred to a VAX computer for processing. The 2D datasets were zero filled to 1024 × 1024 points. Spectral slices containing the individual powder patterns at the vicinity of the peak maxima in the isotropic dimension were extracted from each processed 2D dataset. Principal values of the chemical shift tensor were obtained either by inspection or by fitting of the powder patterns and have an estimated accuracy of ±2 ppm in each of the principal values. Spectra were referenced to an external sample of benzene, and all chemical shifts are given in ppm on the TMS scale.

Calculations. The Gaussian 94 program[15] with a D95 basis set[16] was used for geometry optimizations, calculation of the chemical shielding tensor, and calculation of the bond populations. The chemical shielding calculations were performed using the CHF/GIAO method.[17] The calculated chemical shieldings (σ_c) were converted to the TMS scale by a correlation of the experimental shifts and the calculated shieldings (σ_c). The best fit line was determined to be

$$\delta_c = -0.869\sigma_c + 186.9$$

with a R^2 of 0.995. The slope between the shift and the screening constant is characteristic of Hartree−Fock (HF) level calculations in which the effects of electron correlation are neglected.[18−20] The intercept also can be favorably compared to the theoretical estimate for the chemical shift of TMS, obtained from the calculated shift of methane at the same basis set and theory level (195.6 ppm), adjusted by 7 ppm[21] to account for the difference between gas phase and solution methane chemical shifts. There is a rms difference of 4.1 ppm between the experimental and the calculated principal components of the chemical shift tensors.[22] This level of agreement between theory and experiment is similar to that obtained in studies of other aromatic molecules,[18−20,23] when working with HF optimized structures and chemical shift calculations at the HF level.

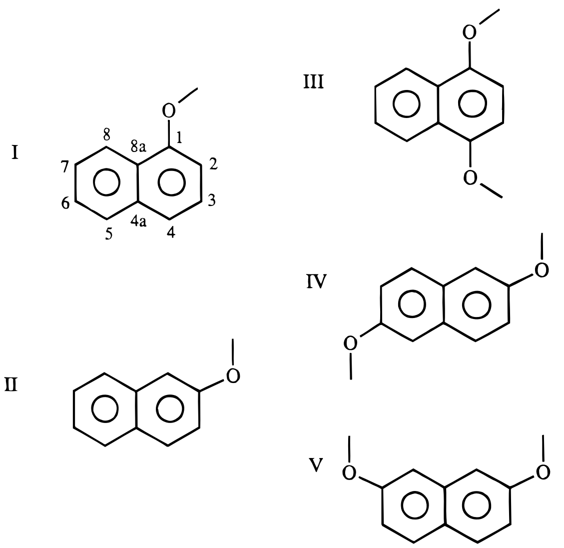

Figure 1. Compounds studied along with numbering system used in paper: (**I**) 1-methoxynaphthalene, (**II**) 2-methoxynaphthalene, (**III**) 1,4-dimethoxynaphthalene, (**IV**) 2,6-dimethoxynaphthalene, and (**V**) 2,7-dimethoxynaphthalene.

To rationalize the NMR shift data in terms of relative differences in the electronic density induced by the substituents, the bond populations were calculated for the optimized structures at the ab initio level using a standard Mulliken formalism.[24] For reference, it is important to note that this approach estimates C−C bond populations of 0.27 for ethane, 0.57 for ethylene, and 0.50 for benzene.

Results and Discussion

The conformation of the methoxy group in the optimized structure along with the numbering system used is shown in Figure 1 for all of the molecules studied. The results of the geometry optimizations place the methoxy groups in the aromatic plane in all of the compounds, as expected for systems without steric hindrance due to the inductive interaction between the highly polar C−O bond with the very polarizable C−C bonds of the aromatic system.[25,26] Of the compounds studied, an experimental structure is available only for **V**,[27] and in terms of the orientation of the methoxy groups the results of the geometry optimization agrees with the X-ray structure. In both **I** and **II** the optimized geometries place the methoxy C−O bond in a *cis* arrangement with respect to the C_1−C_2 aromatic bond. Chemical shift calculations performed on **I** and **II** with the methoxy group *cis* to the C_1−C_2 bond also show better agreement between the experimental and calculated principal values. For **I** the energy of this planar *trans* conformation was calculated to be 10.2 kcal/mol higher than the planar *cis* conformation. The R^2 for the correlation between experimental

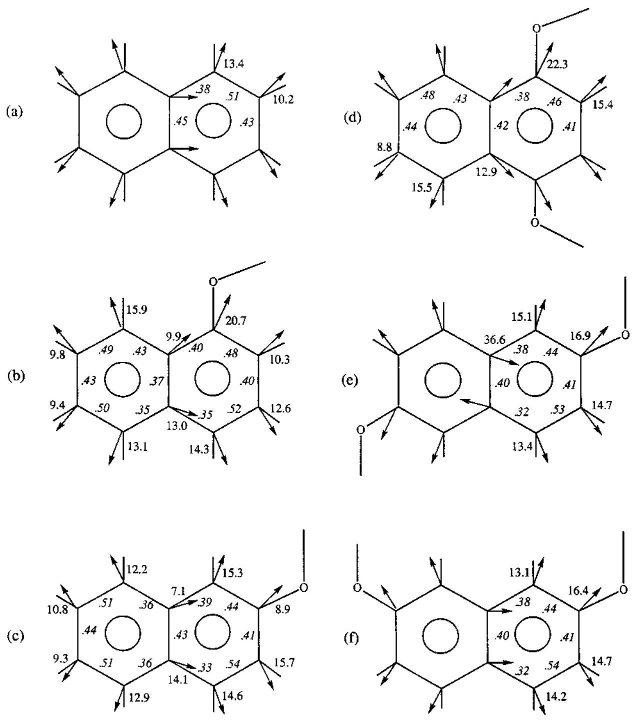

Figure 2. Calculated bond orders (given in italics) and orientations of the δ_{11} component, in degrees from the nearest bond, for the aromatic carbons in (a) naphthalene and (b) 1-methoxy-, (c) 2-methoxy-, (d) 1,4-dimethoxy-, (e) 2,6-dimethoxy-, and (f) 2,7-dimethoxynaphthalene.

and theoretical shifts decreases from 0.996 in the favored *cis* conformation to 0.987 in the planar *trans* conformation, and the rms difference between the experimental and theoretical shifts increases from 3.6 to 8.5 ppm. In the case of **II**, the energy difference is 1.9 kcal/mol, the R^2 correlation factors decreases from 0.996 to 0.994 in going from the *cis* to the *trans* conformation, and the rms difference between the experimental and theoretical shifts increases from 4.2 to 4.7 ppm. Therefore, both the energy and the chemical shift correlations indicate that the preferred conformation of the methoxy group is *cis* to the C_1-C_2 bond.

The preferred orientation of the methoxy group in this series of compounds follows the arguments presented by Biekofsky et al.[28] for the case of anisole derivatives. The same conformational preference has also been observed in methyl aryl ethers[29] and for methyl vinyl ethers.[30] The methoxy group prefers to be *cis* to the aromatic bond with the highest bond order or bond population, owing to an electrostatic interaction between the aromatic π-bond and the methoxy group $O-C_{Me}$ bond. This inductive interaction, stronger for higher π-bond populations, defines the preferred conformation. In naphthalene, the C_1-C_2 bond has a higher bond order than either the C_1-C_{8a} or C_2-C_3 bond.[31] In addition, the results of ab initio bond population calculations, shown in Figure 2 as the values in italics along the bond, for naphthalene and the five methoxy substituted naphthalenes indicate that the C_1-C_2 bond has a higher bond population than either the C_2-C_3 or the C_1-C_{8a} bond in all of the compounds.

A contour plot of the 2D MAT spectrum of **III** along with its isotropic projection is shown in Figure 3. The slices of the five individual powder patterns from this compound are given in Figure 4. Although the isotropic resonance at 127.0 ppm is believed to be due to both $C_{4a,8a}$ and $C_{6,7}$ only the principal values for the bridgehead carbons can be obtained from the anisotropic projection of this resonance. These spectral data are typical of the quality of spectra obtained for these compounds. The principal values that could be extracted from the five MAT spectra of the methoxynaphthalenes are reported in Table 1. Also included in this table are the principal values for the carbons in the parent unsubstituted naphthalene from a single-crystal NMR study.[32] In this single-crystal NMR study it was found that the molecular *mmm* symmetry is lost, making $C_{1,8}$ and $C_{4,5}$ inequivalent as well as $C_{2,7}$ and $C_{3,6}$. However,

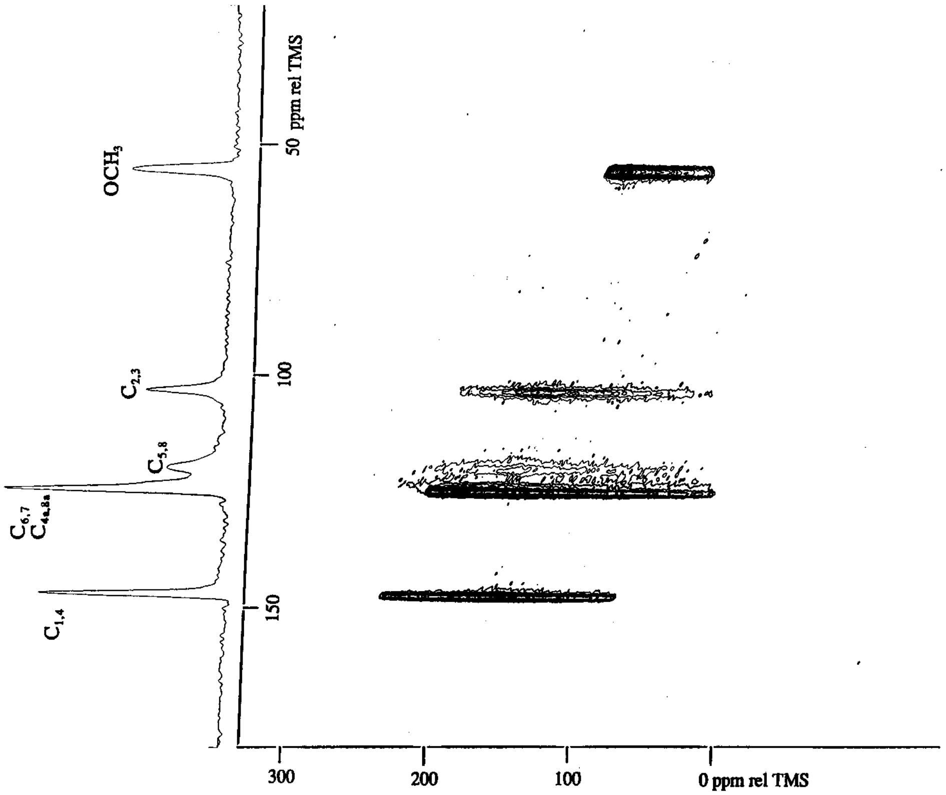

Figure 3. Contour plot of the 2D MAT spectrum of 1,4-dimethoxynaphthalene along with its isotropic projection.

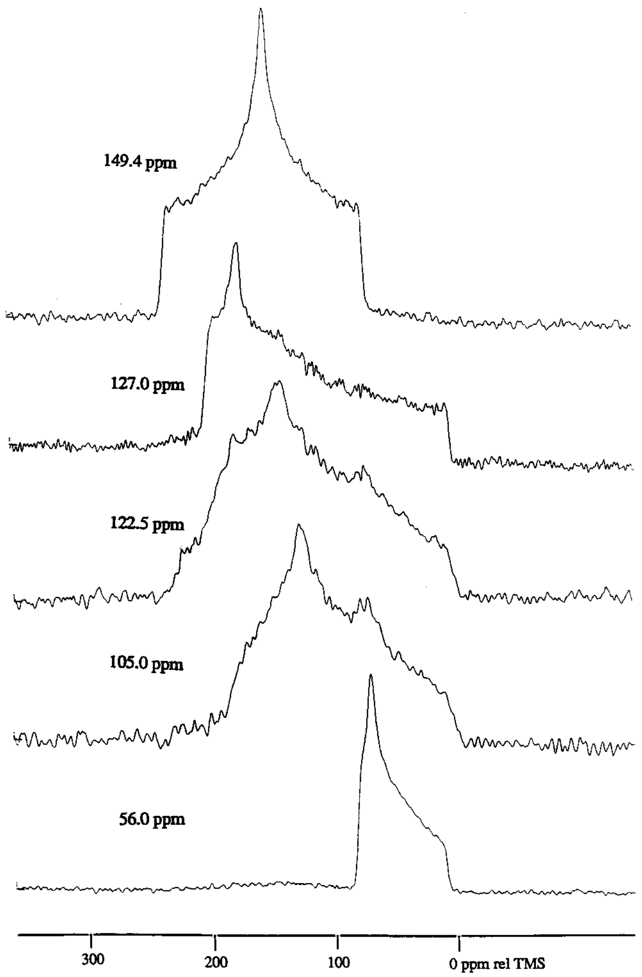

Figure 4. Slices taken from the 2D MAT spectrum of 1,4-dimethoxynaphthalene. The slices are identified by their isotropic chemical shifts. Note that the slice at 122.5 ppm ($C_{5,8}$) contains some signal from the slice at 127.0 ppm because of the low-intensity of the peak and the proximity to the intense peak at 127.0 ppm.

since these differences are sufficiently small and are therefore unobservable in the powder, their average values, reported in Table 1, are used in the determination of the substituent chemical shift parameters.

The degeneracy of carbons in **III**−**V** due to molecular symmetry greatly simplifies the assignment process. All assignments, shown in Table 1, may be made based on the agreement between the solution[33,34] and the solid-state isotropic chemical shifts. Furthermore, these assignments are supported by the theoretical predictions.

Assignments of the shift tensor components to individual carbons in **I** and **II** present more difficulty, since each of the 10 aromatic carbons is magnetically unique. In **II** all 10 aromatic resonances are resolved in the solution spectra,[35] but only nine are observed in the CP/MAS spectrum with the resonance at 128.7 ppm having double intensity. The assignments of C_{Me}, C_1, C_2, C_3, and C_{8a} may be made by comparing the solid-state isotropic chemical shifts with the solution chemical shifts. The principal values of the chemical shift tensor indicate that the nearly axially symmetric powder pattern is due to the bridgehead carbon C_{4a}. The assignment of the remaining carbons (C_4−C_8) proceeds with more difficulty, since all are typical protonated aromatic carbons with little variation among their isotropic shifts or in the individual components of their shift tensors. However, when the individual resonances are resolved in the MAS and the MAT projection, slices can be taken and fit to obtain principal values. Owing to the proximity of the isotropic shifts for C_4, C_5 and for C_6, C_7 these two groups of carbons must be grouped together with only a tentative assignment based on the isotropic shifts. A tentative assignment of C_8 can be made on the basis that it has a δ_{33} component comparable to the δ_{33} of C_4 and C_5. Fortunately, for the purpose of analyzing the substituent chemical shift effects, it is not important to have the assignments of the carbons in the unsubstituted aromatic ring, since they are relatively insensitive to the substituent.

Compound **I** is a liquid at room temperature, and hence, no MAS spectrum was obtained. Instead, the isotropic projection of the low-temperature MAT spectrum was used to obtain the solid-state isotropic chemical shifts. Although all the individual resonances are resolved in a solution spectrum,[35] the isotropic projection of the 2D MAT spectrum shows only five peaks, with the intense peak at 125 ppm having a distinct shoulder on the upfield side. Therefore, many assignments to individual carbons cannot be made at present. However, the resonances of the carbons in the ring containing the methoxy are shifted away from the 125 ppm peak, allowing assignments to be made for C_{Me}, C_1, and C_2. In addition, the assignment of the two bridgehead carbons, C_{4a} and C_{8a}, can be made on the basis of their isotropic chemical shifts and their distinctive, nearly axially symmetric powder patterns. The remainder of the carbons are typical protonated aromatic carbons, and both the calculated chemical shifts and the powder patterns of the slices taken through the peak at 125 ppm and its shoulder are consistent with that expected for protonated aromatic carbons.

Methoxy substituent effects on the principal shift values are reported in Table 2. However, before an analysis to obtain the substituent effect parameters on the principal values can be justified, the orientation of these principal values in the molecular frame due to the substitution relative to their orientation in the unsubstituted parent naphthalene must be considered. Electronic effects are three-dimensional in nature, and they affect the different components of the chemical shift tensor in different ways. When the full tensors are available, the substituent effects can be studied by rotating all of the tensors into a common reference frame and exploring the linear regression analysis in the components in this new frame instead of in the principal axis system. However, the MAT experiments performed for this paper only provide the principal values. The full tensors can only be obtained experimentally from a single-crystal NMR study, a dipolar powder pattern, or a separated local field (SLF) experiment.[36] Therefore, in this case it becomes necessary to use the orientational information obtained from the theoretical calculations in order to complete the analysis. It should be noted that recently a 3D SLF-MAT experiment has been described,[37,38] and the spectra obtained on **IV** using this technique are currently being analyzed for the orientation information. Preliminary analysis of the patterns obtained places the δ_{11} component 13.7° from the C−H bond for C_1, 14.2° for C_3, and 10.0° for C_4, with the rotation being in the same direction predicted by theory.[39] These values are in good agreement with the calculated values of 15.1°, 14.7°, and 13.4°, respectively. If the orientation of the principal axis system for a given carbon does not appreciably change upon substitution, the analysis for the substituent parameters can be done on the principal values.

The calculated orientation of the principal axis system is consistent with previous results on aromatic systems where experimental orientations are known from single-crystal data. In all cases the δ_{33} component is found to be perpendicular to the aromatic plane, as expected, requiring the δ_{11} and δ_{22} components to lie in the plane. In previous studies of aromatic systems, both theoretical and experimental,[30] δ_{11} is designated

TABLE 1: Principal Values of the ^{13}C Shift Tensors in Naphthalene and the Methoxynaphthalenes[a]

assignment	δ_{11}	δ_{22}	δ_{33}	δ_{avg}	δ_{mas}	δ_{soln}
Naphthalene[b]						
$C_{1,4,5,8}$	224.3	143.0	21.6	129.6		128.4
$C_{2,3,6,7}$	227.6	138.8	10.8	125.7		126.4
$C_{4a,8a}$	208.5	202.2	−5.9	134.9		134.1
1-Methoxynaphthalene (**I**)[c,d]						
C_1	234 (242)	161 (153)	71 (59)	155.3 (151.3)		155.3
C_3	178 (180)	124 (118)	7 (14)	103.0 (104.0)		103.6
C_3	(231)	(135)	(17)	(127.7)		125.7
C_4	(217)	(121)	(24)	(120.7)		120.1
C_5	(225)	(131)	(23)	(126.3)		127.3
C_6	(233)	(140)	(14)	(129.0)		126.2
C_7	(226)	(135)	(14)	(125.0)		125.0
C_8	(230)	(142)	(7)	(126.3)		121.9
C_{4a}	204 (206)	200 (199)	−2 (−3)	134.0 (134.0)		134.4
C_{8a}	195 (195)	175 (175)	4 (5)	124.6 (125.0)		125.5
C_{Me}	80 (79)	70 (73)	14 (16)	54.7 (56.0)		55.3
2-Methoxynaphthalene (**II**)[c]						
C_1	177 (178)	121 (113)	18 (24)	105.3 (105.0)	104.3	105.7
C_2	237 (243)	162 (158)	70 (60)	156.3 (153.7)	157.3	157.5
C_3	199 (209)	125 (128)	24 (29)	116.0 (22.0)	117.1	118.7
C_4, C_5[e]	224 (231)	148 (137)	20 (27)	130.7 (131.7)	130.7	129.3
	224 (229)	141 (135)	20 (23)	128.3 (129.0)	128.6	127.6
C_6, C_7[e]	224 (225)	136 (133)	8 (15)	122.7 (124.3)	123.1	123.4
	227 (232)	139 (139)	8 (15)	124.7 (128.7)	125.4	126.3
C_8	225 (226)	140 (130)	18 (23)	127.7 (126.3)	127.7	126.7
C_{4a}	200 (198)	195 (187)	−7 (−4)	129.3 (127.0)	129.2	129.0
C_{8a}	210 (208)	198 (194)	−3 (−3)	135.0 (133.0)	135.4	134.6
C_{Me}	82 (78)	72 (73)	12 (17)	55.3 (56.0)	54.6	55.0
1,4-Dimethoxynaphthalene (**III**)[f]						
$C_{1,4}$	225 (232)	150 (144)	74 (60)	149.7 (145.3)	149.4	149.4
$C_{2,3}$	178 (180)	127 (115)	7 (16)	104.0 (103.7)	104.8	103.1
$C_{5,8}$	221 (227)	137 (140)	9 (7)	122.3 (124.7)	122.2	121.7
$C_{6,7}$[g]	(230)	(138)	(13)	(127.0)	127.0	125.8
$C_{4a,8a}$	200 (199)	176 (176)	7 (7)	127.6 (127.3)	127.0	126.3
C_{Me}	83 (78)	71 (73)	13 (16)	55.7 (55.7)	55.6	55.6
2,6-Dimethoxynaphthalene (**IV**)[h]						
$C_{1,5}$	177 (180)	124 (115)	17 (23)	106.0 (106.0)	105.5	106.9
$C_{2,6}$	236 (239)	163 (156)	71 (61)	156.7 (152.0)	156.9	156.8
$C_{3,7}$	202 (211)	132 (131)	26 (29)	120.0 (123.7)	119.7	119.3
$C_{4,8}$	226 (228)	143 (134)	22 (27)	130.3 (129.7)	130.5	128.7
$C_{4a,8a}$	202 (200)	192 (185)	−2 (−1)	130.7 (128.0)	130.5	130.5
C_{Me}	80 (78)	72 (73)	11 (17)	54.3 (56.0)	53.8	55.6
2,7-Dimethoxynaphthalene (**V**)[h]						
$C_{1,8}$	175 (177)	123 (111)	21 (24)	106.0 (104.0)	105.0	106.1
$C_{2,7}$	237 (246)	164 (160)	72 (61)	157.7 (155.7)	158.4	158.9
$C_{3,6}$	197 (204)	124 (125)	23 (29)	114.7 (119.3)	116.1	116.4
$C_{4,5}$	224 (232)	143 (138)	22 (26)	129.7 (132.0)	130.5	129.6
C_{4a}	190 (189)	184 (178)	−4 (−2)	123.3 (121.7)	124.3	124.8
C_{8a}	207 (209)	200 (195)	2 (0)	136.3 (134.7)	136.8	137.0
C_{Me}	81 (78)	72 (73)	13 (17)	55.3 (56.0)	54.8	55.5

[a] Experimental values are obtained from MAT experiments and are in ppm relative to TMS. The estimated uncertainty is ±2 ppm. Calculated principal values, given in parentheses, are converted to TMS scale as described in text. [b] Values from single-crystal study in ref 32. Values of carbons distinct in the single crystal but equivalent in powder are averaged. [c] Solution assignments from ref 35. [d] No MAS spectra was taken, since this compound is a liquid at room temperature. [e] There is no basis for distinguishing between these two carbons; this is discussed in the text. [f] Solution assignments from ref 33. [g] Components for $C_{6,7}$ are not observed in the slice taken at an isotropic chemical shift of 127.0 ppm because of overlap with the pattern of $C_{4a,8a}$. [h] Solution assignments from ref 34.

as the radial component for protonated or alkyl substituted aromatic carbons, since it is always found to lie nearly along the C−H or C−R bond. Deviations from these bond vectors tend toward a direction that approaches the perpendicular to the aromatic bond with the highest π-bond order. The ab initio calculations performed on these systems support this emperical relationship between the calculated bond populations and the orientation of the in-plane components. The calculated orientation of the δ_{11} component and the ab initio bond populations are shown in Figure 2. In all cases the calculated orientations agree with that expected according to the rules discussed above. The larger deviations of the δ_{11} component from lying along the C−H or C−R bond are observed for the substituted carbon of the 1-methoxynaphthalenes, with the largest deviation, 22.3°, noted in **III**.

The orientations of the two in-plane components for the bridgehead carbons pose a more serious problem, since the difference between the two chemical shift components, 6.3 ppm in naphthalene, is often too small for the calculated orientations to be reliable. This limitation has been discussed in the case of naphthalene.[32] The results of the single-crystal NMR study places the δ_{11} component perpendicular to the central C−C bond (C_{4a}−C_{8a}), which is the bond with the highest bond order. Unfortunately, calculations place either the δ_{11} or the δ_{22} component in this orientation, depending on the basis set used. The corresponding difference between the δ_{11} and δ_{22} bridge-

TABLE 2: Differences in Principal Values of the ^{13}C Shift Tensors in Methoxynaphthalenes Relative to the Same Carbon in Naphthalene[a]

assignment		$\Delta\delta_{11}$	$\Delta\delta_{22}$	$\Delta\delta_{33}$
	1-Methoxynaphthalene			
C_1	*ipso*	10	18	49
C_2	*ortho*−*cis*	−50	−15	−4
C_{4a}	*meta*-bh	−5	−2	4
C_{8a}	*ortho*-bh	−14	−27	10
	2-Methoxynaphthalene			
C_1	*ortho*−*cis*	−47	−22	−4
C_2	*ipso*	9	23	59
C_3	*ortho*−*trans*	−29	−14	13
C_{4a}	*para*-bh	−9	−7	−1
C_{8a}	*meta*-bh	1	−4	3
	1,4-Dimethoxynaphthalene			
$C_{1,4}$	*ipso*, *para*	1	7	52
$C_{2,3}$	*ortho*−*cis*, *meta*	−50	−12	−4
$C_{4a,8a}$	*ortho*-bh, *meta*-bh	−9	−26	13
	2,6-Dimethoxynaphthalene			
$C_{1,5}$	*ortho*−*cis*	−47	−19	−5
$C_{2,6}$	*ipso*	8	24	60
$C_{3,7}$	*ortho*−*trans*	−26	−7	15
$C_{4,8}$	*meta*	2	0	0
$C_{4a,8a}$	*meta*-bh, *para*-bh	−7	−10	4
	2,7-Dimethoxynaphthalene			
$C_{1,8}$	*ortho*−*cis*	−49	−20	−1
$C_{2,7}$	*ipso*	9	25	61
$C_{3,6}$	*ortho*−*trans*	−31	−15	12
$C_{4,5}$	*meta*	0	0	0
C_{4a}	2 *para*-bh	−19	−18	2
C_{8a}	2 *meta*-bh	−2	−2	8

[a] Values are in ppm, taken as the value in the substituted compound minus the value for the same carbon in the parent naphthalene. Bridgehead is abbreviated bh under the entry for the type of substitution effect present.

head components in the methoxy substituted naphthalenes ranges from 4 to 24 ppm. For most of the bridgehead carbons the central C−C bond is determined to have the highest bond populations, and the δ_{11} component is calculated to lie nearly perpendicular to this bond, in agreement with the findings in naphthalene. There were, however, two exceptions to this rule. For C_{8a} in **I** and $C_{4a,8a}$ in **III**, both cases where the bridgehead carbon is *ortho* to a methoxy group substituent, the bond calculated to have the highest bond population was not the C_{4a}−C_{8a} central bond but the C−C bond of the unsubstituted aromatic ring (the C_8−C_{8a} and the C_{4a}−C_5 bond, respectively) and the δ_{11} component is calculated to be nearly perpendicular to these bonds. These two cases are also the two bridgehead carbons having the largest experimental differences between the δ_{11} and δ_{22} components (20 and 24 ppm), making the relative ordering, and therefore the calculated orientations, of the two in-plane components more reliable.

According to the chemical shift tensor calculations, the orientation of the principal axis systems of the protonated carbons does not change significantly between the parent naphthalene and the methoxynaphthalenes, as can be seen from the calculated orientation of the δ_{11} components shown in Figure 2. The largest changes are observed in the case of *ipso* methoxy substitution, showing changes of between 1 and 9°. The remainder of the changes due to other substituent effects are in the 0−5° range. Therefore, as discussed earlier, the linear regression analysis can be completed in the principal axis frame. Table 3 contains the results of this linear regression analysis on the protonated carbons, along with the R^2 value for the analysis. A plot between the experimental chemical shifts and those predicted using the linear regression parameters results in a correlation with a R^2 of 0.999 and a rms of 3.0 ppm, indicating that there is a reasonable correlation. Also presented in Table 3 are methoxy substituent parameters obtained from a linear regression analysis for methoxy substituted benzenes (a combination of the literature values for anisole[40] and for 1,4-dimethoxy-, 1,3,5-trimethoxy-, and 1,2,3-trimethoxybenzene[7]). No adjustment was made to account for the fact that the C_2 methoxy group in 1,2,3-trimethoxybenzene does not lie in the aromatic plane. It should be noted that in the case of the methoxynaphthalenes, since the principal values in naphthalene are well determined, the regression analysis was done on the deviations from the parent compound. In the case of the methoxybenzenes the values for the parent benzene molecule was part of the analysis as literature reports[41] of the principal values in benzene vary.

TABLE 3: Comparison of Methoxy Group Substituent Chemical Shift Parameters for the Protonated Carbons in Benzene and Naphthalene[a]

	$\Delta\delta_{11}$	$\Delta\delta_{22}$	$\Delta\delta_{33}$
	Naphthalene		
ipso	6.2 ± 2.3	29.5 ± 4.5	56.8 ± 4.9
ortho−*cis*	−51.0 ± 2.0	−12.0 ± 3.9	−4.0 ± 4.2
ortho−*trans*	−31.4 ± 2.3	−5.0 ± 4.6	12.8 ± 5.0
meta	−1.8 ± 1.8	7.0 ± 3.6	−0.5 ± 3.8
para	−8.0 ± 1.8	−15.5 ± 3.6	−5.3 ± 3.1
R^2	0.997	0.978	0.990
	Benzene[b]		
ipso	10.5 ± 2.0	29.6 ± 3.1	56.0 ± 2.3
ortho−*cis*	−36.8 ± 1.8	−10.4 ± 2.8	−5.4 ± 2.0
ortho−*trans*	−31.4 ± 1.4	−7.5 ± 2.2	5.7 ± 1.6
meta	0.0 ± 1.3	0.8 ± 2.0	1.4 ± 1.4
para	−9.8 ± 1.9	−13.1 ± 3.0	0.6 ± 2.2
R^2	0.989	0.957	0.990

[a] Values obtained from linear regression analysis as described in text. [b] Values for methoxybenzenes include data from anisole from ref 40 combined with that from di- and trimethoxybenzenes from ref 7.

Several observations can be made directly from Table 3. The measured substituent effects on the protonated carbons are very similar for the methoxynaphthalenes and the methoxybenzenes. The largest effects are observed for the *ipso* and *ortho* carbons in both cases. In the majority of cases the substituent chemical shift effects are within experimental error for the two different groups of compounds. The only instance among the 15 individual parameters where the substituent parameters are significantly different is for the δ_{11} component due to a methoxy group in the *ortho*−*cis* position. In this case, the larger substituent effect can be attributed to a stronger PB−PzB interaction between the C−O bond and the corresponding C−C aromatic bond. The larger bond population of the C_1−C_2 bond (0.51 in naphthalene vs 0.50 in benzene) allows for a stronger inductive effect, which in turn increases the substituent effect on the chemical shift.

The orientation of the two in-plane chemical shift tensor components of the bridgehead carbons is calculated to change significantly between naphthalene and the various methoxy substituted compounds, as may be seen in Figure 2. The changes are calculated to be the largest (approximately 40°) for the situations where there is a methoxy group in the *ortho* position relative to the bridgehead carbon (**I** and **III**). Therefore, the regression analysis to determine the substituent effect parameters in the principal axis system is not appropriate, and the substituent chemical shift parameters due to methoxy substituents cannot be determined unless an experimental determination of the orientation of the principal axis system is performed (i.e., in the NMR measurements on a single crystal) in each of the molecules.

The components of the chemical shift tensor in all methoxy carbons as well as the calculated orientation of these components in the molecular frame are essentially identical. In all calculations the δ_{22} component is perpendicular to the plane defined by the heavy atom $C_{arom}-O-C_{Me}$, the δ_{33} component lies nearly along the C−O bond, and the δ_{11} component is nearly perpendicular (within 5°) to the C−O bond. These theoretical results are very similar to reported experimental orientations for methoxy carbons in aromatic systems.[7]

Conclusions

The principal values of the ^{13}C chemical shift tensors are obtained for five methoxynaphthalene compounds: 1-methoxy-, 2-methoxy-, 1,4-dimethoxy-, 2,6-dimethoxy-, and 2,7-dimethoxynaphthalene using the MAT experiment. In addition, geometry optimizations and quantum chemical calculations of the chemical shielding tensors are completed for each of the molecules. A linear regression analysis is used to quantify the substituent chemical shift effects in the principal values due to the methoxy substitution for the protonated carbons. The substituent parameters obtained for the protonated carbons are very similar to those previously measured for a series of methoxybenzenes.

Bond population calculations illustrate how sensitive the orientation of the two in-plane components in aromatic systems is to the electronic distribution. The calculated orientation of the δ_{11} component is always found to be nearly perpendicular to the bond with the highest bond population. In the bridgehead carbons in this group of compounds, the bond with the highest bond population shifts from the central $C_{4a}-C_{8a}$ bond in the parent naphthalene and the 2-methoxynaphthalenes to the $C_{4a}-C_5$ or C_8-C_{8a} bond in the 1-methoxynaphthalenes, and the orientation of the δ_{11} component changes as expected.

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