

lation combined with tunable lasers thereby offers a substantial practical improvement over previous solid-state isotope separations because of the ease of separating reactants and products. Obviously it will be possible to study other features of the photolysis in the argon matrix, such as yields and time resolved product spectra. Such experiments are planned.

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$$\alpha = R^*/R_i$$

where R^* is the isotopic ratio of excited species. The effective enrichment may be characterized by the factor $\beta = R_i/R_i$ where R_i is the isotopic ratio of enriched products.

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Carbon-13 Magnetic Resonance. 27. The Dependence of Chemical Shifts on Methyl Rotational Conformations and Dynamics in the Methylated Benzenes and Naphthalenes

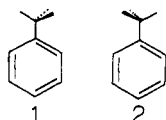
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Abstract: The aromatic carbon-13 chemical shifts of the methylated benzenes are analyzed in terms of the conformational states of the methyl rotors and associated steric, dynamic, and electronic effects. Two formal parametric analyses are developed, based on differing models. The resulting parameters enable highly accurate predicted chemical shift values to be calculated. The analysis is then extended to the carbon-13 chemical shifts of the methylnaphthalenes, incorporating additional features characteristic of this system. The results are compared and contrasted with those previously obtained. Extension of the analysis to more complex systems is investigated by considering the chemical shifts of some methylated derivatives of phenanthrene and anthracene.

Substituted benzenes have been the object of ^{13}C NMR studies for more than 15 years.² It was observed²⁻⁵ that approximately additive chemical shift effects obtain for the aromatic carbons when various substituents are added to the ring, including methyl groups.

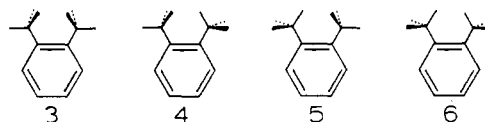
Utilizing least-squares, linear regression techniques, Woolfenden and Grant⁶ demonstrated that the ^{13}C chemical shifts of methyl groups in the methylbenzenes are also additive and exhibit conformational dependence. Although an isolated methyl group such as that found in toluene has available two minimum energy orientations of equal probability, **1** and **2**, the



aromatic portion of the proton-decoupled, ^{13}C spectrum of toluene does not reveal the six lines which would be expected for either of these forms, even at very low temperatures. This results because the sixfold barrier to internal rotation of the methyl in toluene is only 0.06 kcal/mol.⁶ Thus, thermal energies at ambient spectrometer temperatures are sufficient to populate extensively many rotational states beyond the top of the rotational barrier; a methyl group having access to such a continuum of rotational states may appropriately be termed

a "free rotor".⁶ Hence, at ambient temperatures the aromatic portion of the proton-decoupled ^{13}C spectrum of toluene contains only four lines, the chemical shifts of carbons 2 and 6 and carbons 3 and 5 being averaged.

Four symmetrical minimum energy conformations can be proposed for *o*-xylene, **3-6**. However, in this case the various



conformers are not of equal energy. The 2-2 orientation (**3**) is the lowest in steric repulsion energy, while conformations **4** and **5** are of equal, but somewhat higher, energy. The steric strain energy of structure **6** is considerably higher than that of **3**, **4**, or **5**. The assertion that **3** is the lowest energy conformer was introduced in the previously published treatment of the methyl shifts⁶ and was substantiated by the results of the analysis. It is not expected that conformation **6** will contribute significantly to the rotamer population distribution of *o*-xylene or, in fact, to that of any of the methylbenzenes. In instances (vide post) where such conformations must be considered, appreciable structural distortion will probably result.

In the previous treatment⁶ it was assumed (1) that conformations **3**, **4**, and **5** were the only ones which required consid-

Table I. Carbon-13 Chemical Shifts^a for the Aromatic Carbons of the Methylbenzenes

Item	Compd	Position	δ , exptl	δ , calcd ^b	δ , calcd ^c
1	Benzene	1-6	128.6	128.5	128.4
2	Toluene	1	137.7	137.6	137.5
3		2,6	129.2	129.3	129.2
4		3,5	128.4	128.4	128.4
5		4	125.6	125.5	125.6
6	<i>o</i> -Xylene	1,2	136.3	136.3	136.1
7		3,6	129.8	129.8	129.9
8		4,5	126.0	125.9	126.0
9	<i>m</i> -Xylene	1,3	137.4	137.5	137.4
10		2	130.0	130.1	130.0
11		4,6	126.3	126.3	126.4
12		5	128.2	128.3	128.4
13	<i>p</i> -Xylene	1,4	134.4	134.6	134.6
14		2,3,5,6	129.0	129.2	129.2
15	Hemimellitene	1,3	136.0	136.0	136.1
16		2	134.7	134.6	134.7
17		4,6	127.8	127.9	127.8
18		5	125.4	125.3	125.2
19	Pseudocumene	1	133.2	133.3	133.2
20		2	136.2	136.2	136.0
21		3	130.4	130.6	130.6
22		4	135.1	135.0	135.1
23		5	126.6	126.7	126.8
24		6	129.7	129.7	129.8
25	Mesitylene	1,3,5	137.5	137.3	137.4
26		2,4,6	127.3	127.1	127.1
27	Prehnitene ^d	1,4	133.7	133.8	133.9
28		2,3	134.6	134.6	134.6
29		5,6	127.3	127.3	127.1
30	Isodurene	1,3	135.9	135.9	136.0
31		2	131.5	131.6	131.8
32		4,6	128.8	128.6	128.6
33		5	134.2	134.4	134.2
34	Durene	1,2,4,5	133.7	133.7	133.6
35		3,6	131.1	131.0	131.3
36	Pentamethylbenzene ^d	1,5	133.2	133.1	133.3
37		2,4	132.3	132.3	132.4
38		3	134.8	134.8	134.5
39		6	129.2	129.3	128.9
40	Hexamethylbenzene	1-6	132.2	132.2	132.1

^a Extracted from ref 7 (except as noted) and converted to Me₄Si scale using $\delta_{\text{Me}_4\text{Si}} - \delta_{\text{C}_6\text{H}_6} = 128.6$ ppm. All shifts are in parts per million relative to Me₄Si. ^b Utilizing the parameters of Table IV. ^c Utilizing the parameters of Table V. ^d The chemical shifts for this compound as obtained from ref 7 differed significantly from those acquired on the XL-100, so the XL-100 values are used here.

eration when analyzing the conformational population distribution of the methyl groups; (2) that the 2-2 conformation, **3**, is the most stable one and will always exist between at least one pair of adjacent methyl groups, except in hexamethylbenzene where that is not possible without introducing an interaction like that in **6**; and (3) that all allowed 2-2 conformations are equally probable. Least-squares, linear regression analysis of the ¹³C methyl chemical shifts⁶ indicated that methyls in conformation **3** were shifted upfield by -1.9 ppm relative to the CH₃ of toluene, while a methyl in a conformation like that of the right methyl of **4** was shifted upfield by -4.4 ppm, and CH₃'s in conformations like that of the left methyl of **4** experienced a 0.1-ppm downfield shift. Small effects were also noted for methyls in meta and para orientations.

Woolfenden also completed a preliminary least-squares, linear regression analysis on the ring carbons of the methylbenzenes,⁷ the results of which have been summarized by Stothers.⁸ Other authors have published the ¹³C spectral data for one or more methylated benzenes.⁹⁻¹⁴

Although the ¹³C spectra of a few methylated naphthalenes have

been published in the past,¹⁵⁻¹⁸ only recently have more extensive studies been made on these compounds,^{19,20} with approximately additive effects noted for the simpler methyl-substituted naphthalenes. However, no in-depth parametric characterization of such systems has been published.

In this work it is demonstrated that the ¹³C chemical shifts in the methylated benzenes, naphthalenes, and related systems can be analyzed in terms of a dependence on methyl group orientation and dynamics. Steric, dynamic, and electronic effects all appear to be important. Least-squares, linear regression analysis is utilized to develop a formal parametric treatment.

Experimental Section

Data for the methylbenzenes were originally acquired at 15.1 MHz,⁶ but several of the compounds were rerun on a Varian XL-100-15 spectrometer at 25.2 MHz. Significant deviations from previously published values were detected in two cases noted below. All other data included herein were taken on a Varian XL-100-15 spectrometer operating in the Fourier transform mode. High pulse power was supplied by a Heathkit SB-220 linear amplifier, resulting in a $\pi/2$ pulse width of ca. 17 μ s. Decoupling was accomplished by use of a Hewlett-Packard 1505A frequency synthesizer amplified by a Model 310 EN1 power amplifier, and modulated with a noise generator fabricated in our laboratory.

Results and Discussion

The Methylbenzenes. The aromatic carbon-13 chemical shifts of the methylbenzenes are contained in Table I.²¹ The conformational analysis of these data utilized the three postulates given above for the methyl analysis. It should be stressed that parametrization of chemical shift data depends on the choice of a physical model for the regression analysis, and for this reason there is always a degree of arbitrariness in the procedure. To illustrate this point the aromatic chemical shifts of the methylbenzenes have been analyzed in terms of two different models, one emphasizing steric features and a second focusing upon dynamic features. The parameters and factor analyses relevant to the two approaches are given in Tables II and III, respectively, while the parametric results derived from the least-squares, linear regression treatments²² are given in Table I.

Tables II and IV focus upon the steric implications of the constraints imposed on the methylbenzene conformations. The parameters α , β , γ , and δ are positional parameters. This set of four parameters adequately predicts the chemical shifts of all of the compounds which do not have vicinal methyls. The remaining nine parameters, $\alpha_2\beta_2$, $\alpha_2\beta_1$, etc., represent effects which must be considered when adjacent methyls are present. The Greek letters refer to the methyl position relative to the carbon of interest, while the subscripted numeral describes the number of hydrogens which that methyl has oriented toward its vicinal methyl neighbor in a particular minimum energy conformation. For example the chemical shift of carbon positions 1 and 2 in **3** would be influenced by an $\alpha_2\beta_2$ parameter, while the carbon adjacent to the left methylated carbon of **4** would be corrected by a $\beta_2\gamma_1$, etc. It may be noted that there is a significant correction parameter at each ring position when methyls are adjacent.

The value of the α parameter is surprisingly similar to that resulting from methyl substitution in aliphatic systems.²³ The small γ effect is also similar to that found in saturated hydrocarbon systems which are not involved in steric interactions.²³ In the β and δ positions, however, there is a radical departure from the results normally encountered in aliphatic systems, in that the β is much smaller and the δ is much larger for the methylated aromatics. Spiess and Schneider⁹ concluded many years ago that the π electron density was responsible for chemical shift effects at the para position of

Table II. Factor Analysis of the Aromatic ^{13}C Chemical Shifts of the Methylbenzenes Emphasizing Steric Features

Item	Compd	Position	Parameters												
			α	β	γ	δ	$\alpha_2\beta_2$	$\alpha_2\beta_1$	$\alpha_1\beta_2$	$\beta_2\gamma_2$	$\beta_2\gamma_1$	$\beta_1\gamma_2$	$\gamma_2\delta_2$	$\gamma_2\delta_1$	$\gamma_1\delta_2$
1	Benzene	1-6													
2	Toluene	1	1												
3		2,6		1											
4		3,5			1										
5		4				1									
6	<i>o</i> -Xylene	1,2	1	1			1								
7		3,6		1	1					1					
8		4,5			1	1							1		
9	<i>m</i> -Xylene	1,3	1		1										
10		2		2											
11		4,6		1		1									
12		5			2										
13	<i>p</i> -Xylene	1,4	1			1									
14		2,3,5,6		1	1										
15	Hemimellitene	1,3	1	1	1		$1/2$	$1/2$		$1/2$		$1/2$			
16		2	1	2			1		1						
17		4,6		1	1	1				$1/2$	$1/2$		$1/2$		$1/2$
18		5			2	1						1	1		
19	Pseudocumene	1	1	1		1	1								
20		2	1	1	1		1								
21		3		2	1					1					
22		4	1		1	1							1		
23		5		1	1	1							1		
24		6		1	2					1					
25	Mesitylene	1,3,5	1		2										
26		2,4,6		2		1									
27	Prehnitene	1,4	1	1	1	1	$1/3$	$2/3$		$1/3$	$1/3$	$1/3$	$1/3$		$2/3$
28		2,3	1	2	1		$2/3$	$1/3$	1	$1/3$		$2/3$			
29		5,6		1	2	1				$1/3$	$2/3$		$2/3$	1	$1/3$
30	Isodurene	1,3	1	1	2		$1/2$	$1/2$		$1/2$		$1/2$			
31		2	1	2		1	1		1						
32		4,6		2	1	1				$1/2$	$1/2$		$1/2$		$1/2$
33		5	1		2	1						1	1		
34	Durene	1,2,4,5	1	1	1	1	1						1		
35		3,6		2	2					2					
36	Pentamethylbenzene	1,5	1	1	2	1	$1/4$	$3/4$		$1/4$	$1/2$	$1/4$	$1/2$	1	$1/2$
37		2,4	1	2	1	1	$1/2$	$1/2$	1	$1/4$	$1/4$	$1/2$	$1/4$		$3/4$
38		3	1	2	2		$1/2$	$1/2$	1	$1/2$		$3/2$			
39		6		2	2	1				$1/2$	$3/2$		$1/2$	1	$1/2$
40	Hexamethylbenzene	1-6	1	2	2	1		1	1		1	1		1	1

substituted benzenes, and this theory still provides the best explanation of δ effects. It is reasonable that π electron effects are also very important at the β positions, but σ electron effects and steric interactions must also be significant. The β effect for methyl substitution in aliphatic systems is normally about 9 ppm downfield, which may be a combination of inductive²⁴ and steric²⁵ effects. As there is no a priori reason to suppose that these effects would be significantly smaller in aromatic systems, it may be concluded that the small β shift observed obtains because the usual downfield shift is almost balanced out by a comparable upfield shift resulting from variations in the π electron density. As stated above the shifting of the more mobile π electron density is also likely responsible for the relatively large upfield chemical shift at the para position, but in this case no σ -electron shift exists to counterbalance it. This interpretation is consistent with the classical picture of ortho, para directing groups in substituted benzenes and is supported by the chemical shifts noted²⁶ for ethene (122.6 ppm) and C-1 of propene (114.8 ppm), where methyl substitution has caused a large upfield β shift. This is probably due to the fact that the upfield π electron effect is concentrated at a single carbon and cannot be diffused throughout an aromatic system as it is in toluene.²⁷

Rationalization of the correction parameters can be made consistent with the above model. In a benzene system having ortho methyls, every carbon is α , β , or δ to one of the methyls and should thus be rather sensitive to changes in electron dis-

tribution resulting from the various possible steric interactions of the substituents. It may be noted in Table IV that the standard deviation of the fit is only slightly larger than experimental error, indicating that the parameter set chosen is sufficiently complete to characterize totally the factors affecting chemical shifts.

An alternative interpretation of the data, involving fewer parameters and both structural and dynamic features, is presented in Tables III and V. In addition to the three primary assumptions previously used to define the population factors, the principal feature of this model is that it differentiates between "free" and "locked" methyls. For the purposes of this analysis locked methyls were considered to be those involved in threefold barriers to rotation, while free methyls were those whose rotational motion was dominated by sixfold or higher rotational barriers. Examples of sixfold barriers are found in toluene and the center methyl of hemimellitene.²⁸

The parameter set for this second model is given in Table V. The Greek letters indicate as before the position of the carbon of interest relative to the substituent, but in this case they are subscripted with an F to denote when the CH_3 is considered to be a free methyl and similarly with an L for a locked methyl. In the course of executing the regression it was found that the α position was not sensitive to whether a CH_3 was locked or free, so the two parameters were combined. At the β position a satisfactory fit would not obtain using only two parameters, and it was necessary to add some additional dis-

Table III. Factor Analysis of the Aromatic ^{13}C Chemical Shifts of the Methylbenzenes Emphasizing Dynamic Features

Item	Compd	Position	Parameters								
			α	β_{FH}	β_{LH}	β_{FC}	β_{LC}	γ_{F}	γ_{L}	δ_{F}	δ_{L}
1	Benzene	1-6									
2	Toluene	1	1								
3		2,6		1							
4		3,5						1			
5		4								1	
6	<i>o</i> -Xylene	1,2	1					1			
7		3,6			1				1		
8		4,5							1		1
9	<i>m</i> -Xylene	1,3	1					1			
10		2		2							
11		4,6		1							
12		5						2		1	
13	<i>p</i> -Xylene	1,4	1					1		1	
14		2,3,5,6		1							
15	Hemimellitene	1,3	1				1		1		
16		2	1					2			
17		4,6			1			1			1
18		5							2	1	
19	Pseudocumene	1	1					1		1	
20		2	1					1	1		
21		3		1	1				1		
22		4	1						1		1
23		5		1					1		1
24		6			1			1	1		
25	Mesitylene	1,3,5	1					2			
26		2,4,6		2						1	
27	Prehnitene	1,4	1				$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	1
28		2,3	1				$\frac{2}{3}$	$\frac{4}{3}$		1	
29		5,6			1			$\frac{2}{3}$	$\frac{4}{3}$	$\frac{2}{3}$	$\frac{1}{3}$
30	Isodurene	1,3	1				1	1	1		
31		2	1					2		1	
32		4,6		1	1			1			1
33		5	1						2	1	
34	Durene	1,2,4,5	1					1		1	1
35		3,6			2				2		
36	Pentamethylbenzene	1,5	1				$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
37		2,4	1				$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1
38		3	1				1	1	2		
39		6			2				1	1	$\frac{1}{2}$
40	Hexamethylbenzene	1-6	1				2		2		1

Table IV. Linear Least-Squares Regression Parameters for the Chemical Shifts of the Aromatic Carbons of the Methylbenzenes Emphasizing Steric Features

Number of chemical shifts: 40 Regression constant: 128.5 ppm
Standard error of the estimate: 0.12 ppm
Multiple *R*: 0.9997 *F* ratio: 2920

Parameter ^a	Value ^b	No. of cases	<i>F</i> to remove
α	9.0 ± 0.07	20	19 300
β	0.8 ± 0.05	28	284
γ	-0.1 ± 0.05	28	7.1
δ	-3.0 ± 0.07	20	2 110
$\alpha_2\beta_2$	-2.1 ± 0.09	13	576
$\alpha_2\beta_1$	-3.5 ± 0.2	8	277
$\alpha_1\beta_2$	-2.5 ± 0.1	6	638
$\beta_2\gamma_2$	0.6 ± 0.07	15	75.0
$\beta_2\gamma_1$	1.3 ± 0.15	8	73.6
$\beta_1\gamma_2$	0.6 ± 0.15	8	15.4
$\gamma_2\delta_2$	0.5 ± 0.09	13	38.4
$\gamma_2\delta_1$	-0.5 ± 0.1	6	27.4
$\gamma_1\delta_2$	0.9 ± 0.2	8	19.6

^a See text for description of parameters. ^b In parts per million.

inction as to whether the carbon of interest was substituted by hydrogen, indicated by the subscript H, or by a methyl, indicated by subscript C. In this analysis γ_{F} is negligible, and in fact its inclusion decreases the quality of the fit slightly, but

Table V. Linear Least-Squares Regression Parameters for the Chemical Shifts of the Aromatic Carbons of the Methylbenzenes Emphasizing Dynamic Features

Number of chemical shifts: 40 Regression constant: 128.4 ppm
Standard error of the estimate: 0.18 ppm
Multiple *R*: 0.9991 *F* ratio: 1850

Parameter ^a	Value ^b	No. of cases	<i>F</i> to remove
α	9.1 ± 0.09	20	9530
β_{FH}	0.8 ± 0.07	8	128
β_{LH}	1.6 ± 0.07	8	570
β_{FC}	-1.2 ± 0.08	8	205
β_{LC}	-1.4 ± 0.06	11	500
γ_{F}	-0.03 ± 0.06^c	16	0.3
γ_{L}	-0.2 ± 0.05	19	13.1
δ_{F}	-2.8 ± 0.07	12	1610
δ_{L}	-2.2 ± 0.07	10	910

^a See text for description of parameters. ^b In parts per million. ^c This parameter is not significant, but is retained in the analysis to demonstrate that fact.

it is retained to illustrate its conformity with the trends noted for other parameters in the set. The δ parameters are again large and upfield.

Although this parameter set is based upon the dynamical characteristics of the methyls, its interpretation still relates to steric features and their effects on the π electron distribution.

Table VI. Carbon-13 Chemical Shifts^a for Naphthalene and Some of Its Methylated Derivatives^{b,c}

Compd	1	2	3	4	5	6	7	8	9	10	Me(a) ^d	Me(b)	Me(c)	Me(d)
Parent	127.7 (127.8)	125.6 (125.6)							133.3 (133.4)					
1-Methyl	134.0 (134.0)	126.4 (126.5)	125.3 (125.3)	126.2 (126.0)	128.3 (128.4)	125.3 (125.3)	125.4 (125.4)	123.9 (124.0)	133.4 (132.4)	19.2 (19.2)				
2-Methyl	126.7 (126.8)	135.2 (135.1)	127.9 (127.9)	127.2 (127.5)	127.5 (127.4)	124.8 (124.7)	125.7 (125.7)	127.4 (127.3)	133.5 (133.6)	131.6 (131.6)	21.6 (21.5)			
1,2-Dimethyl	130.8 (130.8)	132.8 (132.7)	128.8 (128.8)	125.6 (125.6)	128.3 (128.0)	124.3 (124.4)	125.5 (125.5)	123.5 (123.5)	132.5 (132.7)	132.2 (132.2)	14.4 (14.4)(1)	20.6 (20.6)(2)		
1,3-Dimethyl	133.7 (133.7)	128.7 (128.7)	134.8 (134.7)	125.1 (125.0)	127.7 (127.9)	125.4 (125.3)	124.6 (124.5)	123.7 (123.6)	130.8 (130.6)	133.7 (133.6)	19.1 (19.0)(1)	21.5 (21.4)(3)		
1,4-Dimethyl	132.1 (132.2)	126.0 (126.1)			124.4 (124.6)	125.1 (125.1)			132.5 (132.5)		19.3 (19.3)			
1,5-Dimethyl	134.5 (134.6)	126.2 (126.1)	125.1 (125.1)	122.2 (122.2)					132.5 (132.5)		19.7 (19.8)			
1,6-Dimethyl	133.6 (133.6)	125.5 (125.5)	125.3 (125.3)	125.6 (125.5)	127.3 (127.4)	134.7 (134.7)	127.6 (127.7)	123.7 (123.7)	130.6 (130.6)	133.7 (133.6)	19.1 (19.2)(1)	21.4 (21.5)(6)		
1,7-Dimethyl	133.8 (133.5)	126.4 (126.5)	124.4 (124.4)	125.9 (125.6)	128.1 (128.1)	127.4 (127.5)	135.0 (134.9)	123.0 (122.9)	132.6 (132.6)	131.7 (131.7)	19.2 (19.2)(1)	21.5 (21.5)(7)		
1,8-Dimethyl	135.2 (134.9)	129.2 (129.3)	124.8 (124.9)	127.7 (127.6)					132.9 (132.9)	135.4 (135.4)	25.9 (25.7)			
2,3-Dimethyl	127.3 (127.3)	135.2 (135.2)			126.7 (126.8)	124.8 (124.8)			132.3 (132.3)		20.1 (20.0)			
2,6-Dimethyl	126.5 (126.3)	134.2 (134.2)	128.0 (128.0)	127.0 (126.9)					131.9 (131.8)		21.6 (21.5)			
2,7-Dimethyl	126.0 (126.2)	135.1 (135.2)	127.1 (127.0)	126.9 (127.1)					133.6 (133.7)	129.7 (129.8)	21.7 (21.5)			
2,3,5-Trimethyl	127.9 (127.9)	134.8 (134.8)	135.0 (134.9)	123.6 (123.5)	133.0 (133.0)	125.5 (125.6)	124.5 (124.4)	125.2 (125.1)	132.4 (132.4)	131.3 (131.3)	20.2 (20.0)(2)	19.1 (20.0)(3)	19.1 (19.2)(5)	
2,3,6-Trimethyl	127.0 (126.9)	134.2 (134.2)	135.2 (135.2)	126.6 (126.8)	125.7 (125.8)	134.2 (134.2)	127.0 (127.0)	126.6 (126.5)	130.6 (130.5)	132.5 (132.5)	19.9 (20.0)(2)	19.9 (20.0)(3)	21.3 (21.5)(6)	
1,4,6,7-Tetramethyl	131.2 (131.3)	125.2 (125.2)			124.2 (124.1)	134.5 (134.6)			131.2 (131.4)		19.1 (19.3)(1,4)	20.2 (20.0)(6,7)		
1,3,5,8-Tetramethyl	135.6 (135.2)	131.3 (131.2)	134.0 (134.2)	122.4 (122.4)	133.2 (133.3)	126.1 (125.8)	128.0 (128.0)	132.0 (132.7)	131.1 (131.1)	134.5 (134.5)	25.9 (26.1)(1)	21.3 (21.4)(3)	20.2 (19.9)(5)	25.9 (25.9)(8)

^aIn parts per million from Me₄Si. ^bData for mono- and dimethyl compounds taken from ref 20. Parentheses indicate that assignment was not unambiguous, and the chemical shifts so indicated may need to be interchanged. Measurements were made in CDCl₃ solution, with internal dioxane as the reference. Conversion to Me₄Si scale was made by use of $\delta(\text{diox}) - \delta(\text{Me}_4\text{Si}) = 66.9$ ppm. Assignments were made parametrically in the tri- and tetramethylated compounds. ^cValues predicted by use of the parameters of Tables VII and VIII are given below each line of experimental data. ^dPosition of substitution is indicated by parenthetical number for unsymmetrical cases.

Table VII. Linear Least-Squares Regression Analysis Results for the Methyl Chemical Shifts of the Methyl-naphthalenes

Parameter ^a	Value ^b	No. of cases	F to remove
O ₂₂	-1.5 ± 0.1	7	246
O ₂₁ ^c	-0.9 ± 0.2	1	24.9
O ₁₂ ^c	-5.1 ± 0.2	1	711
Meta	-0.2 ± 0.1	4	3.0
Para	0.2 ± 0.1	4	2.7
O _{21R}	-2.4 ± 0.1	10	608
M ₁₈	4.2 ± 0.1	3	1030
W ₁₅	0.6 ± 0.1	3	24.7

^a See text for description of parameters. ^b In parts per million. ^c These parameters may not be well characterized because of the small number of occurrences in the regression.

The two kinds of β 's (C and H substituted) result from the inherent steric differences. Also for the β and γ parameters the locked methyl creates a larger effect than the freely rotating methyl in every case, as would be expected if the chemical shifts are dependent on steric interactions which may be reduced somewhat by rapid rotational averaging. The more remote δ effects do not conform to this observation, as δ_F is slightly larger than δ_L . It may be that the chemical shift at the δ position is determined by the sum of effects from the two pathways around the aromatic ring which are not symmetrical when the methyl is locked but on average become equal when the methyl approaches the free rotor condition. The two values are sufficiently similar that too elaborate an explanation is probably not justified.

Although the least-squares fit of the data for this set of parameters is not quite as good as for the previous larger set, it is, however, still excellent. It must also be noted that the latter treatment requires only eight parameters (ignoring γ_F), as compared to 13 parameters in the first set.

Naphthalenic Methyl Carbons. The ¹³C chemical shifts for the parent, methyl-, and dimethylnaphthalenes were being obtained in our laboratory when Wilson and Stothers published the complete set of data,²⁰ with many assignments having been made by single frequency decoupling. There are no gross discrepancies between the two data sets, and hence the more complete data set of ref 20, given in Table VI, was utilized in our factor analyses. The data which had been acquired in our laboratory at relatively higher concentrations, while comparing favorably with that given in Table VI in the majority of cases, do exhibit some differences of up to 0.5 ppm due to the high sensitivity of some of the chemical shifts in this series of compounds to solvent effects. Since 0.5 ppm is significant when compared to the 13.4-ppm range observed for the aromatic ¹³C shifts of these compounds, one cannot overemphasize the importance of utilizing uniform conditions of solvent, concentration, etc., when acquiring ¹³C data for purposes of making detailed analyses such as that to be given here. Data for four tri- and tetramethylnaphthalenes, which were commercially available, were acquired using similar conditions and are included in Table VI and the regression analyses.

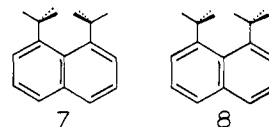
A least-squares, linear regression was executed on the 28 methyl chemical shifts of Table VI, utilizing the parameters of Table VII. O₂₂ is defined by the methyls in **3**, while O₂₁ and O₁₂ refer to the orientations of the methyls on the left and right of **4**, respectively. The Meta and Para parameters correspond to configurations similar to those in disubstituted benzene. The remaining three parameters can occur because two rings are present. O_{21R} corresponds to the orientation to which a methyl substituted at C-1 is constrained by the presence of the fixed

hydrogen at C-8 and is similar to O₂₁; M₁₈ refers to the effect of having CH₃ substituents on both C-1 and C-8. W₁₅ refers to the shift resulting when methyls are in a 1,5 relationship.

The regression parameters of Table VII indicate a successful fit of the data; the fit could probably be improved somewhat by inclusion of smaller transannular effects, which have been ignored. The regression constant corresponds to the chemical shift of an unperturbed C-2 methyl and compares favorably to the experimental values found for isolated, β methyls. The 21.5-ppm value is slightly downfield from that found (or predicted) for the methyl of toluene (21.1 ppm), probably as a result of slightly altered geometry or the presence of the other ring in naphthalene. O₂₂ and O₁₂ compare favorably with the values found for the methylbenzenes (-1.9, -4.4 ppm, respectively), but O₂₁ is of opposite sign and larger than the corresponding benzene parameter (0.1 ppm). O_{21R} is upfield and much larger than O₂₁. These differences probably result from variations in geometry.

The large, long-range effect (W₁₅) noted when methyls are located at C-1 and C-5 may occur because of the planar, all-trans relationship of the substituents; such geometries are known to result in surprisingly large spin-spin coupling constants.³¹ The methyls of 1,8-dimethylnaphthalene are in a parallel relationship not possible in the methylbenzenes, which has resulted in a large downfield shift (M₁₈). Such downfield shifts have been noted for other molecules having similar geometrical arrangements,³² although the origin of such deshielding effects is not known. If the contention that downfield β shifts are the result of steric interactions of (parallel) C-H bonds²⁵ proves to be a viable explanation of those effects, perhaps extension of those arguments to parallel C-C bonds will provide some insights into the nature of the downfield chemical shifts noted here.

As in the case of *o*-xylene one may postulate several symmetrical, minimum energy conformations for the CH₃ groups substituted in the 1,8 positions of naphthalene, as depicted in **7** and **8**. In this case it seems likely that the two conformers are also characterized by different methyl chemical shifts (**8**



producing an average) and are of unequal energy, but which of the two has the lesser conformational interaction is unknown at present. Since relaxation studies²⁹ have demonstrated that the 1,8-methyls of this compound are in the 120° jump regime, a dominant threefold barrier, such as that which would be characteristic of **7**, seems more probable. Methyl rotation in **8** should be governed by a lower energy sixfold barrier. The question could probably be resolved by obtaining the ¹³C chemical shifts of 1,2,8-trimethyl- or 1,2,7,8-tetramethylnaphthalene, or perhaps of 4-methylphenanthrene. In the former two compounds the chemical shifts of the β methyls should indicate the orientation of the α CH₃'s, while in the latter case the methyl should be restricted to one minimum energy conformation like that of the left methyl of **8**. Unfortunately none of these compounds is presently available. The value of M₁₈ produced by the regression is smaller than the observed downfield shift, because the M₁₈ effect is enhanced by the amount of the O_{21R} which was eliminated by the second methyl substitution.

Naphthalenic Aromatic Carbons. Methyl substitution at the α or β position of naphthalene produces ¹³C chemical shifts at almost every position in the molecule, some of which are large even when remote from the substituent (cf. C-6 of 2-methylnaphthalene). Such long-range effects are undoubtedly again a result of the presence of the delocalized π electron system.

Table VIII. Linear Least-Squares Regression Parameters for the Aromatic Carbon-13 Chemical Shifts of the Mono- and Dimethylnaphthalenes^a

Number of chemical shifts: 130		Constants: ^b C ₁ = 127.8, C ₂ = 125.6, C ₉ = 133.4 ppm		Standard error of the estimate: 0.15 ppm		Multiple R: 0.9995		F ratio: 2270	
Position	CH ₃ at 1	No. of occurrences	F to remove	CH ₃ at 2	No. of occurrences	F to remove			
Position Parameters									
1	9.5 ± 0.07	13 ^c	20 200	-1.1 ± 0.07	15	233			
2	-0.4 ± 0.2	13	6.0	9.5 ± 0.07	15 ^c	20 200			
3	-0.3 ± 0.2	13	1.9	2.3 ± 0.07	15	1 150			
4	-2.3 ± 0.2	13	167	-0.3 ± 0.07	15	22.4			
5	0.6 ± 0.06	13	100	-0.4 ± 0.05	15	64.4			
6	-0.4 ± 0.06	13	36.5	-0.9 ± 0.05	15	323			
7	-0.2 ± 0.06	13	13.2	0.06 ± 0.05 ^d	15	1.3			
8	-3.8 ± 0.06	10	3 640	-0.6 ± 0.05	15	119			
9	1.2 ± 0.2	13	39.3	0.2 ± 0.06	15	5.8			
10	0.06 ± 0.2 ^d	13	0.1	-1.8 ± 0.06	15	782			
Ortho-Substitution Parameters ^e									
α ₂ β ₂	-2.2 ± 0.1	6	439						
α ₂ β ₁	-3.3 ± 0.1	11	1 160						
α ₁ β ₂	-2.2 ± 0.2	11	153						
β ₂ γ ₂	0.9 ± 0.1	6	68.7						
β ₂ γ ₁	1.3 ± 0.2	11	52.5						
β ₁ γ ₂	0.1 ± 0.2 ^d	11	0.5						
γ ₂ δ ₂	0.5 ± 0.1	6	24.2						
γ ₂ δ ₁	-0.1 ± 0.2 ^d	11	0.4						
γ ₁ δ ₂	0.5 ± 0.2	11	9.7						
1,8-Dimethyl Parameters ^f									
1,8	-2.4 ± 0.1	3	409						
2,7	4.3 ± 0.2	3	401						
3,6	-0.1 ± 0.2 ^d	3	0.2						
4,5	1.5 ± 0.2	3	49.8						
9	-2.9 ± 0.4	2	57.4						
10	2.1 ± 0.4	2	31.4						

^a Data for monomethyl- and dimethylnaphthalenes was taken from ref 20. ^b The appropriate constant must be used for the position being considered. In the analysis the true regression constant was 127.5 ppm. ^c Only one parameter was used for these two positions; of course a steric correction parameter (α₂β₁) must be applied for a methyl at C-1 to get the total shift. ^d This parameter is insignificant but was retained for the sake of completeness. ^e Applied to appropriate carbons of the substituted ring when methyl occurs ortho to CH₃ or CH. ^f Effects resulting from methyls in a 1,8 configuration.

In considering the parametric approach to be utilized, one similar to that of Table IV was chosen as the more appropriate. The alternative method as given in Table V would also be possible, but is probably less desirable for the present case, because all of the α methyls will always be "locked" while most of the β methyls are "free", as discussed above. The parameter set utilized in the least-squares, linear regression is given in Table VIII. Unfortunately, because of the wide ranging influence of the substituents, a very large parameter set is necessitated. However, even though the number of parameters is large, all of them occur at least ten times in the set.

Although the results are far from identical with those found for the methylbenzenes, some significant parallels may be noted. The α effects are similar to that found in the methylbenzenes. β effects are also comparable, varying from -1.1 to +2.3 ppm. γ effects not involving steric interaction are also unsymmetrical and are near zero, while a δ carbon in the same ring as the substituent experiences a large upfield shift, as in the methylbenzenes. δ effects in the ring not having the substituent are, however, not large. When a methyl is at C-1, C-8 moves upfield 3.8 ppm which we consider to result principally from the steric interaction. The shift is comparable to the value one might expect as a result of an O₁₂ interaction, although the carbon of interest is not a methyl and is not even aliphatic. The ortho parameters, which were applied at all positions of the substituted ring (treating the adjacent carbons of the other ring as a locked ortho substituent when CH₃ was at the α position), are quite similar to those found in methylbenzenes, indicating

that such effects are common to both systems. The 1,8-dimethyl configuration is seen to produce relatively large chemical shifts at every ring position.

The values predicted by use of the parameters in Table VIII are given in Table VI. The fit of the 130 pieces of data is excellent and is almost within experimental error, even though a few larger residuals,³³ up to 0.7 ppm, may be noted. Despite these deviations, it is possible to make most of the assignments of the presently uncharacterized aromatic resonances in the methylated naphthalenes³⁴ with a reasonable level of confidence. The exceptions are those molecules in which structural or electronic features occur which have not been previously encountered, such as in 1,2,3,4-tetramethylnaphthalene, for which at least one methyl must be involved in a conformation equivalent to an O₁₁ interaction, similar to that of the methyls of 6.

Extension to Other Systems. While it may be inferred that one may not directly extrapolate parameters developed for one set of aromatic compounds to another with a high degree of confidence, some general trends may be noted which can assist in interpreting spectra of more complicated systems. This point is illustrated in Figure 1 with data from three compounds, 1- and 2-methylantracene and 3-methylphenanthrene. The anthracene data were extracted from a paper by Caspar et al.,³⁵ while the phenanthrenes were run in CDCl₃ under conditions similar to those used previously. The predicted values given in Figure 1 are those which obtain by a simplistic application of the parameters of Table VIII.³⁶ It is apparent that

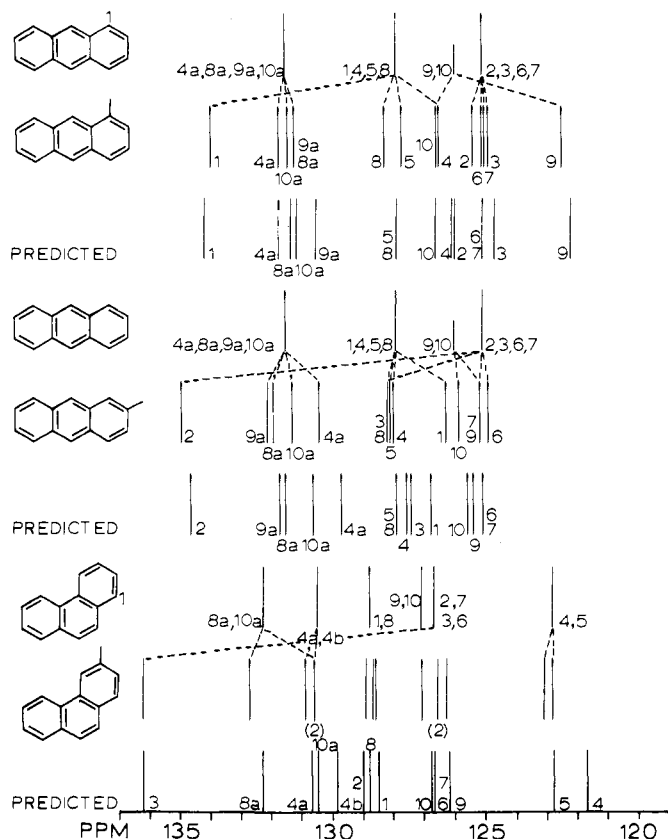


Figure 1. Carbon-13 chemical shift data for 1- and 2-methylanthracene and 3-methylphenanthrene and the respective parent compounds. Predicted values were generated by use of the methylnaphthalene parameters of Tables VII and VIII, illustrating the point that, although parameters developed for one kind of aromatic hydrocarbons cannot predict precisely the chemical shifts of other compounds, they do provide a useful aid in making tentative assignments.

methyl substitution in these compounds produces a detectable chemical shift at almost every position. Although the predicted shifts do not correspond precisely with those found in the methylnaphthalenes, it may be noted that, in those cases where definite assignments have been made, the ordering of the lines in the experimental and calculated spectra are very similar. It is also of interest that methyl substitution produces effects at the α and δ positions which are similar to those previously observed in the benzenes and naphthalenes.

In Figure 2 the chemical shifts of 9-methyl- and 9,10-dimethylanthracene are presented.³⁵ The assignment for the 9-methyl compound has been confirmed by Marshall et al.^{37,38} The data of Figure 2 may be used to estimate the magnitude of some of the conformational effects not found in the methyl derivatives considered above. The resonance of the methyl group of 9-methylanthracene is 6.0 ppm upfield from that of 1-methylanthracene. The only new interaction involving this moiety is a conformation like O_{11} of **6**, for which -6.0 ppm is a reasonable estimate of the size of the parameter. Since the rotation of this methyl is very fast,²⁹ the effect may be somewhat different from that which would be observed for a locked CH_3 . Other related effects which are encountered for the first time in this molecule include $\alpha_1\beta_1$, $\beta_1\gamma_1$, and $\gamma_1\delta_1$. By using the chemical shifts of Figure 2 and the relevant parameters from Table VIII, the following approximate parametric values may be calculated: $\alpha_1\beta_1 = -2.5$ ppm, $\beta_1\gamma_1 = 1.5$ ppm, $\gamma_1\delta_1 = 0.1$ ppm, and the γ effect on the ring resulting from an O_{11} interaction equals about -3.4 ppm.

In principle a linear regression analysis could be performed on the data for the ring carbons of the methylanthracenes given in ref 35 using a parameter set analogous to that of Table VIII.

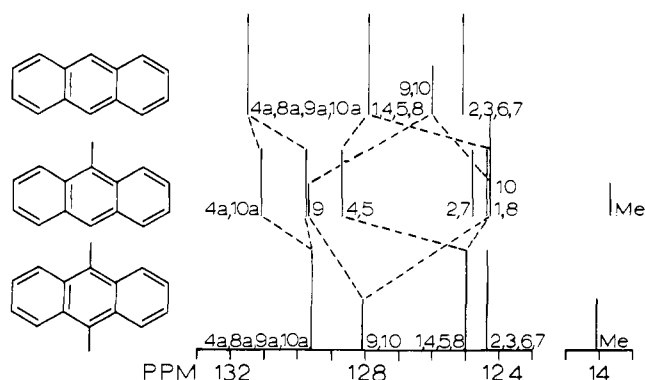


Figure 2. Carbon-13 chemical shifts for anthracene and its 9-methyl and 9,10-dimethyl derivatives. (See text for discussion.)

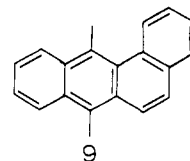
Table IX. Methyl Carbon-13 Chemical Shift Data from Selected Anthracene Derivatives^a

Compd	Methyl position	δ^b
1-Methylanthracene	1	19.7
2-Methylanthracene	2	21.9
9-Methylanthracene	9	13.7
1,4,9-Trimethylanthracene	1	27.1
	9	20.3
1,4,5,8,9-Pentamethylanthracene	1,8	25.9
	9	26.8
7,12-Dimethylbenz[<i>a</i>]anthracene	7	14.0
	12	20.0

^a Extracted from ref 35, with the exception of the benz compound, the spectrum of which was obtained in $CDCl_3$ as before. ^b In parts per million relative to Me_4Si .

However, because of the additional complications introduced into the analysis as a result of the presence of peri methyls, it becomes apparent that the data base is not sufficiently large to accommodate the number of parameters which are necessary. The success of the fit in Figure 1 and inspection of Table 3 of ref 35 indicates that chemical shift effects observed for many of the carbon positions in the methylanthracenes are similar to those found in the methylnaphthalenes.

The methyl chemical shifts of the methylanthracenes are more amenable to analysis and are of considerable interest. Selected methylanthracene chemical shifts plus those of 7,12-dimethylbenz[*a*]anthracene (**9**) are listed in Table IX.



It is expected that conformational effects involving the orientation of peri methyls will be in evidence here, analogous to those of vicinal methyls. The conformations which are expected to be relevant are those illustrated by **7** and **8**: the methyl conformation of **7** is designated as a P_{22} interaction, while that of the left methyl of **8** is a P_{21} and that of the right methyl a P_{12} . A fourth interaction, P_{11} , is possible, but should be of prohibitively high energy and is not expected to occur in this system. The C-9 methyl of a 1,8,9 substituted anthracene should experience both a P_{22} and a P_{12} interaction, while the chemical shift of the 1,8 methyls should be shifted by $\frac{1}{2}P_{22} + \frac{1}{2}P_{22} - O_{21R}$. When 1,9 substitution occurs, the orientation of the center methyl could be either P_{22} or P_{12} , depending on whether the combination of $P_{22} + O_{11R}$ or $P_{12} + O_{21R}$ is of lower energy.⁴¹ In **9**, the C-12 methyl is constrained by a P_{21} interaction and rotates very slowly.²⁹

Table X. Least-Squares Linear Regression Analysis Results for the Methyl Carbons of Selected Anthracene Derivatives^a

Parameter	Value	No. of cases	F to remove
O _{21R}	-2.3 ± 0.2	13	113
O _{11R}	-6.1 ± 0.1	7	1920
P ₂₂	4.5 ± 0.2	6	332
P ₂₁	3.7 ± 0.3 ^c	2	123
P ₁₂	0.1 ± 0.3 ^c	1	0.2

^a Data taken from ref 35 plus that of 7,12-dimethylbenz[*a*]anthracene. ^b In parts per million. ^c These parameters may not be well characterized owing to their limited occurrence in the regression.

Results of the linear regression analysis are presented in Table X. The regression was executed twice, utilizing the two possible orientations of the 1,9 substituted compounds. The parameters in Table X represent the set which results when the 1,9-methyls are assumed to be oriented P₂₂ to one another, which produced a slightly better fit of the data.⁴² Inspection of Table X reveals that parameters O_{21R} and P₂₂ are similar to those obtained for the naphthalenes; P₂₁ produces a downfield shift comparable to that of P₂₂, but a P₁₂ conformation is seen to produce only a very slight chemical shift. Although these tentative parameters will undoubtedly be useful in making assignments and determining methyl conformations in other compounds having peri interactions, data on many other compounds will be needed before these effects can be completely characterized and their origin determined.

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- Of course it is not possible to predict the effects of methyl substitution on C-5 through C-8 of these compounds using parameters derived from methylnaphthalenes.
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- We have also run the parent and 9,10-dimethyl compounds in concentrated CDCl₃ solution. Assignments in the latter compound were confirmed by the method of Gunther et al.³⁹ The chemical shifts obtained by us and those of ref 37 do not agree well with those of ref 35, which were obtained in dilute solution. It is probable that a molecular association phenomenon is producing these effects.⁴⁰
- H. Gunther, H. Schmickler, and G. Jikell, *J. Magn. Reson.*, **11**, 344 (1973).
- R. C. Griffith, D. M. Grant, and J. D. Roberts, *J. Org. Chem.*, **40**, 3726 (1975).
- Two other possibilities exist: (a) that P₂₂ + O_{11R} and P₁₂ + O_{21R} are of similar energy so that some weighted average must be considered; or (b) that the 1-methyl is reoriented so that the center methyl is forced into a P₂₁ + O_{11R} situation. The latter possibility seems to be unlikely because of the success of the least-squares regression, but the other case cannot be totally discounted.
- More data are needed to establish incontrovertibly which conformation is dominant.