Carbon-13 Magnetic Resonance. V.[1] Conformational Dependence of the Chemical Shifts in the Methylbenzenes

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Abstract: The methyl carbon-13 magnetic resonance spectra of all the methylbenzenes have been secured with the proton decoupling technique. Three *ortho* substituent parameters which reflect conformational interactions of two adjacent methyl groups correlate very well the experimental carbon-13 shifts obtained in this study. Additive substituent parameters for *m*- and *p*-methyl groups have also been found and attributed to hyperconjugative effects. Empirical correlations between carbon-13 chemical-shift values and proposed conformational features are further justified by a theoretical consideration of nonbonded repulsion energies existing between the hydrogen atoms in adjacent methyl groups. Proton chemical shifts can be explained by the proton magnetic anisotropy of adjacent *o*-methyl groups. *o*-Methyl substituent shifts are felt to be indicative of significant 1,4-carbon–carbon interactions. Deviation from perfect pairing offers a possible explanation of the effect.

Methyl substituent effects upon the carbon-13 chemical-shift parameter have been studied[1-8] for a variety of compounds. These studies have attempted to find additive substituent parameters which reflect a specific molecular geometry in the methyl-substituted aromatics,[2-5] heterocyclics,[1] alkenes,[6] and alkanes.[2,5,7,8] In several classes of methyl-substituted aromatics, adjacent and *o*-, *m*-, and *p*-methyl substituent parameters have been found by Lauterbur[2-5] to be highly reproducible. Well-characterized exceptions were found to exist, however, in certain *ortho*-disubstituted toluenes in which strong steric interactions between the adjacent substituent groups become important. While the nature of these steric effects upon the ring carbon-13 chemical shifts have been discussed[4] in some detail, variations in the corresponding methyl carbon-13 shifts have not been considered. This study, therefore, is concerned with the effect of *ortho* steric interactions upon the carbon-13 chemical shifts in adjacent methyl carbons. The methylbenzenes form a class of compounds in which steric interactions between *o*-methyl groups do not result in marked distortion in the structure of the aromatic ring system. Nevertheless, the steric features do restrict the free rotation of adjacent methyl groups, and these physical restrictions on the methyl orientation may be used to characterize the spatial dependence of the chemical-shift parameter. In fact, such relationships may be used to specify completely the important methyl conformations existing in the methylbenzenes.

Relatively large methyl substituent effects upon γ carbons in the alkanes[8] (+2.5 ppm) and in the alkenes[6] (+0.1 to +2.5 ppm) have been observed, whereas no such positive γ methyl substituent effects of this magnitude are noted in the aromatics (−0.3 to +0.3 ppm) nor in the linear cumulenes[6] (−1.0 ppm). As molecular coiling is possible in the former set of compounds and not in the latter, it is likely that the unusually large γ effect is due to interactions through space of groups which have coiled back upon one another. As this type of steric interaction would have important consequences in chemical-shift theory, it is desirable to characterize the essential features of these rather sizeable diamagnetic shifts. The steric interaction of 1,4 carbons in the *o*-xylenes also results in a significant diamagnetic shift in the methyl carbon resonance, and as these compounds have the added advantage of being nonflexible systems, they constitute a more favorable system for study. While the spatial orientation would not faithfully represent the structural features existing in a coiled alkane or alkene, the sign and magnitude of the effect are very similar. It, therefore, is likely that the origin of the diamagnetic shift would be similar in each instance.

Lauterbur[3] has published rapid passage carbon-13 spectra on the dispersion mode for several methylbenzenes (*i.e.*, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, durene, and hexamethylbenzene) in which only a single methyl resonance multiplet is observed because of the high molecular symmetry existing for these specific compounds. Utilizing the greater sensitivity and resolution of the proton decoupling technique,[9] it is possible to study the remaining methylbenzenes of lesser symmetry. The symmetrical compounds were also rerun to give carbon-13 chemical-shift data for the 20 different methyl groups.

Experimental Section

A. Equipment and Operational Details. Details of the techniques used in obtaining carbon-13 magnetic resonance spectra with a Varian V-4311 high-resolution spectrometer operating at 15.1 Mcps and a Varian V-4320 proton decoupler have been presented in previous papers[1,7-9] in this series.

B. Compounds. The methylbenzenes were all obtained from standard commercial sources. The compounds which are liquids at room temperature were sealed in tubes as neat liquids after having been degassed by vacuum-freezing techniques. The three solids, durene, pentamethylbenzene, and hexamethylbenzene, were observed as saturated solutions in CS_2, CCl_4, $CHCl_3$, and C_6H_6.

C. Chemical-Shift Values. Experience now indicates that it is more convenient to record the decoupling data as a ratio of the proton decoupler frequency to the carbon-13 transmitter frequency, (f_i/ν_i). This quantity, represented by Γ_i, will remain constant with

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[1] Previous paper in series: T. Page, Jr., T. Alger, and D. M. Grant, *J. Am. Chem. Soc.*, **87**, 5333 (1965).

[2] P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

[3] P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961).

[4] P. C. Lauterbur, *J. Chem. Phys.*, **38**, 1406, 1415, 1432 (1963).

[5] H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722, 731 (1961).

[6] R. A. Friedel and H. L. Retcofsky, *J. Am. Chem. Soc.*, **85**, 1300 (1963).

[7] E. G. Paul and D. M. Grant, *ibid.*, **85**, 1701 (1963).

[8] D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964).

[9] E. G. Paul and D. M. Grant, *ibid.*, **86**, 2977 (1964).

Table I. Methyl Proton and Carbon-13 Chemical-Shift Data for the Methylbenzenes

Item	Compd	Methyl position	Γ_i	δ_H,[a] ppm	$\delta_{C^{13}}$,[b] ppm	Li[d] value
1	Toluene	1	3.9768558	2.09_8	107.3_5	106.8
2	*o*-Xylene	1,2	3.9768626	2.02_1	109.1_2	108.6
3	*m*-Xylene	1,3	3.9768562	2.14_4	107.3_9	107.6
4	*p*-Xylene	1,4	3.9768577	2.14_5	107.7_6	107.1
5	Hemimellitene	1,3	3.9768596	2.06_5	108.3_2	
		2	3.9768803	1.90_9	113.6_8	
7	Pseudocumene	1	3.9768645	(2.03_8)[c]	109.5_8	
8		2	3.9768629	(2.03_8)	109.1_9	
9		4	3.9768577	2.15_7	107.7_6	
10	Mesitylene	1,3,5	3.9768565	2.14_7	107.4_7	107.2
11	Prehnitene	1,4	3.9768588	2.07_7	108.1_2	
12		2,3	3.9768785	1.94_2	113.2_1	
13	Isodurene	1,3	3.9768598	2.07_9	108.3_6	
14		2	3.9768818	1.93_7	114.0_5	
15		5	3.9768578	2.14_7	107.8_0	
16	Durene	1,2,4,5	3.9768628	2.07_0	109.4_5	108.6
17	Pentamethylbenzene	1,5	3.9768581	2.08_0	108.0_0	
18		2,4	3.9768774	(1.98_5)[c]	112.8_7	
19		3	3.9768765	(1.98_5)	112.5_7	
20	Hexamethylbenzene	1–6	3.9768717	2.10_8	111.8_0	109.9

[a] Relative to TMS, lower field resonances given larger positive value. [b] Relative to benzene, higher field resonances given larger positive value. [c] Parentheses indicates that only a single proton resonance peak is observed for these chemically nonequivalent protons. [d] Values obtained on rapid passage conditions from ref 3 were converted from a CS_2 to a C_6H_6 reference by subtracting 65.0 ppm, the carbon-13 chemical shift between these two reference compounds. Values for durene and hexamethylbenzene are for saturated CS_2 solutions.

a variation in the carbon-13 transmitter frequency. Not only do instruments vary one from another but the frequency of a given spectrometer can change slightly on successive days. Thus, an advantage is claimed in reporting the data in this reduced form as the data then can be compared directly with other data obtained at different frequencies. Substitution of Γ_i for f_i/ν_i in eq 2 of ref 9 and rearranging terms yields eq 1a and 1b

$$\delta_{C^{13}} = \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \frac{\Gamma_0}{\Gamma_i}(\tau_i - \tau_0) \cong \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + (\tau_i - \tau_0) \quad (1a)$$

$$\delta_{C^{13}} = \frac{\Gamma_i - \Gamma_0}{\Gamma_i} - \frac{\Gamma_0}{\Gamma_i}(\delta_i - \delta_0) \cong \frac{\Gamma_i - \Gamma_0}{\Gamma_i} - (\delta_i - \delta_0) \quad (1b)$$

where the carbon-13 chemical shift is given by $\delta_{C^{13}}$ and the proton shifts are given either on the τ or δ scales,[10] respectively. The subscripts i and 0 denote the sample and reference compounds, respectively. For benzene, Γ_0 = 3.97644914, τ_0 = 2.83 ppm, and δ_0 = 7.17 ppm. It is well to emphasize that the Γ_i values are field independent, and therefore the experimental values determined for this parameter are not affected by changes in the magnetic field resulting from variations in the bulk magnetic susceptibility of the sample. Thus, if proton chemical shifts are used which are also free of susceptibility errors, the carbon-13 chemical shifts calculated with eq 1a or 1b will not require bulk magnetic susceptibility corrections even though the decoupling data are obtained on two separate neat liquids. However, solvent interactions involving intermolecular association still may affect the Γ_i values determined in the above manner. Such interactions affect the chemical-shift parameter by perturbing directly the electronic structure of the molecule and thus can be considered properly to be a chemical effect.

Results

A. Chemical-Shift Data. Contained in Table I are the decoupling parameters and the proton and carbon-13 chemical-shift data for the methyl carbons in the methylbenzenes. The data for saturated benzene solutions are reported in Table I for the three solid compounds, as it is felt that these values would simulate best the intermolecular interactions which may exist in other liquid methylbenzene samples. To investigate possible solvent effects upon the methyl shifts in the three solid compounds, the chemical shifts were determined also in CS_2, CCl_4, and $CHCl_3$ and compared with that of C_6H_6. As shown in Table II, the solvent shifts do exceed, in some instances, the experimental error of the method, but, nonetheless, these effects are relatively small when compared with the over-all range in the chemical shift values noted for the various methyl groups. The similarity of shift values obtained in the several solvents argues that solvent effects are probably

Table II. The Effect of Solvent upon Carbon-13 Chemical Shifts in Saturated Solutions of the Solid Methylbenzenes

Item	Compd	Methyl positions	Solvent	$\delta_{C^{13}}$, ppm
1	Durene	1,2,4,5	CS_2	109.2_3
2			CCl_4	109.3_8
3			$CHCl_3$	109.3_6
4			C_6H_6	109.4_5
5	Pentamethylbenzene	1,5	CS_2	107.9_4
6			CCl_4	108.1_2
7			$CHCl_3$	108.0_8
8			C_6H_6	108.0_0
9	Pentamethylbenzene	2,4	CS_2	112.9_1
10			CCl_4	112.8_3
11			$CHCl_3$	112.8_8
12			C_6H_6	112.8_7
13	Pentamethylbenzene	3	CS_2	112.6_5
14			CCl_4	112.5_2
15			$CHCl_3$	112.5_7
16			C_6H_6	112.5_7
17	Hexamethylbenzene	1–6	CS_2	111.3_3
18			CCl_4	111.5_8
19			$CHCl_3$	111.7_0
20			C_6H_6	111.8_0

[10] Note: the δ-proton chemical-shift scale, δ_H, increases in opposite field direction from that of both τ_H and the carbon-13 chemical-shift scale, $\delta_{C^{13}}$. Therefore, care must be used in the proper selection of algebraic signs in eq 1a and 1b.

Table III. Populational Factors of the Important Conformational and Geometrical Features in the Methylbenzene

Item	Compd	Methyl position	p_{2-2} (*ortho*)	p_{2-1} (*ortho*)	p_{1-2} (*ortho*)	p(*meta*)	p_1(*para*)	p_2(*para*)
1	Toluene	1	...	...	...	...	...	...
2	*o*-Xylene	1,2	1	...	...	...	...	...
3	*m*-Xylene	1,3	...	...	...	1	...	. .
4	*o*-Xylene	1,4	...	...	...	...	1	...
5	Hemimellitene	1,3	$^1/_2$	...	$^1/_2$	1	...	...
6		2	1	1	...	...	...	...
7	Pseudocumene	1	1	...	...	...	1	...
8		2	1	...	...	1	...	...
9		4	...	...	...	1	1	...
10	Mesitylene	1,3,5	...	...	...	2	...	...
11	Prehnitene	1,4	$^1/_3$	...	$^2/_3$	1	...	1
12		2,3	$^2/_3$	1	$^1/_3$	1	...	...
13	Isodurene	1,3	$^1/_2$	...	$^1/_2$	2	...	...
14		2	1	1	...	...	1	...
15		5	...	...	...	2	1	...
16	Durene	1,2,4,5	1	...	...	1	...	1
17	Pentamethylbenzene	1,5	$^1/_4$	...	$^3/_4$	2	...	1
18		2,4	$^1/_2$	1	$^1/_2$	2	...	1
19		3	$^1/_2$	1	$^1/_2$	1	...	...
20	Hexamethylbenzene	1–6	...	1	1	2	...	1

of minor importance, as it would be unlikely that large effects would be so similar in the different solvents. The greatest solvent deviations are noted for hexamethylbenzene dissolved in CS_2 and C_6H_6, respectively. It is interesting to note that the CS_2 shift is to low field from that of C_6H_6 as predicted by Buckingham, Schaefer, and Schneider[11] for the anisotropy in the susceptibility of these two molecules. Sufficient information for these systems is not available upon which a final conclusion can be based regarding the importance of these solvent effects.

The assignment of some chemical-shift values reported in Table I are based upon uniqueness (items 1–4, 10, 16, 20), as only a single methyl resonance multiplet is observed for some compounds. In other compounds it is possible to use relative peak intensities (items 5, 6, 13, 19) to make an unequivocal assignment. The remaining nine values were assigned on the basis of peak broadening resulting from a small *ortho*-proton coupling in some methyl carbon and/or upon additive substituent parameters to be discussed later. Thus, very sharp peaks were observed for methyls with no *ortho* protons (items 12, 14, 18) and broader resonance peaks for methyls next to an *ortho* proton (items 11, 15, 17). In the case of psuedocumene, the assignment cannot be based on any of the above arguments and depends entirely upon additive effects which are exhibited by all the other methylbenzenes. There is little difficulty in assigning item 9 to the 4 methyl, as the chemical-shift value is characteristic of an isolated methyl carbon. The two very similar values (items 7 and 8) were assigned to the 1 and 2 methyls, respectively, on the basis of an expected +0.34-ppm *para*-substituent effect resulting from the 4-methyl group. The actual shift between these two positions was found to be 0.39 ppm. Negligible *meta* effects were observed in all cases where unequivocal assignments were made upon other criteria, and thus the 2 methyl in pseudocumene exhibits a chemical shift (109.19 ppm) within experimental error of the value noted for *o*-xylene (109.12 ppm).

Arguments based upon the uniqueness and intensity of the proton resonance lines were also used along with a reproducible neighboring group effect to assign the proton chemical-shift values given in Table I. Methyl groups which are not adjacent, adjacent to one, and adjacent to two other methyl substituents were found to exhibit chemical shifts which fall in the following respective ranges: 2.098–2.157, 2.021–2.080, and 1.909–1.985 ppm. The value for hexamethylbenzene (2.108 ppm) constitutes the single exception to the rule. As none of these ranges overlap one another, the values offer a means for characterizing similar methyl chemical shifts in other polymethylaromatics.

B. Linear Regressional Analysis of Data. It was found that factors important in the methyl chemical-shift data could be correlated with a simple linear expression of the form given in eq 2

$$\delta_{C^{13}}(i) = \delta_{C^{13}}(\text{toluene}) + \sum_k p_{ik}\delta_k \qquad (2)$$

where substituent parameters, δ_k, reflect important geometrical features existing in these molecules, and where the population factors relating the *k*th structural feature to the *i*th methyl carbon are given by p_{ik}. A linear regressional analysis was performed on eq 2 for populational factors, p_{ik}, given in Table III in the six independent variables which represent three *ortho*-substituent effects, one *meta*-substituent effect, and two *para*-substituent terms. The three *ortho*-substituent parameters, δ_{2-2}(*ortho*), δ_{2-1}(*ortho*), and δ_{1-2}(*ortho*), respectively, arise from the three conformational orientations proposed in Figure 1 as being of greatest importance for two *o*-methyl groups. Note that the symmetrical relationship existing between structures II and III is removed by the carbon-13 label in one of the methyl groups. The low natural abundance (1.1%) of the carbon-13 isotope precludes the consideration of molecules with carbon-13 nuclei in both methyl groups, whereas molecules with no carbon-13 in any of the methyl groups are of no concern in this study.

To calculate the populational factors of structures I, II, and III, which are identified with the associated substituent parameters, the following empirical rules were initially employed as a working hypothesis.

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[11] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 32, 1227 (1960).

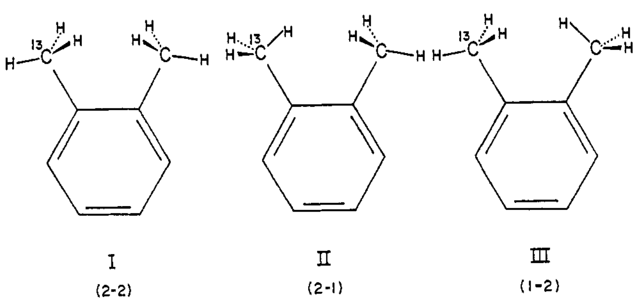

Figure 1. Important conformations in *o*-dimethyl interactions which affect the carbon-13 chemical shift parameter.

(1) Only the three conformational structures (I, II, and III) shown in Figure 1 need be considered as important in the molecular structure whenever two or more methyl groups occupy adjacent benzene ring positions.

(2) The 2–2 conformation (I) is assumed to be the most stable of the three structures allowed by rule 1, and therefore it will always exist between at least one pair of adjacent methyl groups except in the case of the completely substituted hexamethylbenzene where the molecular structure does not favor this geometrical orientation.

(3) All possible 2–2 conformations (I) allowed by the molecular geometry for a series of adjacent methyl groups are equally probable.

The application of these rules is illustrated in a consideration of prehnitene (1,2,3,4-tetramethylbenzene). The number of important conformers for this compound is limited by rules 1 and 2 to the three shown in Figure 2. It is readily seen that the presence of one 2–2 conformation prohibits the existence of an additional 2–2 conformation in the same series of adjacent methyl substituents. Finally, structures IV, V, and VI are each weighted equally by rule 3. Again, it should be remembered that a carbon-13 label in any of the four methyl groups removes the symmetry inherent in structure V and eliminates the symmetrical relationship existing between structures IV and VI. As there are only two nonequivalent methyl carbons in this compound, it is sufficient to consider the two distinct compounds with a carbon-13 label in the 1- or 2-methyl positions, as compounds labeled in the 4 or 3 position will exhibit the same geometrical relationships, respectively. Thus, the populational factors, p_{ik}, given in Table III for prehnitene are derived from Figure 2 in the following manner. A carbon-13 atom in the 1- or 4-methyl group is affected by 2–2 (I) and 1–2 (III) adjacent conformations for 33 and 67% of the time, respectively, whereas a carbon-13 in the 2- or 3-methyl group experiences an adjacent 2–2 conformation (I) 67% of the time, a 2–1 conformation (II) 100% of the time, and a 1–2 conformation (III) only 33% of the time. Based upon this very simple approach, the fractional population factors given in Table III for p_{2-2}(*ortho*), p_{2-1}(*ortho*), and p_{1-2}(*ortho*), respectively, are obtained for both the 1,4- and 2,3-methyl groups. In a similar manner, the *ortho* populational factors given in Table III for all of the remaining compounds are computed from the simple model specified by the three postulated rules restricting the molecular conformation.

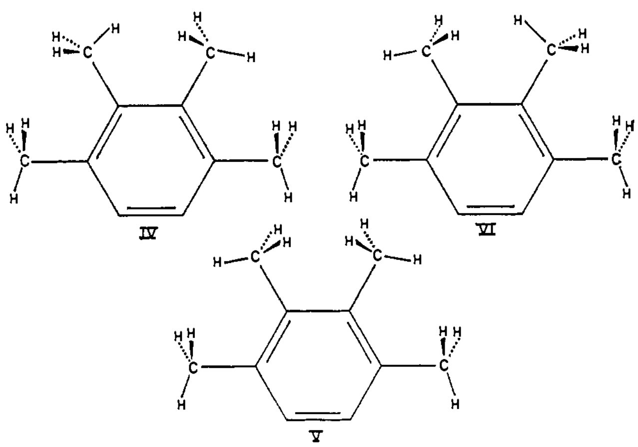

Figure 2. The three equally weighted conformer of prehnitene.

No attempt was made to include conformational features in the *meta* interaction, and thus, *p*(*meta*) is taken to be identical with the number of *m*-methyl groups relative to the *i*th methyl group labeled with a carbon-13. Finally, it became necessary to distinguish between two types of *para* carbon–carbon interactions with statistical weights p_1(*para*) and p_2(*para*) to achieve a good regressional fit of the data. One factor, p_1(*para*), is used when either one or both of the *p*-methyl groups have no adjacent *o*-methyl neighbors, and the second, p_2(*para*), is used in molecules in which both *p*-methyl groups have at least one neighboring *o*-methyl group.

The results of the regressional analysis in the six parameters are given in column A of Table IV. Three of the parameters, δ_{1-2}(*ortho*), δ(*meta*), and δ_2(*para*), have very low magnitudes and this affects directly the F test which measures the reliability of the variable as a valid predictor of the chemical shift. These three parameters were deleted and a second analysis in the three major variables was undertaken. The statistical data for this three-parameter fit are found in column B of Table IV. It is evident from the statistical analysis that the significant features of the chemical-shift values can be correlated with only three parameters, and no significant benefit is derived from the inclusion of more variables. The six-parameter analysis is included, as it is conceptually valuable to note the negligible magnitude of the three additional parameters. Furthermore, it is well to emphasize that while the substituent parameter for the 1–2 conformation (III) is negligible, its inclusion in the calculation of the populational weights is essential to achieve the excellent fit in only three parameters. Figure 3 exhibits a plot of the predicted *vs.* experimental values for the three-parameter fit, and all points are found to lie on the line within experimental error. The standard deviation of the fit is 0.1 ppm which is comparable with the estimated experimental error (0.05 to 0.07 ppm) in the method.

All attempts to find additive relationships for the methyl proton shifts, which were equivalent to the above carbon-13 results, were unsuccessful. The differences in the proton shifts were sufficiently small that the values reflected only the gross structural features (*i.e.*, the number of adjacent methyl groups) noted in the previous section.

Table IV. Regressional Analysis of Carbon-13 Chemical-Shift Parameters in the Methylbenzenes

	A		B	
Number of observations	20		20	
Number of independent variables	6		3	
Multiple correlation coefficient R squared	0.9992		0.9986	
Standard deviation in predicted shifts	0.08 ppm		0.10 ppm	
Constant term-dependent variable	107.35		107.42	
Parameter	Value	F test to remove	Value	F test to remove
δ_{2-2}(*ortho*)	1.87 ± 0.05 ppm	1224.5	1.85 ± 0.06 ppm	1074.1
δ_{2-1}(*ortho*)	4.43 ± 0.04	9904.2	4.42 ± 0.05	7676.0
δ_{1-2}(*ortho*)	−0.14 ± 0.09	2.2	. . .	
δ(*meta*)	0.05 ± 0.03	2.5	. . .	
δ_1(*para*)	0.38 ± 0.05	62.0	0.34 ± 0.05	43.2
δ_2(*para*)	0.14 ± 0.06	6.8	. . .	

Discussion

A. Justification of the Conformational Postulates. The excellent fit of all 20 chemical-shift values with a simple model, utilizing a limited number of conformationally dependent variables, provides sufficient justification, in itself of the validity of the three hypothesized rules. This conclusion is supported by the fact that the values of the two conformationally dependent parameters, δ_{2-2}(*ortho*) and δ_{2-1}(*ortho*) are much larger than the third remaining parameter, δ_1(*para*). However, as supplementary and corroborative evidence, the semitheoretical formalism of Mason and Kreevoy[12] is used to calculate nonbonded repulsion energies between methyl protons in various geometrical orientations, as a means of justifying rules 1 and 2. Given in eq 3 and 4 are the potential functions proposed by these workers for such proton–proton interactions

$$V = f(\varphi_1, \varphi_2) = K\sum_i\sum_j \varphi(r_{ij}) \qquad (3)$$

$$\varphi(r_{ij}) = 3.7164 \times 10^3 \exp(-3.078 r_{ij}) - 89.52/r_{ij}^6 \qquad (4)$$

where i and j are indices for interaction protons, r_{ij} is the internuclear proton–proton distance in A, and K is an empirical constant with a value which should fall between 0.5 and 1.0. The intermediate value of 0.75[13] selected in this work compensates in part for the neglect of proton–carbon repulsion energies which are not considered in the treatment.

The repulsion energy between a single methyl proton and one of the *ortho*-ring proton is given in Figure 4a as a function of the angle of methyl rotation. As would be expected, maximum repulsion is found when the methyl proton eclipses the benzene ring with its associated *o*-hydrogen. If all six proton–proton interactions between the two *o*-hydrogens and the three methyl hydrogens are considered, the energetics of methyl rotation in toluene can be studied. Given in Figure 4b is a partial plot of this sixfold barrier to rotation. Maxima and minima in the curve are only separated by 0.06 kcal/mole which is considerably less than ambient thermal energies. Therefore, with the accuracy of eq 3 and 4, the methyl group can be considered to be "freely" rotating. Based on this calculation, the effect of ring protons upon the conformation of an isolated methyl group is assumed to be negligible.

Interactions between protons in adjacent methyl groups, such as found in *o*-xylene, result in considerably larger variations in the conformational energies. The two generalized rotational coordinates required to describe the conformational features in *o*-xylene are given in Figure 5, and the corresponding potential energy surface for the interaction of these two *o*-methyl groups is contained in Figure 6. Here, all nine interactions existing between the two sets of three protons were considered, but the interaction between methyl protons and *o*-hydrogens in the benzene ring have not been included in the calculation. This potential energy surface repeats itself every 120° in both φ_1 and φ_2, and the dashed lines in Figure 6 represent the minimum energy pathways for methyl rotation in *o*-xylene. For the symmetrical rolling motion shown by the dashed lines, the methyl proton–ring proton interaction is given in Figure 4c, and it can be easily seen that this type of interaction favors a different conformational orientation. The repulsion between the two methyl groups yields a barrier (ΔE = 2.58 kcal/mole), which is greater than that due to the *ortho* proton effect (ΔE = 1.06 kcal/mole). Combining the two effects gives a predicted 1.52-kcal/mole barrier for the rotational motion and this is in reasonable agreement with the recently determined 2.0-kcal/mole barrier reported by Fateley, Miller, and Witkowski.[14] Theory, therefore, predicts that the 2–2 conformation (I) is more stable by 1.5 kcal/mole than structures II or III as shown in Figure 1. Thus, rule 2 is justified by this semiempirical calculation. The existence of a 2–2 conformation (I) requires that the benzene ring be eclipsed by one proton in each of the participating methyl groups. Once this pattern is established, additional methyl substituents will then adjust to the conformations of lowest energy which are compatible with the 2–2 oriented pair of methyls. As can be seen from Figure 6, this condition is satisfied when the additional methyl groups assume conformations specified by structures II and III. Thus, rule 1, as well as rule 2, is given a semitheoretical basis. Rule 3 is a reasonable assumption and no further justification beyond the experimental one is felt to be necessary. When considered together, the repulsion calculation and the empirical correlation of the carbon-13 chemical-shift values form a strong basis for assuming that the conformational features are specified by the previously proposed rules.

The dotted line in Figure 6 represents the rotational pathway of lowest energy which must be followed by the

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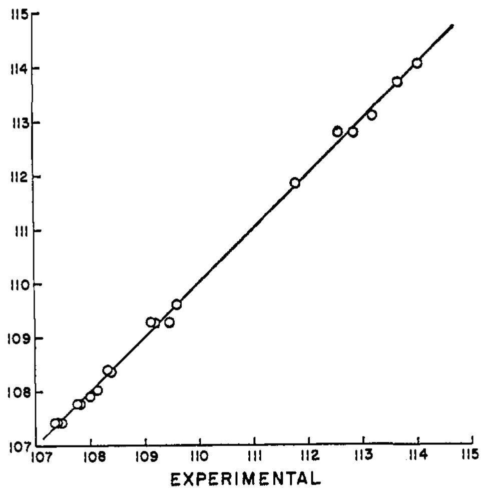

Figure 3. Predicted *vs.* experimental values of the methyl carbon-13 chemical shifts for the methylbenzenes.

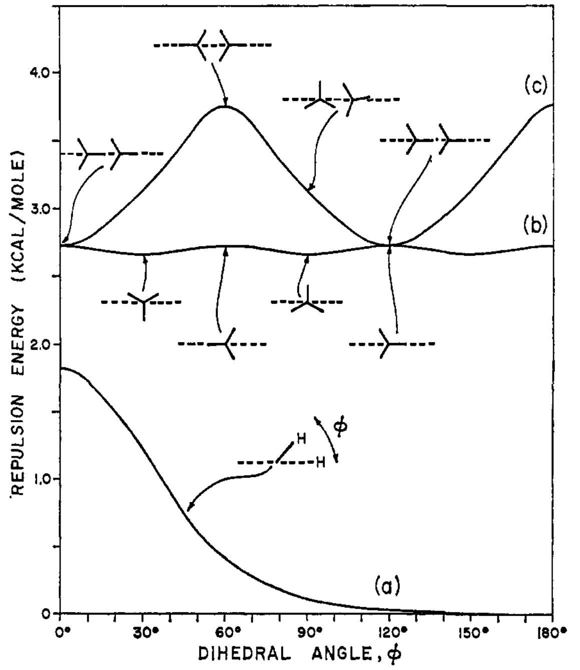

Figure 4. (a) The repulsion energy for a single methyl proton–ring proton interaction. The angle is measured from the eclipsed structure. (b) The combined repulsion energies of all six proton–proton interactions between the three methyl hydrogens and the two *o*-hydrogens in toluene. A negligible barrier of 0.06 kcal/mole is observed for isolated methyl groups. (c) The repulsion contribution of *ortho* protons to the rotational energy barrier in *o*-xylene. The rotation of one methyl group is given by φ and the orientation of the other methyl is specified by the potential energy surface given in Figure 6.

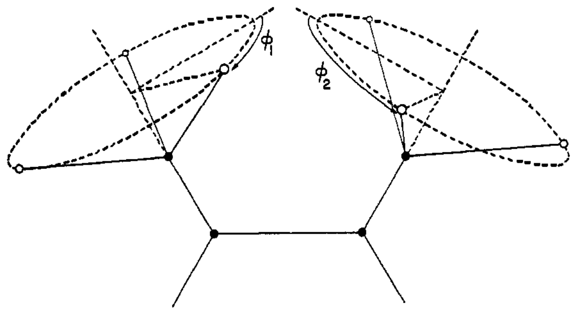

Figure 5. The two generalized coordinates, φ_1 and φ_2, used to define the geometrical orientation of *o*-dimethyl groups.

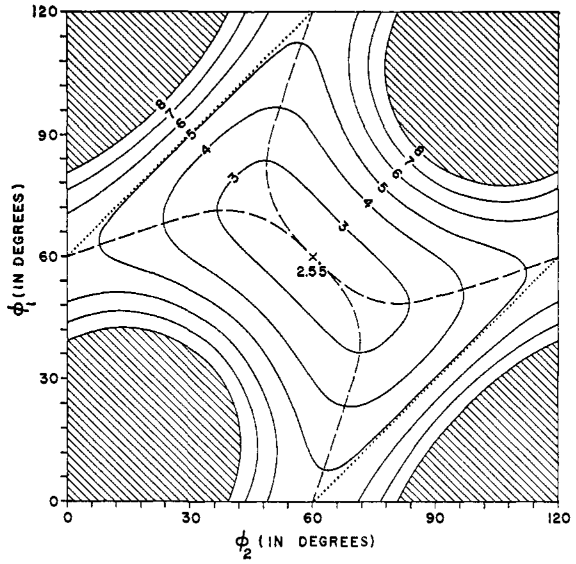

Figure 6. Potential energy surface in kcal/mole for the interaction of *o*-dimethyl groups in various geometrical orientations. Shaded areas indicate high-energy regions in which eq 3 is not valid.

six methyl groups in hexamethylbenzene. "Geared" motion of all the methyl groups in this compound prevent any two adjacent methyl groups from assuming the 2–2 conformation which is found at the minimum energy on the potential surface. It is interesting to note that this rotational motion follows essentially a constant energy contour, and thus a negligible barrier to methyl rotation would be expected for this compound providing the proper phase relationship is maintained between the six rotating methyl groups. The S_6 symmetry noted by Schnepp and McClure[4,15] for hexamethylbenzene in the solid state is in good agreement with this conclusion as the molecule exhibits this symmetry for all but two instances during the rotational process. This study offers no indication that hexamethylbenzene is highly unusual from the other members of the series, and it must be concluded that discrepancies noted for other properties in the methylbenzenes[16] are not important in the carbon-13 chemical-shift data. Nonetheless, the existence of significant ring puckering in the ground state due to steric strain appears unlikely, as the model used to account for the carbon-13 chemical-shift data emphasizes the importance of conformational features. Any significant ring distortion would be expected to create measurable deviations in the methyl carbon-13 chemical-shift value of hexamethylbenzene. As a negligible barrier is expected for the freely rolling symmetrical motion in hexamethylbenzene, it must be concluded that interactions important in the carbon-13 chemical-shift parameter average to give the same value expected for the conformation of hexamethylbenzene in a C_6 symmetry as specified by II or III in Figure 1 and by the empirical rules proposed above. It may be significant, however, that the greatest solvent shifts were noted for this compound (*e.g.*, the saturated CS_2 solution). Furthermore, the marked deviation of the proton chemical shift may possibly be indicative of the importance of freely rotating methyl groups in this compound.

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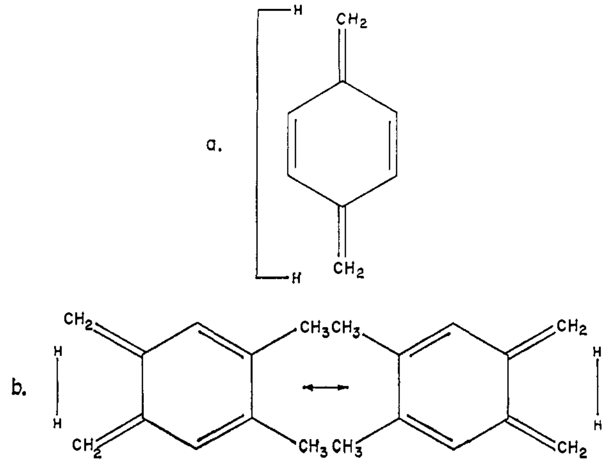

Figure 7. (a) Hyperconjugative structure for *p*-xylene. (b) Important hyperconjugative structures in durene. Possible *para*-resonance terms of the type shown in a are apparently less important in durene.

B. *ortho*-Substituent Effects upon the Methyl Proton and Carbon-13 Chemical Shifts. In this study the methyl proton resonance was observed to move to higher fields as the number of *o*-methyl substituents increases. This trend is similar to that observed for sterically hindered hydrogens at the *endo* position in the norbornenes.[17-19] Steric interactions, however, in the octahydrophenanthrene series[20] have been used to explain a downfield shift in the resonance of hydrogens which are spacially crowded by other proximate hydrogens. In derivatives of mesitylene and durene both upfield and downfield shifts were noted[21] for various substituents. The F, OH, NH_2, and NO_2 substituents increase the shielding in *o*-methyls while Cl, Br, and I groups result in deshielded *o*-methyl protons. Steric shifts to lower fields have been attributed[11,22-24] to van der Waal type interactions, but the opposite upfield trend noted in the proton shifts in the methylbenzenes obviously cannot be rationalized in this manner. However, the internuclear distances and geometrical orientation of adjacent *o*-methyl groups are such that a diamagnetic shift of the proper magnitude can be expected from the anisotropy in the magnetic susceptibility[25,26] of the carbon–carbon bond associated with the adjacent methyl group. If the reasonable value of 4×10^{-6} cm^3/mole[27-32] is used for $\Delta\chi_{C-C}$, one obtains a +0.1-ppm value for the *o*-methyl substituent shift in good agreement with the experimental data contained herein. The change with substitution in methyl proton shifts, therefore, is adequately explained by the magnetic anisotropy of adjacent groups.

The small magnitudes of anisotropic shifts, however, are unable to account for the much larger *ortho*-carbon-13 substituent shifts. The similarity in magnitude and in sign of the two *ortho*-substituent shifts with certain γ-substituent shifts in the alkanes[33] suggests that the interaction has the same origin in both cases. It is felt that these relatively large substituent shifts over three C–C bonds can be explained[34] best for molecules, having two or more closely positioned C–H bonds, by deviations from perfect pairing. The conformational dependence of this interaction in the methylbenzenes may also indicate the importance of additional π-electron delocalization with the interacting methyl groups. Such terms would be similar to those used to account for π-electron effects in adjacent geminal coupling constants.[35,36] Theoretical assessment of the importance of such terms in the methyl carbon-13 chemical shifts is presently underway.

C. Long-Range Interactions between *p*-Methyl Groups. The existence of a *para*-substituent effect in some molecules but not in other constitutes an unusual observation. As this effect is relatively small (0.34 ppm) it may not have any parallel in the chemical properties of these compounds. However, the effect is clearly exhibited in the carbon-13 chemical-shift data, as both *para* situations are each reflected in five chemical-shift values (see Table III). Thus, any attempt to theoretically interpret this long-range interaction should distinguish between the two cases. It is tentatively assumed that a hyperconjugative resonance effect of the valence-bond-type structure given in Figure 7a may account for the δ_1(*para*) parameter, whereas no such simple resonance structure can be drawn for *m*-xylene. If this assumption is correct, a negligible δ_2(*para*) parameter indicates that such hyperconjugative interactions between *p*-methyls are absent whenever both groups can interact in some manner with an *o*-methyl. The hyperconjugative interactions shown in Figure 7b for durene may diminish the importance of the *para* interaction represented by Figure 7a. As an alternative explanation, we note that the long-range interaction is never found when the rotation of both methyl groups is restrained. If this observation is pertinent then the methyl orientation relative to the benzene ring is important in delocalized structures of the type given in Figure 7a. Both methyl groups are in eclipsed structures of the type specified by Figure 1 whenever the *para*-substituent effect is negligible but at least one methyl is freely rotating in all cases where a δ_1(*para*) is observed.

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