

## AN ALTERNATIVE TO "STERIC C-H COMPRESSION" AS THE SOURCE OF UPFIELD CARBON-13 NMR SHIFTS IN POLYMETHYLARENES.

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**KEYWORDS:** Carbon-13 nmr, steric extension, C-C bond lengths, MM2 calculations

### INTRODUCTION

Vicinal alkyl groups attached to benzenoid rings or cycloalkane moieties in a tetralin-like configuration are commonly postulated features in structural models of bituminous coals [for examples, see [1]]. Formation of cyclic carboxylic acid anhydrides (analogous to phthalic anhydride) from mild oxidations of such coals [2] is one item of evidence in support of this postulate, and it would be expected that features from vicinal alkyl species should be readily identifiable if highly resolved carbon-13 nmr spectra of coals were to be obtained. This expectation should be readily testable since in polymethylarenes, methyl carbon-13 nmr shift patterns are observed in which ortho-related methyl carbon signals are significantly upfield (up to 7 ppm) from those of isolated methyl groups. These patterns are usually interpreted by suggesting that non-bonded repulsion between alkyl hydrogen atoms [3-5] leads to **steric compression** of C-H bonds. Many other carbon-13 "steric shifts" are rationalized similarly, with electron migration postulated in the sense  $\delta^* \text{H-C} \delta$  [6,7]. However, bond length and angle distortions occur more readily for C-C bonds than for C-H bonds (compare  $\nu \text{CH}$ ,  $\sim 3000 \text{ cm}^{-1}$ ;  $\nu \text{CC}$ ,  $\sim 1000 \text{ cm}^{-1}$ , and  $\delta \text{CH} \sim 1450 \text{ cm}^{-1}$ ;  $\delta \text{CC} \sim 700 \text{ cm}^{-1}$ ), so hydrogen-hydrogen repulsions are not likely to be the only significant steric factors. Further, the methyl proton shifts in ortho-xylene are also upfield from those in the meta and para isomers [8].

### PROCEDURES AND DISCUSSION

I have tested the validity of the **steric compression** postulate, using Allinger's MM2 force field approach [9] with the commercial application Chem3D Plus™ [10] on a Macintosh II microcomputer. I calculated equilibrium geometries of various methylarenes (benzenes, naphthalenes, anthracenes). The steric interactions were minimized iteratively, considering contributions from compression-stretching, bending, stretch-bend, van der Waals, dipole-dipole, and torsional forces. Ten to one hundred iterations are sufficient to reach self-consistent minima. Calculations for ten distinct environments for methyl groups suggest (see Table 1) that the major variations in geometry minimizing non-bonded repulsions are bond extensions of the aryl C - alkyl C bonds, and appropriate angular changes.

Bond length and angle distortions occur more readily for C-C bonds than for C-H bonds, consistent with the appropriate force constants.

The methyl carbon-13 shifts are linearly correlated with aryl C - alkyl C bond lengths: shift increases as bond length decreases (Figure 1). The hybridization of the alkyl carbons is unchanged; one-bond carbon-13 - proton coupling constants are within 0.5 Hz of 125 Hz.

I interpret these results as decreased hyperconjugative interactions between the methyl groups and the attached aromatic species with increasing aryl C - alkyl C bond length, and as a direct consequence, decreased C-methyl carbon-13 shifts. In this series of compounds, there is **steric extension** of carbon-carbon bond lengths to avoid the hydrogen-hydrogen repulsions in the steric compression model proposed by Grant and coworkers.

This is not to discount the possible significance of non-bonded hydrogen-hydrogen repulsion effects under appropriate circumstances. In the polycyclic aromatic phenanthrene a similar MM2 treatment may be applied to deduce the preferred geometry. In this species, the two hydrogens of the C-H bonds in a bay environment are shortened significantly, but the major predicted changes are systematic deformations of the entire ring geometry and bending of the bay C-H bonds with increased angles. The predicted C-C bond lengths in the phenanthrene skeleton show excellent correlations with those observed from neutron diffraction measurements (see Figure 2).

#### ACKNOWLEDGEMENTS

This work was catalysed by an opportunity provided by a Project SERAPHIM Fellowship held in summer 1988 at the Department of Chemistry of Eastern Michigan University, Ypsilanti, Michigan. Thanks are accorded for this award.

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Table 1  
Carbon-13 shifts for methyl groups in methylarenes

Compound	Shift, ppm	MM2 bond length, nm
Toluene	21.3	0.1509
o-Xylene	19.6	0.1511
9-Methylanthracene	13.7	0.1516
9,10-Dimethylanthracene	14.1	0.1517
1,2,3-trimethylbenzene	15.2(2)	0.1514
1-Methylnaphthalene	19.1	0.1511
1-Methylanthracene	19.7	0.1512
2-Methylnaphthalene	21.4	0.1509
1,2,3,5-tetramethylbenzene	14.6(2)	0.1515
	20.9(5)	0.1508

