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INTERRELATIONSHIPS AMONG HEATS OF FORMATION AND MOLECULAR MECHANICS STERIC ENERGIES

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Abstract: A procedure for the calculation of the heat of formation (WH_f) of alkyl-substituted aromatic hydrocarbons from molecular mechanics steric energies is discussed. The simple protocol requires the choice of a model that accurately reflects the structural characteristics present in the molecular system, especially with regard to steric interactions.

INTRODUCTION

The calculation of molecular thermodynamic properties by molecular mechanics (MM) methods[1] is of considerable topical interest.[2] Particular attention has focused recently on the calculation of the heats of formation for aliphatic and aromatic hydrocarbons. While highly successful, the methods developed to date[2] are largely dependent upon group incremental schemes and/or ancillary quantum mechanical calculations. A simple method (i.e., one that does not depend on these supplemental schemes) that is at the same time reliable, has not been reported. A recent pairwise difference method[2d] relating heats of formation and steric energy provides a possible solution to this problem, however, it is dependent upon both polar and resonance corrections. Thus, in the present work, we investigate a relationship between molecular mechanics (MM2)[3a] calculated steric energies (SE) and the experimental heats of formation (WH_f) for polyalkylbenzenes in an attempt to establish a more direct method for obtaining reasonable estimates of this thermodynamic information.

For this analysis, we consider two sets of molecules, {M} and {N}, that are composed of the same numbers and types of groups (i.e., homodesmic sets[3b]). We may readily define differential steric energies (δSE) and differential heats of formation ($\delta\Delta H_f$) for these two sets by equations 1 and 2, respectively. The simplest approximate relationship between the quantities

$$\delta SE = SE\{M\} - SE\{N\} \qquad (1)$$

$$\delta\Delta H_f = \Delta H_f\{M\} - \Delta H_f\{N\} \qquad (2)$$

δSE and $\delta\Delta H_f$ is that they are equal (i.e., $\delta SE = \delta\Delta H_f$).[4] If valid, such an equivalence would allow for the calculation of heats of formation directly from MM2 SEs and available ΔH_f data (Eq. 3). The present work is concerned with testing the limits of this

$$\Delta H_f\{M\} = SE\{M\} - SE\{N\} + \Delta H_f\{N\} \qquad (3)$$

proposed equivalence for polyalkylbenzenes.

COMPUTATIONAL DETAILS

All calculations were performed using the molecular mechanics method[1] and the program MM2.[3] Calculations were performed on benzene (1), toluene (2), o-xylene (3), m-xylene (4), p-xylene (5), 1,2,3-trimethylbenzene (6), 1,2,4-trimethylbenzene (7), 1,3,5-trimethylbenzene

(8), 1,2,3,4-tetramethylbenzene (9), 1,2,3,5-tetramethylbenzene (10), 1,2,4,5-tetramethylbenzene (11), 1,2,3,4,5-pentamethylbenzene (12), hexamethylbenzene (13), ethylbenzene (14), o-diethylbenzene (15), m-diethylbenzene (16), p-diethylbenzene (17), hexaethylbenzene (18), ethylene (19), propene (20), Z-2-butene (21), E-2-butene (22), 1-butene (23), Z-3-hexene (24), and E-3-hexene (25). Previously reported stretching parameters for benzene[5] were used for all benzene rings. All reasonable conformations were investigated in searching for the global minimum, and all geometries were completely optimized. Calculated steric energies for ground-state conformations are reported in Table 1. Schematic representations reporting substituent torsion angles for geometry optimized structures of 2 - 18 are shown in Figure 1 and selected bond lengths and angles are reported in Figure 2.

Table 1. Calculated Ground-State Steric Energies (SE) For 1 - 25[a]

Compound	SE						
1	-2.69	7	-2.73	13	5.78	19	0.42
2	-2.89	8	-3.26	14	-1.92	20	0.24
3	-2.51	9	-0.18	15	-0.11	21	1.56
4	-3.09	10	-1.59	16	-1.21	22	0.13
5	-3.11	11	-2.34	17	-1.20	23	1.48
6	-1.39	12	1.13	18	14.09	24	3.60
						25	2.50

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[a] In kcal/mol.

RESULTS AND DISCUSSION

The MM2 calculated steric energies for the ground-state conformations of 1 - 25 (Table 1) correspond to the SEs of isolated molecules. In testing the validity of $\delta SE = \delta\Delta H_f$, it is therefore most relevant to use experimentally determined, gaseous heat of formation ($\Delta H_f(g)$) data in our analysis.[6] We have focused on the xylenes and trimethylbenzenes in our initial test calculations.

In general, for polyalkylbenzenes, the differential steric energy (δSE) is defined as:

$$\delta SE = SE(C_6H_xR_{6-x}) - (6-x)SE(C_6H_5R) + (5-x)SE(C_6H_6) \quad (4)$$

(where R = alkyl substituent). Similarly, the differential heat of formation ($\delta\Delta H_f$) is defined as:

$$\delta\Delta H_f = \Delta H_f(C_6H_xR_{6-x}) - (6-x)\Delta H_f(C_6H_5R) + (5-x)\Delta H_f(C_6H_6) \quad (5)$$

We use the monosubstitued benzenes as our model for these calculations in order to incorporate any polar or resonance effects inherent to the molecular system. By looking at this homologous series we eliminate all corrections except those that are due to steric interactions. For the specific case of the xylenes (3 - 5), these equations become:

$$\delta SE = SE(C_6H_4(CH_3)_2) - 2SE(C_6H_5CH_3) + SE(C_6H_6) \quad (6)$$

and

$$\delta\Delta H_f = \Delta H_f(C_6H_4(CH_3)_2) - 2\Delta H_f(C_6H_5CH_3) + \Delta H_f(C_6H_6) \quad (7)$$

For o-xylene (3), the calculated value for δSE is 0.6 kcal/mol. Similarly, for m-xylene (4) and p-xylene (5), we obtain $\delta SE(4)$ = 0.0 kcal/mol and $\delta SE(5)$ = 0.0 kcal/mol, respectively. Experimental $\Delta H_f(g)$ values for 3 - 5[6] allow for the calculation of the corresponding $\delta\Delta H_f$ values: $\delta\Delta H_f(3)$ = 0.3 kcal/mol, $\delta\Delta H_f(4)$ = -0.2 kcal/mol,and $\delta\Delta H_f(5)$ = 0.0 kcal/mol. From the square root of the sum of the squares of the ΔH_f error values[6] for 3 - 5, one can obtain an average error for the $\delta\Delta H_f$ of the xylenes ($\varepsilon(\delta\Delta H_f)$) of 0.3 kcal/mol. Thus, considering the experimental error for these $\delta\Delta H_f$ values, we see that the simple equivalence for δSE and $\delta\Delta H_f$ holds for 3 - 5.

In order to test the proposed equivalence for a more highly substituted system, we applied equations 4 and 5 to the trimethylbenzenes (6 - 8) and obtained: δSE(6) = 1.9 kcal/mol, $\delta\Delta H_f$(6)= 1.1 kcal/mol; δSE(7) = 0.6 kcal/mol and $\delta\Delta H_f$(7) = 0.1 kcal/mol; δSE(8) = 0.0 kcal/mol and δWH_f(8) = -0.4 kcal/mol. Assuming that the error in the described procedure is additive, error limits for the trimethylbenzenes can be obtained in a simple manner from the observed differences between δSE and $\delta\Delta H_f$ for the xylenes. For 6, for example, we calculate ε(6) = 2ε(ortho-R) + ε(meta-R)where ε(ortho-R) = 0.3 kcal/mol, ε(meta-R) = 0.2 kcal/mol, and ε(para-R) = 0.0 kcal/mol. The ε(6) value would therefore be 0.8 kcal/mol and similarly, ε(7) and ε(8) are 0.5 and 0.6 kcal/mol, respectively. Thus, within these error limits, the equivalence described by equation 3 also holds for the more substituted benzenes 6 - 8.

These initial findings for the xylenes and the trimethylbenzenes encouraged us to investigate a wider range of polyalkylbenzene derivatives. We therefore applied the same methodology to 9 - 18. The δSE, $\delta\Delta H_f$, $|\delta SE - \delta\Delta H_f|$, and additive error estimates (ε) for 9 - 18 are reported in Table 2. For 9 and 10, experimental $\Delta H_f(g)$ values are currently unavailable. In these systems, we therefore obtained the necessary $\Delta H_f(g)$ values by employing $\Delta H_f(g) = \Delta H_f(l) + \Delta H_v$.[7a] The heat of vaporization, ΔH_v, in this equation was obtained from the well-established empirical relation[8] for hydrocarbons (ΔH_v = 1.12 n_c + 0.31 n_q + 0.71) where n_c and n_q are the number of non-quaternary and quaternary carbons, respectively. We have tested the accuracy of this relation for these particular types of compounds by calculating ΔH_v values for compounds 1 - 5 and comparing them with experimental data and note that, on average, the predicted ΔH_v values are too low by 0.6 kcal/mol. This correction was applied to the calculated ΔH_f data for 9 and 10 (Table 2). For 11, $\Delta H_f(g)$ was obtained from experimental values of $\Delta H_f(s)$ and the heat of sublimation, ΔH_s, using $\Delta H_f(g) = \Delta H_f(s) + \Delta H_s$.[7a]

From inspection of the data in Table 2, one can see that the equivalence relationship described by Eq. 3 also provides reasonable agreement for 9 - 18. The greatest deviations in δSE and uncorrected $\delta\Delta H_f$ data are observed for 9 - 13. When the ΔH_f data for 9 and 10 are corrected for the error in ΔH_v (+0.6 kcal/mol, see above), a significant improvement is noted, leaving only 11 - 13 outside the range of experimental error. These discrepancies for 11 - 13 may be signs of the limitations of our proposed equivalence (see discussion below).

For the ethylbenzenes (14 - 18), relevant differential steric and enthalpic data along with additive error values are reported in Table 2. For 15 - 17, ΔH_f data can be calculated from the available $\Delta H_f(l)$[6] and predicted ΔH_v.[8] Since the experimental value for ΔH_v of $C_6H_5C_2H_5$ is 10.1 kcal/mol[6] and the predicted value is 9.7 kcal/mol,[8] the approximate error in applying this empirical equation to this class of compounds is 0.4 kcal/mol.[9] Inspection of the data reported in Table 2 reveals reasonable agreement between the δSE and the $\delta\Delta H_f$ values for 15 - 17.

For the most highly substituted ethylbenzene, hexaethylbenzene (18), the $\Delta H_f(g)$ value can be obtained from heat of combustion ($\Delta H_c(s)$, -2635.4 kcal/- mol[10]) and heat of sublimation (ΔH_s,

Table 2. Comparison of δSE and $\delta\Delta H_f$ for Alkylbenzenes 3 - 13 and 15 - 18^a

Compound	ΔH_f	δSE	$\delta\Delta H_f$	$\|\delta SE - \delta\Delta H_f\|$	Error Estimate (ε)^b
1	19.7^e				
2	12.0^e				
3	4.6^e	0.6	0.3	0.3	---
4	4.1^e	0.0	-0.2	0.2	---
5	4.3^e	0.0	0.0	0.0	---
6	-2.3^e	1.9	1.1	0.8	0.8
7	-3.3^e	0.6	0.1	0.5	0.5
8	-3.8^e	0.0	-0.4	0.4	0.6
9	-9.7^f	3.3	1.4(2.0^c)	1.9(1.3^c)	1.3
10	-11.1^f	1.9	0.0(0.6^c)	1.9(1.3^c)	1.2
11	-11.7^g	1.2	-0.6	1.8	1.0
12	-16.3^i	4.8	2.5	2.3(1.7^c)	2.0
13	-20.8^f	9.7	5.7	4.0	3.0
14	7.1^e				
15	-4.5^f	1.0	1.0(1.4^d)	0.0(0.4^d)	---
16	-5.7^f	-0.1	-0.2(0.2^d)	0.1(0.3^d)	---
17	-5.5^f	-0.1	0.0(0.4^d)	0.1(0.5^d)	---
18	-59.5^h	12.2	-3.6	15.8	5.7

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[a] In kcal/mol. [b] Based on ε(3), ε(4), and ε(5) for 3 - 13 and on ε(15), ε(16), and ε(17) for 15 - 18 as discussed in the text. [c] With benzene ring correction (+0.6 kcal/mol) as discussed in the text. [d] With benzene ring correction (+0.4 kcal/mol) as discussed in the text. [e] Experimental $\Delta H_f(g)$ value.[6] [f] Experimental $\Delta H_f(l)$ value[6] and calculated ΔH_v value from Eq. 11.[8] [g] Experimental $\Delta H_f(s)$[6] and ΔH_s[7] values. [h] Calculated $\Delta H_f(s)$ value from $\Delta H_c(s)$[9] and experimental ΔH_s value.[7b] [i] Experimental $\Delta H_f(s)$ and ΔH^m values used to calculate $\Delta H_f(l)$. ΔH_v from Eq. 11[8] used to calculate $\Delta H_f(g)$.

22.7 kcal/mol[7b]) data. Calculating $\Delta H_f(s)$ for 18 from the combustion reaction we obtained -82.2 kcal/mol. Using ΔH_v, we calculate that $\Delta H_f(g, 18) = 59.5$ kcal/mol. The δSE value for 18 is 12.2 kcal/mol, and $\delta\Delta H_f$ for 18 is calculated to be -3.6 kcal/mol. Using the approximation that errors are additive, we determine ε(18) to be 5.7 kcal/mol. Thus, with this error limit, hexaethylbenzene (18) does not show agreement for the proposed equivalence relationship. Since the most sterically crowded methylbenzenes also deviated from the proposed relationship (see above), it seems that sterically crowded systems cannot be accurately described by such a macroincremental analysis with the monosubstituted benzene model.[11] Since the less substituted homologs do not possess the interactions responsible for the steric strain found in the higher members of the series, such a result is not unreasonable.

If the deviation observed above is due only to steric crowding in the higher homologs, it should be possible to more accurately calculate heat of formation data using homodesmic reactions that incorporate the effects of steric crowding. We therefore explored the use of alkylethylenes in our thermodynamic analysis for this potentially more accurate model.

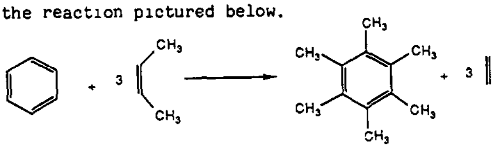
Calculated steric energies for 19 - 25 are listed in Table 1. To initially test this approach on alkyl-substituted ethylenes, we calculated differential SE and ΔH_f data for 21-25.[12] For Z-2-butene (21), we have: δSE(21) = SE(Z-$CH_3CH{=}CHCH_3$) - 2SE($CH_3CH{=}CH_2$) + SE($CH_2{=}CH_2$) and $\delta\Delta H_f$(21) = ΔH_f(Z-$CH_3CH{=}CHCH_3$) - 2ΔH_f($CH_3CH{=}CH_2$) + ΔH_f($CH_2{=}CH_2$). Applying this method to 21-25 yields excellent agreement between differential steric energies and enthalpies for these compounds (δSE(21) = 1.5 kcal/mol, $\delta\Delta H_f$(21) = 1.2 kcal/mol; δSE(22) = 0.1 kcal/mol, $\delta\Delta H_f$(22) = 0.2 kcal/mol; δSE(24) = 1.1 kcal/mol, $\delta\Delta H_f$(24) = 1.1 kcal/mol; and δSE(25) = 0.0 kcal/mol, $\delta\Delta H_f$(25) = -0.5 kcal/mol).

As a further attempt to explore the utility of this type of treatment, we considered the general reaction for the calculation of ΔH_f of substituted benzenes from the SE of substituted alkenes that is shown below. For a specific case, when

R_1 = CH_3 and R_2 = H, the δSE is then 0.0 kcal/mol and $\delta\Delta H_f$ is also 0.0 kcal/mol

In an analogous manner, the δSE and $\delta\Delta H_f$ for a series of R_1 and R_2 substituents were calculated and the results are reported in Table 3. As inspection of this data shows, agreement between calculated and measured ΔH_f data is very good.

In order to test the use of this type of macroincremental approach to the calculation of ΔH_f of sterically crowded alkylbenzenes, we recalculated the differential thermodynamic data for hexamethylbenzene using the reaction pictured below.



Using this method we are able to obtain a ΔH_f for 13 of -17.9 kcal/mol. This is meaningfully closer to the experimental value of -20.8 kcal/mol than the value obtained in our initial calculations (-16.8 kcal/mol). Since some of the steric strain found in 13 is incorporated into the alkylethylene used for this calculation (21), this finding supports the hypothesis that the previous lack of agreement between experiment and calculation is due to the neglect of such steric interactions. A similar use of 6 as the model yields a ΔH_f for 13 of -18.4 kcal/mol. Use of 3 and 9 as the models leads to ΔH_f for 13 of -19.0 kcal/mol. This suggests that a greater incorporation of steric interactions into the model compounds selected leads to a more reliable value for ΔH_f.

Table 3. Calculated δSE and $\delta\Delta H_f$ for Dialkylbenzenes and Ethylenes[a]

R_1	R_2	δSE	$\delta\Delta H_f$	$\lvert\delta SE - \delta\Delta H_f\rvert$
CH_3	H	0.0	0.0	0.0
C_2H_5	H	-0.3	-0.1	0.2
CH_3	CH_3	-1.0	-0.9	0.1
C_2H_5	C_2H_5	-0.6	-0.3(0.1[b])	0.3(0.7[b])

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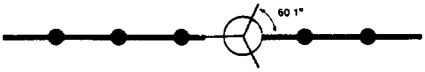
[a] In kcal/mol. [b] With benzene ring correction as discussed in the text (+0.4 kcal/mol).[8]



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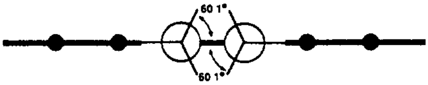

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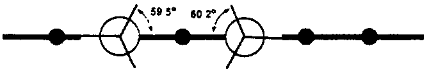

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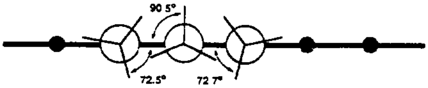

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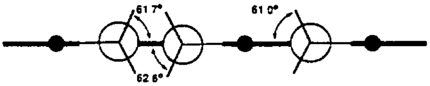

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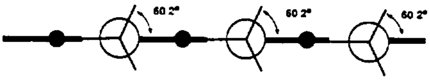

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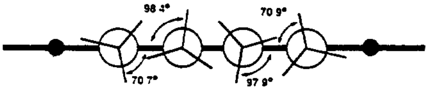

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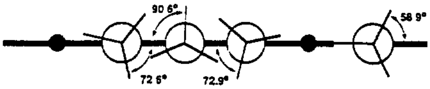

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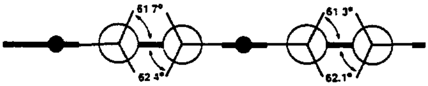

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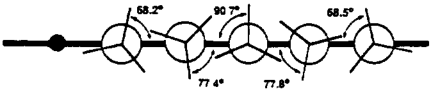

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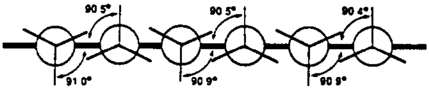

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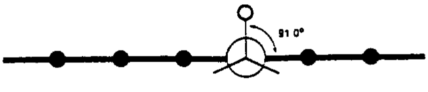

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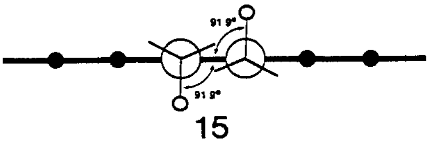

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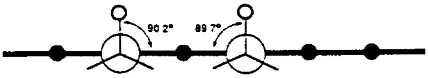

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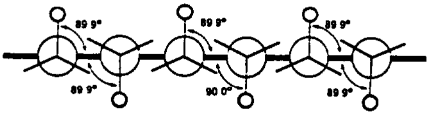

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Figure 1. Schematics of substituent torsion angles for optimized structures for methylbenzenes 2 - 13 and ethylbenzenes 14 - 18. These schematics are viewed from around the ring perimeter with filled circles representing aromatic hydrogen atoms. Newman projections are down the C_{alk} - C_{ar} bonds. For 14 - 18, open circles represent terminal methyl groups.

In order to further substantiate the hypothesis that steric crowding is responsible for the deviation from the proposed equivalence relationship, we further explored the structural details of these compounds.

Geometry optimization of benzene (1) yields a structure of D_{6h} symmetry in accord with experimental findings.[14] For toluene (2) we obtain a structure of approximate C_s symmetry in which one of the methyl C-H bonds eclipses the aryl ring.[15] We calculate ground-state conformations of o-, m- and p-xylene (3, 4, and 5)[16] to be of approximate C_{2v}, C_{2v}, and C_{2h} symmetry, respectively. For the trimethylbenzenes, both 6 and 7 are of approximate C_s symmetry after geometry optimization, while 8 adopts a structure of approximate C_{3h} symmetry. Optimization of the tetramethylbenzenes (9, 10, and 11) leads to ground-state structures of approximate C_2, C_1, and D_{2h} symmetry, respectively. Pentamethylbenzene (12), after geometry optimization, yields a ground-state structure with C_s symmetry. For 13,[17] we obtain an approximate D_{3d} conformation as the ground state in agreement with previous molecular mechanics,[18a] ab initio calculations,[18b] and single-crystal neutron diffraction analysis.[18c] For ethylbenzene (14), the ground state is of C_s symmetry. The diethylbenzenes (15, 16, and 17) are of approximate C_2, C_s, and C_{2v} symmetry, respectively. Hexaethylbenzene (18) is of approximate D_{3d} symmetry in the ground state, in agreement with previous configurational analyses.[19] In all cases, observed bonding parameters for 1 - 18 may be considered normal. Alkyl group torsion angles for 2 - 18 are reported schematically in Figure 1 and selected bond lengths and angles are reported in Figure 2.

The average C_{ar}-C_{ar} bond distances show some deviation for 1 - 18 and range from 1.398 Å in 1 to 1.410 Å in 18. The sterically crowded structures 12, 13, and 18 all have C_{ar}-C_{ar} bond distances (1.405, 1.408 and 1.410 Å, respectively) that are significantly greater than the 1.398 Å found for 1. Ring substitution patterns also affect the C_{ar}-C_{alk} bond distances. For example, in the relatively uncrowded 2, the C_{ar}-C_{alk} distance (1.508 Å) is significantly shorter than the average C_{ar}-C_{alk} distance in the relatively sterically crowded 18 (1.525 Å). Furthermore, all of the compounds studied yield very similar values for the C_{ar}-C_{alk} bond distances except for 12, 13, 15 and 18, i.e., the four most sterically crowded compounds.

The average C_{ar}-CH_2-CH_3 angles for the ethylbenzenes are also indicative of steric strain in these compounds. These bonding parameters range from 110.8° to 111.8° with hexaethylbenzene (18) exhibiting the largest value. This value is in reasonable agreement with previous mol-

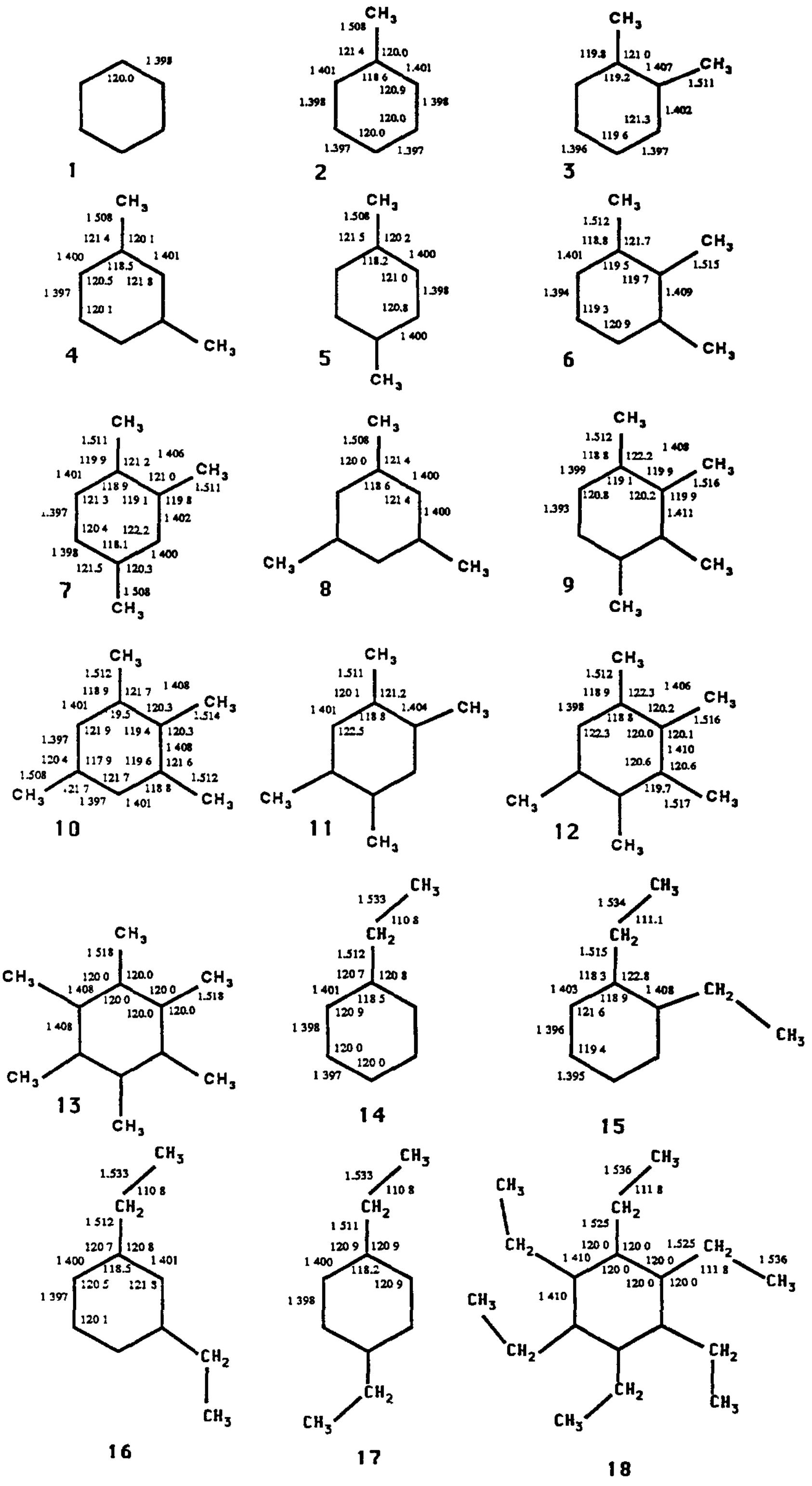

Figure 2. Schematic representation of selected calculated structural features f benzene and its substituted derivatives (1 - 18).

ecular mechanics calculations[19] on hexaethylbenzene that yielded a C_{ar}-CH_2-CH_3 angle of 113.5° for the $\underline{D}_{3d}$ conformation and with X-ray crystallographic analysis[19] that revealed 112.8° for average C_{ar}-CH_2-CH_3 angles.

The torsion angles of the methyl- and ethylbenzenes reveal more information about steric effects in these compounds. These torsion angles are reported schematically in Figure 1.

For the methylbenzenes, we can classify alkyl group interactions by the number of hydrogens directed toward the adjacent carbon: (1,1), (2,1) and (2,2) interactions represents adjacent (ortho) methyl groups that have two, three and four hydrogens directed toward each other, respectively.

For structures with two adjacent methyl substituents, a (2,2) conformation is favored (3 and 11). This (2,2) conformation is also observed for 4, but for 5, the most stable conformation is a (2,1) structure. The ground state of 8 is the (2,1);(2,1);(2,1) conformation of $\underline{C}_{3h}$ symmetry and 7 adopts a conformation with a (2,2) arrangement for the 1,2-dimethyl substituents and a (1,2) arrangement for the 2,4-dimethyl substituents.

Three or more adjacent methyl substituents yield an approximately alternating, "up-down"[19] configuration in which hydrogens are located alternately above and below the mean plane of the benzene ring and in which terminal methyl C-H bonds are close to eclipsing the aryl ring plane (6, 9, 10, and 12). Hexamethylbenzene (13) adopts a $\underline{D}_{3d}$ conformation in its ground state in accord with previous molecular mechanics,[18a] and *ab initio* calculations,[18b] as well as neutron diffraction experiments.[18c]

Also of structural interest is the planarity of the benzene ring. Our calculations reveal an essentially planar ring with only 0.1° to 0.8° of puckering as measured by ring torsion angles. The greatest deviations from planarity are seen for 13 and the smallest deviations are noted for the least sterically crowded alkyl benzenes.

For the ethylbenzenes, stable conformations are those in which methyl groups reside above or below the mean plane of the aryl ring. The ground-state conformations for 16 and 17 have the methyl groups on the same side of the benzene ring. We feel that attractive Van der Waals interactions[20] may be responsible for this observation.

Thus, the uncrowded alkyl-substituted benzenes are very similar in structure with relatively normal bond distances, angles, and torsion angles. Sterically-crowded compounds like 13 and 18, however, deviate from this trend and show longer bond distances and torsional distortions consistent with steric crowding. While the differences are small, we conclude that these calculated differences in structural parameters are consistent with the suggestion of steric crowding in the higher homologs considered in this work. This observation is consistent with our proposal that deviations from the equivalence relationship are due to steric crowding that is not evident in the less substituted systems, thereby leading to poor predicted ΔH_f values due to the inappropriate nature of the model.

CONCLUSIONS

The equivalence relation between δSE and $\delta \Delta H_f$ is supported in many cases by the above energetic and heat of formation calculations. We are cautious to note that the method appears to be most accurate for carefully chosen models that reflect the structural characteristics of the compounds of interest, especially with respect to steric interactions.

REFERENCES AND NOTES

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(4) The question arises as to whether this equation is reasonable from a theoretical standpoint. For the sets {M} and {N}, differences in SEs and ΔH_f values should largely be the result of the neglect of zero-point vibrational energies (ZPE) as well as translational and rotational energy (E_{tr} and E_{rot}, respectively) in the former. Since we are concerned with differences in SE and ΔH_f values for the molecules in question, if the δZPE, δE_{tr} and δE_{rot} are negligible or zero, then the difference in steric energy (δSE) should equal the difference in the heats of formation ($\delta\Delta H_f$).[2e] Similar relationships for molecular conformations are well established.[2d] No corrections were made for conformational population since this effect should be small.[2e]

(5) For C_{ar}-C_{ar} bonds, l_o = 1.3937 and k_s = 8.0667 mdyn/Å. See: Ōsawa, E.; Onuki, Y.; Mislow, K. J. Am. Chem. Soc. 1981, 103, 747.

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(7) a) Eqs. 10 and 12 are exact for enthalpies determined at the same temperature. All data for ΔH_f in this work are obtained at 298 K. The ΔH_v and ΔH_s data used in this work were obtained under standard conditions for the measurement of these parameters. b) Chickos, J. S.; Annunziata, R.; Ladon, L. H.; Hyman, A. S.; Liebman, J. F. J. Org. Chem. 1986, 51, 4311.

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(9) The similarity of correction values for ΔH_v for the methyl and ethyl benzenes (0.6 and 0.4 kcal/mol) suggests that an average value of 0.5 kcal/mol could serve adequately for both systems. For 6, 7, and 8 experimental ΔH_v values are 11.7, 11.5 and 11.4 kcal/mol[6] and calculated ΔH_v is 10.8 kcal/mol,[8] indicating an average correction for trisubstituted benzenes of 0.7 kcal/mol.

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(12) In order to demonstrate that the homodesmic nature of the reaction is important we considered a similar calculation on 1-butene (23).[13] Since Eq. 3 would then not be a homodesmic reaction we expect the calculation to fail. We calculated for 23 wSE(23) = 1.4 kcal/mol; and $\delta\Delta H_f$(23) = 2.9 kcal/mol.The lack of agreement for this simple uncrowded system demonstrates the homodesmic requirement for this procedure.[3b]

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