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A TEST OF THE AM1 MODEL FOR CALCULATING ENERGIES AND STRUCTURAL PROPERTIES OF BENZENE, TOLUENE, NAPHTHALENE, 1-METHYL AND 2-METHYLNAPHTHALENE

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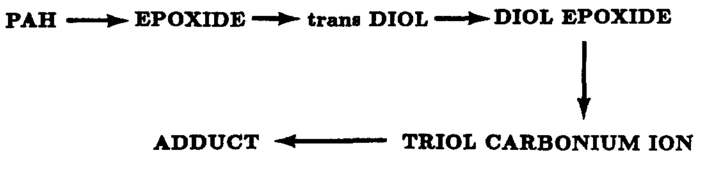
Abstract - AM1 results are compared with those obtained for benzene and toluene using the 6-31G and 6-31G*(5D) basis sets, and those for naphthalene, 1-methylnaphthalene and 2-methylnaphthalene using the 6-31G basis set. There is good agreement both with regard to the relative stability of the various rotamers and many geometrical features. This new parametric quantum mechanical model is thus well-suited for calculations designed to explore the origin of the specific effects of methyl group substitution on the carcinogenic activity of PAHs.

INTRODUCTION

It is now well-established that the carcinogenic activity of polycyclic aromatic hydrocarbons (PAHs) and their methyl derivatives is due to the end products in a sequence of oxidative metabolic reactions,



The diol epoxide, or equivalent triol carbonium ion, alkylates either DNA or possibly another information-carrying cellular macromolecule such as a nuclear protein that reacts with DNA, forming an adduct[1,2a].

The structure of many of these PAH molecules contains a phenanthrene ring system, and the oxidative substitution occurs around a terminal angular ring ljacent to the so-called "bay region", see Figs. 1A and B[2b].

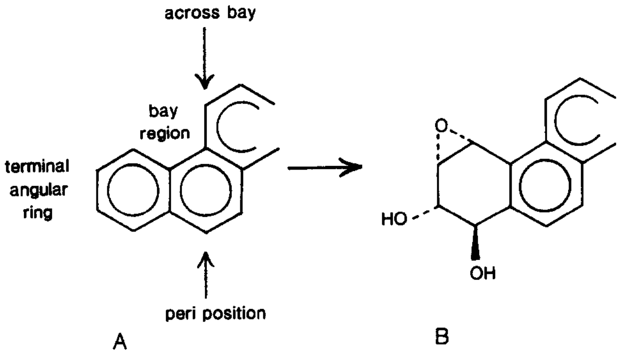


FIGURE 1. Oxidative attack on the terminal angular ring, A, leads to the formation of a diol-epoxide, B.

The presence of a methyl group across the "bay" enhances the activity, e.g. 12-methylbenz[a]anthracene, 5-methylchrysene and 11-methylbenzo[a]pyrene; whilst the presence of an additional methyl group in a peri position with respect to the angular ring, see Fig. 1A, diminishes it, e.g. 5,12-dimethylchrysene[2c]. As would be expected, substitution in the terminal angular ring around which the oxidative attack occurs abolishes it altogether[2d].

X-ray crystallographic studies have shown methyl group substitution across the "bay" to have significant structural consequences[2e]. In addition to inplane distortion the crowded environment of the methyl group results in the molecule becoming nonplanar in some cases, thereby reducing the steric strain, and if the PAH is already nonplanar the out-of-plane distortion becomes more accentuated. The buckling of the molecule occurs primarily by torsion about the ring bonds rather than by a departure from planarity of the bonding about individual carbon atoms.

The angular rings in the oxidative metabolites to which the epoxide, diol groups, etc. are attached contain carbon atoms with a connectivity of four, and are, of course, nonplanar to begin with. The presence of a methyl group across the "bay" serves to make these rings even more nonplanar[2e].

To investigate in detail how methyl group substitution affects the various stages in the above reaction sequence, and so gain a better understanding of the essentially indirect mechanisms by which the carcinogenic activity is either enhanced or diminished, calculations are in progress using the new general purpose quantum mechanical model Austin Model 1 (AM1)[3]. Full geometry optimization is employed in order to characterize the ring distortion, any nonplanarity that may be present and the orientation of the methyl C-atom and H-atoms with respect to the ring bonding, and tc evaluate the relative stability of the various rotamers and the destabilization of the ring system due to the methyl substitution[4a,b,5a].

Comparison with experiment can be made in only a few instances, so an important consideration at the outset has been to explore the extent to which the results obtained using this semiempirical program show the same trends as those found using _ab initio_ methods.

Calculations on naphthalene and its 1-methyl and 2-methyl derivatives have therefore been carried out using the 6-31G basis set[5a], and, along with previous results for benzene and toluene using the 6-31G and 6-31G*(5D) basis sets[6a,b], comparisons are made in the present paper with the corresponding AM1 results.

Calculations on 9-methylanthracene and 4-methylphenanthrene have already been completed[5b].

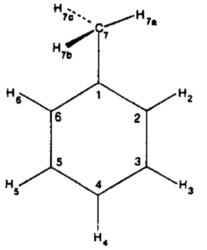
COMPUTATIONAL PROCEDURE

The calculations were carried out on a VAX 11/780 computer using the AMPAC program [7] and the Austin Model 1, AM1,[3] with gradient optimization. Full geometry optimization was employed in the search for the most stable rotamers. In all cases the PRECISE option was used to provide higher precision geometries within the AM1 model. Methyl group rotational transition states were identified by the appearance of a single imaginary frequency in a vibrational analysis.

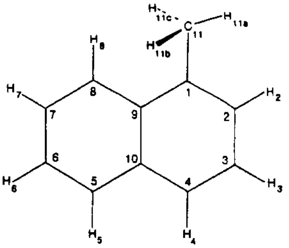
A calculation on naphthalene using the 6-31G* basis set[8] was carried out using a MULTIFLOW Trace 7/200 supermini computer.

RESULTS

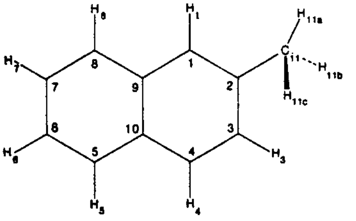
The numbering used to identify the bond lengths and angles, and the characterization of the "staggered-eclipsed" and "eclipsed-staggered" orientations of the methyl H-atoms with respect to the ring bonding in toluene, 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN) are shown in Fig. 2.



Staggered-Eclipsed Toluene



Staggered-Eclipsed
1-Methylnaphthalene



Eclipsed-Staggered
2-Methylnaphthalene

FIGURE 2. The characterization of the "staggered-eclipsed" (s-e) orientation of the methyl H-atoms with respect to the ring bonding in toluene and 1-MN, and the "eclipsed-staggered" (e-s) orientation in 2-MN. Rotation of the methyl group through 180° generates the e-s and s-e orientations respectively. Also shown are the numbering systems used to identify the bond lengths and angles.

ENERGY

A. Rotamer Stability and the Barrier to Rotation

The AM1 calculations, like those using the 4-21, 6-31G and 6-31G*(5D) basis sets, find the orthogonal rotamer of toluene with the C-atom of the methyl group and the ring atoms out-of-plane to be the most stable, and the s-e (e-s) rotamer to be the transition state for rotation of the methyl group. In keeping with the very low experimental value for the energy barrier[9], 0.059 kJ mol^{-1}, the calculated values are all of the same magnitude, see Table 1.

TABLE 1. Calculated energy barrier for rotation of the methyl group in toluene, kJ mol^{-1}.

orthogonal structure ⟶ s-e rotamer (barrier structure)[a]

STO-3G[10a]	4-21[10b]	4-31G[10a]	6-31G[5a]	6-31G*(5D)[5a]	AM1
0.012[b]	0.013[c]	0.017[b]	0.029[c]	0.017[c]	0.037[c]

a. The e-s rotamer is identical by reason of symmetry.

b. Assuming that the ring atoms in the orthogonal structure are coplanar.

c. Fully optimized orthogonal structure.

With 2-MN the e-s rotamer is found to be the most stable and the s-e rotamer the least. Although the structural environment of the methyl group is very similar to that in toluene, i.e. abutted by two 'ortho' H-atoms in the ring, the energy barrier is much higher, 3.1 and 0.8 kJ mol^{-1} in the 6-31G and AM1 calculations respectively. On the other hand with 1-MN it is the s-e rotamer that is the most stable and the e-s rotamer the least. But, probably in response to the close proximity of the peri H-atom in the adjacent ring to the methyl group, the energy barrier is still higher, 10.2 and 5.5 kJ mol^{-1} in the 6-31G and AM1 calculations respectively — values which lie on either side of experimental values of 8.8 [11a] 9.0 [11b] and 9.6 [11c] kJ. mol^{-1}.

In vibrational analyses using AM1 a single imaginary frequency was found for the s-e rotamer of toluene, and for the e-s rotamer of 1-MN, thereby confirming that these are transition state structures.

B. The Stability of s-e 1-MN Relative to e-s 2-MN.

There is good agreement for the difference in energy between the most stable rotamers of 1-MN and 2-MN. The AM1 value is 4.5 and the 6-31G value 5.1 kJmol^{-1} with e-s 2-MN more stable than s-e 1-MN.

C. Destabilization due to the Methyl Group Substitution.

Utilizing cis-1,3-butadiene and cis-isoprene as reference molecules, the energy change for the reaction in which the methyl group is transferred from an aromatic molecule to cis-1,3-butadiene,

e.g. toluene + cis-1,3-butadiene ⟶ benzene + cis-isoprene

gives a measure of the stabilization or destabilization, as the case may be, brought about in the parent aromatic structure by the methyl substitution. In such a reaction not only do the reactants and products contain equal numbers of C-C bonds between C-atoms of the same connectivity and equal numbers of each kind of C-atom bonded to the same number of H-atoms so that energy contributions arising from a mismatch in bonding are minimized, i.e. the reaction is homodesmotic[12a-d], but in addition there is a formal matching of the steric environment of the methyl group to furthur minimize extraneous energy contributions.

The AM1 energy changes show the same ranking, from most negative to least negative (or most positive) as those calculated using the 6-31G basis set.

	1-MN	: Toluene :	2-MN	
AM 1	-3.4	+0.7	+1.1	kJ mol^{-1}
6-31G	-5.3	-2.1	-0.3	kJ mol^{-1}

Taken together the values for toluene and 2-MN, lying on either side of zero and at most by only 2.1 kJ mol^{-1}, imply that relative to the diene reference molecules there is no significant stabilization or destabilization. The larger negative values for 1-MN, on the other hand, indicate a perceptible destabilization in this molecule, which is consistent with the more crowded environment of the methyl group.

D. The Gain in Energy Accompanying Relaxation of the Planarity Constraint in the Orthogonal Rotamers of Toluene and I-MN

In studying the orthogonal rotamer of toluene the geometry and energy of the structure in which the methyl C-atom and the ring atoms were constrained to be coplanar were determined first, and then the planarity constraint was relaxed utilizing full geometry optimization. This final structure was found to be more stable by only 0.08 kJ mol^{-1} using both the 6-31G and the 6-31G*(5D) basis set[6b], and the AM1 value is even smaller, 0.02 kJ mol^{-1}. There is thus no significant force driving the methyl C-atom and the ring atoms out-of-plane in this particular orthogonal structure.

In the case of both 1-MN and 2-MN the constrained coplanar orthogonal form was found to have an energy intermediate between the energies of the s-e and e-s , and the e-s and s-e rotamers as would be expected, see Table 2.

TABLE 2. Energy of the constrained coplanar orthogonal form compared to that of the most and least stable rotamer, kJ mol^{-1}, calculated using the 6-31G basis set[5a], with AM1 values in parentheses.

1-MN	s-e	orthogonal	e-s
	reference zero	+5.0(+2.7)	+10.2 (+5.5)
2-MN	e-s	orthogonal	s-e
	reference zero	+1.6	+3.1

It was not practicable to carry out full geometry optimization using the 6-31G basis set. Using AM1, however, the gain in energy upon relaxation of the constraint in the case of 1-MN was found to be 0.12 kJ mol^{-1}, which may indicate that the presence of the fused ring favors nonplanarity to a slightly greater extent compared to that in toluene, but certainly not enough to alter the stability relationship in Table 2.

GEOMETRY

A. The Ring Geometry in Naphthalene.

There quite a striking lack of agreement between the ranking of the lengths of the "long" bonds as determined both by experiment and by MO calculations, see Table 3. The AM1 values give

$$C_2\text{-}C_3 < C_{10}\text{-}C_9 < C_9\text{-}C_1$$

the same ranking as the other semiempirical methods, MINDO/3 [20] and MNDO [21], three X-ray diffraction studies [13a-c] and an early electron diffraction study[14]. A neutron diffraction study on perdeuteronaphthalene [16] also gives this ranking. On the other hand a more recent electron diffraction study [15], and *ab initio* calculations using STO-3G[17], 4-21[18], and 6-31G[5a,17] basis sets give

$$C_{10}\text{-}C_9 < C_2\text{-}C_3 < C_9\text{-}C_1$$

The inclusion of polarization functions does not affect this ranking - the same result is obtained with the 6-31G* as with the 6-31G basis set, see Table 3.

However the 4-21 values corrected to give an r_e structure, and further refined by fitting a set of predicted vibrational frequencies to the corresponding observed ones[19], give yet another ranking

$$C_2\text{-}C_3 < C_9\text{-}C_1 < C_{10}\text{-}C_9$$

In view of these discrepancies, which arise from bond length differences of a few thousandths of an Ångstrom, it will be particularly interesting to see how future AM1 calculations on larger PAHs and their derivatives compare with the extensive X-ray crystallographic data which are available.[2e]

TABLE 3. Experimental and calculated values for the bond lengths in the naphthalene ring: see Fig. 2 for the numbering system.

		Long			Short
TECHNIQUE	Ref.	C_9-C_1	C_2-C_3	C_{10}-C_9	C_1-C_2
X-ray Diffraction	13a	1.421	1.415	1.418	1.364
X-ray Diffraction	13b	1.424	1.411	1.421	1.377
X-ray Diffraction	13c	1.425	1.417	1.424	1.377
Electron Diffraction	14	1.422	1.412	1.420	1.371
Electron Diffraction	15	1.422	1.417	1.412	1.381
Neutron Diffraction[a]	16	1.423	1.401	1.412	1.372
STO-3G	17	1.432	1.426	1.405	1.353
4-21	18	1.420	1.415	1.409	1.350
4-21[b]	19	1.424	1.417	1.426	1.373
6-31G	17,5a	1.420	1.416	1.413	1.362
6-31G*	c	1.421	1.417	1.409	1.358
MINDO/3	20	1.447	1.427	1.441	1.382
MNDO	21	1.439	1.429	1.435	1.382
AM1	3	1.422	1.416	1.421	1.373
AM1	c	1.422	1.416	1.419	1.373

a. Perdeuteronaphthalene

b. The values in reference 18 corrected to give an r_e structure and further refined by fitting a set of predicted vibrational frequencies to the corresponding observed ones.

c. This work

B. The Inward Bowing of the Peri Hydrogen Atoms.

The 6-31G calculations[5a] confirmed the inward bowing of the peri H-atoms which Brock and Dunitz noted in their low temperature X-ray diffraction study of naphthalene [13c] and found the same feature in both 1-MN and 2-MN. AM1 calculations give similar results, see Table 4.

TABLE 4. Inward Bowing of the Peri Hydrogen Atoms

	H_4----H_5 : C_4---C_5 (Å)		
Molecule	Expt.	6-31G	AM 1
Naphthalene	2.45 : 2.49[13c]	2.479 : 2.486[a]	2.464 : 2.484
s-e 1-MN	--	2.450 : 2.474	2.443 : 2.476
e-s 1-MN	--	2.429 : 2.466	2.421 : 2.467
e-s 2-MN	--	2.470 : 2.485	2.458 : 2.482
s-e 2-MN	—	2.469 : 2.484	2.461 : 2.482

a. The corresponding values calculated from the geometry reported by Sellers and Boggs[18] using the 4-21 basis set are very similar, i.e., 2.479 : 2.485.

C. Distortion of the Ring in the Methyl Derivatives

In Table 5 the AM1 values for the changes in the bond lengths, the bond angles and the ring area in the conversion of benzene into s-e toluene are compared with those obtained using the 4-21[9b], 6-31G[5a] and 6-31G*(5D) basis sets, and in Table 6 the corresponding AM1 and 6-31G values for the conversion of naphthalene into s-e 1-MN and e-s 2-MN. In the vast majority of cases the increments have the same sign.

TABLE 5. Changes in the bond lengths (Å), bond angles (degrees), and ring area (Å^2) in the conversion of benzene into s-e toluene.

Increment	4-21[9b]	6-31G[5a]	6-31G*(5D)[5a]	AM 1
C_1-C_2	$+0.001_8$	$+0.002_3$	$+0.002_2$	$+0.004_2$
C_2-C_3	$+0.001_1$	$+0.000_9$	$+0.002_1$	-0.000_7
C_3-C_4	-0.002_8	-0.002_7	-0.002_8	-0.000_8
C_4-C_5	$+0.001_0$	$+0.000_8$	$+0.001_6$	$+0.000_3$
C_5-C_6	-0.002_9	-0.002_8	-0.002_9	-0.002_1
C_6-C_1	$+0.006_0$	$+0.006_1$	$+0.006_7$	$+0.005_9$
$\angle C_6C_1C_2$	-1.4_3	-1.6_6	-1.6_8	-0.7_6
$\angle C_1C_2C_3$	$+0.7_8$	$+0.9_2$	$+0.9_5$	$+0.3_2$
$\angle C_2C_3C_4$	$+0.1_8$	$+0.2_0$	$+0.1_7$	$+0.1_6$
$\angle C_3C_4C_5$	-0.4_9	-0.5_7	-0.5_7	-0.1_9
$\angle C_4C_5C_6$	$+0.1_7$	$+0.1_9$	$+0.1_9$	$+0.1_1$
$\angle C_5C_6C_1$	$+0.7_8$	$+0.9_2$	$+0.9_4$	$+0.3_6$
Ring Area	+0.0045	+0.0050	+0.0077	+0.0081

The change in area of the aromatic ring system has proved to be a sensitive index for distinguishing between the influence of substituent groups on the net bonding between the carbons in many monosubstituted benzene derivatives[6a]. The AM1 calculations, like the *ab initio*, show a similar increase in area in the ring to which the methyl group is attached in 1-MN and 2-MN, see Table 6, as in the case of toluene, see Table 5. Furthermore the AM1 calculations show there to be a perceptible decrease in the area of the unsubstituted ring in 2-MN, in contrast to a small increase in 1-MN.

A much more delicate interplay of structural factors might be anticipated in the rotation whereby s-e toluene is converted into the orthogonal form with the C-atom of the methyl group and the ring atoms no longer coplanar. Nevertheless, there is equally good agreement between the AM1 and *ab initio* [5a,10b] values for the increments in bond lengths and angles, see Table 7.

Moreover the *type* of nonplanarity found using AM1 is identical to that obtained using the 6-31G and 6-31G*(5D) basis sets (see Fig. 3) although the nonplanarity is not quite so pronounced with AM1. It was not feasible to use the 6-31G basis set with full geometry optimization in order to study nonplanarity in the orthogonal rotamers of 1-MN and 2-MN. AM1 calculations on the former have, however, been carried out, and reveal a significant difference from the nonplanarity in orthogonal toluene as can be seen from a comparison of Figs. 3 and 4.

In the case of toluene, the"orthogonal" H-atom of the methyl group shifts in unison with the methyl C-atom and the top three C-atoms of the ring in relation to the reference plane, and the other two methyl H-atoms shift in the opposite direction[6b]: whereas in the case of 1-MN, it is these other two methyl H-atoms that shift in unison, and the "orthogonal" methyl H-atom shifts in the opposite direction. Furthermore the nonplanarity in each of the two rings is much greater than that in toluene.

TABLE 6: Changes in the bond lengths (Å), bond angles (degrees), and ring areas (Å^2) in the conversion of naphthalene into 1-methyl and 2-methylnaphthalene.

	s-e 1-MN		e-s 2-MN	
Increment	6-31G^{5a}	AM1	6-31G^{5a}	AM1
C_9-C_1	$+0.013_0$	$+0.007_4$	$+0.001_0$	-0.000_8
C_1-C_2	$+0.003_4$	$+0.005_8$	$+0.001_8$	$+0.004_1$
C_2-C_3	-0.000_9	-0.002_4	$+0.007_5$	$+0.006_1$
C_3-C_4	-0.003_4	-0.001_0	-0.002_4	-0.002_0
C_4-C_{10}	0	-0.000_3	$+0.000_4$	$+0.000_3$
C_{10}-C_5	-0.001_3	$+0.000_3$	-0.001_6	-0.000_7
C_5-C_6	0	-0.000_4	$+0.000_9$	$+0.000_3$
C_6-C_7	-0.003_0	-0.001_0	-0.001_0	-0.000_4
C_7-C_8	$+0.001_6$	$+0.000_1$	$+0.000_9$	$+0.000_2$
C_8-C_9	$+0.000_9$	$+0.000_7$	-0.000_9	$+0.000_1$
C_9-C_{10}	$+0.002_2$	$+0.000_6$	-0.001_6	-0.000_5
$\angle C_{10}C_9C_1$	$+0.3_8$	$+0.0_2$	$+0.1_3$	$+0.1_5$
$\angle C_9C_1C_2$	-1.8_2	-0.8_3	$+0.9_2$	$+0.3_3$
$\angle C_1C_2C_3$	$+1.4_3$	$+0.6_2$	-1.6_2	-0.7_6
$\angle C_2C_3C_4$	-0.0_4	-0.0_1	$+0.9_2$	$+0.3_5$
$\angle C_3C_4C_{10}$	-0.4_5	-0.1_9	$+0.0_7$	$+0.1_1$
$\angle C_4C_{10}C_9$	$+0.5_0$	$+0.3_9$	-0.4_2	-0.1_8
$\angle C_{10}C_5C_6$	$+0.1_8$	$+0.1_3$	-0.0_3	-0.0_3
$\angle C_5C_6C_7$	-0.3_2	-0.2_4	-0.1_0	-0.0_2
$\angle C_6C_7C_8$	$+0.1_6$	$+0.0_5$	$+0.0_6$	-0.0_1
$\angle C_7C_8C_9$	$+0.3_2$	$+0.3_5$	-0.0_2	-0.0_1
$\angle C_8C_9C_{10}$	-0.6_9	-0.5_4	-0.0_8	-0.0_3
$\angle C_9C_{10}C_5$	$+0.3_5$	$+0.2_5$	$+0.1_7$	$+0.0_8$
Ring Area I^a	+0.0170	+0.0123	+0.0075	+0.0086
Ring Area II	+0.0003	+0.0003	-0.0004	-0.0012

a. The ring to which the methyl group is bonded.

TABLE 7: Changes in the bond lengths (Å) and bond angles (degrees) in the conversion of s-e toluene into orthogonal toluene with the ring and methyl C-atom no longer in the same plane.

Increment	4-21^{10b}	6-31G^{5a}	6-31G*(5D)	AM1
C_1-C_2	$+0.001_8$	$+0.002_0$	$+0.002_0$	$+0.000_8$
C_2-C_3	-0.001_7	-0.001_8	-0.002_7	-0.000_7
C_3-C_4	$+0.001_6$	$+0.001_7$	$+0.001_9$	$+0.000_6$
C_4-C_5	-0.002_2	-0.001_8	-0.002_5	-0.000_5
C_5-C_6	$+0.002_3$	$+0.001_9$	$+0.002_3$	$+0.000_7$
C_6-C_1	-0.002_4	-0.001_8	-0.002_5	-0.000_8
$\angle C_6C_1C_2$	--	0	-0.0_2	-0.0_6
$\angle C_1C_2C_3$	--	0	$+0.0_1$	$+0.0_6$
$\angle C_2C_3C_4$	--	-0.0_1	$+0.0_1$	-0.0_3
$\angle C_3C_4C_5$	--	$+0.0_1$	-0.0_1	-0.0_1
$\angle C_4C_5C_6$	--	0	-0.0_1	$+0.0_2$
$\angle C_5C_6C_1$	--	0	$+0.0_2$	$+0.0_2$

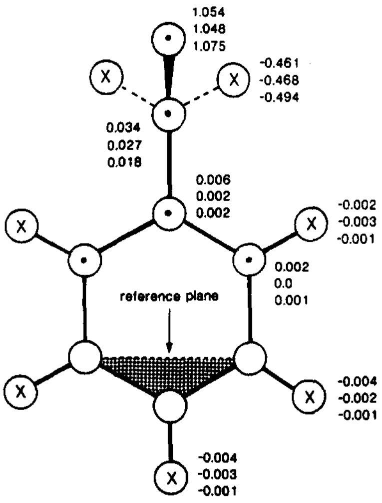


FIGURE 3. Nonplanarity of the orthogonal rotamer of toluene in Ångstrom units, above ⊙ and below ⓧ the reference plane, calculated using the 6-31G and 6-31G*(5D) basis sets, and the AM1 model (values reading from top to bottom).

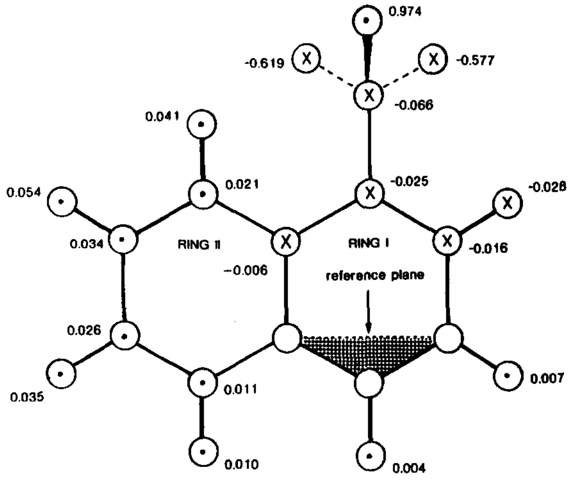


FIGURE 4. Nonplanarity of the orthogonal rotamer of 1-methylnaphthalene in Ångstrom units, above ⊙ and below ⓧ the reference plane, calculated using the AM1 model.

The ipso angle in benzene derivatives, namely the angle in the ring subtended by the substitutent group, has been the focal point in the discussion and analysis of structural data for many years[22]. The values in Tables 5 and 6 show the ipso angle in toluene, 1-MN and 2-MN to be systematically less than the corresponding angle in the parent hydrocarbon in all the calculations. In s-e toluene, the 4-21, 6-31G, 6-31G*(5D) and AM1 values for $\angle C_6C_1C_2$ are approximately 118.6, 118.3, 118.3 and 119.2° respectively, in relation to the 120° angle in benzene, compared to experimental values of 118.7 ± 0.4° and 119.1 ± 0.3° from electron diffraction[23] and microwave measurements[24] respectively [25]. In s-e 1-MN, the 6-31G and

AM1 values for $\angle C_9C_1C_2$ are approximately 119.0 and 119.7°, in relation to the 120.8 and 120.5° respectively for position 1 in naphthalene. In e-s 2-MN the corresponding values for $\angle C_1C_2C_3$ are approximately 118.6 and 119.6°, in relation to 120.2 and 120.4° respectively for position 2.

D. Orientation of the Methyl C-atom with respect to the Ring Bonding.

The tilt of the methyl C-atom,[6a] evaluated as the difference between the angles at the left-hand side and the right-hand side of the bond to the ring, is systematically negative to the extent of about 1° for s-e toluene, i.e., $\angle C_7C_1C_6 - \angle C_7C_1C_2$ is -0.8, -0.8, -0.9 and -1.0° in the 4-21,[10b] 6-31G,[5a], 6-31G*(5D)[5a] and AM1 calculations.

The change in the tilt angle in 1-MN and 2-MN as the methyl group is rotated from the s-e into the e-s position is very similar in the 6-31G and AM1 calculations. In 1-MN, $\angle C_{11}C_1C_9 - \angle C_{11}C_1C_2$ goes from approximately +0.3 to +4.8°, and from -0.4 to +5.0°, respectively; while in 2-MN, $\angle C_{11}C_2C_1 - \angle C_{11}C_2C_3$ goes from approximately +1.0 to +2.6°, and from +0.8 to +2.5°, respectively.

E. Rotational Dependence of the H-C Bond Length in the Methyl Group

Both 4-21[10b] and 6-31G[5a] calculations found the H-C bond length in the methyl group in toluene to vary as the group is rotated, passing through a minimum value when the H-C bond is orthogonal. The 6-31G calculations found a similar variation for 1-MN,[5a] and, as shown in Table 8, the AM1 calculations also give the same kind of variation.

TABLE 8: Minimum and maximum values for the methyl H-C bond lengths, Å.

	Minimum (H-C in plane)		Maximum (H-C orthogonal)	
Molecule	6-31G[5a]	AM1	6-31G[5a]	AM1
Toluene[a]	1.082_9	1.117_4	1.086_2	1.119_5[b], 1.119_5[c]
1-MN	1.082_1	1.117_8	1.086_1	1.119_5[b], 1.119_3[c]

a. Values using the 4-21 basis set, 1.081_8 and 1.085_9 Å respectively[10b]

b. Orthogonal structure with the methyl C-atom and the ring atoms constrained to be coplanar.

c. Orthogonal structure with relaxation of the planarity constraint.

F. The Orientation of the In-plane Methyl Hydrogen Atom in Relation to the Ring Bonding in the Most Stable Rotamers of 1-MN and 2-MN.

The in-plane H-atom of the methyl group in s-e 1-MN and e-s 2-MN eclipses C_1-C_2, the ring bond, which compared to C_9-C_1, has the greater double bond character. These structures are thus analogous to those of the most stable forms of many aliphatic molecules of the type CH_3-CH=CHX, in which a methyl H-atom eclipses the carbon-carbon double bond.[5a] Moreover C_1-C_2 is slightly shorter in the more stable rotamers, see Table 9, indicating that greater stability is associated with a slight enhancement of the bond localization already present.

TABLE 9. Length of the C_1-C_2 bond, Å.

Rotamer		6-31G[5a]	AM 1
1-MN	s-e	1.365_7	1.378_8
	e-s	1.368_8	1.382_2
2-MN	e-s	1.364_1	1.377_1
	s-e	1.367_0	1.378_6

A Comparison of AM1 and MNDO for calculating ΔH_f^o of Benzene and Polycyclic Aromatic Hydrocarbons.

MINDO/3[20] and MNDO[21] give values of H_f^o for benzene and naphthalene that are more positive than experiment,[27] and the MNDO values obtained by Hites and Simonsick[28] for larger PAHs show the same trend. In calculations prior to the study of their methyl derivatives similar behavior has been found in the case of anthracene, phenanthrene, chrysene and benz[a]anthracene, see Table 10.

TABLE 10. $\Delta H^o{}_f$ values, kcal mol^{-1}.

Molecule	Expt.[27]	MNDO[28]	AM1[a]
Benzene[b]	+19.74 + 0.17	+21.20	+22.02
Naphthalene[b]	+35.92 ± 0.36	+38.13	+40.58
Anthracene	+55.19 ± 0.53	+58.57	+62.92
Phenanthrene	+49.59 ± 0.41	+55.39	+57.44
Chrysene	+64.48 ± 1.60	+74.67	+76.22
Benz[a]anthracene	+70.03 + 1.03	+74.55	+78.24

a. This work.

b. MINDO/3 values, 28.8 and 57.3 kcal mol^{-1} respectively.[20]

The values become progressively more positive than experiment the larger the ring system in accord with the following linear equations,

MNDO : $\Delta H_f^o(\text{calc.}) = -1.06 + 1.115 \ \Delta H_f^o(\text{Expt.})$

AM1 : $\Delta H_f^o(\text{calc.}) = -0.59 + 1.156 \ \Delta H_f^o(\text{Expt.})$

with correlation coefficients of 0.994 and 0.998 respectively.

Summary and Conclusion

Results very similar to those determined using ab initio calculations have been found with the AM1 model for various properties of toluene, naphthalene, 1-MN and 2-MN, notably

(i) the relative stability of the various methyl group rotamers of 1-MN and 2-MN,

(ii) the destabilization of the parent molecule brough about by the methyl group substitution,

(iii) the inward bowing of peri H-atoms.

(iv) the distortion of the ring in the methyl derivatives,

(v) the orientation of the methyl C-atom with respect to the ring bonding, and the orientation of the in-plane H-atom of the methyl group in the most stable rotamers of 1-MN and 2-MN.

(vi) the rotation dependence of the H-C bond length in the methyl group.

These similarities thus provide a good basis for the further use of the AM1 model to explore the origin of the specific effects of methyl group substitution on the carcinogenic activity of PAHs.

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