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Structure and Conformation of Dihydroaromatic Compounds. 1-Alkyl-1,4-dihydrobenzenes, 1-Alkyl-1,4-dihydronaphthalenes, and 9-Alkyl-9,10-dihydroanthracenes

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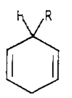
Abstract: The molecular geometries of 1-alkyl-1,4-dihydrobenzenes, 1-alkyl-1,4-dihydronaphthalenes, and 9-alkyl-9,10-dihydroanthracenes have been evaluated by empirical force-field calculations. Unlike the parent dihydroaromatics, the alkyl-substituted hydrocarbons all exhibit optimum geometries that are nonplanar, and the distortion from planarity increases with the steric bulk of the substituent. In contrast to earlier suggestions of a boat-to-boat equilibrium, all of the 1,4-dihydrobenzenes studied have a single energy minimum in which the substituent occupies a pseudoaxial position. Several of the dihydronaphthalene and dihydroanthracene derivatives exhibit two distinct nonpolar energy minima, but the pseudoaxial conformation is much more stable than the pseudoequatorial form in each case. Consequently, even these compounds can be considered to exist in a single conformation.

The preferred conformations of 1,4-cyclohexadienes (1,4-dihydrobenzenes) (**1**), 1,4-dihydronaphthalenes (**2**), and 9,10-dihydroanthracenes (**3**) have been the subject of considerable controversy, and a consistent interpretation of the many conflicting reports in the literature has only recently begun to emerge.[1,2] In addition to resolving fundamental questions about molecular structure, the biological importance of heterocyclic[3] and quinone[4] analogues of **1–3** demands a thorough understanding of the conformational behavior of these dihyroaromatic systems. We have previously reported a computational study of the parent hydrocarbons (**1a–3a**).[2a] We found that a planar geometry is preferred for all three compounds, although the energy required for distortion is small, particularly for **3a**, the nonplanar form of which is slightly more stable according to some of the computational methods. We now turn our attention to alkyl-substituted derivatives which are expected[2a] to behave somewhat differently.



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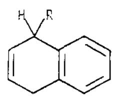

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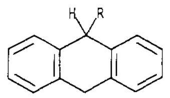

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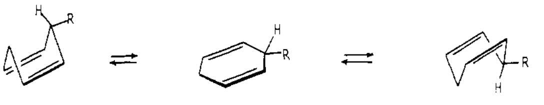
a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = i-C_3H_7
e, R = t-C_4H_9

In view of the flexible nature of these hydrocarbons (as illustrated for a substituted 1,4-cyclohexadiene in eq 1), we pose the following fundamental questions: Is the planar conformation an energy minimum? If the planar (or near-planar) conformation is instead a maximum on the multidimensional potential surface and represents a transition state between two equilibrating boat conformers, which boat is more stable?



(1)

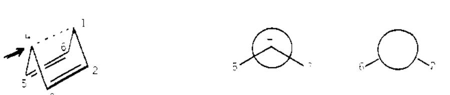
Our previous study[2a] demonstrated that empirical force-field calculations[5] accurately describe the conformational behavior of these systems, and we have consequently utilized this computational technique to evaluate a series of alkyl-substituted derivatives of **1–3**.

Methods

Empirical force-field calculations were carried out using Allinger's MMI and MMPI programs.[5b] For derivatives of **1** and **2** the C(2)–C(3)–C(4)–C(5) torsional angle was varied systematically, and all other geometric parameters were optimized for each torsional angle. In the case of the 9,10-dihydroanthracene and derivatives, the corresponding torsional angle of the dihydro ring is C(9a)–C(4a)–C(10)–C(10a) and this was varied accordingly.

Derivatives of **2** and **3** possess aromatic rings for which MMI does not include all of the necessary parameters. Calculations on these compounds were carried out in two ways: (1) with MMPI, and (2) following Allinger's[5b] suggestion and defining a new "aromatic" sp^2 carbon atom. All parameters for this atom type are identical with those of olefinic sp^2 carbons except the optimum C=C bond length (1.397 Å) and the C=C force constant (8.0667 mdyn/Å). The two methods of calculation gave energy profiles which were virtually identical.

The use of the dihedral driver option of the MMI program precludes imposition of rigorous symmetry on the structures being evaluated. Consequently, a description of **1–3** and their derivatives in terms of two intersecting planes is only an approximation, since the two "halves" of the molecule are not strictly planar. We have therefore defined a "folding angle", α, which accurately describes the geometries of the structures we reported here. The folding angle is defined as the arithmetic mean of two dihedral angles about a line joining the saturated carbon atoms as illustrated for 1,4-cyclohexadiene (**1**).[6] Thus a planar structure would have α = 180°. The deviations from C_{2v} symmetry are most pronounced for small values of α, i.e., for highly puckered rings, but even then



$$\alpha = [(5)-(4)-(1)-(3) + (6)-(4)-(1)-(2)]/2$$

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Table I. Optimized Structures of 1-Substituted 1,4-Dihydrobenzenes[a, b]

compd	R	folding angle, α (deg)	strain energy (kcal/mol)
1a	H	180	−1.6
1b	CH_3	174	−0.7
1c	C_2H_5	173	−0.7
1d	*i*-C_3H_7	169	0.1
1e	*t*-C_4H_9	160	1.8
1f	C_6H_5	176	*c*

[a] Complete geometry optimizations with MMI.[6] [b] The preferred orientation of the substituent is axial in each case. [c] Not calculated; MMI does not contain the necessary heat of formation parameters for aromatic compounds.

the individual dihedral angles are all within ±5° of the average of the two.

Results and Discussion

1,4-Dihydrobenzenes. The 1,4-cyclohexadiene ring was for many years generally considered to be boat-shaped[7] despite a vibrational spectral analysis in 1949 suggesting a planar structure.[8] Although subsequent reports involving Raman and infrared analysis,[9-11] electron diffraction,[12] NMR,[13] and force-field and molecular orbital calculations[14] also supported a planar conformation, there were conflicting reports involving electron diffraction[15] and NMR,[16] as well as semiempirical molecular orbital calculations,[17] that supported a boat-shaped geometry. The use of lanthanide shift reagents ultimately provided a complete NMR analysis of simple 1,4-cyclohexadiene derivatives,[18,19] indicating planar or nearly planar structures. Moreover, it appears that all existing NMR data can now be rationalized[1] without discrepancies, including interpretation of the homoallylic coupling constants which has been a matter of debate.[19-21] The report by Oberhammer and Bauer[15] constituted the major evidence against a planar structure, but their conclusion was based on an erroneous interpretation of the experimental data.[2b,5a] The conformation of 1,4-cyclohexadiene itself must closely correspond to the parabolic potential energy curve involving wide amplitude vibrations around the planar form as described by Laane and Lord[11] and supported by the force-field calculations of Allinger and Sprague.[14a]

Our own extensive molecular mechanics and molecular orbital calculations[2a] as well as molecualr orbital calculations by Boggs[2b] and Radom[2c] have confirmed this behavior for the parent compound, **1a**, but what of substituted dihydrobenzenes, **1b–e**? The introduction of a single substituent at the 1 position of a 1,4-dihydrobenzene reduces the symmetry of the molecule, and a planar conformation with $\alpha = 180°$ is no longer expected to be an energy minimum. This expectation is confirmed by the empirical force-field calculations (Table I), where the distortion from planarity increases with the steric bulk of the substituent. While the optimum geometry for **1b–e** is nonplanar in each case, we are reluctant to describe these structures as "boats" because the distortions are small. Even the *tert*-butyl derivative ($\alpha = 160°$) is bent by only 20° whereas Dreiding models of the dihydroaromatics exhibit distortions about twice as large ($\alpha = 145°$). Moreover, **1a–e** each exhibit a *single energy minimum*. Hence the boat–boat equilibrium of eq 1 does not describe the behavior of this system. The energy profile for strain energy vs. folding angle of 1-methyl-1,4-dihydrobenzene is typical and is shown in Figure 1 together with the energy profile for the parent compound **1a**. Figure 1 clearly shows that the major effect of substitution at the 1 position is to skew the energy profile slightly relative to that of **1a**. The energy minimum for **1b** is at 174° rather than 180°, but the curves are very similar in other respects.

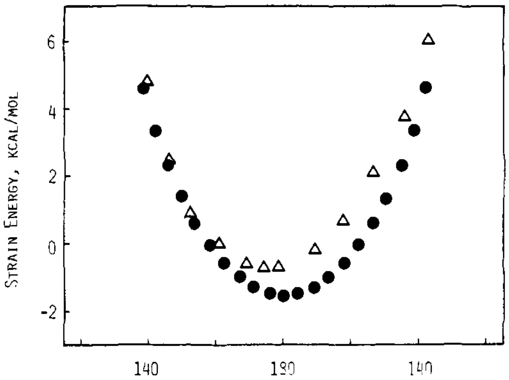
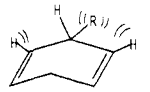


Figure 1. Energy vs. folding angle for 1,4-dihydrobenzene (**1a**, circles) and 1-methyl-1,4-dihydrobenzene (**1b**, triangles).

One major consequence of these calculations is the demonstration that a bulky substituent in a nonplanar conformation preferentially occupies the *pseudoaxial* position. There is no energy minimum for conformations in which the substituent is pseudoequatorial even though it has long been assumed that the equatorial position would be the favored location for substituents. This original suggestion was made on the basis of space-filling models,[16b] and appears to have been accepted without serious question for almost 10 years. This erroneous interpretation was almost certainly aided by the behavior of Dreiding models (which exhibit a clear preference for nonplanar geometries for **1–3**) and by analogy with cyclohexane derivatives. Unfortunately such comparisons are invalid and misleading. Dreiding models reflect only angle strain, whereas the conformations of the dihyroaromatics are determined by the interplay of angle strain, torsional effects, and nonbonded interactions.[2] The preferred equatorial conformations of substituted cyclohexane reflect a decrease in the unfavorable 1,3-diaxial interactions of the axial conformer. In contrast, nonbonded interactions in the dihydroaromatic series are minimized in the axial conformation and maximized in the equatorial conformation, where the substituent is eclipsed with the adjacent vinyl hydrogen.



The calculations of **1a–f** fully support our interpretation. In each instance the preference for a nonplanar conformation can be viewed as a destabilization of the planar form resulting from steric interactions between the substituent and the adjacent vinyl groups. These nonbonded interactions are alleviated by distortion from planarity, and this in turn causes an increase in angle strain. Increasing steric bulk of the substituent results in a monotonic change in folding angle along the series **1a–e** and a corresponding change in strain energy (Table I). Introduction of an alkyl substituent at the 1 position of 1,4-dihydrobenzene therefore leads to several changes in the energy profile (Figure 1). The optimum structure is no longer planar, and the strain energy of this structure is greater than for the unsubstituted compound (**1a**). An even

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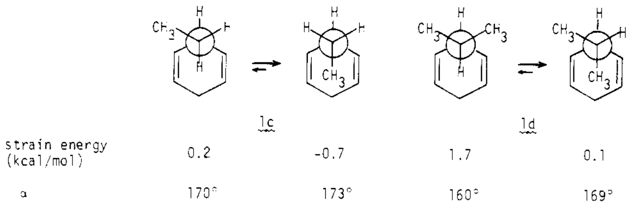
Table II. Optimized Structures of 1-Substituted 1,4-Dihydronaphthalenes[a, b]

compd	R	folding angle, α (deg)	rel strain energy[c] (kcal/mol)
2a	H	180	0
2b	CH_3	164	1.3
2e	t-C_4H_9	149	4.3
		132[d]	13.6[d]

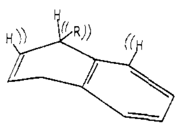
[a] Complete geometry optimizations with MMI.[6] [b] Preferred orientation of the substituent is axial in each case. [c] Relative to the planar form of 2a. The absolute strain energy is not calculated because MMI does not contain the necessary heat of formation parameters for aromatic compounds. [d] The substituent is equatorial.

greater increase in strain energy is seen for those geometries in which the methyl group has an equatorial orientation. For geometries which are distorted from the optimum geometry but with an axial methyl group, the curve for **1b** becomes nearly superimposable on that for **1a**.

The ethyl and isopropyl derivatives **1c** and **1d** provide further evidence that the major structural feature governing the nonplanar distortion is the interaction of the alkyl substituent with the adjacent vinyl groups (allylic strain[21]). Both of these compounds have two nonequivalent rotamers of the alkyl substituent, each of which is an energy minimum. The more stable rotamer for each compound (which is entered in Table I) is that in which interactions with the vinyl CH are minimized. Both the strain energy and the folding angle appear to be determined almost entirely by the groups which are gauche to vinyl CH. For example, the less stable (C_s symmetry) rotamer of **1d** is folded to the same extent as the *tert*-butyl derivative, **1e**, and also has nearly the same strain energy. The same comparison can be made between the more stable rotamer of **1c** and the methyl derivative **1a**, and between the two *unsymmetrical* rotamers of **1c** and **1d**. Finally, the small distortion from planarity of the phenyl derivative reinforces these arguments. Although the phenyl group has a greater steric bulk than an isopropyl group in cyclohexyl systems,[22] the phenyl derivative **1f** exhibits a smaller distortion than any of the alkyl derivatives **1b–e**. By adopting a perpendicular geometry it is possible for **1f** to minimize the unfavorable interactions between the phenyl ring and vinyl CH groups.



1,4-Dihydronaphthalenes. We have previously shown that the optimum geometry of the unsubstituted dihydronaphthalene, **2a**, is planar.[2a] However, the results obtained with 1,4-dihydrobenzene derivatives strongly suggested that similar results would be obtained in the dihydronaphthalene series. Moreover, the unfavorable nonbonded interactions of the alkyl substituent in **2** are expected to be even more severe than in **1**. When an alkyl substituent is in a pseudoequatorial arrangement,. the nonbonded interactions involve the vinyl hydrogen on one side and the aromatic ring with its peri hydrogen on the other side. The calculations for **2a**, **2b**, and **2e** (Table II) substantiate these expectations.



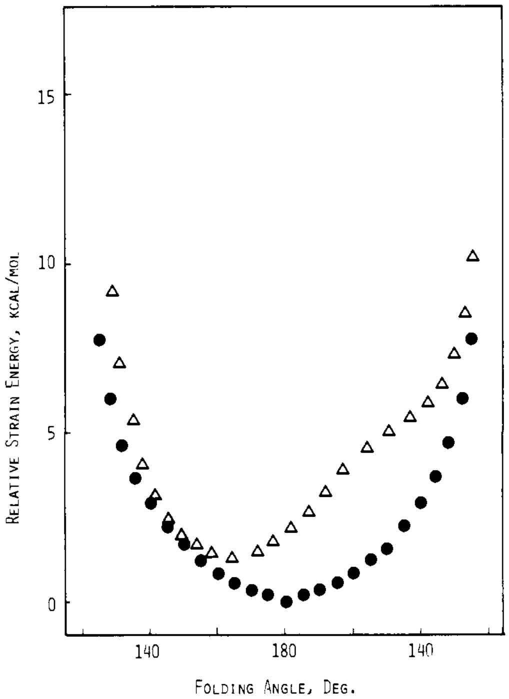


Figure 2. Energy vs. folding angle for 1,4-dihydronaphthalene (**2a**, circles) and 1-methyl-1,4-dihydronaphthalene (**2b**, triangles).

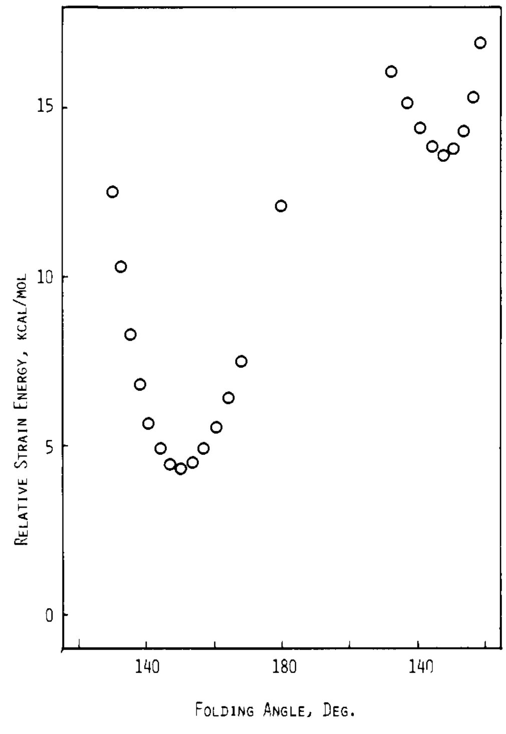


Figure 3. Energy vs. folding angle for 1-*tert*-butyl-1,4-dihydronaphthalene (**2e**).

The change in strain energy along the series **2a–e** is greater than for **1a–e**, and the distortions from planarity are also greater for derivatives of **2**.

The energy profile of the methyl derivative, **2b**, is shown in Figure 2 together with that of the parent compound, **2a**. As in the case of the dihydrobenzenes, the major effect of methyl substitution is to increase the energy of those geometries where the substituent is pseudoequatorial. Thus the portion of the curve for **2b** where the methyl group is axial is nearly superimposed on the curve for **2a**. Only when the substituent becomes equatorial does the relative strain energy differ substantially from that of **2a**.

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Table III. Optimized Structures of 9-Substituted 9,10-Dihydroanthracenes[a,b]

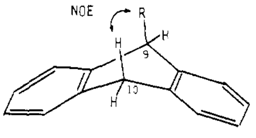
compd	R	folding angle, α (deg)	rel strain energy[c] (kcal/mol)
3a	H	180	0
3b	CH_3	148	0.9
		131[d]	4.6[d]
3c	$t\text{-}C_4H_9$	143	5.2
		126[d]	15.0[d]

[a] Complete geometry optimizations with MMI.[6] [b] Preferred orientation of the substituent is axial in each case. [c] Relative to the planar form of 3a. The absolute strain energy is not calculated because MMI does not contain the necessary heat of formation parameters for aromatic compounds. [d] The substituent is equatorial.

The *tert*-butyl derivative, **2e**, exhibits a new feature in its energy profile (Figure 3). Unlike the dihydrobenzenes, **1a–f**, and the other dihydronaphthalenes, **2a** and **2b**, this compound has two distinct energy minima. From a theoretical point of view this is a boat-to-boat equilibrium, but in practice it is a moot point because the energy minima differ by more than 9 kcal/mol and fewer than one out of 10^6 molecules would exist in the pseudoequatorial conformation at room temperature. As in the case of the dihydrobenzenes, the dihydronaphthalenes **2b** and **2e** can be effectively described as existing in a single conformation with the substituent in the psuedoxial orientation. Our results are also in agreement with previous experimental conclusions that many derivatives of **2** exist as a "flattened boat",[23] and that greater distortions from planarity are found for dihydronaphthalenes with a single large substituent.[24]

9,10-Dihydroanthracenes. The energy of the parent dihydroanthracene, **3a**, is extremely insensitive to the folding angle.[2a] The calculated energy minimum with MMI is a planar structure, although a folding angle of 145° is found in the solid state.[25] We anticipated that alkyl substitution would substantially alter the situation because nonbonded interactions involve two aromatic rings. Indeed these nonbonded effects strongly destabilize the planar form, resulting in folded structures that are preferred for both **3b** and **3e** (Table III). As was observed with **2e**, both of these substituted dihydroanthracenes show two energy minima (Figure 3). Once again the energy difference between the two forms is quite large; e.g., the minima for **3b** differ by 3.7 kcal/mol. At room temperature the pseudoequatorial form would not be experimentally detectable by NMR. Consequently these molecules are still best described as existing in a single conformation, where substituents can cause large distortions from planarity.

How do these computational results compare with the substantial body of experimental work that has been carried out for 9,10-dihydroanthracenes? Most of the experimental work has been interpreted in terms of a boat-to-boat equilibrium corresponding to eq 1, and the evidence for this interpretation is threefold.[1] First, the X-ray crystallographic structure of the parent compound, **3a**, is nonplanar, and this would strongly suggest an equilibrium between two equivalent structures in solution. The failure to detect the individual confomers by low-temperature NMR[26] was interpreted to indicate a very small energy barrier for conformational interconversion. Second, the observation of a nuclear Overhauser effect (NOE) for substituted derivatives such as **3e** demonstrated the presence of at least some of the nonplanar conformer in which the alkyl group is pseudoaxial.[27] In view of other evidence that pseudoequatorial conformer would be more stable,[1] this pseudoaxial form was considered to be part of a conformational equilibrium. Third, evaluation of homoallylic coupling constants (i.e., between the protons on the 9 and 10 positions)[27,28] was judged to indicate a mixture of two conformers for several derivatives of **3**.



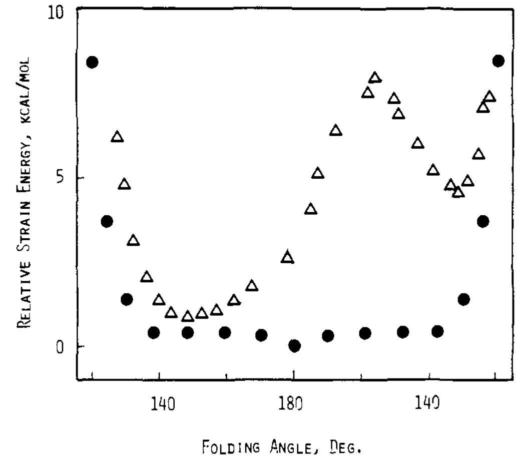
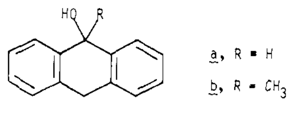


Figure 4. Energy vs. folding angle for 9,10-dihydroanthracene (**3a**, circles) and 9-methyl-9,10-dihydroanthracene (**3e**, triangles).

None of these experimental results are in conflict with our calculations. The extremely flat potential energy surface found[2a] for **3a** indicates that even rather small crystal packing forces could result in the nonpolar structure observed in the solid state. This in no way argues against an optimum planar geometry in solution. The NMR measurements[26–28] of **3** and its derivatives are also consistent with a single conformation where a substituent is pseudoaxial. Quantitative correlation between molecular geometry and NOE or coupling constants is difficult, particularly in the absence of a reliable structure model. Changes in NOE or coupling constants for different derivatives of **3** were previously interpreted in terms of shifts in a boat-to-boat equilibrium. Our calculations demonstrate that no single "boat" geometry exists for different derivatives of 9,10-dihydroanthracene. The changes in NOE and homoallylic coupling constants therefore reflect a systematic variation in the molecular structure of a single conformer in which the substituent has a pseudoaxial orientation.

The preference for a substituent to occupy a pseudoaxial position is dramatically illustrated by the recent report of Miller and Marhevka[29] who found that the acid-catalyzed ionization of the secondary alcohol **4a** proceeds nearly twice as fast as reaction of the tertiary alcohol **4b**. As suggested by these authors[29] this highly unusual reactivity pattern (secondary faster than tertiary) undoubtedly reflects different conformations for **4a** (hydroxyl pseudoaxial) and **4b** (methyl pseudoaxial). The pseudoaxial methyl group in **4b** requires a pseudoequatorial hydroxyl group, and this precludes effective orbital overlap in the developing cation. The normally large rate enhancement (ca. 10^6) expected for methyl substitution at a cationic center[30] is therefore overwhelmed by



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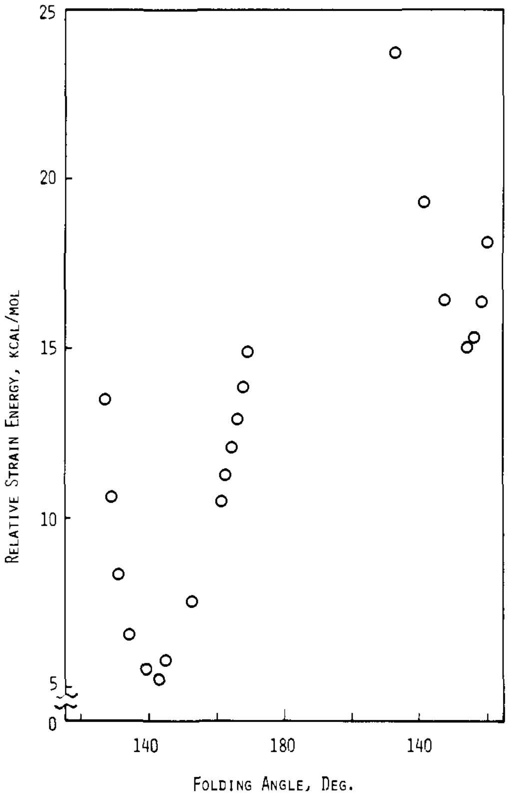

Figure 5. Energy vs. folding angle for 9-*tert*-butyl-9,10-dihydroanthracene (**3e**).

removal of the benzylic character at the transition state for ionization of **4b**.

Conclusions

The conformational behavior of the dihydroaromatic compounds **1**–**3** is unusual. All of the compounds we have studied can be classified as effectively existing in a single conformation, despite previous suggestions that an equilibrium analogous to eq 1 might be expected. Very little energy is required to substantially distort these structures from their minimum energy conformations, however, and rather large vibrational amplitudes should be expected. The parent compounds **1a**–**3a** have optimum geometries which are planar, and distortion becomes progressively easier proceeding from **1a** to **3a**.[2a] Indeed the energy of **3a** is virtually unchanged for folding angles in the range of 135–180°.

The ease of distortion is not greatly affected by 1-alkyl substitution for the dihydrobenzenes, and the cost of a 15° folding distortion from the optimum structure is about 0.6 kcal/mol for both **1a** and **1b**. Alkyl substitution has an increasingly large effect on the benzannulated derivatives, **2** and **3**, however. A 15° distortion requires only 0.5 kcal/mol for **2a**, and comparable folding for the methyl derivative requires 0.5 and 0.7 kcal depending on the direction. The energy for 15° distortion of the parent dihydroanthracene (**3a**) is further decreased to less than 0.4 kcal/mol, but the methyl derivative requires 0.9 or 2.5 kcal depending on the direction of the distortion. These effects can be seen graphically by comparison of the steepness of the various curves in Figures 1–5. Clearly alkyl substitution in the dihydroanthracenes, and to a lesser extent in the dihydronaphthalenes and dihydrobenzenes, results in a much steeper energy well. This in turn should greatly reduce the vibrational amplitudes and result in experimental behavior which is much more consistent with a single, well-defined molecular geometry.

In all three of the dihydroaromatic systems, substitution at one of the reduced positions distorts the optimum geometry from a planar conformation to one in which the substituent occupies an axial position. The preferred axial orientation results largely from minimizing nonbonded interactions between the substituent and the adjacent vinyl or peri hydrogens. These steric interactions are greater in the derivatives of **2** and **3**. Hence the energy profiles are much steeper for derivatives of **2** and **3** than for **1**. Similarly, the nonplanar distortion of the optimum geometry increases from **1** to **2** to **3** with any particular alkyl substituent. For any one of the dihydroaromatics **1**–**3** an increase in steric bulk of the substituent results in greater distortion from planarity. The calculations we report here provide a uniform and consistent explanation for the structures and conformational behavior of dihydroaromatics compounds. Moreover, this explanation is in agreement with all of the available experimental information for monosubstituted derivatives of **1**–**3**.

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Registry No. **1a**, 628-41-1; **1b**, 2050-31-9; **1c**, 81157-94-0; **1d**, 81157-95-1; **1e**, 5178-95-0; **1f**, 4794-05-2; **2a**, 612-17-9; **2b**, 21564-70-5; **2e**, 65482-09-9; **3a**, 613-31-0; **3b**, 17239-99-5; **3e**, 13387-48-9.