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Structure and Conformation of Dihydro Aromatic Compounds. 3. Cis- and Trans-Disubstituted 1,4-Dihydrobenzenes, 1,4-Dihydronaphthalenes, and 9,10-Dihydroanthracenes

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Abstract: The conformational effects of cis and trans substituents on 1,4-dihydrobenzene, 1,4-dihydronaphthalene, and 9,10-dihydroanthracene were investigated with an empirical force field. It is found that steric repulsions between the substituents and the ortho ring hydrogens (peri interactions) lead to complex structural behavior. The possibility of chair-like structures and the interconversion between chair and boat forms is discussed.

The preferred geometries of 1,4-dihydrobenzene (**1** = DHB), 1,4-dihydronaphthalene (**2** = DHN), and 9,10-dihydroanthracene (**3** = DHA), and their derivatives, have been the source of many investigations and the center of considerable controversy.[1] The key structural features are (1) planar vs. boat shape geometries for the dihydro aromatic ring which could, of course, in the latter case involve boat-to-boat inversion processes, and (2) pseudoaxial vs. pseudoequatorial location of substituents. Rotational preferences of substituents has also attracted some interest, but this has been largely confined to system **3**.[1]


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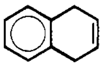
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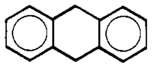
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Although Dreiding models strongly suggest the boat conformation for **1–3**, vibrational spectroscopy[2] has indicated a planar structure for **1**. While conflicting electron diffraction studies exist,[3] the most recent experimental results, including NMR,[4] do seem to confirm the planar structure.

A boat structure has been assumed for **3** due, in part, to the fact that X-ray analysis indicates a boat form in the solid state[5] with a "folding angle" of 145°. More recently, solid-state ^{13}C NMR data have also been provided in support of boat conformations.[6] In solution, however, the anticipated boat-to-boat interconversion has never been demonstrated by dynamic NMR approaches, and this has usually been attributed to a very low barrier to interconversion.[7] The preferred location of substituents was also the subject of debate, but NMR experiments employing nuclear Overhauser enhancements have established the pseudoaxial position as the geometry of choice.[1]

The 1,4-dihydronaphthalene system (**2**) has received the least amount of attention. NMR data have suggested a boat conformation for monosubstituted derivatives, but with less puckering than in the 9,10-dihydroanthracene series.[1] A greater tendency for planarity with **2** is also supported by the suggestion that *trans*-1,4-di-*tert*-butyl-1,4-dihydronaphthalene is flat (or nearly so).[8] Thus, experimental evidence suggests a trend toward planarity in the series **3** < **2** < **1**, and planar structures have not generally been suggested for **3** or its derivatives.

Previous studies of **1** involving ab initio[9] and semiempirical,[10,11] molecular orbital methods as well as molecular mechanics[10,12] calculations have all indicated an energy minimum corresponding to the planar structure. (Molecular mechanics is a nonquantum mechanical method of computing structures, energies, vibrational spectra, and a limited number of physical properties of molecules. The calculations, based on empirical parameterization of intramolecular interactions, are several orders of magnitude faster than quantum mechanical calculations and are extraordinarily accurate.[22]) However, the potential energy surface is such that only ca. 1 kcal/mol is required for a 20° distortion from planarity (i.e., folding angle 180° to 160°). Similarly, MMI[23] calculations with **2** and **3** (as well as MINDO/3 for 3) also indicate planar minima, but with even flatter potential wells (see Figure 1). Hence **3** is calculated to have large puckering amplitudes at room temperature since the calculated difference between planar (180°) and puckered (160°) forms is only 0.4 kcal/mol.

A subsequent MMI/MMPI force field study on monosubstituted derivatives of **1–3** shows little difference in the energy profile for **1** except that the minima are skewed away from 180° according to substituent size.[10b] For example, 1-methyl-1,4-dihydrobenzene shows a folding angle of 174°, whereas it is 160° for 1-*tert*-butyl-1,4-dihydrobenzene. Both exhibit a pseudoaxial preference for the substituent. As might be expected, **2** and **3** have larger folding angles due to increased peri interactions. Large substituents on **2**, and all substituents on **3**, show minima for both pseudoaxial and pseudoequatorial geometries. In most cases the pseudoaxial geometry is sufficiently more stable so as to render the other isomer experimentally undetectable (4–10-kcal/mol difference). The reason for this can be understood by considering

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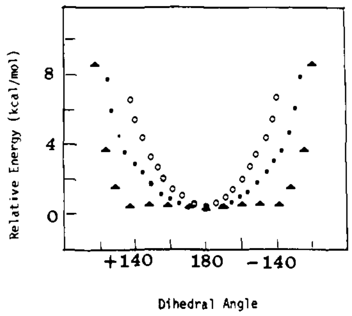


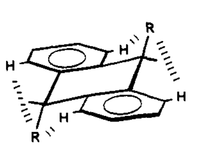
Figure 1. Relative total energy computed with the Allinger MMPI force field as a function of ring pucker: open circles, 1,4-dihydrobenzene; filled circles, 1,4-dihydronaphthalene; triangles, 9,10-dihydroanthracene.

a mechanical model of 9-methyl-9,10-dihydroanthracene. With the model in the boat conformation (mechanical models always "incorrectly" prefer the boat form for **1–3**)[10] such that the methyl group is in the pseudoaxial position, the methyl–peri interactions are minimized. During ring flipping to the other boat form, one finds a steady increase in steric interactions as the Me is transformed from a pseudoaxial to a pseudoequatorial position. In the pseudoequatorial position (folding angle 145°) we have maximized the methyl–peri interactions. If we were to further compress the folding angle of the pseudoequatorial conformer to 130°, the methyl–peri interactions are decreased but the ring strain from excessive puckering offsets this effect and the energy again increases. Consequently a double minimum exists with the pseudoequatorial 9-methyl-9,10-dihydroanthracene 3.7 kcal/mol less stable than the pseudoaxial form. Experimental detection of the equatorial conformation is therefore not expected.

In an earlier paper[10a] we pointed out that mechanical models must be used with caution in these systems because they improperly treat the inner ring angle deformations and ultimately provide misleading information about ring puckering. Any mechanical model that maintains rigid bond angles and bond lengths, e.g., Dreiding models, is especially bad. Computational models are superior in this regard. In this paper we further explore the conformational properties of disubstituted dihydroaromatics.

Results and Discussion

Traditional views on the stereochemical preferences of disubstituted dihydroaromatics would include planar forms (particularly for DHB's) and boat-to-boat interconversions (particularly for DHA's).[1] Moreover, in the latter case with cis isomers, it has been held that such an equilibrium lies heavily to the side with both substituents pseudoaxial. In DHA's especially, important experimental evidence has been an evaluation of the long range proton NMR coupling constants ($J_{H_9H_{10}}$) and nuclear Overhauser enhancements from H_4 to H_{10} and R_{10} = *t*-Bu to H_9, as well as crystal structures for *cis*-9-Me-10-EtDHA[13] and *trans*-9-Me-10-i-PrDHA.[14] Our results (MMPI and in some cases MM2 calculations) show that the conformational properties of DHB's, DHN's, and DHA's may be far more complex than previously believed (illustrated in Figure 3). The origin of this greater complexity is due chiefly to nonbonded interactions between the alkyl substituents and the peri hydrogens. This interaction increases, of course, in the series DHB < DHN < DHA as well as Me < *t*-Bu. Two significant consequences of these peri interactions are illustrated with **4** and **5**. We may view **4** as inherently planar but where nonbonded interactions produce a distortion into a chair-like conformation. Interestingly, although considerable controversy has existed concerning the stereochemistry of these dihydrobenzenes, chair structures have never been seriously proposed. The only experimental evidence for such a deformation is an X-ray structure of *trans*-bis(trimethylsilyl)-9,10-dihydroanthracene.[15] Structure **5** illustrates another way in which these peri interactions can be avoided. An unusually high degree of ring folding will result from the R group sterically interacting with (and "passing by") the ortho hydrogens. Such a distorted boat was calculated as a minimum in several cases with the trans isomers (vida infra). We contend that the available NMR evidence is not inconsistent with the structures discussed herein. Boat-to-boat interconversions of highly folded structures such as **5** support the observation of substantial nuclear Overhauser effects from R_{10} to H_9. A boat-to-boat inversion is required, otherwise R_9 and R_{10} (for trans isomers with $R_9 = R_{10}$) are not NMR equivalent. This is, of course, not the case for **4** regardless of any equilibration processes.



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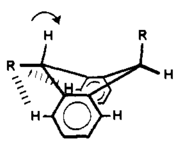

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An additional and final point of interest appears in the rotational orientation of *tert*-butyl substituents. The ss rotation (see Figure

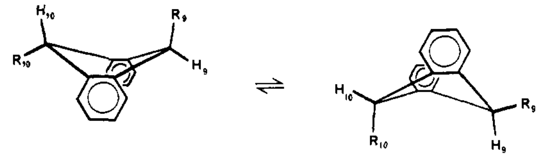

Figure 2. Presumed boat-to-boat inversion for 9,10-dihydroanthracenes.

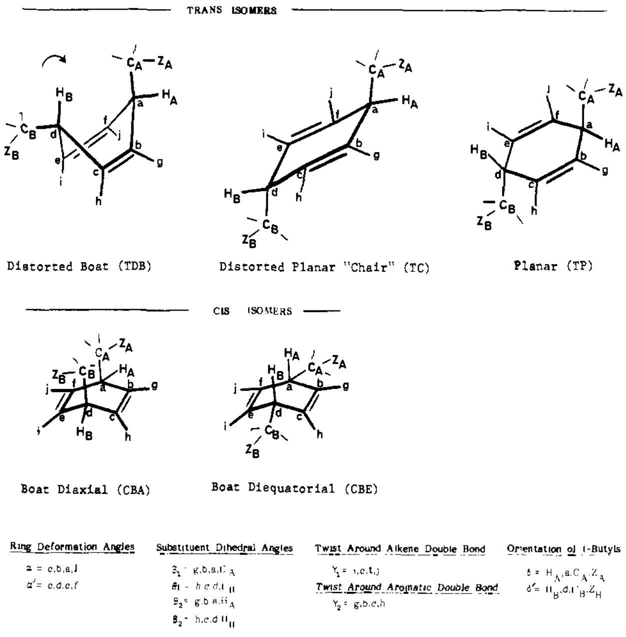

Figure 3. Conformations of *cis*- and *trans*-dimethyl- and di-*tert*-butyldihydrobenzenes (DHB), -dihydronaphthalenes (DHN), and -dihydroanthracenes (DHA). For DHN, e–f is the olefinic double bond.

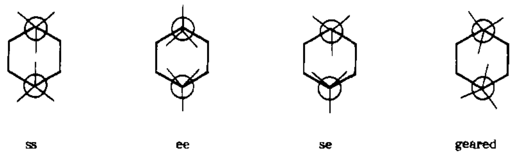

Figure 4. Orientation of the *tert*-butyl groups in the DHA system. The nomenclature we adopt refers to the Newman projection of the *tert*-butyl groups on the six-membered ring; ss = staggered-staggered, ee = eclipsed-eclipsed, se = staggered-eclipsed.

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Table I. MMPI Calculations for *cis*- and *trans*-Dimethyl- and Di-*tert*-butyl-1,4-dihydrobenzenes, -1,4-dihydronaphthalenes, and -9,10-dihydroanthracenes[a]

Compound[b]	Conformational Minimum[c] (folding angle-deg)[d]	--Ring Deformation-- angles-deg[e]		--Substituent Dihedral-- angles-deg[e]				--Double Bond-- Twist Angles-deg[f]		--Orientation of-- t-Bu Groups-deg		Total Steric Energy (kcal/mol)
		α	α'	β_1	β_1'	β_2	β_2'	γ_1	γ_2	δ	δ	
Cis-DiMeDHB	CBA (170)	10	10	64	64	-57	-57	---	---	---	---	4.5
Cis-Di-*t*-BuDHB	CBE (172)	8	8	-58	-58	60	59	---	---	176	176	13.8
Cis-DiMeDHN	CBA (160)	20	20	73	74	-47	-47	---	---	---	---	11.1
Cis-Di-*t*-BuDHN	CBA (157)	23	24	68	71	-50	-48	---	---	16	15	26.7
Cis-DiMeDHA	CBA (155)	25	25	77	77	-43	-43	---	---	---	---	17.3
Cis-DiMeDHA	CBE (134)	46	46	2	2	114	114	---	---	---	---	24.7
Cis-Di-*t*-BuDHA	CBA (153)	27	27	69	70	-46	-45	---	---	13	12	34.8
Trans-DiMeDHB	TP	1	0	57	-57	-63	63	1.0	1.0	---	---	4.8
Trans-Di-*t*-BuDHB	TP[g]	8	-2	60	-53	-60	67	3.1	3.0	178	178	15.0
Trans-DiMeDHN	TP[g]	3	-4	61	-60	-60	61	0	3.0	---	---	12.9
Trans-Di-*t*-BuDHN	TDB (140)	44	37	81	9	-38	118	---	---	0	180	31.6
Trans-Di-*t*-BuDHN	TC	15	-8	72	-70	50	-53	17	9	180	180	30.2
Trans-DiMeDHA	TP[g]	8	-6	64	-63	-56	57	3	3	---	---	21.5
		[4]	[-3]	[61]	[-61]	[-57]	[58]	[2]	[2]			[3.2]
Trans-DiMeDHA	TDB (142)	36	41	87	5	-31	110	---	---	---	---	21.7
		[37]	[39]	[92]	[11]	[-27]	[105]					[2.4]
Trans-Di-*t*-BuDHA	TC	21	-19	77	-75	-44	45	13	13	180	180	43.9
		[14]	[-13]	[72]	[-72]	[-47]	[48]	[8]	[8]	[180]	[180]	[30.4]
Trans-Di-*t*-BuDHA	TDB (136)	39	50	83	22	-34	128	---	---	0	180	39.9
		[40]	[46]	[88]	[15]	[-30]	[122]	---	---	[0]	[180]	[23.4]

[a] Values in parentheses are MM2. [b] DHB = 1,4-dihydrobenzene; DHN = 1,4-dihydronaphthalene; DHA = 9,10-dihydroanthracene. [c] CBA = cis boat axial; CBE = cis boat equatorial; CP = cis planar; TDB = trans distorted boat; TP = trans planar, TC = trans chair (see Figure 3 for illustrations). [d] Represents the deviation from planarity (180°) of the central ring and is 180° − α (or the average when $\alpha \neq \alpha'$). [e] Angles measured in an upward fashion relative to the point of origin with orientation as shown in Figure 3 are taken as positive in sign. [f] See Figure 3 for orientations. In DHN, γ_1 represents twist around the olefinic double bond. [g] Categorized as planar, since deviation from planarity is small.

4 for nomenclature) appears to minimize peri interactions and is usually adopted in the absence of any transannular interference. (Transannular interactions refer to attractive or repulsive interactions of substituents located on opposite sides of a ring.) However, incorporation of a second *tert*-butyl group on the same side of the ring will cause a "gearing" effect of the two groups, whereas a hydrogen across the ring can "split" the methyls of a *tert*-butyl causing an ee geometry. Three of these four possibilities actually result as minima according to the calculations discussed below.

Cis-Disubstituted DHB's. The calculated folding angle (see Table I for data) for *cis*-DiMeDHB indicates a flattened boat with only a 4° increase in pucker as compared to the monomethyl derivative (174°). Since β_1 and β_1' are larger than β_2 and β_2', the methyl groups are both in the pseudoaxial position. Interestingly, *cis*-Di-*t*-BuDHB shows a slight pseudoequatorial preference for the *tert*-butyl groups indicating that transannular steric interactions may be important. It should be noted that the preferred orientation of large substituents in DHB's has been controversial,[16] but recent experimental results indicate that a single large substituent forces a modest deviation from planarity with the substituent pseudoaxial (NMR results with a dimethylcarbinol group),[17] whereas two large groups in a cis isomer produce a nearly planar ring with the groups very slightly pseudoequatorial (X-ray results with cis-phenyl and -trityl substituents).[18] Hence our MMPI calculations are in agreement with available experimental results. Rotational preferences also become important with *tert*-butyl groups, and in this case, δ and δ' are close to 180° indicating the ee arrangement as illustrated in Figure 4.

Cis-Disubstituted DHN's. As expected, *cis*-DiMeDHN and *cis*-Di-*t*-BuDHN show more ring folding, 160° and 157°, respectively, due to increased peri interactions from the ortho aryl hydrogens. This folding produces an additional steric problem with *cis*-Di-*t*-BuDHN, in that the *tert*-butyl groups are brought relatively close together. This results in a gearing of these substituents (Figure 4), with σ = 16° and σ' = 15°.

Cis-Disubstituted DHA's. *cis*-DiMeDHA presents an interesting case in that MMPI shows two minima: a diaxial boat and a diequatorial boat. With methyl substituents, continued folding of the diequatorial boat results in the methyls eventually passing the peri hydrogens leading to a decrease in energy. However, the calculations suggest a 7-kcal/mol difference in total steric energy between the two possible boat forms and so the diequatorial conformation is not expected to be observed. Not unexpectedly, *cis*-Di-*t*-BuDHA is highly folded (153°), and the *tert*-butyl groups are, once again, in a geared arrangement.

Trans-Disubstituted DHB's. Experimental results[1,8] have suggested that trans DHB's are probably planar particularly with identical or similar substituents. Our calculations confirm a planar geometry for *trans*-DiMeDHB, but *trans*-Di-*t*-BuDHB is beginning to show a chair-like distortion which becomes important for the DHN's and DHA's discussed below. The *tert*-butyl groups

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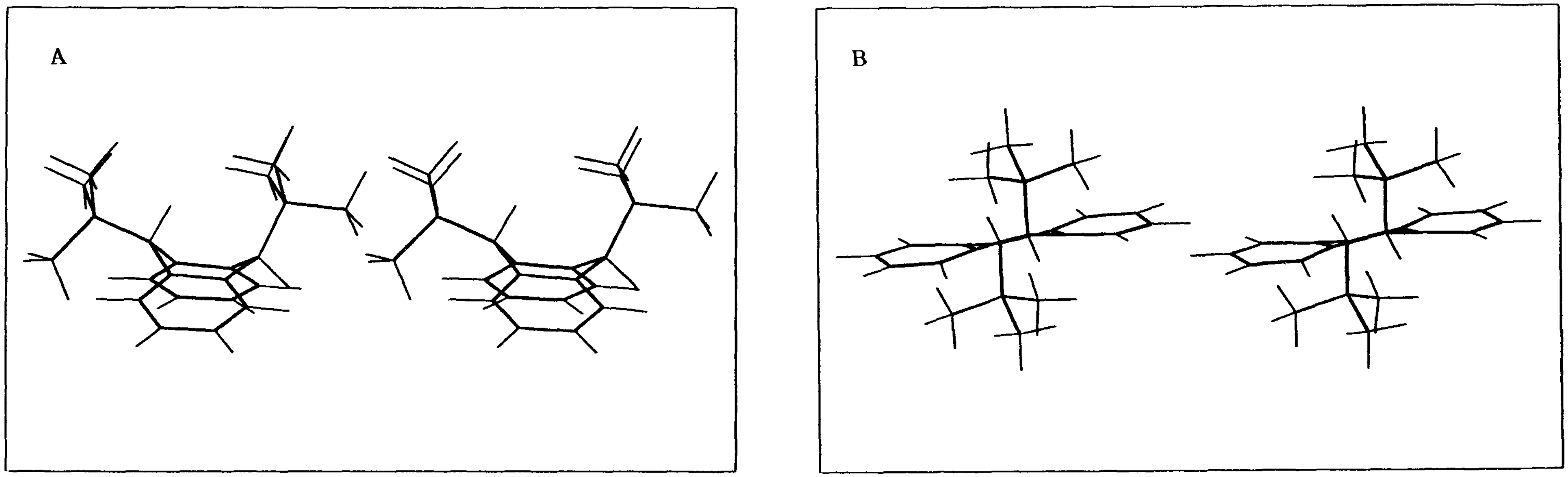

Figure 5. Stereoviews of *trans*-1,4-di-*tert*-butyl-1,4-dihydronaphthalene. A is the boat form and B is the chair form.

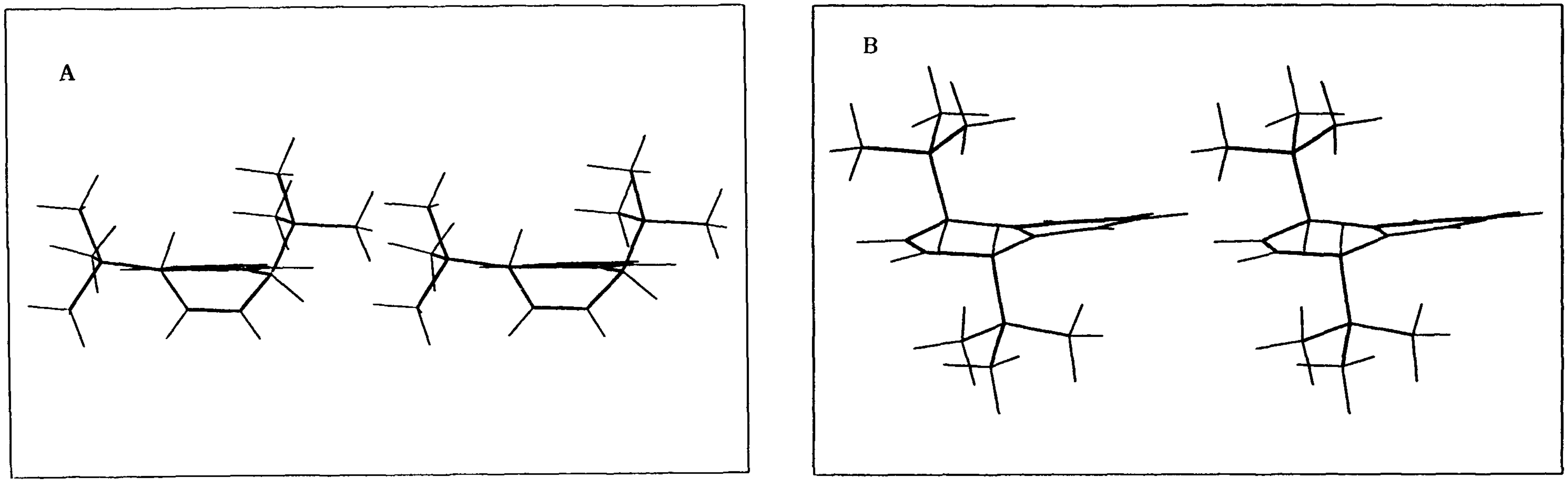

Figure 6. Stereoviews of *trans*-9,10-di-*tert*-butyl-9,10-dihydroanthracene. A is the boat form and B is the chair form.

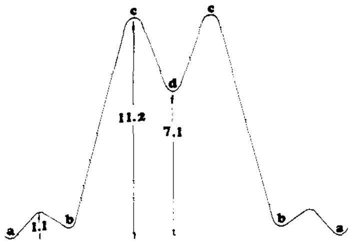

Figure 7. The MM2 reaction coordinate for boat-to-boat isomerization of *trans*-9,10-di-*tert*-butyldihydroanthracenes. Computed structures a–d are shown in Figure 8. Energies are in kcal/mol.

are oriented in the ee arrangement, which is the preferred rotational orientation in the absence of serious, transannular steric effects (cf. *cis*-DiMeDHB).

Trans-Disubstituted DHN's. *trans*-Di-*t*-BuDHN is especially interesting since the chair and distorted boat conformations are energetically different by less than 1.5 kcal/mol, and both conformations represent somewhat nonconventional structures for this ring system (see Figure 5 for stereoviews). In both cases, serious distortions that relieve steric interactions between the *tert*-butyl group and the peri hydrogens are evident. In the boat form the DHN is considerably folded (142°) with one end turned up allowing the pseudoequatorial *tert*-butyl to "pass" the ortho hydrogens. In the chair form similar steric interactions lead to twisting about the olefinic (17°) and aromatic (9°) double bonds.[19] Furthermore, the orientation of the *tert*-butyl groups is different for these conformational isomers. In the flattened state, the groups are ee minimizing the interaction with the peri positions. In the distorted boat, hydrogen H_B is forced into the pseudoaxial *tert*-butyl group across the ring and so "splits" the methyl producing an se relationship. Analogous geometries arising from similar transannular interactions have been observed experimentally with isopropyl groups in the DHA series.[20,21]

Trans-Disubstituted DHA's. Both MMPI and MM2 calculations suggest two conformations of nearly equal energy for *trans*-DiMeDHA. The planar structure shows only a slight chair-like distortion by MMPI, and even less so by MM2. This is expected since the origin of the distortion is van der Waals repulsions which MMPI overestimates. The boat conformation shows a considerable distortion and the phenomenon of a methyl group "passing by" the peri interactions appears significant for both MMPI and MM2.

As expected, the *trans*-Di-*t*-BuDHA provides the most distorted structures in both the chair and boat form (see Figure 6). In the boat form, two stable conformations were found. The lowest energy structure possessed staggered equatorial and eclipsed axial *tert*-butyl groups while the 0.3 kcal mol^{-1} less stable boat conformer had both *tert*-butyl groups staggered. The transition state for axial *tert*-butyl rotation between these boat forms is 1.1 kcal mol^{-1} above the most stable boat conformation.

The chair conformation was found to be 7.1 kcal mol^{-1} (MM2) and 4.0 kcal mol^{-1} (MMPI) higher in energy than the se boat conformation. Although the symmetry of the chair form (C_{2h}) requires the mean planes of the aryl rings to be coplanar, there is considerable twisting of each ring (endocyclic torsion angles up to 7.7° by MM2 and 13° by MMPI). The central ring is a flattened chair with torsion angles near ±15°. The *tert*-butyl groups in the chair conformer are both staggered. The staggered/eclipsed chair conformation represents the transition state for *tert*-butyl rotation among chair topomers; the barrier is only 0.5 kcal mol^{-1}.

Interconversion Pathways

The geometric constraints of trans-disubstituted DHN's and DHA's are such that two boat forms and two chair forms exist. The dynamics of boat-to-boat, chair-to-chair, and boat-to-chair interconversions have never been considered and for this reason we decided to explore the minimum energy reaction pathway for these isomerizations. We report here our initial findings of the boat-to-boat interconversion of *trans*-9,10-di-*tert*-butyldihydroanthracene.

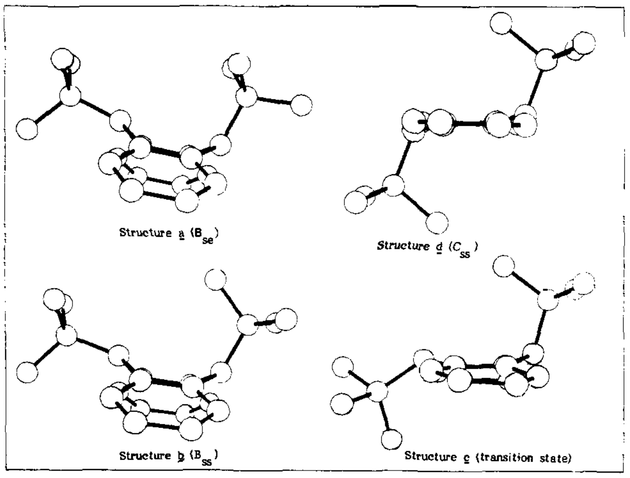

Figure 8. MM2 computed conformations of structures a–d along the reaction coordinate in Figure 7. The computer symmetries are the following: a (C_S); b (C_S); c (C_1); d (C_{2h}).

The interconversion of topomeric boat forms of 9,10-Di-*t*-Bu-DHA is unexpected. Dreiding models suggest that all DHA's undergo a boat-to-boat inversion through a planar transition state. The boat-to-boat interconversion pathway based on computer models is more complex (see Figure 7). We find that the most stable boat conformation (a, 23.40 kcal mol^{-1}) must first rotate the axial *tert*-butyl group to the eclipsed conformation (b, 23.68 kcal mol^{-1}, E_a = 1.09 kcal mol^{-1}). From this conformation, the tricyclic system begins to flatten. The asymmetric transition state (c, E_a = 11.16 kcal mol^{-1}) is reached just before the C_{2h} chair conformation is attained (d, 30.46 kcal mol^{-1}). Continuation of the interconversion process is isometric to that just described. The dominant structural distortion involves passing the equatorially substituted ring carbon through the mean plane of the ring system. There are also small orthogonal distortions involving *tert*-butyl rotation.

This boat–chair–boat interconversion is remeniscent of the cyclohexane chair–boat–chair isomerization (both barriers near 11 kcal mol^{-1}). On the basis of our computed isomerization barrier, it is anticipated that low-temperature DNMR studies are feasible. In addition, it may be possible to thermally populate the chair conformer and trap it on a cryogenic surface for IR and UV spectroscopic analysis.[24] The synthesis of this molecule and further explorations on the potential energy surfaces of dihydroaromatic molecules are in progress.

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Registry No. *cis*-Me_2DHB, 24560-92-7; *trans*-Me_2DHB, 24560-93-8; *cis*-*t*-Bu_2DHB, 89773-84-2; *trans*-*t*-Bu_2DHB, 89773-86-4; *cis*-Me_2DHN, 21947-40-0; *trans*-Me_2DHN, 89773-87-5; *cis*-*t*-Bu_2DHN, 89773-85-3; *trans*-*t*-Bu_2DHN, 74877-15-9; *cis*-Me_2DHA, 13417-34-0; *trans*-Me_2DHA, 13417-35-1; *cis*-*t*-Bu_2DHA, 54974-10-6; *trans*-*t*-Bu_2DHA, 54974-11-7.

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(19) For a discussion of the NMR spectrum of this compound, see ref 8.

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(23) MMI, MMPI, and MM2 refer to empirical force fields developed by N. L. Allinger at the University of Georgia. These force fields are available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA. For a detailed discussion see ref 22b.

(24) Cryogenic trapping of thermally unstable molecular conformations for spectroscopic and kinetic analysis is well established. See, for example: Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657.