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An Investigation of Substituent Effects on the Conformation of 9,10-Dihydroanthracenes by Molecular Mechanics Calculations and X-ray Structure Analysis.

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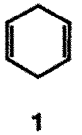
Abstract: MM2 calculations for a series of 9-R-9,10-dihydroanthracenes (DHAs) and *cis*-9-R-10-R'-9,10-dihydroanthracenes were performed to investigate the effect of substituents on the geometry of the central ring in 9,10-dihydroanthracenes. In general, the observed variation in central ring folding as compared to 9,10-dihydroanthracene itself is rather small for the monosubstituted compounds, but is quite pronounced for the *cis*-9-R-10-R' disubstituted deriviatives. These variations in conformational preferences are rationalized in terms of the 1,4 transannular effect of substituents across the ring, and by the *peri* interaction between the substituents and the neighboring aromatic hydrogens. X-ray structure determinations on two monosubstituted compounds, 9-Me-DHA and 9-$SiMe_3$-DHA, and two disubstituted compounds, *cis*-9-$SiMe_3$-10-Me-DHA and 9-$SiMe_3$-10-iPr-DHA, provide strong support for the validity of the calculations in predicting optimum structures for monosubstituted and *cis*-disubstituted DHAs.

Introduction

The stereochemistry of 1,4-cyclohexadiene (**1**), 1,4-dihydronapthalene (**2**), 9,10-dihydro-anthracene (**3**; DHA) and their derivatives have been the subject of considerable interest.[1,2] Unlike the parent **1**, whose planar structure was resolved recently after a long controversy,[2] **3** has been shown by X-ray diffraction to be nonplanar[3] in the solid state with a folding angle of $\beta = 145°$ (i.e., the angle between the two planes containing the benzene ring). It has been assumed that the boat conformation of **3** also predominates in solution, and the failure to observe separate ^{1}H NMR resonances for the pseudoaxial and pseudoequatorial protons at C9 and C10, even at low temperatures, has been attributed to rapid boat-to-boat inversion.[4]



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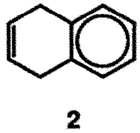

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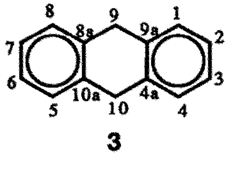

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The tendency towards a boat conformation[5] increases in the series **1**<**2**<**3**. However, molecular mechanics calculations, as well as MNDO and *ab initio* molecular orbital calculations,[6] indicate a small energy difference between the boat and planar conformations of **3**, and so appropriately placed substituents may be expected to exert a considerable influence on the overall conformation of 9,10-dihydroanthracenes.

The solid state geometry of numerous DHA derivatives has been investigated by X-ray crystallography.[7-16] Depending upon the nature and the position of the substituents, the central ring adopts either planar (or nearly planar), boat, or even chair-like conformations in the crystalline state confirming the sensitivity to the nature of the substituents. Moreover, polar substituents have been present in some structures introducing an additional complication.[2] Thus steric, inductive, hydrogen bond and dipole-dipole interactions may all be important towards conformational changes, and the relative magnitudes of these effects are difficult to sort out. Herein, several 9-monosubstituted and *cis*-9,10-disubstituted-DHAs are examined in an attempt to develop some rationale about the effect of these substituents on DHA geometry. The choice of substituents has been limited to those providing mainly steric interactions in order to simplify the analysis of the results. Molecular mechanics calculations have been performed for a series of 9-monosubstituted and *cis*-9,10-disubstituted-9,10-DHAs, and crystal structure determinations were made for 9-Me-DHA, 9-$SiMe_3$-DHA, *cis*-9-$SiMe_3$-10-Me-DHA and *cis*-9-$SiMe_3$-10-iPr-DHA.

Experimental Section

Calculations. Molecular Mechanics calculations were carried out by application of the MM2(87) program package.[17] No symmetry restriction were imposed during the calculations.

Materials. All the four DHAs utilized for X-ray structural determination are known compounds, and were synthesized by the reported procedure.[18]

Crystallographic Data. Intensity data were collected on Enraf-Nonius CAD4 diffractometers using graphite-monochromated CuKα (λ=1.54184Å) or MoKα (λ=0.71073Å) radiations, and all calculations were carried out using the Enraf-Nonius MolEN programs. Intensity data were measured using ϖ-2Θ scans of variable rate. Refinement was carried out by full- matrix least squares based on F, with weights $w= \sigma^{-2} (F_o)$. Nonhydrogen atoms were refined anisotropically, while hydrogen atoms were located by difference maps and handled as shown in table 3. Crystal data, particulars of the experiments and final R factors are also given in Table 3. Thermal-ellipsoid plots, atom positional and thermal parameters, table of bond lengths and angles, torsion angles and least-squares planes calculations have been deposited as supplementary material.

Results and Discussion.

9-Monosubstituted-9,10-Dihydroanthracenes. The value $\Sigma\Theta$ is used as a measure of the degree of nonplanarity of the central ring. It represents the sum of the absolute values of all six torsional angles defined by the carbon atoms within the central ring. For a planar ring, the expected value of $\Sigma\Theta$ is 0^o, while higher values represent deviation from planarity. Since $\Sigma\Theta$ reflects the change in planarity about the entire central ring, it has been chosen as a better measure of the substituent effect than any single selected torsional angle (i.e., it takes unsymmetrical distortions into account).

MM2 calculations were performed for a series of 9-R-DHAs with R = H, CH_3, iPr, tBu $SiMe_2H$ and $SiMe_3$ to systematically investigate the effect of substituents on the degree of nonplanarity of the central ring. It has been concluded from previous molecular mechanics calculations[19] that the size of the substituent at C9 influences the degree of nonplanarity of the central ring in 9-R-DHAs. These calculations indicated that nonplanarity of the central ring decreases in the order tBu > Me > H. However, the present, expanded study leads us to conclude that the size of a single substituent at C9 has much less effect on central ring folding than previously considered. *Cis* disubstitution, on the other hand, does have a very substantial impact on geometry. For example, the MM2 calculated $\Sigma\Theta$ values are 129.6, 125.9, 152.1, 130.4, 131.9 and 114.7° for R = H, Me, iPr, tBu, $SiMe_2H$ and $SiMe_3$ respectively as shown in table 1:

Table 1. MM2 Calculated Angles for 9-R-9,10-Dihydroanthracenes.

R	$\Sigma\Theta^a$ (deg)	$\alpha_1{}^b$ (deg)	$\alpha_2{}^c$ (deg)
H	129.6	32.4	32.4
Me	125.9	31.7	30.3
iPr	152.1	38.9	34.6
tBu	130.4	33.6	28.7
$SiMe_2H$	131.9	33.4	31.5
$SiMe_3$	114.7	29.3	26.5

[a] Sum of absolute values of all six torsional angles defined by carbon atoms within the central ring. [b] Torsional angle C10a-C8a-C9-C9a = C4a-C9a-C9-C8a. [c] Torsional angle C8a-C10a-C10-C4a = C9a-C4a-C10-C10a.

Thus, the degree of nonplanarity of the central ring in 9-tBu-DHA is almost equal to that in DHA itself despite the fact that the tBu group is the most bulky in the series considered. This rather unexpected result is also verified by X-ray crystal structure determination, and so we may conclude that the degree of nonplanarity of 9-substituted DHAs is rather insensitive to the size of the substituent; this is in contrast to the behavior of the structurally related 10-R-9-anthrones.[20] A likely explanation is as follows. Unsubstituted DHA exhibits a large degree of folding. The placement of a small substituent at C9 in the favored pseudoaxial position does not introduce significant repulsions with the *peri* hydrogen atoms located at C1 and C8, and therefore does not change the degree of planarity significantly (e.g., 9-Me-DHA). Increasing bulkiness of the substituent, however, does cause some van der Waals overlap with the *peri* hydrogens, and this causes a moderate increase in folding of the central ring (e.g., 9-iPr-DHA). With even larger substituents like tBu or $SiMe_3$, a second steric effect appears to become important: the transannular repulsion of the substituent with the pseudoaxial hydrogen atom located at C10. This effect, previously recognized[21] to be important for *cis*-9,10-disubstituted-DHAs, appears to be the controlling factor for the degree of nonplanarity of 9-R-DHAs. Since the *peri*-repulsions and the transannular interactions act in opposite directions, they cancel each other to some extent, and this explains the minimal sensitivity of central ring folding to substituent size.

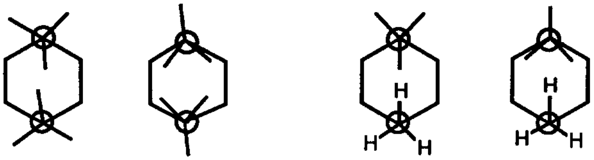
The importance of transannular repulsion is nicely demonstrated by a comparison of 9-iPr-DHA and 9-tBu-DHA. The lowest energy conformations of the iPr and tBu group are illustrated in Figure I. If only *peri* interactions are considered, both iPr and tBu should have very similar effects on the nonplanarity of the central ring. However, the transannular repulsions are quite different, being much more pronounced in the case of tBu-DHA leading to a flatter central ring in this case (Table 1). Interestingly, 9-$SiMe_3$-DHA is more planar than any of the other monosubstituted cases considered. This can be rationalized by the fact that the C-Si bond is longer than a C-C bond, and so the effective radius of the $SiMe_3$ group is smaller than that of tBu. This reduces *peri* repulsion relative to the tBu case, and the fact that 9-$SiMe_3$-DHA exhibits less folding than 9-tBu-DHA can be understood. However, Table 1 shows that 9-$SiMe_3$-3 is even flatter than the parent DHA itself. The van der Waals overlap of the methyl groups from the $SiMe_3$ fragment with the pseudoaxial hydrogen at C10 is apparently big enough to force the central ring to flatten moderately to lower the energy of the molecule. Thus, consideration of the balance between *peri* interactions and transannular interactions of the substituents allows an understanding of the variation in the degree of nonplanarity in DHAs.

9-iPr-3 **9-tBu-3**

Figure I. Orientation of iPr and tBu groups in the DHA system.

***cis*-9-10-Dialkyl-9,10-Dihydroanthracenes:** To further evaluate these two opposing effects, MM2 calculations were performed on a series of *cis*-9-R-10-R'-DHAs. The steric interaction of a large substituent with the aryl ring hydrogens (*peri* interaction) promotes greater puckering, whereas the van der Waals repulsions between the bulky substituents at C9 and C10 favors ring flattening (transannular effect). These effects were noted previously with *cis*-dimethyl- and *cis*-di-tBu-DHA using MMP1 calculations.[21a] In both cases the potential energy minimum was a boat conformation with substituents in pseudoaxial positions and with almost identical folding of the central ring: 150° for dimethyl and 153° for di-tBu. Once again, the similarity in calculated folding angle is attributed to the cancellation of the two opposing steric effects. Our MM2 studies on various *cis*-dialkyl derivatives (9,10-diMe, 9-Me-10-Et, 9-Me-10-t-Bu, 9-tBu-10-iPr 9,10-di-tBu and 9-tBu-10-$SiMe_3$) show only modest changes in folding of the central ring as compared to the parent compound (Table 2). Thus the suggestion that opposing steric effects cancel in *cis*-disubstituted derivatives holds up well over a series of structures.

MM2 calculations for 9,10-di-tBu-DHA show that the tBu groups prefer slightly distorted eclipsed (ee) conformations; this arrangement is almost 5 kcal mol more stable than the staggered-staggered (ss) geometry (Figure II). On the other hand, 9-tBu-10-Me-DHA shows the ss conformation as the global minimum, only slightly lower in energy than the se form. Similar results were also obtained for 9-$SiMe_3$-10-Me-DHA. Hence the ss arrangement is to be expected except when transannular interactions become large.



	ss	ee	ss	se
MM2 Steric energy (kcal mol^{-1}) =	22.2	17.53	7.23	7.34
	Di-tBu-3		**tBu-Me-3**	

Figure II. Orientation of tBu and Me groups in the DHA system. ss = staggered-staggered, ee =eclipsed-eclipsed, se = staggered-eclipsed. Nomenclature refers to Newman projection of the tBu and Me groups on the six membered ring.

Table 2. MM2 Calculated Angles for *cis*-9R-10R'-9,10-Dihydroanthracenes.

R	R'	$\Sigma\Theta^a$ (deg)	$\alpha_1{}^b$ (deg)	$\alpha_2{}^c$ (deg)
Me	Me	97.2	24.3	24.3
Et	Me	110.8	25.0	28.5
iPr	Me	126.8	33.4	25.7
tBu	Me	102.2	27.9	17.2
tBu	iPr	112.2	27.5	28.2
tBu	tBu	103.4	25.2, -25.9	25.2, -25.9
$SiMe_3$	Me	81.6	21.5	16.7
$SiMe_3$	iPr	129.2	26.5	33.9
$SiMe_3$	tBu	104.0	20.8	27.4
$SiMe_3$	$SiMe_3$	80.2	19.8, -20.0	19.8, -20.0

[a] Sum of absolute values of all six torsional angles defined by carbon atoms within the central ring. [b] Torsional angle C10a-C8a-C9-C9a = C4a-C9a-C9-C8a. [c] Torsional angle C8a-C10a-C10-C4a = C9a-C4a-C10-C10a.

The largest values of ring puckering were noted for the isopropyl derivatives, 9-methyl-10-iPr-DHA and 9-trimethylsilyl-10-iPr-DHA, which show ΣΘ = 126.8° and 129.2° respectively. The minimum energy conformations are illustrated for both compounds in Figure III. The preferred orientation of the isopropyl group allows minimization of the transannular interaction while increasing the *peri* interactions; this forces the central ring to become considerably more folded. The greater *peri* interaction of the iPr group in 9-iPr-10-Me-3 is illustrated by a comparison of the torsional angle α_2 = 33.4° on the isopropyl side with α_1 = 25.7° on the methyl side. A similar examination of the torsional angles in 9-SiMe$_3$-10-iPr-3 shows α_1 = 33.9° and α_2 = 26.5°. Further, among the various *cis*-9,10-diakyl DHAs studied, 9-SiMe$_3$-10-Me-3 and 9,10-bis-SiMe$_3$-3 show the least puckering of the central ring: ΣΘ 81.6 and 80.2 respectively. This observation may be explained on the grounds that the C-Si bond is longer than the C-C bond, reducing the effective radius of the SiMe3 group. This reduces *peri* repulsions and allows some flattening of the central ring.

9-iPr-10-Me-3 **9-SiMe$_3$-10-iPr-3**

Figure III. Orientaton of iPr, Me, and SiMe$_3$ groups in the DHA system.

Crystal Structure Studies: X-ray crystal structures of some model compounds were necessary to verify the theoretical results. Three such reports have already appeared, 9-*t*-Bu-DHA[9], *cis*-9-Et-10-Me-DHA[10] and *cis*-9,10-di-SiMe$_3$-DHA[13], and we undertook additional crystal structure determinations for two monosubstituted (9-Me-DHA and 9-SiMe$_3$-DHA) and two *cis* disubstituted derivatives (9-SiMe$_3$-10-Me-DHA and 9-SiMe$_3$-10-iPr-DHA). All of the monosubstituted and *cis*-disubstituted DHAs investigated by X-ray exhibit nonplanarity of the central ring as a boat or pseudo-boat conformation with substituents in the pseudoaxial positions. The crystal structure data for these compounds are collected in Table 3 with selected structural parameters presented in Table 4. There is generally good agreement between the structures found in the solid state and the MM2 calculated results. Moreover X-ray results for DHA, 9-Me-DHA and 9-tBu-DHA show nearly identical folding of the central ring (β= 145°, 145.06° and 146.6° respectively) confirming the theoretical results that central ring folding in monosubstituted-DHAs is generally insensitive to substituent size.

A closer comparison of the degree of folding in the central ring may be achieved by comparing the torsional angles, keeping in mind that ΣΘ is the sum of six torsional angles. There is little difference between calculated and experimental values. For example, the calculated values for 9-Me-DHA and 9-SiMe3-DHA are ΣΘ = 125.9° and 114.7° respectively, whereas X-ray determination shows corresponding values of 136.4° and 121.5°. Similarly, X-ray analysis of 9-SiMe3-10-Me-DHA and 9-SiMe3-10-iPr-DHA shows ΣΘ = 85.44° and 140.36°, with calculated values of 81.6° and 129.2° respectively. The maximum folding of the central

Table 3. X-ray Crystal Data for 9-R-10-R'-9,10-Dihydroanthracenes.

	R=Me R' = H	R = $SiMe_3$ R' = H	R = $SiMe_3$ R' = Me	R = $SiMe_3$ R' = iPr
mol. formula	$C_{15}H_{14}$	$C_{17}H_{20}Si$	$C_{18}H_{22}Si$	$C_{20}H_{26}Si$
mol. weight	194.3	252.4	266.5	294.5
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$Pca2_1$	$P2_12_12_1$	Pbca	$Pna2_1$
cell constants				
a, Å	12.0694 (13)	6.2190 (3)	9.3063 (4)	20.702 (2)
b, Å	12.0456 (10)	11.2142 (10)	22.3870 (8)	10.0464 (13)
c, Å	7.6907(8)	21.133 (3)	15.1806 (9)	8.7817 (5)
Z	4	4	8	4
no. of variables	136	244	173	234
D_{calc}, g cm^{-3}	1.154	1.138	1.119	1.071
radiation	CuKα	CuKα	MoKα	CuKα
temp, K	294	294	297	298
Θ range, deg	2 - 75	2 - 75	1 - 29	2-75
decay %	___	2.0	___	19.2
min. transmission, %	96.58	86.16	___	96.42
unique data	1245	2924	4197	3696
observed data	1083	2835	2575	3489
criterion	$I>1\sigma(I)$	$I>3\sigma(I)$	$I>1\sigma(I)$	$I>3\sigma(I)$
R	0.040	0.030	0.061	0.039
R_w	0.052	0.041	0.053	0.052
hydrogen atoms	fixed	refined	fixed	Me fixed,others refined

Table 4. Selected Structural Parameters Describing the Folding of the Central Ring of 9R- and *cis* -9-R-10-R'- 9,10-Dihydroanthracene as determined by X-ray

R	R'	δ^a (deg)	$\alpha_1{}^b$ (deg)	$\alpha_2{}^c$ (deg)	$\Sigma\Theta$ (deg)
CH_3	H	145.06	34.76	31.40	136.42
			-34.75	-31.55	
$SiMe_3$	H	150.02	31.45	26.82	121.56
			-31.44	-26.82	
$SiMe_3$	Me	158.33	23.16	18.00	85.44
			-21.94	-16.77	
$SiMe_3$	iPr	143.90	28.58	37.61	140.36
			-27.58	-36.47	

[a] dihedral angle between the two planes containing the benzene rings.

[b] torsional angle C10a-C8a-C9-C9a and C4a-C9a-C9-C8a

[c] torsional angle C8a-C10a-C10-C4a and C9a-C4a- C10-C10a

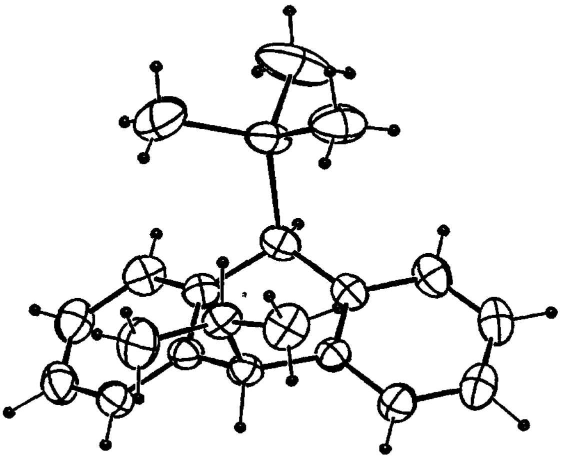


Figure IV. ORTEP view of the structure of 9-trimethylsilyl-10-isopropyl-9,10-dihydroanthracene.

ring observed in 9-SiMe$_3$-10-iPr-DHA has already been attributed to strong *peri* interactions encountered by the iPr group. This is verified by examination of the torsional angle $\alpha_2 = 37.61°$ on the iPr side as compared to $\alpha_1 = 28.58°$ on the SiMe$_3$ side. The orientation of the iPr group provides minimum transannular interaction as seen by the ORTEP picture in Figure 4.

Conclusions

Single substituents show little effect on the folding of the central ring in 9,10-dihydroanthracenes regardless of size. This is in sharp contrast to the structually related 10-substituted-9-anthrones where both computational and X-ray structural analysis reveal a high degree of sensitivity of central ring folding to substituent size. The effect of *cis*-disubstitution is to flatten the central ring in 9,10-dihydroanthracenes due to the transannular steric effect between substituents. However, such flattening leads to an increase in the *peri* interactions with the nearby aromatic protons, and so this former effect is minimized. In general, the conformational preferences of 9,10-dihydroanthracenes can be rationalized by the opposition between the *peri* effects and the transannular effects. Finally, the good agreement between the MM2 results and the X-ray data provide strong support for the validity of the calculations in predicting optimum structures for both monosubstituted and *cis*-disubstituted-DHAs.

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Supplementary Material Available. Thermal-ellipsoid plots, tables of bond lengths and angles, torsion angles and atom positional and thermal parameters for 9-Me-9,10-dihydro-anthracene, 9-SiMe$_3$-9,10-dihydroanthracene,*cis*-9-SiMe$_3$-10-Me-9,10-dihydroanthracene,and *cis*-9-SiMe$_3$-10-iPr-9,10-dihydroanthracene (31 pages). Ordering information is given on any current masthead page.

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