# Conformational Analysis of 9,10-Dihydroanthracenes. Molecular Mechanics Calculations and ^{13}C NMR

Peter W. Rabideau,* Jennifer L. Mooney, and Kenny B. Lipkowitz

Contribution from the Department of Chemistry, Purdue School of Science, Indiana University–Purdue University at Indianapolis, Indianapolis, Indiana 46223. Received July 17, 1986

Abstract: The conformational analyses of 9,10-dihydroanthracene and several of its methylated and ethylated derivatives are studied by empirical force field calculations (MM2 and MMPI). The computational results are considered in light of previous and current carbon NMR data. Model compounds are examined which involve fixed, planar, and boat-shaped conformations about the central ring, and these ^{13}C NMR data are then compared with flexible systems. It is concluded that carbon chemical shifts and carbon–hydrogen coupling constants are consistent with the results of molecular mechanics calculations which indicate a greater tendency for planarity around the central ring than previously considered.

The preferred geometries of 1,4-cyclohexadiene, its derivatives, and related compounds have been the subject of a number of investigations and the source of considerable controversy.[1] However, it now appears that 1 is planar, and substituent groups cause only a modest deviation from this preferred conformation.[2]
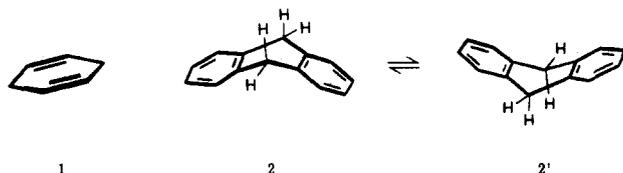
On the other hand, 9,10-dihydroanthracene (DHA) was found to exist in a puckered conformation in the solid state[3] with a folding angle (angle between the planes containing the benzene rings) of 145°. Since solution NMR at low temperatures did not resolve individual pseudoaxial (pa) and pseudoequatorial (pe) protons in the central ring, it was assumed that DHA exists as rapidly equilibrating boat conformations (2 ⇌ 2′).[4] It has been assumed that substituted derivatives of 2 also exist as boat conformations with equilibrium positions being appropriately shifted by the preferred pa geometries of 9 and 10 position substituent groups. A number of NMR studies have appeared which seem to support this position,[1] and this includes a recent solution and solid-state ^{13}C NMR investigation[5] on DHA and several of its methylated derivatives.[6] Subsequently, force field calculations[7] have suggested a tendency for planar structures in DHA and many of its derivatives (i.e., symmetrical 9,9 and trans-9,10 disubstitution).[8] For example, MM2 and MMPI calculations on 2 indicate little difference between planar and boat forms (0.4 kcal/mol or less). Moreover, trans-9,10-dipropyl-9,10-dihydroanthracene has very recently been found to be planar in the solid state by X-ray

analysis.[9,10] Thus in view of the general reliability of force field calculations together with recent experimental results, a reexamination of the ^{13}C NMR spectral behavior of these compounds seems warranted.

Dalling et al.[5] studied DHA and several of its methylated derivatives by solution and solid-state ^{13}C NMR. Clearly 3 and 4 exist as boat conformations in the solid state since separate resonances were observed for pseudoaxial (pa) and pseudoequa-

torial (pe) methyl groups in each case. In solution however, only single methyl signals were observed, even at low temperature (~ -70 °C), and this was attributed to a rapid boat-to-boat inversion process. We have carried out molecular mechanics calculations on 3 and 4 with the MM2 and MMPI force fields,[7c] and plots of total steric energy vs. ring pucker are shown in Figure 1. The calculations predict three minima in each case: two boat forms and a planar conformation.

Theory suggests little difference in energy between planar 3 and its boat-shaped conformer. Moreover, the barrier to interconversion is also predicted to be quite low, especially when it is realized that the energy profile in Figure 1 represents a symmetry-constrained folding process which may not be the lowest energy pathway.[8c] A planar conformation is even more favorable with 4 and, in contrast with 3, is calculated to be the global minimum. This is presumably due to the fact that the gem dimethyls are bisected by the ortho hydrogens in the planar state.

Experimentally, Dalling et al. observed a smaller difference between pa and pe methyl solid state chemical shifts in 4 than would be expected on the basis of the γ effect resulting from interactions with the nearby peri hydrogens. This "rather suprising" result was attributed to a flattening of the central ring even in the solid state. This is, of course, quite consistent with our calculations. It is expected that this effect should be even more important for tetramethyl-DHA, and this is exactly what

(1) For a review, see: Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

(2) Rabideau, P. W.; Wetzel, D. M.; Paschal, J. W. *J. Org. Chem.* **1982**, *47*, 3993 and references therein.

(3) (a) Ferrier, W. G.; Iball, J. *Chem. Ind. (London)* **1954**, 1296. (b) Sygula, A.; Holak, T. A. *Tetrahedron Lett.* **1983**, *24*, 2893.

(4) Smith, W. B.; Shoulder, B. A. *J. Phys. Chem.* **1965**, *69*, 2022.

(5) Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.

(6) Variation in the degree of puckering in the central ring was noted by these investigators, and, in fact, 9,9,10,10-tetramethyl-DHA was found to be planar.

(7) (a) Boyd, D. B.; Lipkowitz, K. B. *J. Chem. Educ.* **1982**, *59*, 239 and references therein. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; Americal Chemical Society: Washington, DC, 1982; ACS Monograph No. 177. (c) 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, IN 47405.

(8) (a) Lipkowitz, K. B.; Rabideau, P. W.; Raber, D. J.; Schleyer, P. v. R.; Kos, A. J.; Kahn, R. A. *J. Org. Chem.* **1982**, *47*, 1002. (b) Raber, D. J.; Hardee, L. E.; Rabideau, P. W.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2843. (c) Rabideau, P. W.; Lipkowitz, K. B.; Nachbar, R. B., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3119.

(9) Ahmad, N-u-d.; Goddard, J.; Hatton, I. K.; Howard, A. K.; Lewis, N. J.; MacMillan, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1859. See also: Ahmad, N-u-d.; Cloke, C.; Hatton, I. K.; Lewis, N. J.; MacMillan, J. *Ibid.* **1985**, 1849.

(10) In addition, 9,9,10,10-tetrachloro-9,10-dihydroanthracene has been shown to be planar in the solid state,[11] and trans-bis(trimethylsilyl)-9,10-dihydroanthracene appears to be flat with a chair-type deformation.[12]

(11) Germain, G.; Main, P.; Woolfson, M. M. *Acta. Crystallogr., Sect. A* **1971**, *27*, 368.

(12) (a) Davey, M. Ph.D. Thesis, L'Universite De Bordeaux I, 1978. (b) Leroy, F.; Courseille, C.; Daney, M.; Bouas-Laurent, H. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2792.

(13) Grant, D. M.; Cheny, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315.

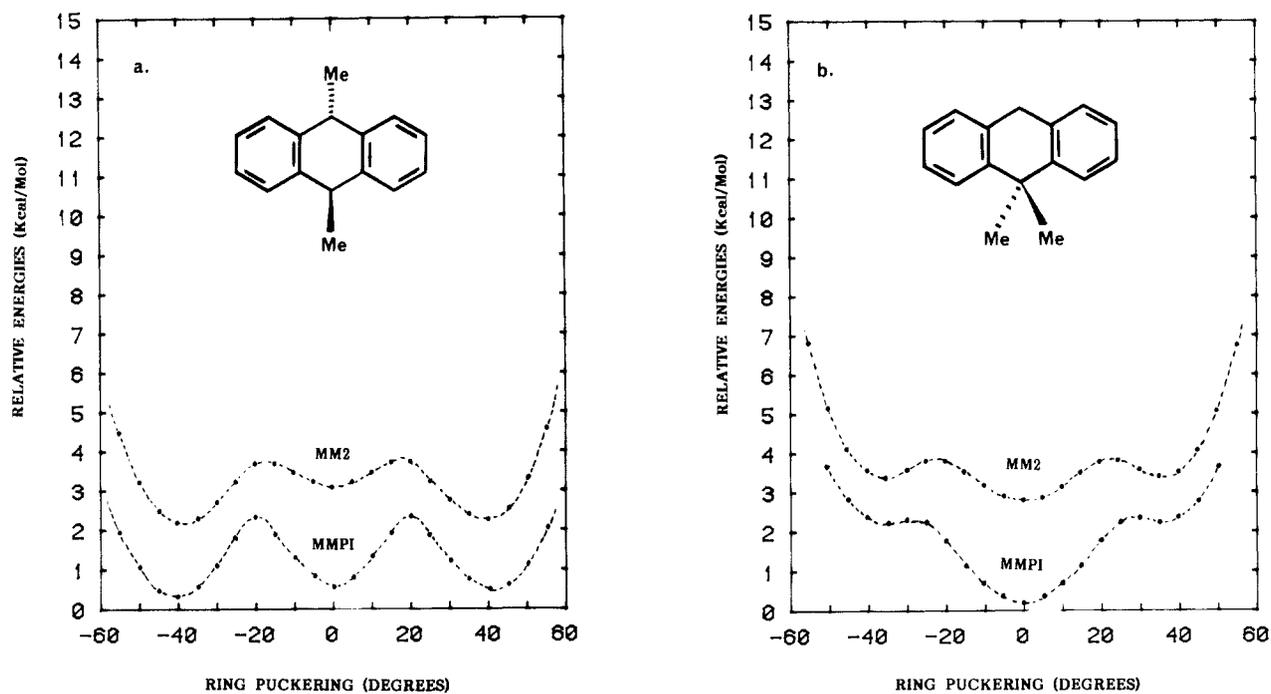(14) Grossel, M. C.; Perkins, J. *Nou. J. Chim.* **1979**, *3*, 285.

Figure 1. MM2 and MMPI calculations for (a) *trans*-9,10-dimethyl-9,10-dihydroanthracene and (b) 9,9-dimethyl-9,10-dihydroanthracene.
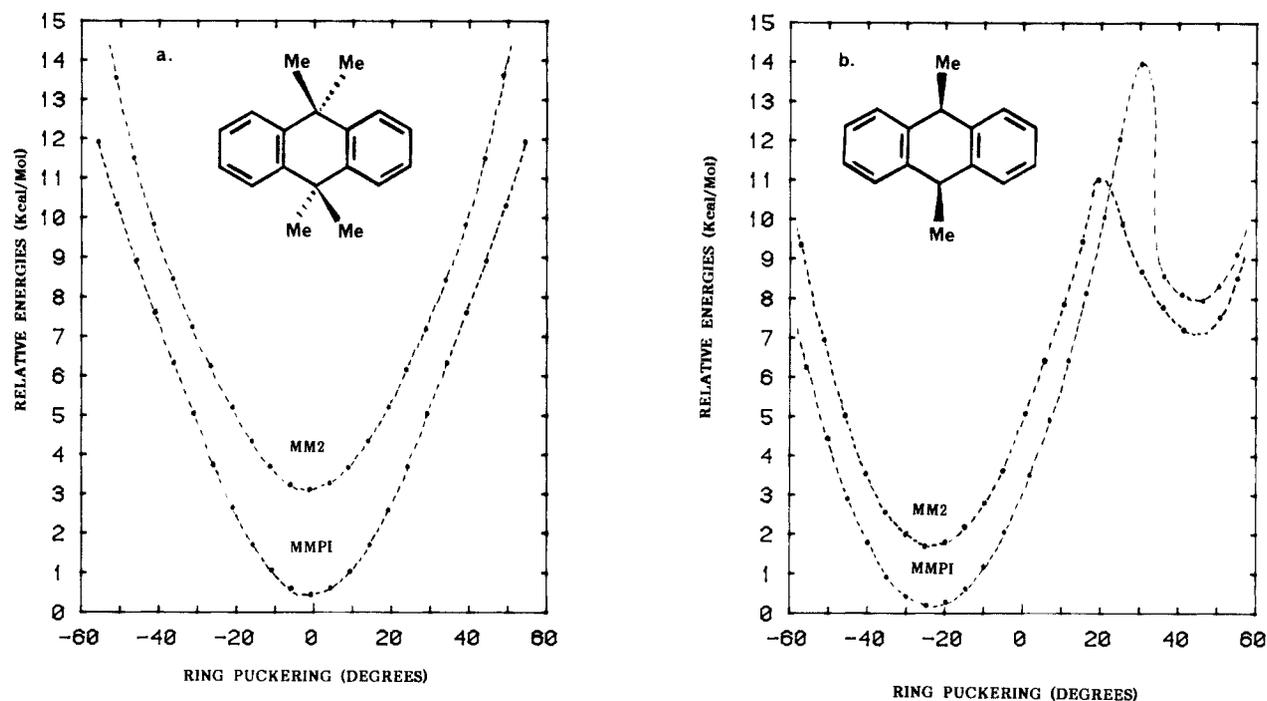

Figure 2. MM2 and MMPI calculations for (a) 9,9,10,10-tetramethyl-9,10-dihydroanthracene and (b) *cis*-9,10-dimethyl-9,10-dihydroanthracene.

is predicted by force-field calculations (Figure 2). In this case ^{13}C NMR also indicated planar structures in both liquid and solid states.

In solution, *cis*-9,10-dimethyl-9,10-dihydroanthracene shows a temperature-dependent carbon NMR spectrum with a ca. 1.5 ppm change in methyl resonances over a temperature range of +40 to –70 °C. This was interpreted as a change in the equilibrium population involving dipseudoaxial and dipseudoequatorial conformations (**5 ⇌ 5′**). On the other hand, force field calcu-

5   **5′**
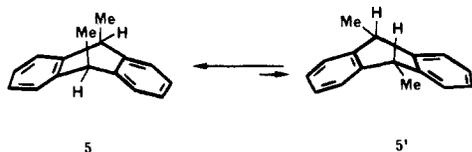
lations indicate no contribution from **5′** at all. As shown in Figure

2, the di-pe form is more than 5 kcal/mol higher in energy than the di-pa conformation. It is our contention that one need not invoke **5′** to describe the NMR temperature dependence of **5**. We base this on the well-established, parabolic surface for the parent 1,4-cyclohexadiene which shows a temperature dependence of proton homoallylic coupling constants (d_6 analogue). Hence it is possible that wide amplitude oscillations are solely responsible for the observed temperture-dependent NMR results.

One question that we wish to address is whether or not the fully puckered, boat-shaped conformation adopted by many DHAs in the solid state is also the geometry in solution, since it is possible that the former may be affected by crystal packing forces. Dalling et al. approached the problem by comparing the bridge carbon (C_9 and C_{10}) chemical shifts in both solid and liquid states. Their measured values fell within a range of 0.2–0.6 ppm leading them to conclude that "this agreement argues rather forcibly for the position that the geometry of each of these compounds does not

8132 *J. Am. Chem. Soc., Vol. 108, No. 26, 1986*

Rabideau et al.

Table I. Carbon Chemical Shifts for 9,10-Dihydroanthracene and Derivatives[a]

| compound	C-1, C-4[b,c]	C-2, C-3[b,c]	C-4a, C-8a[b]	C-9	C-10	CH$_2$CH$_3$	CH$_2$CH$_3$	other
DHA	127.2 (127.6)[d]	126.0 (126.3)[d]	136.0 (136.9)[d]	36.1 (36.2)[d]				
9-EtDHA	127.8, 127.6	125.9, 125.8	135.5, 139.9	48.8	31.3	35.3	12.1	
cis-9,10-diEtDHA	128.6	125.7	139.3	48.3		35.5	13.4	
trans-9,10-diEtDHA	126.7	125.8	138.6	43.8		27.0	10.0	
cis-9-Et-10-t-BuDHA	129.0, 130.9	124.6, 125.8	136.5, 140.1	47.6	55.8	33.3	14.8	3.51,[e] 30.0[f]
trans-9-Et-10-t-BuDHA	125.9,[g] 130.5	124.6, 125.4[g]	138.1, 138.3	40.1	57.2	21.6	8.0	38.9,[e] 28.5[f]
9-t-Bu-DHA	130.7, 127.9	126.1, 125.1	137.8, 138.2	57.5	37.2			39.1,[e] 28.1[f]

[a] Dilute solutions in CS$_2$. Chemical shifts measured from internal Me$_4$Si. [b] These assignments could be reversed. [c] The α (C-1, C-4) and β (C-2, C-3) carbons can generally be distinguished in the coupled or off-resonance decoupled spectrum by the "fingerprint method". Günther, H.; Schmickler, H.; Jikeli, G. *J. Magn. Reson.* **1973**, *11*, 344. Jikeli, G.; Herrig, W.; Günther, H. *J. Am. Chem. Soc.* **1974**, *96*, 323. [d] Values in parentheses are from ref 5 and represent CDCl$_3$ solutions. [e] tert-Butyl quarternary. [f] tert-Butyl methyls. [g] These assignments may be reversed. Signal overlap makes the "fingerprint method" (footnote c) difficult to apply.

vary greatly between the liquid and solid states". Since this is not consistent with our molecular mechanics calculations, we decided to investigate the carbon chemical shifts of bridge carbons in a number of systems with *well-defined* geometries.

Regardless of whether one invokes the rapid boat-to-boat inversion concept or relies on the MM2/MMPI results, the (average) NMR spectrum of **6** should reflect a puckered conformation with
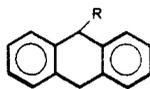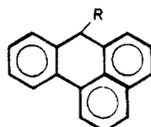

6

7
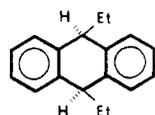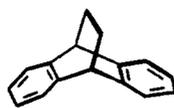
δ^{13}C (C$_9$ 48.4 ppm

δ^{13}C (C$_9$ 48.4 ppm

di-pa substitution. In fact, the chemical shift of the bridge carbon (C$_9$) in **6** compares quite favorably with the analogous position in **7**. This latter compound is, of course, fixed as a puckered DHA with "ethyl" substitution.


2. R H, δ^{13}C, C$_9$ 36.1 ppm

2a. R Et, δ^{13}C, C$_9$ 48.7 ppm

8, R H, δ^{13}C, C$_9$ 34.5 ppm

8a. R Et, δ^{13}C, C$_9$ 45.7 ppm

We selected **8** as a planar model with the expectation that the "added" aromatic ring would be sufficiently remote (and bond order changes sufficiently small) so as not to greatly influence the chemical shift values of interest. This appears to be justified since the methyl chemical shifts of toluene and 2-methylnaphthalene are within 0.1 ppm of one another.[15] Hence we are able to estimate the effect of ring puckering on the chemical shift of the bridge carbon by a comparison of **2a** and **8a** (**2a** is actually expected to be more puckered than **5** since transannular interactions can induce flattening in the latter). This difference is 3.0 ppm. When the unsubstituted derivatives **2** and **8** are compared, the difference in chemical shifts at C$_9$ is only 1.6 ppm. The fact that the shift difference is only half as large in this case is consistent with the molecular mechanics results for **2** which predict significant contributions from both planar and folded conformations. As mentioned above, MMPI indicates a planar minimum with only 0.4 kcal/mol required for a 20° change in folding angle about the central ring.

So far we have considered cases where an ethyl substituent becomes more pseudoaxial with increased ring folding. It will also be of interest to examine systems where this substituent may be located in the pseudoequatorial position. Thus we can "lock" an ethyl substituent in either the pa or pe position with the isomeric

9-ethyl-10-*tert*-butyl DHAs, **9** and **10**. In **10**, the resonance position of C$_9$ is slightly upfield as compared to **2a** and **5** (see Table
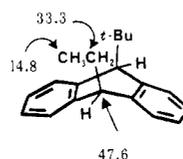

[δ ^{13}C(ppm)]
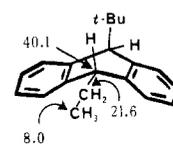
I), and this is attributed to a transannular steric shift from the *tert*-butyl across the central ring (ca. −1 ppm). Consistent with the trends above, C$_9$ in **9** absorbs at much higher field reflecting the effect of a pe ethyl substituent (−7.5 ppm). This is exactly the same value observed by Dalling et al. for the difference between pa and pe methylated C$_9$'s in the solid state and would appear to confirm the highly puckered nature of **9** and **10**. The positions of pa CH$_3$CH$_2$ and pe CH$_3$CH$_2$ are also quite different, with the latter appearing at 11.7 ppm higher field. This value is slightly smaller than the difference between pa and pe methyls in solid-state *trans*-diMeDHA (12.8 ppm), and once again it is consistent with a −1.0-ppm shift caused by steric interaction of pa CH$_3$CH$_2$ with the *tert*-butyl group in **9**.

The pe CH$_3$CH$_2$ also shows an upfield shift, −6.8 ppm, relative to **9**. However, this difference is only due in part to an upfield shift for CH$_3$CH$_2$ in **10**, since CH$_3$CH$_2$ in **9** is slightly downfield when compared to the other ethylated derivatives. Nonetheless, there does seem to be an upfield δ effect in **10**, which is interesting since it is opposite in direction to the effects presumed to be steric in origin (δ-synaxial effects).[16] Hence we investigated the steric environment of the ethyl substituent in **10** by molecular mechanics calculations. As illustrated, the most stable geometry has the methyl group antiperiplanar to the C$_9$ methine hydrogen (this is 2.0 kcal/mol more stable than when the methyl is synperiplanar).
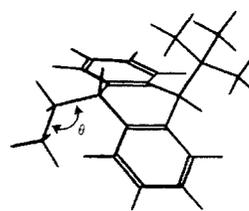
10

(MM2 generated, hydrogens omitted throughout)

θ = 114°

In this conformation, the CH$_3$CH$_2$ carbon is 2.94 Å from the ortho hydrogens and steric interactions are expected. The expanded bond angle θ (114°) is a direct consequence of this interaction. We must also note that the geometric relationship (i.e., angle) between CH$_3$CH$_2$ and the ortho hydrogens is quite different from that required for a synaxial arrangement.

Since solid DHA is known to exist in a boat conformation, it would be very informative to compare bridge carbon chemical

(15) 1-Methylnaphthalene is actually the correct structural arrangement, but its methyl shift cannot provide a reference point due to the effect of H$_8$.

(16) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Wiley: New York, 1983; p 39.

(17) Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* **1982**, *23*, 31.

Conformational Analysis of 9,10-Dihydroanthracenes

J. Am. Chem. Soc., Vol. 108, No. 26, 1986 8133

Table II. One-Bond ^{13}C-H Coupling Constants for DHA and Related Compounds in Hz[a]

Compound	J_{13C-H}	Compound	J_{13C-H}
	127.6 (128±2)[b]		125.9
	126.9		128.0
	128.5		126.7
	122.6		127.9[c]
			138.7[d]

[a] Run as ~0.5 M solutions in CS$_2$ with internal Me$_4$Si as reference and coaxial D$_2$O as lock. [b] Value from: Smith, W. B.; Shoulders, B. A. *J. Phys. Chem.* **1965**, *69*, 2022. [c] Measured from the triplet although it is, strictly, an ABX. [d] Run in CDCl$_3$.

shifts in both solution and solid state. Unfortunately solid-state NMR could not provide this value due to a broadened resonance line.[5] In an attempt to solve this problem and provide data for a "known", boat-shaped geometry, we undertook the study of 11. The ethane bridge locks the DHA into a boat conformation. Futhermore, the "ethyl substituent" is pe not pa, and this is important since a pa substituent does, in fact, affect the bridge carbon chemical shift across the ring. The chemical shift of C$_{10}$ in 11 is 36.1 ppm. Hence, by comparing this puckered model with the planar one (8), it appears that ring folding alone produces a
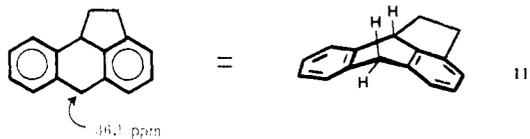
downfield shift of approximately 1.6 ppm at the bridge carbons. Interestingly, the chemical shift of the model is identical with the solution value for 9,10-dihydroanthracene (2) itself, and so we must conclude that boat conformations contribute significantly to the overall geometry of 2. This is consistent with the calculations which indicate a shallow potential well within the range of ±35° folding about the central ring.

As a final point, we note that geometry changes in the central ring should show up in the one-bond ^{13}C-H coupling constants at the bridge carbon(s). Baum, et al.[17] have shown that coupling constants in hydrocarbons of the type RCH$_2$R are given by the equation

$$^1J = 250(1 + \cos \theta_0)/(1 - \cos \theta_0)$$

where the interorbital angle (θ_0) is related to the C-C-C internuclear bond angle (θ_n) by the expression

$$\theta_0 = 84.82 + 0.3853\theta_n - 0.001473\theta_n^2$$

Using MM2 values for the C-C$_9$-C angle in puckered (θ = 111.0°) and planar (θ = 116.9°) 2, we calculated coupling constants of J = 125.2 and 123.8 Hz, respectively. The relative, if not absolute, values may be of some significance (see Table II). Hence, we can expect to observe a ca. 1.4-Hz difference in J_{13C_9-H} between planar and folded structures witth the latter being larger. Application of this approach to our models, planar 8 (J = 126.7 Hz) and puckered 11 (J = 127.9 Hz), shows a difference of 1.2

RING PUCKERING (DEGREES)
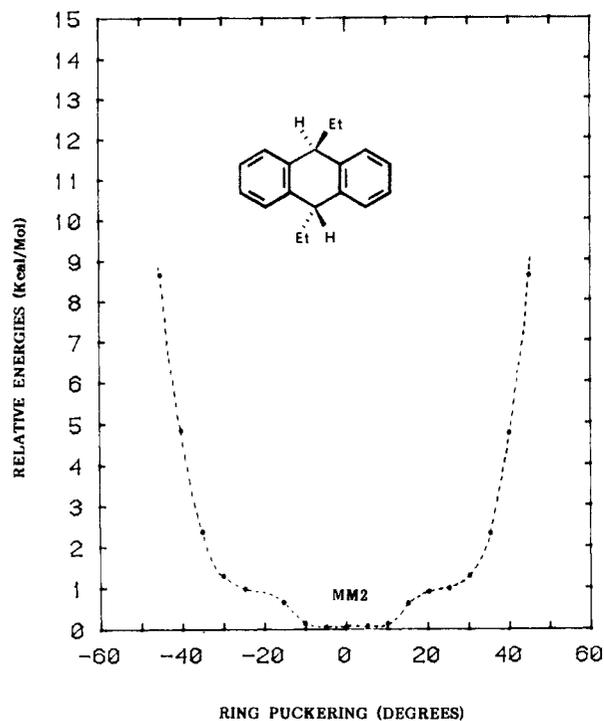
Figure 3. MM2 Calculation for *trans*-9,10-diethyl-9,10-dihydroanthracene.

Hz which is in reasonable agreement.

We pointed out above that the parent compound 2 resembles the puckered model with regard to C$_9$ chemical shift data. This is also the case with the coupling constant data. In 2, J = 127.6 Hz which is only slightly smaller than in 10. However, a comparison of the *cis*- and *trans*-diethyl compounds clearly suggests a difference in conformations, since J_{13C_9-H} = 128.5 Hz in the former and 126.9 Hz in the latter. This does support our argument that the *trans*-diethyl isomer is essentially planar (see Figure 3). With the 9-ethyl-10-*tert*-butyl isomers, it is expected that both will be nonplanar favoring a pa *tert*-butyl group. However, the trans compound should be somewhat flattened. Comparison of the J values shows a 1-2-Hz increase in the cis compound. DHAs with a lone substituent should also be puckered, and 9-ethyl-DHA shows J_{13C_9-H} = 128.0 Hz, just slightly less than the (puckered) *cis*-diethyl compound.

Dalling et al.[5] favor the boat-to-boat inversion model for DHAs but recognize the flexible nature of the central ring and the possibility of "flattening" in some cases. Our conclusions are somewhat different because we argue more strongly in favor of planar or nearly planar structures (in some cases). We also note that the previous solid-state study only dealt with methyl substitution which involves a relatively small steric perturbation. This is illustrated by the comparison of force field calculations between *trans*-9,10-dimethyl-DHA and *trans*-9,10-diethyl-DHA (Figures 1a and 3, respectively). It would be expected, of course, that even larger groups would have a more significant effect, and we noted that *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene was found to be planar even in the solid state.[10] Hence we feel that force-field calculations do a good job in describing the complex conformational properties of DHAs and that the results are consistent with experimental (NMR) findings.

Experimental Section

General. Calculations were performed with the Allinger MM2 molecular mechanics program.[7b,c] Aromatic carbon atoms were defined in terms of the optimum C=C bond length (1.397 Å) and the C=C force constant (8.067 mdyn Å). NMR spectra were recorded on a Varian CFT-20 with ca. 0.5 M solutions in CS$_2$ with internal Me$_4$Si as reference and coaxial D$_2$O as lock.

9,10-Dihydroanthracene (2) was obtained commercially and recrystallized twice from 95% ethanol.

9-Ethyl-9,10-dihydroanthracene (2a) was prepared from ethylanthracene by Li/NH$_3$ reduction.[18]

cis-9,10-Diethyl-9,10-dihydroanthracene (cis-6) was prepared by reductive alkylation of anthracene.[19]

trans-9,10-Diethyl-9,10-dihydroanthracene (trans-6) was prepared by Li/NH₃ reduction of 9,10-diethylanthracene.[18]

9,10-Ethano-9,10-dihydroanthracene (7) was prepared from dibenzobarrelene by Li/NH₃ reduction.[20]

Benzanthrene (8) was prepared from commercial benzanthrone by reduction with a fourfold excess of LiAlH₄/AlCl₃.[21]

Ethylbenzanthrene (8a) was prepared from **8** (0.55 g, 2.5 mmol) by proton abstraction with n-butyllithium (3.1 mmol) in THF at -78 °C followed by the addition of excess bromoethane. Ether extraction yielded **8a** as a yellow oil which was microdistilled for analysis. NMR (CCl₄) δ 0.5 (t, 3 H), 1.7 (quintet, 2), 4.1 (t, 1), 7.5 (m, 10).

Anal. Calcd for C₁₉H₁₆: C, 93.39; H, 6.61. Found: C, 93.66; H, 6.04. Mass spectrum, m/e 228.

trans-9-Ethyl-10-tert-butyl-9,10-dihydroanthracene (10) was prepared from 9-tert-butyl-9,10-dihydroanthracene by proton abstraction with n-butyllithium followed by alkylation with bromoethane.[22]

cis-9-Ethyl-10-tert-butyl-9,10-dihydroanthracene (9) was prepared by epimerization of **10**.[22]

1,9-Ethano-9,10-dihydroanthracene (11) was prepared from aceanthrene[23] (230 mg, 1 mmol) and sodium (60 mg, 2.5 mmol) according to the general procedure for metal–ammonia reduction. After normal quenching with dilute ammonium chloride solution and ether extraction, the solid product was recrystallized from methanol/water to yield 1,9-ethano-9,10-dihydroanthracene as white crystals: mp 81–82 °C (60 mg, 0.3 mmol, 33%); NMR (CDCl₃) δ 2.0 (m, 1 H), 2.9 and 3.1 (m, 3), 3.8 (m, 3), 7.1 (br d, 7).

Anal. Calcd for C₁₆H₁₄: C, 93.15; H, 6.85: Found: C, 93.36; H, 6.60.

(18) Harvey, R. G.; Arazadon, L.; Grant, J.; Urberg, K. J. Am. Chem. Soc. 1969, 91, 4535.

(19) Harvey, G. R.; Arazadon, L. Tetrahedron 1969, 25, 4887.

(20) Rabideau, P. W.; Jessup, D. W.; Ponder, J. W.; Beekman, G. F. J. Org. Chem. 1979, 44, 4594.

(21) See: Fieser, W.; Fieser, M. Reagents for Organic Synthesis; Wiley: New York, 1967; Vol. III, p 176.

(22) Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. J. Am. Chem. Soc. 1975, 97, 1145.

(23) Aceanthrene was prepared starting from aceanthrenequinone according to the synthesis reported by Becker et al. (Becker, H. D.; Hansen, L.; Nadersson, K. J. Org. Chem. 1985, 50, 277) with one exception. 2-Aceanthrone was prepared with pyridine hydrochloride reagent as described by Plummer et al. (Plummer, B. F.; Al-Saigh, Z. Y.; Arfan, M. J. Org Chem. 1984, 49, 2069). Melting points of intermediate compounds were identical with those reported by Becker et al.

The Complexation of Sodium Ion by the Cryptand 4,7,13-Trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C₅) in a Range of Solvents. A ²³Na Nuclear Magnetic Resonance Kinetic Study

Stephen F. Lincoln,*† Ian M. Brereton,‡ and Thomas M. Spotswood‡

Contribution from the Department of Physical and Inorganic Chemistry, and the Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia 5001, Australia. Received March 24, 1986

Abstract: The exchange of Na⁺ between the solvated state and the cryptate [Na·C21C₅]⁺ has been studied in acetonitrile, propylene carbonate, acetone, methanol, dimethylformamide, and pyridine solvents by ²³Na NMR spectroscopy. The decomplexation rate constants k_d(298.2 K) = 19.4 ± 0.5 and (2.88 ± 0.03) × 10⁴ s⁻¹ determined in propylene carbonate and dimethylformamide, respectively, encompass the variation of lability toward decomplexation exhibited by [Na·C21C₅]⁺ in the six solvents studied. The [Na·C21C₅]⁺ formation rate constants 10⁻⁵k_f(298.2 K) = 4.9 and 214 dm³ mol⁻¹ s⁻¹ determined in pyridine and dimethylformamide, respectively, encompass the much smaller variation of the lability of the formation process and demonstrate that the variation of k_d dominates the variation of the stability of the cryptate with the nature of the solvent. By comparison k_d for [Na·C211]⁺ is 500–2000 times less than that for [Na·C21C₅]⁺, and the greater lability toward decomplexation of the latter cryptate is attributed to C21C₅ possessing only three oxygen donor atoms whereas C211 has four such atoms. However, k_f for [Na·C211]⁺ is smaller than k_f for [Na·C21C₅]⁺ by a factor of 10 or less. These observations and the dependence of k_f and k_d on the nature of the solvent are used to postulate reaction mechanisms for the two cryptates.

Since the introduction of the polyoxadiazabicycloalkane or cryptand ligands by Lehn the solution chemistry of the complexes, or cryptates, formed between alkali metal ions and cryptands has been the subject of extensive study.[1–12] Investigations of the effect of metal ion size and cryptand cavity size on stability and lability have produced a substantial understanding of the mechanism of cryptate formation,[5–8,10] but there is a relative paucity of systematic data on the effect of the cryptand donor atoms on these characteristics. This study seeks insight into this aspect of the cryptates through a kinetic investigation of Na⁺ exchange on the cryptate formed by 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C₅) in a range of solvents and a comparison of the derived kinetic

Chart I
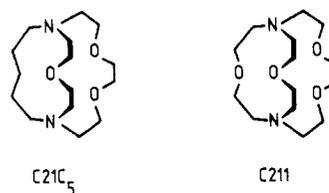
parameters with those characterizing the closely related 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) sys-

†Department of Physical and Inorganic Chemistry.
‡Department of Organic Chemistry.

(1) Lehn, J.-M. Struct. Bonding (Berlin) 1973, 16, 1–69.
(2) Lehn, J.-M.; Sauvage, J. P. J. Am. Chem. Soc. 1975, 97, 6700–6707.