Conformational Analysis of 1,4-Cyclohexadienes. Carbon–Proton Spin–Spin Coupling Constants in Dihydroaromatic Carboxylic Acids

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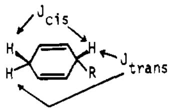
Abstract: [2,3,4,5,6-$^{2}H_5$; *carboxyl*-^{13}C]-1,4-dihydrobenzoic acid (**2**), [2,3,4,5,6,7,8-$^{2}H_7$; *carboxyl*-^{13}C]-1,4-dihydro-1-naphthoic acid (**3**), and [*carboxyl*-^{13}C]-9,10-dihydro-9-anthroic acid (**4**) were synthesized and studied by proton NMR spectroscopy to obtain all homoallylic carbon–proton couplings. The ratio J_{CH}/J_{HH} is 0.6, as previously observed for other systems. It is observed that these carbon–proton couplings are just as sensitive as proton–proton couplings to the degree of puckering of the dihydro ring. A comparison of theoretical and empirical J values is consistent, whereby the ratio $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ (for J_{HH}) decreases, and the ratio $J_{ax\text{-}ax}/J_{ax\text{-}eq}$ (for J_{CH}) increases throughout the series **2–4,** showing the extent of puckering of **3** is intermediate between that of **2** and that of **4**. Thus are generated three categories—"flat", "flattened boat", and "true boat"—to compare the geometries of **2–4.** Considerations of other types of coupling constants (vicinal and allylic) in the series **2–4** and in other compounds supports the designation of these separate categories.

It is clear that 1,4-dihydrobenzene and its monosubstituted derivatives are planar,[2-5] and that 9,10-dihydroanthracenes are puckered with 9-substituents axial.[6] However, some uncertainty shrouds the NMR conformational analysis of dihydroaromatic compounds in general, because the ratio of the two proton-proton homoallylic coupling constants $^{5}J_{cis}/^{5}J_{trans}$ (see **1**) remains close to 1 throughout a series of compounds.[2,7] Indeed, it has been proposed that this ratio of homoallylic coupling constants should not be used as a conformational tool.[2b] This hypothesis is somewhat surprising, because a strong geometrical dependence of $^{5}J_{HH}$ had been previously shown (in single-path olefins).[8]



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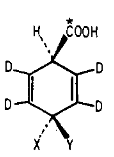
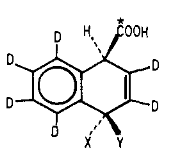
In the present account it is shown that part of the past difficulty in utilizing the ratio $^{5}J_{cis}/^{5}J_{trans}$ arises from the fact that in proton-proton couplings this ratio uses axial-equatorial and equatorial-equatorial couplings. Perhaps better suited to the conformational analysis are axial-axial and axial-equatorial couplings, whose $^{5}J_{cis}/^{5}J_{trans}$ ratio does not remain so close to 1. Since the substituent is axial, one must then use couplings to the substituent. In the present study the substituent was labeled with ^{13}C, and proton couplings to this labeled carbon were used. It is then realized, from data generated from this and from past studies, that there is a consistent trend in the ratio $^{5}J_{cis}/^{5}J_{trans}$ (both $^{5}J_{ax\text{-}ax}/^{5}J_{ax\text{-}eq}$ and $^{5}J_{eq\text{-}eq}/^{5}J_{ax\text{-}eq}$) throughout a series of dihydroaromatic compounds.

Results and Preliminary Remarks

Spectral Analysis. The compounds synthesized in this study are **2–4**. Compounds **2** and **3** were deuterated as shown so as to remove interfering couplings from the olefinic protons (the proton NMR of **2** and **3** with no deuteration exhibited patterns too complex to analyze). It was apparent from the proton NMR spectra of **2** and **3** that a roughly 50:50 product distribution resulted in both cases. Table I gives the proton NMR parameters obtained from **2–4.**



2a X=H, Y=D
b X=D, Y=H



3a X=H, Y=D
b X=D, Y=H

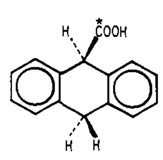


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Figure 1 shows, as an example of the NMR analysis conducted herein, the deuterium-decoupled proton spectrum of **2**. With a *mixture* of **2a** and **2b,** *two* AB portions of an ABX (proton-proton-carbon) system should appear, giving rise to two overlapping spectra of eight lines each. The chemical shifts of the methylene proton in **2a** and **2b** were slightly different (by 0.015 ppm), and accordingly two closely overlapping four-line methylene patterns could be recognized (Figure 1b). Thus, the two $^{5}J_{HH}$ splittings and the two $^{5}J_{CH}$ splittings could be discerned. The chemical shifts of the methine proton in **2a** and **2b** were virtually identical, and the two overlapping four-line methine patterns were essentially superimposed (Figure 1a). From the methine pattern the $^{2}J_{CH}$ splitting could be discerned. The total spectrum of **2** was analyzed as a "six"-spin system to give the data presented in Table I.

The deuterium-decoupled proton NMR spectrum of **3** was analyzed in an identical fashion. The spectrum of **3** differed from that of **2** in that the chemical shifts of the methylene protons in **3a** and **3b** were substantially different (0.15 ppm), and consequently the two four-line methylene patterns were separate.

The analysis of **4,** with no deuteriums, was a more straightforward aromatic proton-decoupled analysis of the ABC portion of an ABCX pattern.

The $^{5}J_{HH}$ values for **2** taken from Table I should be considered to be more accurate than those obtained in a previous study[9] in which the two splittings were not specifically resolved, and these values appearing in Table I should replace the previous values.

Spectral Assignments. The uncertainty that existed in the data for **2** and **3** was the correct assignment of the two AB patterns; e.g., in **2** it was certain that the isotopic isomer with $^{5}J_{CH}$ = 4.65 also had $^{5}J_{HH}$ = 9.19 Hz, but from spectral analysis itself, it could not be ascertained whether these two values belonged to the trans-J_{CH} and cis-J_{HH} (**2a**), or to the cis-J_{CH} and trans-J_{HH} (**2b**). The assignments that were made for **2** were based on two considerations: (1) for 1,4-dihydrobenzene itself,[10] $^{5}J_{cis}$ has been shown to be larger than $^{5}J_{trans}$;

Table I. Carbon–Proton and Proton–Proton Coupling Constants for Dihydroaromatic Carboxylic Acids **2–4**

Compd	Coupling constant, Hz[a]						Chemical shift of proton[b]		
	cis-$^5J_{HH}$	trans-$^5J_{HH}$	cis-$^5J_{CH}$	trans-$^5J_{CH}$	$^2J_{HH}$	$^2J_{CH}$[e]	δ(1)	δ(4c)[c]	δ(4t)[d]
2	9.19	7.56	5.75	4.65	(−22.0[f])	(−)10.97	3.705	2.574	2.559
3	3.84	4.36	5.44	2.86	(−21.9[g])	(−)9.85	4.30	3.34	3.19
4	<0.5	0.9	3.2	0.7	−18.1	(−)9.0	4.99	4.25	3.90

[a] Considered accurate to 0.1 Hz. [b] In parts per million downfield from internal standard Me_4Si. [c] Orientation cis to carboxyl group. [d] Orientation trans to carboxyl group. [e] Sign known to be negative (ref 12). [f] Value not available in the present study, but obtained from ref 2a. Value not available in the present study, but obtained from ref 7a.

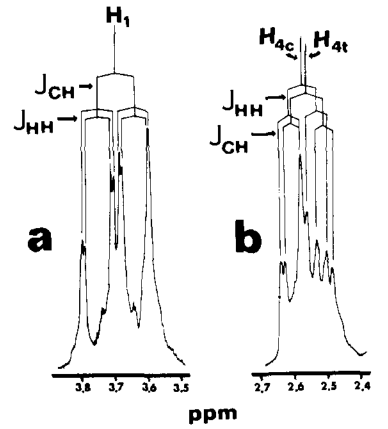


Figure 1. Deuterium-decoupled proton NMR spectrum of the mixture **2a**/**2b**, showing (a) the methine region (H(1)) and (b) the methylene (H(4)) region. The H(4c) proton, cis to the carboxyl group, belongs to **2b**; and the H(4t) proton, trans to the carboxyl group, belongs to **2a** (see Figure 2).

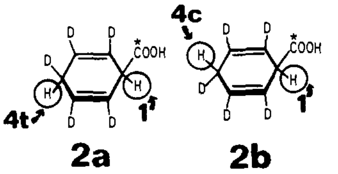


Figure 2. Structures of **2a** and **2b**, whose NMR spectra are shown in Figure 1. The protons H(1), H(4c), and H(4t) are specifically labeled.

(2) a lanthanide induced shift study of 1,4-dihydrobenzyl alcohol[2a] has shown that the homoallylic proton signal with the smaller coupling moves faster than the other homoallylic proton signal, and a corresponding lanthanide induced shift study of *cis*- and *trans*-2,4a-dihydrotriptycene carboxylates[2b] has shown that this downfield signal belongs to the proton cis to the 1-substituent.

For **3**, the $^5J_{HH}$ assignments have previously been made for the parent compound.[2,11] Thus assigned, it is observed from Table I that cis-J_{CH} > trans-J_{CH}, just as would be anticipated (an axial-axial coupling should be large).[8]

The spectral assignments for **4** follow directly from previous work[6] that has established chemical shifts for the 9-substituted-9,10-dihydroaromatic system.

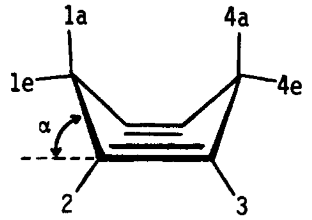
Justification for Using J_{CH} Values: the J_{CH}/J_{HH} Ratio. In the present study it was assumed that homoallylic J_{CH} values correlate with homoallylic J_{HH} values. The basis for this assumption is a previous study[12] in which it was shown that for labeled carboxylic acids, J_{CH} correlates with J_{HH} for 2-, 3-, 4-, and 5-bonded couplings in olefins, aromatics, acetylenes, and aliphatics (correlation coefficient = 0.98). For a given type of coupling it was shown[12] that J_{CH}/J_{HH} is about 0.6 (the slope of the plot was 0.62). Since compound **2** is flat, then the geometry of cis-$^5J_{CH}$ should approximate that of cis-$^5J_{HH}$, and likewise the geometries of trans-$^5J_{CH}$ and trans-$^5J_{HH}$ should be similar. Compound **2** thus offers a system suitable to test this correlation for homoallylic couplings. Indeed, from Table I these ratios are calculated to be: cis-J_{CH}/cis-J_{HH} = 5.75/9.19 = 0.63, and trans-J_{CH}/trans-J_{HH} = 4.65/7.56 = 0.62. This excellent agreement between cis-J_{CH}/cis-J_{HH}, trans-J_{CH}/trans-J_{HH}, and the previously observed ratio of 0.62 is no doubt to some degree fortuitous, for *identical* geometries are not to be expected for a J_{CH} geometry and its respective J_{HH} geometry, but it is nevertheless clear that homoallylic J_{CH} values in the conformational analysis of **2–4** can be related to the geometrically equivalent J_{HH} values. Thus, cis-trans ratios for J_{CH} should be just as meaningful as cis-trans ratios for J_{HH}. Indeed, for flat **2**, it is calculated from Table I that cis-J_{CH}/trans-J_{CH} = 1.24, and that cis-J_{HH}/trans-J_{HH} = 1.22; thus, it is clear that the cis-J/trans-J ratio for this flat system is about 1.21, for both proton–proton and carbon–proton systems. Previously observed cis-J_{HH}/trans-J_{HH} ratios for flat systems have been 1.20 for dihydrobenzene,[10] 1.2 for 1,4-dihydrobenzyl alcohol,[2a] and 1.1 for 3-fluoro-1,4-dihydrobenzyl alcohol.[2a]

A further check is possible on the suitability of using $^5J_{CH}$ values in the conformational analysis of **2–4**. From the ^{13}C-satellite proton spectrum of dihydroanthracene itself, an axial-axial proton–proton homoallylic coupling constant of 4.8 Hz has been determined.[5] The axial-axial carbon–proton homoallylic value of 3.2 Hz taken from Table I for **4** thus generates a ratio of J_{CH}/J_{HH} = 3.2/4.8 = 0.67, again close to the previously observed[12] value of 0.62.

Theoretical Considerations

A previous theoretical study[8] of (monoolefin) homoallylic coupling constants indicates a straightforward trend in which the calculated coupling constant increases as either, or (to a much greater degree) both, of the C–H bonds approach a parallel alignment with the atomic p orbitals of the π system. Subsequently, in an attempt to extend this trend to cyclohexadiene (dual path), the calculated coupling constants of the first study have been multiplied by a factor of 2.[5] To ascertain if this latter approach might be too simplistic, SCF-INDO-FPT calculations[13] were done in the present study on 1,4-cyclohexadiene itself at various conformations. Table II gives the results. In Table II proton–proton coupling constants are given as the puckering angle α varies (defined as the dihedral angle of the plane defined by the sp^2 carbons and the plane defined by $C_{(6)}$–$C_{(1)}$–$C_{(2)}$). The geometry of cyclohexadiene is taken from an electron diffraction study,[14] and for the various values of α in Table II constant bond lengths and constant independent bond angles were retained. The maximum value of α was taken at 35°, because at this value the C–H bond is parallel to the olefinic p orbitals (within 0.1°). In order to determine the effect of a dual path vs. a single path, calculations for 2-butene were also done utilizing an identical geometry; these values also appear in Table II. This calculated value for 2-butene is somewhat larger than that done by Barfield and Sternhell (compare 4.8 with 2.8); the cause for this difference most probably arises from the shorter bond lengths and larger internal angles of cyclohexadiene cited in the electron diffraction study[14] (Barfield and Sternhell used "standard" bond lengths and bond angles).

Table II. Calculated[a] Proton–Proton Coupling Constants of 1,4-Cyclohexadiene at Various Puckering Angles



Puckering angle, α, deg	Calculated J, Hz: 1a, 4a (cis)	1e, 4e (cis)	1a, 4e (trans)	1a, 2	1e, 2	1a, 3	1e, 3	1a, 1e	Energy, kcal/mol
0	16.06	16.06	12.45	4.10	4.10	−2.30	−2.30	−13.85	0.0
10	21.96	9.73	11.22	3.20	5.28	−3.26	−1.10	−13.01	0.67
20	25.44	4.55	8.05	2.86	6.41	−3.85	0.18	−10.85	3.08
30	25.13	1.23	4.29	3.16	7.14	−4.02	1.37	−8.24	8.08
35	23.41	0.31	2.65	3.53	7.26	−3.95	1.89	−7.04	11.89
35[b]	22.83		2.79	3.58		−4.01		−6.52	
2-Butene, 0°[c]	4.78	4.78	4.59	3.85	3.85	−2.18	−2.18	−9.44	

[a] Calculated by SCF–INDO–FPT;[13] geometry taken from an electron diffraction study.[14] All bond lengths and independent bond angles are not changed, except for the puckering angle α, defined as the dihedral angle of the plane of C(2)–C(3)–C(5)–C(6) and the plane of C(2)–C(1)–C(6). [b] Done as for the previous 35° case except that all overlap integrals between C(1) and its hydrogens, and C(4) and its hydrogens, have been reduced to zero. [c] Geometry exactly the same as for 1,4-cyclohexadiene at α = 0°.

Several interesting observations can be made from Table II. First, the calculated homoallylic coupling constants are surprisingly large. In particular, the axial-axial couplings (1a,4a) attain in excess of 25 Hz, while the largest experimental axial-axial proton-proton coupling constant is 12 Hz. This is consistent with previous observations that the INDO approach overestimates σ–π contributions.[15]

Second, notwithstanding the overestimation of the INDO approach of these contributions, comparison of the calculated ^5J values in cyclohexadiene vs. that in 2-butene in Table II shows that a dual path does not just "double" the coupling, but that additional enhancement is occurring. This may be related to the enhancement factor previously observed[16] for 2,5-dihydrofurans, in which a second potential coupling path apparently does not contribute directly to the coupling, but instead increases the normal homoallylic coupling by a "substituent" effect. In cyclohexadienes, apparently each olefin "substituent" has a similar enhancement factor on the coupling path of the other olefin, and of course this phenomenon occurs twice. This enhancement factor clearly appears in the experimental data where single-path homoallylic couplings are typically 1–2 Hz,[8] while dual-path homoallylic couplings are a magnitude greater.

Third, a surprising observation is that the axial-axial couplings do not steadily increase as α increases; instead, $^5J_{ax\text{-}ax}$ increases rapidly until $\alpha = 20°$, when $^5J_{ax\text{-}ax}$ begins to drift. The origin of this effect could arise from two possible sources: (1) As the H(1)–H(4) distance decreases (as α increases), a through-space negative contribution to the overall coupling constant may occur. (2) The enhancement factor (vide infra) may become less effective as the substituent (one olefin) and the coupling path (the other olefin) fall further from mutual planarity. In an attempt to ascertain which of the two explanations were correct, the through-space contribution to the homoallylic coupling was removed by making the overlap integrals zero between C(1) (and its hydrogens) and C(4) (and its hydrogens) in a technique previously described.[17] The last entry of Table II for α = 35° shows the results as this contribution is removed: very little happens. Thus, reason 1 appears *not* to be the correct one.

Table III. Theoretical $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ and $J_{ax\text{-}ax}/J_{ax\text{-}eq}$ Ratios (from Table II) for Various Puckering Angles

Puckering Angle, α[a]	$J_{eq\text{-}eq}/J_{ax\text{-}eq}$[b]	$J_{ax\text{-}ax}/J_{ax\text{-}eq}$[b]
0	1.29	1.29
10	0.87	1.96
20	0.57	3.16
30	0.29	5.86
35	0.17	8.83

[a] Defined in Table II. [b] Both these ratios are J_{cis}/J_{trans}.

Table IV. Empirical $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ and $J_{ax\text{-}ax}/J_{ax\text{-}eq}$ Ratios for Compounds **2–4**

Compd	$J_{eq\text{-}eq}/J_{ax\text{-}eq}$[a]	$J_{ax\text{-}ax}/J_{ax\text{-}eq}$[b]
2	1.22	1.24
3	0.88	1.90
4	<0.55 (0.3–0.7[c])	4.6

[a] cis-J_{HH}/trans-J_{HH}. [b] cis-J_{CH}/trans-J_{CH}. [c] This range is for a series of 9-alkyl-9,10-dihydroanthracene compounds (ref 6a).

This third observation has a strong implication on the utilization of the value of $^5J_{ax\text{-}ax}$ as a measure of the degree of puckering of the dihydro ring. At larger values of α, $^5J_{ax\text{-}ax}$ may be relatively insensitive to the degree of puckering, and claims to the "maximum extent of puckering" based on the "largest possible $^5J_{ax\text{-}ax}$" may be faulty.

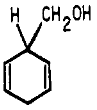
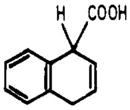
Fourth, as α increases, the equatorial-equatorial and equatorial-axial couplings decrease while the axial-axial couplings increase. This suggests that the $J_{ax\text{-}ax}/J_{ax\text{-}eq}$ ratio should be as sensitive as the $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ ratio (if not more so) to the degree of puckering of the dihydro ring and prompts a close look at the J_{CH}(cis)/J_{CH}(trans) ratios of the present series.

Discussion

A Comparison of the Ratios $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ and $J_{ax\text{-}ax}/J_{ax\text{-}eq}$. Table III gives a comparison of the theoretical $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ and $J_{ax\text{-}ax}/J_{ax\text{-}eq}$ ratios, generated directly from Table II. It is observed that the former ratio decreases, and the latter ratio increases, as α increases. The sensitivity of both ratios to α is about the same ($J_{ax\text{-}ax}/J_{ax\text{-}eq}$ is slightly more sensitive).

The assumption that J_{CH} ratios can be compared with J_{HH} ratios (vide supra) is now utilized. Table IV shows empirical $J_{eq\text{-}eq}/J_{ax\text{-}eq}$ ratios (J_{HH}) and $J_{ax\text{-}ax}/J_{ax\text{-}eq}$ ratios (J_{CH}) for compounds **2–4**. Again, the former ratio decreases, and the latter ratio increases, throughout this series. And again, the

Table V. Comparison of Theoretical and Empirical Proton–Proton Coupling Constants

		$^3J_{1e\text{-}2}$		$^3J_{1a\text{-}2}$		$^4J_{1e\text{-}3}$		$^4J_{1a\text{-}3}$		
Compd	Ref	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Concluded[d] category
	2a	3.1	4.1[a]	3.1	4.1[a]	(−)1.5	−2.3[a]	(−)1.5	−2.3[a]	Flat
	7a	4.6	5.3[b]	2.4	3.2[b]	−1.2	−1.1[b]	−2.4	−3.3[b]	Flattened boat
5	2b			2.5	3.2[c]			(−)3.0	−4.0[c]	True boat
6	2b	5.8	7.1[c]	2.5	3.2[c]	≤1.0	1.37[c]	(−)3.0	−4.0[c]	True boat

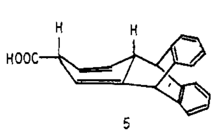
[a] Calculated coupling constants taken from Table II for $\alpha = 0°$. [b] Calculated coupling constants taken from Table II for $\alpha = 10°$. [c] Calculated coupling constants taken from Table II for $\alpha = 30°$. [d] This comparison of observed and calculated J values is not to imply specific values of α to the indicated compounds, but merely to illustrate that these three designated categories are empirically supportable. See text.

latter ratio appears to be slightly more sensitive to structural changes.

The agreement between Tables III and IV is quite reasonable: as one progresses from a flat dihydro system ($\alpha = 0°$) to a more highly puckered system, $J_{\text{eq-eq}}/J_{\text{ax-eq}}$ steadily decreases from an original value of ~1.25, and $J_{\text{ax-ax}}/J_{\text{ax-eq}}$ steadily increases from an original value of ~1.25.[18]

This agreement between the data of Tables III and IV suggests that quantifying the puckering in a dihydro ring may be possible such that a "true boat" or a "flattened boat"[7b] might have numerical significance. It would be an extreme overinterpretation of the data to suggest that from Tables III and IV true values of α can be obtained for **2–4**, but it does seem reasonable that separate categories can be formulated for **2** ("flat"), **3** ("flattened boat"), and **4** ("true boat"). In an attempt to see if the data of Tables III and IV do reflect true values of α for dihydro systems, one can extrapolate the $J_{\text{ax-ax}}/J_{\text{ax-eq}}$ value for **4** (4.6 Hz) to obtain a predicted value of $\alpha \simeq 25°$. The x-ray value for 9,10-dihydroanthracene itself is $\alpha \simeq 28°$.[19] Thus, it is possible that empirical homoallylic ratios can reflect the true degree of puckering of dihydroaromatic rings with a reasonable amount of accuracy.

$J_{\text{ax-ax}}/J_{\text{ax-eq}}$ in a Proton–Proton System. As pointed out above, J_{CH} ratios were needed to utilize the $J_{\text{ax-ax}}/J_{\text{ax-eq}}$ ratio, since the substituent lies thermodynamically in the axial orientation. However, a limited number of $J_{\text{ax-ax}}/J_{\text{ax-eq}}$ ratios are available from the literature. In the dihydrotriptycene carboxylic acids **5** and **6**,[2b] this ratio is 2.6 and is indeed greater than for the "flattened boat" **3**. In another example of kinetic control in the [2.2]paracyclophane series where the substituent was equatorial,[20] this $J_{\text{ax-ax}}/J_{\text{ax-eq}}$ ratio was greater than 8.8 ($J_{\text{ax-eq}} < 1$ Hz, $J_{\text{ax-ax}} = 8.8$ Hz). This very large ratio indicates a very highly puckered system, notwithstanding a "modest" $J_{\text{ax-ax}}$ value. Indeed, as stated above, the most highly puckered systems may not have the largest $J_{\text{ax-ax}}$ values.



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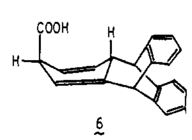

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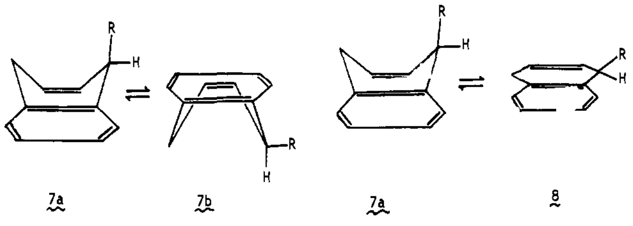
Coupling Constants Other Than Homoallylic, Theoretical vs. Observed. Table V compares theoretical proton-proton coupling constants, generated from 1,4-cyclohexadiene for α = 0, 10, 30°, with empirical proton-proton coupling constants from various derivatives. This comparison shows that the calculated values from the adopted geometry[14] of cyclohexadiene are consistently too large. That the calculated J values are too large both for homoallylic and nonhomoallylic coupling constants suggests that the published geometry[14] of cyclohexadiene may suggest too compact a molecule (bond lengths too short, internal ring angles too small, placing C(1) too close to C(4)), as suggested above. Nevertheless, a consistent trend emerges whereby in all types of couplings, the observed and calculated coupling constants increase or decrease respectively in the same manner. This table is not to imply specific values of the puckering angle α for the compounds in Table V, but merely to illustrate that the three separate categories—"flat", "flattened boat", and "highly puckered"—are empirically supportable for couplings other than homoallylic.

Geminal Couplings. If a steady trend occurs for the compounds **2–4**, then the geminal aliphatic couplings should become less negative through the series[21] (i.e., as the plane of the olefins becomes further skewed from bisection of the geminal H-H angle). Indeed, the data from Table I shows this for both the geminal H-H and C-H coupling constants.

Carbon–Carbon Couplings. In a previous study,[15] carbon-carbon couplings were obtained for a series analogous to **2–4**, and from this study also it was concluded that a monotonic increase in the extent of puckering existed throughout this series.

The Possibility of Rapidly Introconverting Conformers for 3. Dihydroanthracene rapidly equilibrates, and "freezing out" the separate conformers in NMR proton spectroscopy cannot be done, even at −60 °C.[22] A similar attempt was made in the present study for 1,4-dihydro-1-naphthoic acid. Down to −60 °C no change in the proton NMR spectrum was observed; below this temperature the solubility of the compound was too low to allow an NMR study. Since these studies could not be conducted at extremely low temperatures, then they should be considered inconclusive.

Therefore, the possibility should be considered of rapidly equilibrating conformers of 1,4-dihydro-1-naphthoic acid. In this treatment, two possibilities will be considered: boat ⇄ boat (**7a** ⇄ **7b**) and boat ⇄ flat (**7a** ⇄ **8**).



7a 7b 7a 8

(1) Boat ⇄ boat (**7a** ⇄ **7b**). The possibility of substantial amounts of both **7a** and **7b** can be fairly easily eliminated. First, vicinal proton-proton coupling constants of both H(4) protons with H(3) should be similar (compare the actual values 4.60 with 2.44 Hz[7a]). Second, the ratio $J_{\text{cis}}/J_{\text{trans}}$ should be similar for both carbon-proton and proton-proton couplings (but

compare the actual values of 0.88 and 1.90 from Table IV). Third, from Table II the theoretical ratios of $J_{\mathrm{cis}}/J_{\mathrm{trans}}$ can be calculated to be large (for $\alpha = 20°$, this ratio should be 1.9, for both J_{CH} and J_{HH}). The actual ratio is 0.88 for J_{HH} and 1.90 for J_{CH}. Fourthly, allylic coupling constants of both H(4) protons with H(2) should be similar (but compare −1.24 with −2.97).

(2) Boat $\rightleftarrows$ flat (**7a** $\rightleftarrows$ **8**). The possibility of substantial amounts of both **7a** and **8** is real, because the observed vicinal and allylic coupling values for 1,4-dihydro-1-naphthoic acid could be interpreted to be an "average" between those for flat and puckered conformations (see Table V). Furthermore, predicted ratios of homoallylic $J_{\mathrm{cis}}/J_{\mathrm{trans}}$ calculated from the data in Table II give $J_{\mathrm{cis}}/J_{\mathrm{trans}} = [\frac{1}{2}J_{\mathrm{eq\text{-}eq}}(30°) + \frac{1}{2}J_{\mathrm{ax\text{-}ax}}(0°)]/[\frac{1}{2}J_{\mathrm{ax\text{-}eq}}(30°) + \frac{1}{2}J_{\mathrm{ax\text{-}eq}}(0°)] = [0.62 + 8.03]/[2.14 + 6.22] = 1.03$, and for carbon–proton couplings $J_{\mathrm{cis}}/J_{\mathrm{trans}} = [\frac{1}{2}J_{\mathrm{ax\text{-}ax}}(30°) + \frac{1}{2}J_{\mathrm{eq\text{-}eq}}(0°)]/[\frac{1}{2}J_{\mathrm{ax\text{-}eq}}(30°) + \frac{1}{2}J_{\mathrm{ax\text{-}eq}}(0°)] = [12.56 + 8.03]/[2.14 + 6.22] = 2.46$. These values are in fair agreement with the respective values of 0.88 and 1.90 (Table IV). Thermodynamically, however, the existence of two energy minima over a range of α (of, say, 0–35°) does not appear to be plausible. The factor that renders the puckered conformation more stable in **4**—the peri interaction of the carboxylate group with the aromatic protons and/or the angle strain[23]—would cause a monotonic decrease in energy in **3** as α increases. Meanwhile, the factor, that renders the flat conformation the most stable for **2**—the staggered arrangement of the aliphatic and olefinic protons (the torsional factor[23])—would cause a monotonic increase in energy in **3** as α increases. The net result would be one energy minimum.

Conclusions

Both proton–proton and carbon–proton homoallylic coupling constants can be dependably used in the conformational analysis of dihydrobenzenes, dihydronaphthalenes, and dihydroanthracenes provided enough data is available to generate a $^5J_{\mathrm{cis}}/^5J_{\mathrm{trans}}$ ratio. From such ratios for dihydrobenzenes, dihydronaphthalenes, and dihydroanthracenes it is clear that the degree of puckering follows a monotonic increase in this series of compounds. This conclusion is consistent with other data including: vicinal and allylic proton–proton coupling constants, geminal proton–carbon and proton–proton coupling constants; and various carbon–carbon coupling constants.

Experimental Section

Proton NMR spectra were done on a JEOL PS-100 NMR spectrometer utilizing internal lock mode and deuterium decoupling. The spectra were first order and no differences were noted between J values obtained by first-order analysis and those generated by LAOCOON III analysis.[24] The J values obtained in this study are considered to be accurate within 0.1 Hz.

Synthesis. Compounds **2** and **3** were synthesized using procedures identical with those previously described for the analogues without the ^{13}C label.[7b,9] The ^{13}C label was introduced in a manner identical with that for the nondeuterium analogues of **2** and **3**.[15] Compound **4** has been previously synthesized.[15]

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