Stereochemistry of 1,4-Cyclohexadienes. Planar vs. Boat-Shaped Conformations

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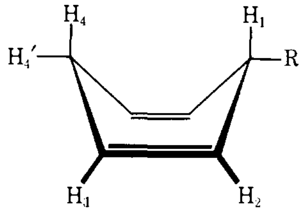
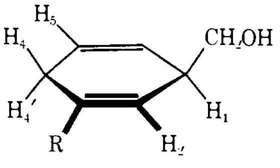
Abstract: The problem of planar vs. boat-shaped 1,4-cyclohexadiene ring systems is attended to through the conformational analysis of restricted, rigid systems such as *cis*- and *trans*-methyl 2,4a-dihydrotriptycene-2-carboxylate (*cis*- and *trans*-**4**), as well as the unrestricted 1,4-dihydrobenzyl alcohol (**2a**) and 3-fluoro-1,4-dihydrobenzyl alcohol (**2b**). NMR analysis using Eu(fod)$_3$ and triple irradiation techniques indicates that **2a** and **2b** are, in fact, planar, and the NMR parameters from these compounds together with the boat-shaped *cis*- and *trans*-**4** are presented for the general analysis of the 1,4-cyclohexadiene ring system. The significance of the homoallylic coupling constants and their variation with geometry in these compounds is also discussed.

For a number of years, the 1,4-cyclohexadiene ring system was generally considered to be boat-shaped (**1a**),[1] even though a planar structure was suggested in 1949 on the basis of vibrational spectral analysis.[2] Interestingly, the last 10 years have seen a series of conflicting reports[3-14] almost evenly divided between the boat-shaped and planar conformations. A major cause of these difficulties has been the fact that NMR analysis provides unusually large coupling constants across the ring (homoallylic coupling constants typically 8-9 Hz), but due to a remarkable number of chemical shift equivalences in a variety of derivatives, allylic and vicinal coupling constants cannot be measured from the deceptively simple spectra.[6,10-14] Thus, the ratio of cis and trans homoallylic coupling constants has been the basis of conformational assignments, and, for example, led to the suggestion[12] that 1,4-dihydrobenzoic acid exists in a boat with the substituent pseudoequatorial (i.e., **1b**). Unfortunately, there has been some disagreement[7,11,12] concerning the "predicted value" of the J_{cis}/J_{trans} ratio expected for the planar form.[15]



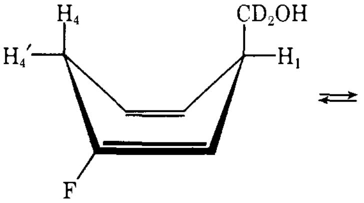
1a, R = H
b, R = CO$_2$H



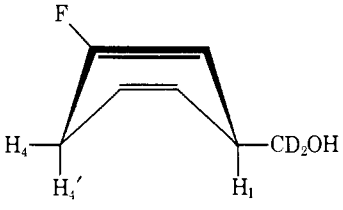
2a, R = H
b, R = F

In a preliminary communication of these results,[17] we reported the complete NMR analysis of two 1,4-cyclohexadiene derivatives (**2a** and **2b**), and concluded that these structures are, in fact, planar. Thus, the NMR spectrum of 1,4-dihydrobenzyl alcohol (see Figure 1a) presents the usual problems of this system in that protons H_1, H_4, and $H_{4'}$ are strongly coupled to each other, but the appearance of the combined $H_4H_{4'}$ signal as a doublet gives the false suggestion that these "accidentally" equivalent protons are equally coupled to H_1. However, the addition of Eu(fod)$_3$ with simultaneous decoupling of both vinyl signals (Figure 1b) facilitates the appearance of H_4[18] and $H_{4'}$ as an AB quartet with each signal further split by H_1. As illustrated, the homoallylic coupling constants are indeed different (see Table I), and it should be noted that the cis/trans ratio, $J_{1,4'}/J_{1,4}$ = 1.16, is in good agreement with the value of 1.12 calculated for a planar ring.[15] Two additional results from Table I also suggest a planar ring, the large $J_{4,4'}$ value,[19] and the equality of the vicinal coupling constants $J_{3,4}$ and $J_{3,4'}$, which indicates that H_3 must bisect the angle between H_4 and $H_{4'}$.

In order to investigate the possibility of rapid boat to boat inversion which would also lead to equal $J_{3,4}$ and $J_{3,4'}$ values, we prepared 3-fluoro-1,4-dihydrobenzyl alcohol-d_2[20] (**3**) on the assumption that ring inversion would average in relatively large H_4F and $H_{4'}F$ coupling constants (i.e., H_4F and $H_{4'}F$ dihedral angles become small in **3b** and **3a**, respectively).[21] Comparison of the ^1H NMR spectrum (60 MHz) with and without ^{19}F heteronuclear decoupling indicates that there is strong coupling between fluorine and H_2 (17.5 Hz), H_5 (7.5) (note the W relationship), and H_6 (4.8). However, coupling between F and H_4,$H_{4'}$ appears to be quite small, <2 Hz, and could not be measured even though attempts were made under a variety of conditions. Once again, however, using Eu(fod)$_3$[24] (see Table II) we were able to observe $H_4H_{4'}$ (see Figures 2 and 3) which originally appeared as an AB pattern with strong coupling from H_1, and by decoupling H_2 and H_6, $J_{4,5}$ and $J_{4',5}$ were determined to be equal (3.5 Hz). Similar to **2a**, the ratio of cis/trans homoallylic coupling constants (1.11) is almost identical with that calculated for a planar ring.[15] Hence, on the basis of (1) small H_4F and $H_{4'}F$ coupling constants, (2) equality of $J_{4,5}$ and $J_{4',5}$ and (3) agreement of "predicted" cis/trans homoallylic coupling constant ratio with theory, we conclude that **3** is planar (or less likely, involves *very shallow* boat conformations undergoing fast ring inversion).



3a



3b

In addition to the verification that there are, in fact, planar 1,4-cyclohexadienes, we had hoped that making available the values for the cis and trans homoallylic coupling constants ($J_{1,4'}$ and $J_{1,4}$), allylic coupling constants ($J_{2,4}$ and $J_{2,4'}$), and vicinal coupling constants ($J_{4,5}$ and $J_{4',5}$)

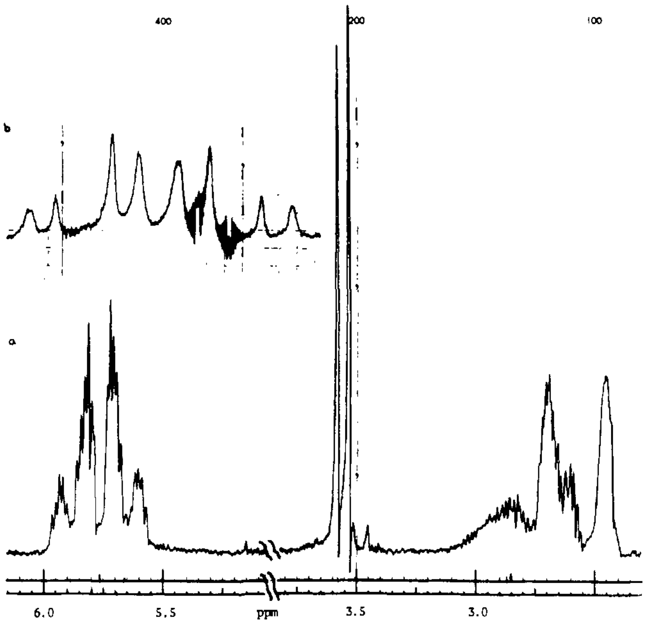


Figure 1. NMR spectrum ($CDCl_3$; 100 MHz) of 1,4-dihydrobenzyl alcohol (**2a**): upper trace, H_4 and $H_{4'}$ with $Eu(fod)_3$ added and vinyl protons decoupled.

Table I. 100 MHz NMR Data for 1,4-Dihydrobenzyl Alcohol (2a) with $Eu(fod)_3$

Signal obsd	Decoupled protons[a]	Signal pattern	Results
$H_2,H_6; H_3,H_5$[b,c]	$H_1; H_4,H_{4'}$	4 line AB	$J_{2,3} = 10.3$ Hz
$H_2,H_6; H_3,H_5$	$H_4,H_{4'}$	4 lines (AB) each split into a doublet	$J_{1,2} = 3.1$,[d] $J_{1,3} = 1.5$[e]
$H_2,H_6; H_3,H_5$	H_1	4 lines (AB) each split into a triplet	$J_{3,4} = J_{3,4'} = 3.0$[f] $J_{2,4} = J_{2,4'} = 1.5$[g]
$H_4,H_{4'}$[h]	$H_1; H_3,H_5$	4 line AB	$J_{4,4'} = 21.7$[i]
$H_4,H_{4'}$	$H_2,H_6; H_3,H_5$	4 lines (AB)[j] each split into a doublet	$J_{1,4} = 7.4$,[d] $J_{1,4'} = 8.6$[e]

[a] Triple irradiation, two external oscillators used. [b] $Eu(fod)_3$ added until vinyls crossed and become separated. [c] The upfield half of the vinyl AB system moves fastest with $Eu(fod)_3$ addition, crosses the other half, and becomes the downfield portion. Hence, it is assigned to $H_{2,6}$. [d] From coupling of downfield doublet pairs. [e] From coupling of upfield doublet pairs. [f] Upfield triplet pairs. [g] Downfield triplet pairs not well resolved. [h] More $Eu(fod)_3$ added until $H_4,H_{4'}$ is observed as an AB system. [i] $H_2(H_6)$, $H_4(H_{4'})$ coupling not observed under these conditions. [j] Appropriately treated as first order, since $\delta_{4,4'} = 35$ Hz at this point (see also footnote *c*, Table II); confirmed by LAOCN3.

Table II. 100 MHz NMR Data for 3-Fluoro-1,4-dihydrobenzyl Alcohol-d_2 (3) with $Eu(fod)_3$

Signal obsd	Decoupled nuclei[a]	Signal pattern	Results
$H_4,H_{4'}$	H_2,H_6	4 line AB each split into a doublet of doublets[b]	$J_{4,4'} = 22.0$ Hz $J_{4,5} = 3.5$ $J_{4',5} = 3.5$
$H_4,H_{4'}$	H_5,H_6	4 line AB each split into doublets[c,d]	$J_{1,4} = 7.5$ $J_{1,4'} = 8.3$
H_5,H_6	$H_1,H_4,H_{4'}$	4 line AB each split into doublets[d]	$J_{5,6} = 10.5$ $J_{5,F} = 7.5$ $J_{6,F} = 4.8$
H_2	$H_1,H_4,H_{4'}$	Doublet[e]	$J_{2,F} = 17.5$ $J_{2,6} = 1.4$
H_2	$H_1,H_4,H_{4'}$	Doublet of doublets	$J_{1,2} = 3.4$

[a] Triple irradiation, two external oscillators used. [b] Major secondary coupling from H_1. However, $J_{H_1H_4}$ and $J_{H_1H_{4'}}$ were more accurately measured by decoupling H_5,H_6. [c] Plus small additional coupling. [d] Appropriately treated as first order, since $\delta_{4,4'} = 42$ Hz at this point, and in addition, $J_{1,4}$ and $J_{1,4'}$ are unchanged with increased chemical shift (i.e., more shift reagent). [e] In several decoupling attempts, an additional coupling of 1.4 Hz was observed. A similar coupling had also been observed with H_6, and therefore we assigned this to $J_{2,6}$.

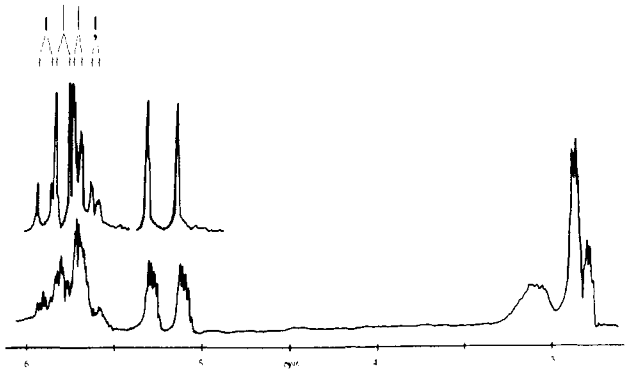
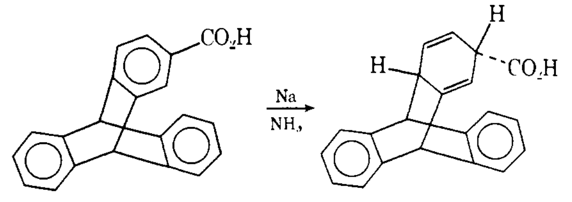
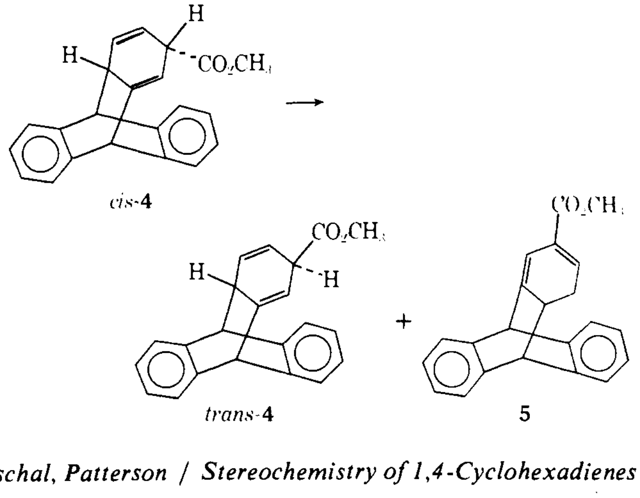


Figure 2. NMR spectrum ($CDCl_3$; 100 MHz) of 3-fluoro-1,4-dihydrobenzyl alcohol-d_2 (**3**): upper trace with decoupling of H_1, H_4, and $H_{4'}$.



would provide a basis for the analysis of additional (as well as previously reported) 1,4-cyclohexadiene systems. Interestingly, these results raise the important question of whether all conformationally free 1,4-cyclohexadienes are, in fact, planar, or if suitable substitution can cause the adoption of a boat conformation. Thus, in order to recognize a boat structure, if encountered, we felt that suitable, unambiguous NMR parameters must be made available, and this led us to the preparation of a rigid, boat-shaped derivative.

The reduction of triptycene-2-carboxylic acid with sodium in liquid ammonia[25] provides *cis*-2,4a-dihydrotriptycene-2-carboxylic acid in good yield. However, in order to obtain the desired NMR parameters, the trans isomer was needed as well, and to this end the corresponding methyl ester was prepared. Interestingly, attempted isomerization under a variety of conditions, including standing for 30 min in pyridine, led only to **5**. However, if *cis*-**4** is dissolved in



cis-**4**

trans-**4**

5

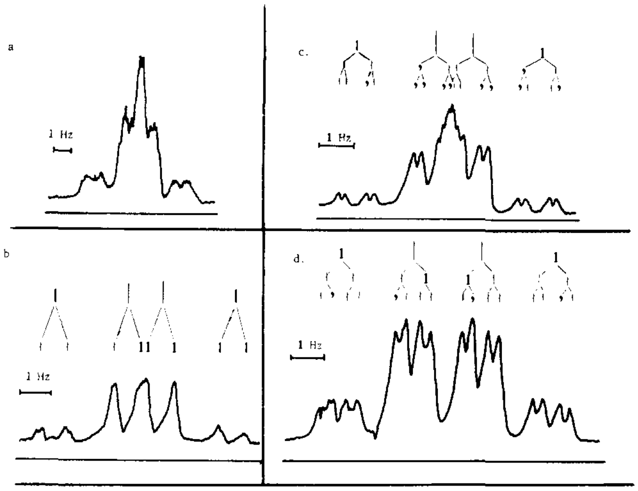


Figure 3. NMR spectrum ($CDCl_3$; 100 MHz) of compound **3** showing protons H_4 and $H_{4'}$ in the presence of Eu(fod)$_3$: (a) with no decoupling; (b) decoupling all vinyl protons; (c) decoupling H_2 and H_6, (d) same as c, but with additional Eu(fod)$_3$.

Table III. 100 MHz NMR Data for *cis*-2-Carbomethoxy-2,4a-dihydrotriptycene (4)[a]

Signal obsd	Decoupled protons[b]	Signal pattern	Results
H_2	H_1,H_3,H_4	Doublet	$J_{2,4a} = 12.0$ Hz[c]
H_{4a}	H_1,H_3,H_4	Doublet of doublets	$J_{2,4a} = 12.0; J_{4a,10} = 2.0$
H_{10}	H_1,H_3,H_4	Doublet	$J_{4a,10} = 2.0$
H_{4a}	H_4,H_{10}	Doublet of triplets[d]	$J_{1,4a} = J_{3,4a} = 3.0$[d]
H_2[e]	H_1,H_3	Doublet of doublets	$J_{2,4} = 3.0$
H_4[e]	H_2,H_{4a}	Doublet	$J_{3,4} = 9.6$
	H_{4a}	Doublet of doublets	$J_{3,4} = 9.6, J_{2,4} = 3.0$
	H_2	Doublet of doublets	$J_{3,4} = 9.6, J_{4,4a} = 2.5$

[a] $CDCl_3$. [b] Double or triple irradiation as necessary. [c] Confirmed by irradiation of H_{4a}. [d] Presumably a valid measurement since H_1 and H_3 have identical chemical shifts, are not coupled to one another, and have exactly the same geometric relationship to H_{4a}. [e] Eu(fod)$_3$ added to separate H_4 from H_1 and H_3.

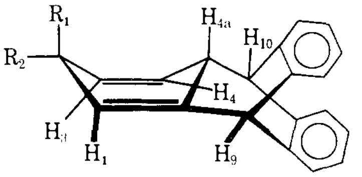
Table IV. 100 MHz NMR Data for *trans*-2-Carbomethoxy-2,4a-dihydrotriptycene (**4**)[a]

Signal obsd	Decoupled protons	Signal pattern[b]	Results
H_2	H_1,H_3,H_4	Doublet	$J_{2,4a} = 4.7$ Hz
	H_4	Doublet of triplets[c]	$J_{2,1} = J_{2,3} = 5.8$
H_4		Doublet of doublets[d]	$J_{4,4a} = 2.5$
	H_2	No significant change	$J_{2,4} \geqslant 1.0$
H_1H_3	H_4	Doublet of doublets[c]	$J_{1,2} = J_{1,3} = 5.5$ $J_{1,4a} = J_{3,4a} = 3.0$
H_{10}	H_1,H_3,H_4	Doublet	$J_{4a,10} = 2.0$
H_1[e]	H_{4a}	Broad doublet	$J_{1,2} = 5.7$[f]

[a] $CDCl_3$. [b] Double or triple irradiation as necessary. [c] Presumably a valid measurement since H_1 and H_3 have identical chemical shifts, are not coupled to one another, and have exactly the same geometric relationship to H_2 (see alternate measurement below). [d] Measurement confirmed by decoupling H_4 and observing H_{4a}. [e] Eu(fod)$_3$ added, H_1 and H_3 separated but broad. [f] The values of 5.8, 5.5, and 5.7 for $J_{1,2}$ are presumably a reflection of the experimental error encountered in measuring this value by three different ways.

pyridine for 5 min and then recovered, the cis and trans isomers are furnished in equal amounts without **5**, and *trans*-**4** is obtained by recrystallization.

It should be noted that the 1,4-cyclohexadiene ring in both of these isomers is quite rigid, and models suggest that the degree of puckering is "normal" as compared with the Drieding model of unsubstituted, boat-shaped 1,4-cyclohexadiene. In addition, the cis isomer affords a pseudoaxial/pseudoaxial homoallylic relationship, and the trans a pseudoaxial/pseudoequatorial proton interaction.



cis-4: $R_1 = H_2$; $R_2 = CO_2CH_3$

trans-4: $R_1 = CO_2CH_3$; $R_2 = H_2$

The NMR analysis was accomplished by double and triple irradiation together with the use of Eu(fod)$_3$, and the results are presented in Tables III and IV. The important features for *cis*-**4** include the homoallylic coupling constant $J_{2,4a}$ = 12.0 Hz (*to our knowledge this is the largest homoallylic coupling constant ever reported*), the allylic coupling constant $J_{2,4}$ = 3.0, and the vicinyl coupling constant $J_{4,4a}$ = 2.5.[26] As expected,[27,19] the homoallylic coupling constant for *trans*-**4** is considerably smaller ($J_{2,4a}$ = 4.7) due to the pseudoaxial/pseudoequatorial relationship, and the vicinyl coupling constant ($J_{1,2}$ = 5.7) is considerably larger than the allylic coupling constant involving a pseudoequatorial proton ($J_{2,4}$ = 1).[28]

Experimental Section

General. NMR spectra were recorded with deoxygenated samples, ca. 10% in $CDCl_3$, on a Varian HA100 or a JEOL C60HL (^{19}F). Eu(fod)$_3$ was added in small increments, and double or triple irradiation was employed to observe each signal as it became amenable to analysis. Typically, no more than four or five additions of Eu(fod)$_3$ could be made since line broadening hampered decoupling.[18b]

1,4-Dihydrobenzyl Alcohol (2a). Lithium aluminum hydride (1 g, 26 mmol) was added to a cooled, stirred solution of 1,4-dihydrobenzoic acid[30] (0.8 g, 6.5 mmol) in anhydrous ether (100 ml). The mixture was refluxed for 1 hr, cooled, and quenched cautiously with water. Usual workup resulted in an oil which was purified by preparative GLC to provide 0.3 g of **2a** (43% yield). See Figure 1 for NMR.

Anal. Calcd for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 76.18; H, 9.22.

3-Fluoro-1,4-dihydrobenzoic Acid.[31] Sodium metal (24 mmol, 3 eq) was added to *m*-fluorobenzoic acid (1 g, 8 mmol) in 60 ml of liquid ammonia containing 10 ml of anhydrous ethanol. After the blue color disappeared, 20 ml of saturated ammonium chloride solution was added and the ammonia was allowed to boil off. After 1 hr, the remaining solution was acidified with HCl (cooling), and the product was isolated by ether extraction. The residue was distilled to give 0.5 g (50%) of a colorless oil: bp 94° (0.7 mm); NMR ($CDCl_3$) δ 10.7 (bs, 1 H), 5.8 (m, 2), 5.4 (m, 1), 3.9 (m, 1), 2.8 (m, 2).

Anal. Calcd for $C_7H_7O_2F$: C, 59.16; H, 4.96; F, 13.37. Found: C, 58.87; H, 5.08; F, 13.16.

3-Fluoro-1,4-dihydrobenzyl Alcohol (3). This was prepared from the above acid and $LiAlH_4$ (or $LiAlD_4$) according to the procedure used for **2a**. See Figure 2 for NMR.

Anal. Calcd for C_7H_9OF: C, 65.62; H, 7.03; F, 14.85. Found: C, 65.47; H, 6.89; F, 14.97.

***cis*-2,4a-Dihydrotriptycene-2-carboxylic Acid.** Anhydrous ammonia (500 ml) was condensed (−78°) into a flask (under helium) containing 2-triptycenecarboxylic acid (3 g, 10 mmol) in anhydrous ethanol (250 ml). Sodium metal (0.81 g, 35 mg-atoms) was added in pieces (10 min). The solution was allowed to stir at −78° for an additional 15 min after the color disappeared, and solid NH_4Cl was added. The ammonia was allowed to evaporate, and the ethanol was removed by rotary evaporation. Cold water was then added, and the solution was acidified with cold, dilute HCl and extracted with chloroform. The solution was then washed several times with water, dried, and evaporated to give an oil. Ether was added followed by filtration, and the addition of chloroform produced white crystals: 1.2 g (40%); mp 212–215°; NMR

($CDCl_3$) δ 9.9 (bs, 1 H), 7.1 (m, 8), 6.0 (bs, 3), 4.9 (s, 1), 4.4 (d, 1), 3.5 (d, 1), 2.6 (m, 1); ir (mull) 1652 cm^{-1} (C═O); mass spectrum M^+ *m/e* 300 ($C_{21}H_{16}O_2$).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.08; H, 5.56.

***cis*-Methyl 2,4a-Dihydrotriptycene-2-carboxylate (*cis*-4).** The above acid (1.2 g) was refluxed for 2 hr with BF_3 etherate (0.6 ml) in 100 ml of methanol.[32] Upon cooling, *cis*-**4** crystallized (1.0 g, 80%) mp 154-6°: NMR ($CDCl_3$) δ 7.1 (m, 8H), 6.0 (m, 3, olefinic), 4.9 (s, 1; H_9), 4.4 (d, 1; H_{10}), 3.7 (s, 3), 3.4 (d, 1; H_2), 2.6 (d, 1; H_{4a}), ir ($CHCl_3$), 1673 cm^{-1} (C═O); mass spec M^+ *m/e* 314 ($C_{22}H_{18}O_2$).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.85; H, 5.79.

***trans*-Methyl 2,4a-Dihydrotriptycene-2-carboxylate (*trans*-4).** The above ester (*cis*-4; 0.5 g) was dissolved in 5 ml of pyridine and shaken for 1 min. The pyridine was then evaporated as quickly as possible without heat, and the residue was washed with water, extracted with ether, and again evaporated. Slow recrystallization from ether afforded *trans*-**4:** 0.1 g (20%); mp 150-152° (depressed mixture melting point with *cis*-**4a**); NMR ($CDCl_3$) δ 7.1 (m, 8 H), 6.1 (d of m, 1), 5.8 (m, 2), 4.9 (s, 1; H_9), 4.4 (bs, 1, H_{10}), 3.8 (m, 1; H_2), 3.6 (s, 3), 2.9 (m, 1; H_{4a}).

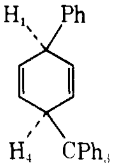
Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.27; H, 5.67.

Methyl 3,4-Dihydrotriptycene-2-carboxylate (5). Treatment of *cis*-**4** in pyridine as above but for extended periods led to the formation of **5** which was also recrystallized from ether, mp 150-152° (depressed mixture melting point with *trans*-**4**). The fact that **5** was yet a third dihydro isomer was established by mass spectrum (M^+ *m/e* 314; $C_{22}H_{18}O_2$), and the structure was assigned by NMR ($CDCl_3$) δ 7.2 (m, 8 H), 6.7 (m, 1), 6.3 (bd, 1), 4.8 (s, 1), 4.2 (bs, 1), 3.7 (s, 3), 2.45 (m, 2), 1.7 (m, 1); uv (methanol) 267 (ε 2900), 275 (3100), 295 mμ (2700).[33]

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.90; H, 5.61.

Discussion

The object of our study has been to obtain NMR parameters for both planar and boat-shaped 1,4-cyclohexadienes so as to provide a general approach to the conformational analysis of this ring system. Thus, we feel that sufficient data are now available, and, as an example, we will consider compounds **6, 7, 8,** and **9**, *all of which have been the subject of controversy concerning their stereochemistry.*



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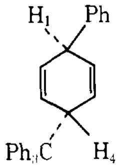

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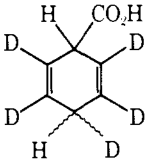

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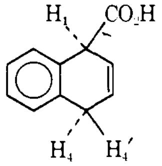

9

A boat conformation was suggested for **6**[10,11] with both substituents pseudoequatorial, and we would agree since the homoallylic coupling constant of 11 Hz compares favorably to 12 Hz found for the diaxial proton relationship in our rigid boat (*cis*-**4**). However, we disagree with the suggestion that **7** is also a boat, since its trans homoallylic coupling constant is 7.5 which does not agree well with the value of 4.5 for *trans*-**4**, but matches the values of 7.4 and 7.5 found for the two planar derivatives.[29] For the same reason, we also suggest (contrary to earlier reports[12,13]) that **8** is planar, since the homoallylic coupling constants of 8.3 and 8.9 are not even close to the values of 4.7 and 12.0 found for the boat system (**4**), but compare reasonably well with 7.4 and 8.6 found for planar **2**.

In the case of **9**, a "nearly planar" or "flattened boat" structure was suggested[14] mainly on the basis of the homoallylic coupling constants (or more exactly their ratio). We feel, however, that since these values are quite different when an aromatic ring is substituted for an olefinic double bond (i.e., 1,4-cyclohexadienes vs. 1,4-dihydronaphthalenes), the application of their ratios to determine conformation may not be analogous (cf. introductory section). In any event, the vicinal and in particular the allylic coupling constants[21] should be indicative of the ring conformation. The vicinal coupling constants ($J_{3,4}$ and $J_{3,4'}$) are 4.6 and 2.44, and the allylic coupling constants ($J_{2,4}$ and $J_{2,4'}$) are 1.24 and 2.97. The analogous values for boat-shaped **4** are vicinal 5.7 and 2.5, and allylic ≥1 and 3.0, and on this basis we conclude that **9** has about the same degree of puckering as **4** which compares favorably to a normal, boat-shaped Drieding model of 1,4-cyclohexadiene.

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References and Notes

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(15) Recently, a value of J_{cis}/J_{trans} = 1.12 was suggested on the basis of an INDO treatment.[16] See ref 14.

(16) M. Barfield and S. Sternhell, *J. Am. Chem. Soc.*, **94**, 1905 (1972).

(17) J. W. Paschal and P. W. Rabideau, *J. Am. Chem. Soc.*, **96**, 272 (1974).

(18) (a) H_4 assigned as the signal moving downfield fastest, i.e., closest proximity to CH_2OH. (b) Since the signals moved downfield at different rates, it was sometimes possible to take advantage of overlapping signals during "crossing", and simultaneous decoupling of two signals with one oscillator was achieved. Thus, a large number of spectra were recorded for each compound (a few of these are shown for **2b** in Figures 2 and 3), and it was desirable to add $Eu(fod)_3$ in several small unmeasured increments.

(19) S. Sternhell, *Q. Rev., Chem. Soc.*, **23**, 238 (1969), and references therein.

(20) Deuteration was necessary to reduce the peak width of H_1 so that it could be effectively decoupled.

(21) The angular dependence of J_{HF} vicinal coupling constants is similar to the Karplus treatment of J_{HH} systems, except the values are much larger in the 0 and 180° range of dihedral angles. It would be difficult to estimate an "expected" value of J_{HF} for the gauche relationship in a planar **4** because of the double bond and distortions at C_4 expected for a planar ring. However, we feel that it is reasonable to expect relatively large J_{HF} values from a boat conformation due to the much smaller dihedral angle. In 2-fluoropropene, for example, J_{F,CH_3} = 16.0 Hz.[23]

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(24) In this case, $J_{H_1H_2}$, J_{FH_5}, and J_{FH_6} were measured before and after addition and were found to be unchanged. Hence, the $Eu(fod)_3$ is not affecting the conformational preferences of **4** or the coupling constants.

(25) A preliminary account concerning the metal–ammonia reduction of triptycene has been presented (American Chemical Society Great Lakes Regional Meeting, 1974, West Lafayette, Ind.) with details to be published.

(26) The fact that the allylic coupling constant is larger than the vicinal coupling constant is not unexpected, since the pseudoaxial protons H_2 and H_{4a} approach a 90° relationship with the vinyl protons which maximizes allylic coupling and minimizes vicinyl coupling.

(27) See also A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J.

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(28) Isomer assignment was made on the basis of these values, together with the fact that Eu(fod)$_3$ causes substantially greater downfield shifts of H_{4a} in one isomer (assigned trans).

(29) An additional possibility is a rapid boat-to-boat inversion which could produce a comparable homoallylic coupling constant. However, if one substituent can be accommodated by a planar 1,4-cyclohexadiene (i.e., compound **2**), presumably a second could be accommodated similarly, provided it is on the other side of the ring.

(30) M. E. Kuehne and B. F. Lambert, *J. Am. Chem. Soc.*, **81**, 4278 (1959); *Org. Synth.*, **43**, 23 (1963).

(31) Attempts at complete NMR analysis with shift reagents were unsuccessful with this compound.

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(33) Structure was assigned to this dihydro isomer, since only one bridgehead proton showed significant coupling and there are only two vinylic protons which are shifted downfield. In addition, uv shows conjugation.

Proton Magnetic Shielding Tensors from Spin-Rotation Measurements on H_2CO and NH_3

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Abstract: The spin-rotation tensor for H_2CO was obtained from very high resolution beam maser measurements of rotational transitions. Spin-rotation tensor elements are $M_{aa} = -4.12 \pm 0.36$ kHz, $M_{bb} = 2.45 \pm 0.32$ kHz, and $M_{cc} = -2.10 \pm 0.34$ KHz in the principal axis system. These results are combined with previous molecular orbital calculations of diamagnetic shielding to obtain total absolute shielding tensor elements of $\sigma_{aa} = 15.9$, $\sigma_{bb} = 40.7$, and $\sigma_{cc} = -1.7$ ppm and an average shielding of 18.3 ppm with uncertainties of ±2 ppm or better. A similar analysis is carried out for NH_3. Spin-rotation tensors and shielding tensors are given for proton and nitrogen sites with estimated accuracy better than 1 ppm. For NH_3 $\sigma_{zz}(H) = 26.5$ ppm and $\bar{\sigma}(H) = 31.2$ ppm. The absolute shielding scale is discussed.

The average of the diagonal elements of the magnetic shielding tensors, more commonly known as the "chemical shift", has been extremely useful in structure determinations and characterizing particular types of bonding in functional groups. Since there are relatively large changes in shielding as the field direction is changed relative to molecular axes, a better understanding of magnetic shielding can be obtained from the shielding tensor. Shielding tensors have been obtained previously by orienting molecules in liquid crystals,[1] using multiple-pulse techniques on single crystals,[2] or molecular beam Zeeman measurements.[3,4] Relatively few experiments have yielded accurate shielding tensors or quadrupole coupling tensors using liquid crystal techniques. Results which are in good agreement with other measurements were obtained for linear or symmetric top molecules.[1] Difficulties appear to arise in establishing the order parameter. This problem is much more serious for asymmetric tops since the "orientation" axis is often not known and two-order parameters must be specified. Excellent results have been obtained from the multiple pulse measurements for larger molecules which may be frozen into rigid crystals and do not contain nuclei with quadrupole moments. Occasionally there are problems with this technique in determining the direction of shielding tensor axes relative to the bond directions. Direct measurements of shielding tensors for ^{19}F and ^{13}C have been obtained from high resolution molecular Zeeman measurements on molecular beams. These measurements are limited to a few small molecules with favorable magnetic and electric moments.

It was shown by Ramsey[5] that the magnetic shielding tensor for diatomic molecules could be separated into diamagnetic and paramagnetic parts. The diamagnetic part is expressed as first-order matrix elements between ground-state wave functions. The paramagnetic part depends on second-order terms for the mixing of excited electronic states having nonzero orbital angular momentum with the ground state. This type of treatment for diatomics was extended to symmetric-top and asymmetric-top molecules by Flygare[6] and coworkers. The diamagnetic terms may be easily and accurately obtained from ab initio molecular orbital calculations. The paramagnetic terms are very difficult to calculate and accuracy is poor. The paramagnetic terms, however, are related to electron contributions to the spin-rotation tensor by a numerical constant. This suggests that accurate magnetic shielding tensors may be obtained by combining calculated diamagnetic terms with paramagnetic terms from spin-rotation measurements. This method was used previously for fluorine shielding tensors.[7,8]

Formaldehyde rotational transitions were observed using a beam maser by Takuma, Shimizu, and Shimoda,[9] by Thaddeus, Krisher, and Loubser,[10] by Krupnov and Skvortsov,[11] and by Shigenari.[12] More accurate measurements on $J = 1$ and $J = 2$ K-type doublets were reported by Tucker, Tomasevich, and Thaddeus.[13]

The resolution of the two-cavity maser spectrometer[14] using Ramsey's method of separated oscillating fields is significantly better than the resolution of single cavity masers. Measurements of the 1_{10}-1_{11} transition of H_2CO using a two-cavity maser were reported previously.[15]

Experimental Section

The two-cavity maser spectrometer was described previously.[14,15] For the present measurements the beam was produced with a 0.1 mm diameter stainless steel nozzle. Formaldehyde vapor was obtained by heating a paraformaldehyde-silicone oil slurry. The upper state was focussed using a quadrupole lens. Two OFHC copper cavities excited in the TM_{010} mode were used to observe resonances. The cavity separation was 76 cm and the width of the central peak of the resonance pattern was 390 Hz. A "fast scan" recorder trace of all observed components is shown in Figure 1. The upper trace (a) is the "single-cavity" spectrum and the lower trace (b) was obtained using the two-cavity maser. Both spectra are shown as derivatives of the emission spectrum due to the frequency modulation with lock-in detection used in the apparatus.

Spin-Rotation Tensor

The strongest lines of the $2_{11} \rightarrow 2_{12}$ transition and our previous data on the $1_{10} \rightarrow 1_{11}$ transition were analyzed to determine the spin-rotation tensor and spin-spin interac-