Carbon-13 Magnetic Resonance of Hydroaromatics. 2.[1] Conformation of Tetralin and Tetrahydroanthracene and Their Methyl Derivatives

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Abstract: Carbon-13 chemical shift data have been acquired for 36 methylated tetralins and tetrahydroanthracenes. A least-squares regression analysis has been undertaken on the ring carbons of compounds of unequivocal conformation to determine methyl substituent parameters for the two distinct aliphatic positions and the results have been used to estimate the position of equilibrium of conformationally mobile compounds. It is concluded that 1-methyltetralin exists in essentially equally populated conformers at room temperature but that the 2-methyl derivative is dominated by the conformation with an equatorial methyl group. Substituent parameters are compared with those previously determined for methylated cyclohexanes. A similar analysis of the methyl chemical shifts was unsuccessful owing, in part, to the highly flexible nature of the saturated ring.

Introduction

The importance of hydrogen donor solvents in coal liquefaction processes is well known.[2,3] Tetralin and its methylated derivatives have been the subject of various studies over the years, and it has long been known that the saturated ring exists in a half-chair form similar to cyclohexene.[4,5] A circular dichroism study[6] has further concluded that a methyl group at C-1 preferentially orients pseudoaxially, while a methyl at C-2 prefers the equatorial position. The substituent positions at C-1 are not truly equatorial or axial in the sense used for cyclohexanes, and this is acknowledged by the pseudo prefix. Proton nuclear magnetic resonance (NMR) suggests that *trans*-2,3-dimethyltetralin prefers the diequatorial form as its predominant conformer,[7] and another ^1H NMR study has been undertaken on several other methylated tetralins.[8] Nonetheless, a comprehensive investigation of these conformationally interesting compounds has been lacking. The application of carbon-13 NMR to the investigation of an extenisve set of mono-, di- and trimethyltetralins and related tetrahydroanthracenes was a logical consequence to a previous study of methylated 9,10-dihydroanthracenes.[1] The central ring of the dihydroanthracenes, while held fairly rigidly in the boat form in the parent dihydro compound or its lightly substituted analogues, was found to undergo distortions to a more planar structure when heavily substituted. The saturated ring in tetralins, and in the related tetrahydroanthracenes, however, is much more flexible and offers an interesting contrast to the dihydroanthracenes.

To organize and to systematize the conformational dependent shifts in these systems, a linear, least-squares regression analysis has been undertaken for the ^{13}C chemical shifts utilizing methyl substituent parameters similar to those used to analyze the ^{13}C chemical shifts in the methyl-substituted cyclohexanes.[9]

Experimental Section

^{13}C spectra were obtained on a Varian SC-300 spectrometer operating at 75.5 MHz. A 12-KHz spectral window and 16K data table were employed. Samples were run as 50% solutions in $CDCl_3$ with tetramethylsilane $(CH_3)_4Si$ as internal standard. Proton spectra were obtained at 300 MHz on the same instrument. Solid ^{13}C spectra were taken on a Bruker CXP-100 using carbon-proton cross polarization and magic angle spinning (CP/MAS).

Synthesis

Tetralins. Table I lists numbers and names of all the tetralins used in this study.

Parent (1) and Monomethyl Derivatives (2, 3). The parent **1** was obtained by distillation of a commercial sample, bp 86 °C (17 mm) [lit.[10] 59–59.5 °C (1.8 mm)]. Compound **2**, obtained by Clemmensen reduction[11] of 4-methyl-1-tetralone (Aldrich) (72.7%), boiled at 102–105 °C (17 mm) [lit.[12] 87–88 °C (7 mm)]. Similarly **3** from 2-methyl-1-tetralone (Aldrich) (77%) boiled at 102–105 °C (17.5–20 mm) [lit.[13] 97–98 °C) (10 mm)].

***cis*- (4) and *trans*-1,2-Dimethyl-THN (5).**[14] Reduction of 2.21 g of 3,4-dimethyl-DHN[15] in 60 mL of ethanol over 0.57 g of 10% palladium–carbon gave 1.75 g (78%), bp 61 °C (0.05 mm), of pure *cis*-**4**. Hydrogenation of 1.88 g of 1,2-dimethyl-1-tetralol, mp 62–65 °C (a 2:1 mixture of geometrical isomers by ^1H NMR) (lit.[15] 65.5–66 °C), in 215 mL of methanol and 2.3 mL of 70% perchloric acid with 1.5 g of 10% palladium–carbon and 33 psi of hydrogen at room temperature for 1 h gave 1.06 g (62%), bp 119–120 °C (26.5 mm). This was a 1:1 mixture of **4** and **5**.

***cis*- (6) and *trans*-1,3-Dimethyl-THN (7).** Addition of 1.7 g of 3-methyl-1-tetralone[16] in 24 mL of benzene to etheral methylmagnesium iodide (from 0.48 g of magnesium) gave after the usual isolation 1.22 g (from cold hexanes) (65.4%), mp 78–82 °C. Sublimination at 70–90 °C (bath) and 0.01 mm gave pure **1-hydroxy-1,3-dimethyl-THN**, mp 79–83 °C, a single isomer by ^1H NMR. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.65; H 9.18. Hydrogenation of the carbinol (1.31 g) in 150 mL of methanol with 1.6 mL of 70% perchloric acid, 1.06 g of 10% palladium–carbon at room temperature, and 33 psi of hydrogen for 4 h gave 0.80 g (67.2%), bp 128–130 °C (36 mm) [lit.[15] 78 °C (1 mm)]. By ^1H NMR this was a 1:1 mixture of 6 and **7**.

***cis*- (8) and *trans*-1,4-Dimethyl-THN (9).** 1,4-Dimethyl-DHN (2.21 g), bp 134–135 °C (29 mm) [lit.[15] 87–88 °C (0.8 mm)], in 60 mL of 95% ethanol with 0.57 g of 10% palladium–carbon shaken at room temperature under hydrogen gave 1.77 g (79.3%), bp 119–121 °C (20 mm) [lit.[17] 63–64 °C (0.4 mm)]. This by ^1H NMR was an 85:15 mixture of **8** and **9**.

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Table I. Carbon-13 Chemical Shifts of Tetralin and Its Methylated Derivatives[a]

compound	1	2	3	4	4a	5	6	7	8	8a	CH_3 (position)
parent (1)	29.6	23.6			137.1	129.4	125.8				
	(30.0)	(23.3)									
1-methyl (2)	32.7	31.8	20.8	30.2	136.7	129.3	125.8	126.0	128.3	142.1	23.0
2-methyl (3)	38.3	29.4	31.7	29.4	136.8[b]	129.2[b]	125.7	125.7	129.1[b]	136.5[b]	22.1
	(38.6)	(29.1)	(31.9)	(30.0)							
cis-1,2-dimethyl (4)	37.8	32.3	26.0	29.1	135.8	129.1	125.7	125.7	129.1	143.2	17.3 (1)
	(37.7)	(32.7)	(26.5)	(28.7)							18.4 (2)
trans-1,2-dimethyl (5)	40.1	35.8	28.9	28.2	136.5	129.1	125.5	126.0	128.7	141.5	22.1 (1)
											20.4 (2)
cis 1,3-dimethyl (6)	33.5	42.3	29.5	39.4	136.9	129.0	125.7	126.0	126.9	141.3	21.8 (1)
	(33.4)	(41.7)	(29.1)	(39.6)							22.5 (3)
trans-1,3-dimethyl (7)	32.5	39.0	24.3	38.6	136.2	129.1	125.7	125.9	128.9	141.8	24.4 (1)
	(32.4)	(38.7)	(23.7)	(38.6)							22.1 (3)
cis-1,4-dimethyl (8)	33.0	28.9			141.9	128.0	125.9				22.7
	(33.4)	(28.9)									
trans-1,4-dimethyl (9)	33.0	28.4			141.7	128.4	125.9				23.3
cis-2,3-dimethyl (10)	35.6	32.1			135.8	129.5	125.7				15.7
	(35.5)	(32.9)									
trans-2,3-dimethyl (11)	38.6	35.5			137.1	128.8	125.7				19.6
1,1-dimethyl (12)	33.7	39.6	19.9	30.8	135.9	129.3	125.5	126.1	126.7	145.7	31.9
	(34.5)	(39.9)	(20.0)	(31.0)							
2,2-dimethyl (13)	43.5	29.4	36.0	26.5	136.4	129.7[b]	125.6[b]	125.7[b]	129.0[b]	135.7	28.1
	(43.3)	(29.7)	(36.6)	(26.7)							
5-methyl (14)	30.3	23.8[b]	23.2[b]	26.8[b]	136.5	135.5[b]	127.4[b]	125.5[b]	127.3[b]	137.1[b]	19.4
	(30.0)	(23.3)	(23.3)	(26.9)							
1,8-dimethyl (15)	29.4	30.7	18.0	29.9	136.2	127.6[b]	125.7	128.2[b]	135.9	140.7	21.1 (1)
	(29.3)	(30.1)	(17.9)	(30.0)							18.9 (8)
1,1,8-trimethyl (16)	34.7	44.2	19.8	32.6	137.1[b]	128.1	125.5	130.9	136.8[b]	143.3	29.3 (1)
											23.6 (8)
1,1,3-trimethyl (17)	34.9	48.5	25.8	39.8	136.0	129.1	125.5	126.1	126.6	145.3	31.8 (1e)
	(34.5)	(48.5)	(25.7)	(39.6)							32.8 (1a)
1,2,2-trimethyl (18)	43.6	31.8	32.4	26.4	135.2	128.9[b]	125.5[b]	125.9[b]	129.3[b]	142.5	27.8 (2e)
											25.9 (2a)
											18.7 (1)
1,1,4-trimethyl (19)	34.0	36.1	27.7	33.5	141.2	128.5	125.8	126.1	126.8	145.5	32.0 (1e)
											32.0 (1a)
											23.1 (4)
1,3,3 trimethyl (20)	30.3	46.6	30.0	44.5	136.3	129.6	125.8	126.1	127.0	140.6	32.0 (3e)
	(30.1)	(46.4)	(29.7)	(44.2)							25.2 (3a)
											21.9 (1)
2,2,3 trimethyl (21)	44.7	32.1	37.5	35.4	136.4[b]	129.4[b]	125.7[b]	125.6[b]	128.8[b]	136.1[b]	28.8 (2e)
											20.0 (2a)
											15.7 (3)
1α,2α,3α-trimethyl (22)	38.4	39.1	33.8	34.1	136.5	128.7	125.6	126.1	127.0	140.0	19.7 (3)
	(38.1)	(38.7)	(33.8)	(34.2)							17.7 (1)
											6.1 (2)
1α,2α,3β-trimethyl[d] (23)	38.4[b]	39.1[b]	29.4	38.5[b]	136.2	128.8	125.6	125.6	128.8	143.4	19.9 (3)
											17.9 (1)
											16.6 (2)
1,1,2-trimethyl (24)	37.1	39.3	27.4	29.3	135.7	129.2	125.4	126.1	127.1	146.4	30.0 (1)
											25.8 (1)
											16.6 (2)
1α,2α,4α-trimethyl (25)	38.8	31.9	35.4	33.4	143.8	127.3	125.7[b]	126.0[b]	129.3	141.0	17.4 (1)
	(38.7)	(32.7)	(36.3)	(33.4)							19.4 (2)
											22.1 (4)
1α,2α,4β-trimethyl (26)	38.1	27.6	33.6	32.2	*c*	129.1	125.8	125.8	129.1	*c*	17.4 (1)
	(37.7)	(27.3)	(33.3)	(32.4)							18.5 (2)
											24.8 (4)
5,8-dimethyl-5,6,7,8-tetrahydro-2-naphthoic acid (27)	33.4[b]	28.5	28.5	32.9[b]	142.7	130.2	127.1	127.7	128.4	149.1	22.5
											173.5 (carbonyl)

[a] Parentheses indicate calculated shifts using parameters of Table IV. [b] Ambiguous assignments. [c] Compound was present as minor constituent and unprotonated carbons were not observed. [d] Compound was present as minor constituent with extensive overlap with signals of 22.

***cis*- (10) and *trans*-2,3-Dimethyl-THN (11).** The Reformatsky reaction[18] on 1-phenyl-2-propanone (2.68 g) with 8.24 mL of ethyl 2-bromopropionate gave 4.14 g (87.5%), bp 84–88 °C (0.03 mm). This on dehydration with phosphorus pentachloride[16] gave 3.40 g (89.1%), bp 72–77 °C (0.01 mm), shown to be a mixture of isomeric olefinic esters by ^{1}H NMR. Reduction of 3.27 g in 140 mL of methanol with 0.25 g of platinum oxide at slightly above atmosperic pressure, filtration, and saponification gave on acidification an oil which was collected in benzene, dried over sodium sulfate, and cyclized with 168 g of polyphosphoric acid (PPA[19]) by heating for 2 h in a boiling water bath. The usual workup gave 1.57 g (60.1% from the olefinic esters) of a mixture of 2,3-dimethyltetralones, bp 67–71 °C (0.008 mm). Reduction with lithium aluminum hydride followed by dehydration in benzene with *p*-toluenesulfonic acid[20] gave 0.91 g of 2,3-dimethyl-DHN (74.2% from the ketones), bp 42–43 °C (0.01 mm), shown to be pure by ^{1}H NMR. This in ethyl acetate on reduction with 10% palladium–carbon at near at-

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mospheric pressure gave 0.70 g (76%), bp 113–115 °C (16 mm), shown by ^{1}H NMR to be a 65:35 mixture of **10** and **11**.

1,1-Dimethyl-THN (12). Compound **12** was prepared as reported but with cyclization in PPA (87.5%), bp 104–106 °C (13.5 mm) [lit.[21] 40 °C (0.04 mm)].

2,2-Dimethyl-THN (13). 2-Methyl-1-tetralone (3.2 g) in 37 mL of glyme with 2.24 g of 50% sodium hydride (washed with petroleum ether) was refluxed for 3 h, chilled, combined with 5 mL of methyl iodide, stirred for 30 min while warm, and then refluxed for 30 min. The usual treatment gave 3.21 g (92.2%), bp 131–135 °C (11 mm). Clemmensen reduction[11] of 3.45 g of ketone gave **13** (2.16 g, 62.8%), bp 98–101 °C (10 mm).

5-Methyl-THN (14). 4-(2-Methylphenyl)butanoic acid[22] (4.3 g, mp 52–57 °C) was cyclized with PPA[19] to give 2.86 g (74%) of 5-methyl-1-tetralone, bp 153–156 °C (12.5 mm), mp 43–51.5 °C (lit.[22] bp 116–117 °C (1 mm), mp 50–51 °C). Clemmensen reduction[11] of 2.82 g gave 2.02 g (78.4%) of **14**, bp 104.5–105 °C (10.5 mm) [lit.[23] 143.8 °C (57 mm)], pure by ^{1}H NMR.

1,8-Dimethyl-THN (15). Conjugate addition[24] of methylmagnesium iodide (from 1.83 g of magnesium and 0.1 g of copper(I) chloride) to 13.1 g of diethyl 2-methylbenzalmalonate, bp 135–141 °C (0.6–0.7 mm) [lit.[25] 148–149 °C (4 mm)], gave after saponification 8.19 g (73.8%), mp 113–120 °C dec. From benzene–hexanes it melted at 119–121 °C dec. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.16; H, 6.38. Heating at 180–186 °C (bath) gave (72%) crystals, mp 47–49 °C. These on sublimation melted at 48–50 °C (lit.[26] 48–49 °C). Homologation of 3-(2-methylphenyl)butanoic acid by the Arndt–Eistert reaction[18] gave 4-(2-methylphenyl)pentanoic acid as an oil. This was converted to 4,5-dimethyl-1-tetralone (2.31 g, 65.5% over two steps) by heating for 4 h at 130–140 °C (bath) with 158 g of PPA. The ketone boiled at 163–165 °C (15 mm), mp 44–54 °C [lit.[26] bp 171–173 °C (21 mm), mp 56–58 °C)]. Reduction of 2.31 g of the ketone by lithium aluminum hydride gave 2.10 g (89.5%), mp 108–113 °C, raised to 116–118 °C by crystallization from aqueous methanol and from benzene–hexanes. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.17; H, 9.22. Dehydration of the carbinol (1.5 g) with *p*-toluenesulfonic acid[20] gave 1.17 g (87%) of 1,8-dimethyl-DHN, bp 115–118 °C (16 mm). This in 30 mL of 95% ethanol with 0.3 g of 5% palladium–carbon gave 0.87 g (73.4%) of **15**, bp 124–125 °C (20.5 mm) [lit.[27] 60 °C (0.5 mm)], pure by ^{1}H NMR.

1,1,8-Trimethyl-THN (16). Conjugate addition[24] of *o*-tolylmagnesium bromide (from 13.68 g of 2-bromotoluene and 1.83 g of magnesium) to 10 g of diethyl isopropylidenemalonate in the presence of 0.1 g of copper(I) chloride followed by saponification gave 9.21 g (78%) of the malonic acid, mp 103–118 °C. A sample from benzene–hexanes melted at 118–122 °C. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.69; H, 6.90. Decarboxylation of 8.21 g at 175–184 °C (bath) gave 4.93 g, mp 67–70 °C, and 0.9 g of second crop, mp 62–66 °C (total 87.4%). A pure sample from pentane after sublimation melted at 69–71.5 °C. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.45; H, 8.36. Homologation via Arndt–Eister reaction[18] on 4.15 g gave 2.02 g (42.5%) of **methyl 4,4-dimethyl-4-(2-methylphenyl)butanoate**, bp 126 °C (1.0–1.9 mm). This was saponified to give 1.69 g (89.4%) as an oil. The oil on cyclization with PPA[19] gave 1.01 g (65.5%), bp 108–109.5 °C (0.33 mm). A 2.42-g sample of this ketone was reduced with lithium aluminum hydride; the carbinol was dehydrated[20] to yield 1.82 g (82.2% over two steps) of **1,1,8-trimethyl-DHN**, bp 140–142 °C (25 mm). Reduction of this in 45 mL of methanol with 0.43 g of 10% palladium–carbon gave 1.55 g (84.1%) of **16**, bp 133–135 °C (20 mm).

1,1,3-Trimethyl-THN (17). 3-Methyl-4-phenylbutanoic acid[28] was esterified (methanol–acetyl chloride) in 82.2% yield, bp 147–148 °C (24 mm). The ester (2.67 g) in 55 mL of benzene was added at 0 °C to 30 mL of ether and 35 mL of 1.4 M methyllithium, refluxed for 3 h, and stirred at room temperature overnight. The **2,4-dimethyl-5-phenyl-2-pentanol** obtained after the usual treatment was cyclized with 166 g of PPA.[19] Workup gave 2.23 g (92.1% from the methyl ester), bp 115–117 °C (16 mm) [lit.[29] 116 °C (10 mm)]. The purity and structure of the compound were established by ^{1}H NMR.

1,2,2-Trimethyl-THN (18). 2,2-Dimethyl-1-tetralone (2.61 g), described above, with methylmagnesium iodide (from 1.44 g of magnesium) gave an oil after the usual treatment. This in 10 mL of toluene with 1.2 mL of thionyl chloride was warmed on the steam bath for 15 min and distilled, bp 135–137 °C (24 mm). The product, 2.32 g (90% from the ketone), proved to be the *exo*-methylene compound by ^{1}H NMR. It was reduced in 125 mL of absolute ethanol with 0.18 g of platinum oxide to yield 1.54 g (65.5%) of **18**, bp 123–128 °C (25 mm), pure and the expected structure by ^{1}H NMR.

1,1,4-Trimethyl-THN (19). 4-Phenylpentanoic acid (2.03 g) (Pfaltz and Bauer) on esterification (methanol–acetyl chloride) gave 2.04 g (92%), bp 151–152 °C (27 mm). This added to ethereal methylmagnesium iodide (from 0.56 g of magnesium) and stirred at room temperature overnight gave an oil after the usual treatment. The oil was cyclized with 118 g of PPA. The product **19**, 1.66 g (90.9% from the methyl ester), bp 131 °C (31 mm), was pure by ^{1}H NMR.

1,3,3-Trimethyl-THN (20). Dimethylation of 4 g of 4-methyl-1-tetralone with 4.81 g of sodium hydride (50%) and 6.25 mL of methyl iodide as described above gave 4.44 g (94.4%) of **2,2,4-trimethyl-1-tetralone**, bp 159–163 °C (28 mm), 95% pure by ^{13}C NMR. Clemmensen reduction[11] of 3.56 g gave 2.77 g (84.1%), bp 125–127 °C (25 mm), shown to be **20** by ^{1}H NMR.

2,2,3-Trimethyl-THN (21). The dimethylation reaction above on 3-methyl-1-tetralone[16] (2.19 g) with 2.56 g of sodium hydride and 3.33 mL of methyl iodide gave 2.47 g (95.6%) bp 72–75 °C (0.01 mm), shown to be pure and to be **2,2,3-trimethyl-1-tetralone** by ^{13}C NMR. It was reduced with 1.8 g of lithium aluminum hydride to give 2.13 g (85.5%), mp 75–91 °C. Proton NMR indicated 90–95% purity and that the 1-hydroxy and the 3-methyl groups were equatorial. A sample from hexanes melted at 95–97 °C. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.22; H, 9.47. A solution of 0.7 g of the carbinol in 200 mL of methanol and 1 mL of 70% perchloric acid with 1 g of 10% palladium–carbon was reduced at 33 psi pressure and at room temperature for 1 h. After addition of anhydrous potassium carbonate, filtration, evaporation, the oil, 0.35 g (54.6%), bp 112–113 °C (14 mm) [lit.[30] 64 °C (0.4 mm)], was found to be pure **21** by ^{1}H NMR.

1α,2α,3α- (22) and 1α,2α,3β-Trimethyl-THN (23). A subsequent preparation of 2,3-dimethyl-1-tetralone (described above under **10** and **11**) was shown to consist of equal parts of cis and trans isomers by ^{13}C NMR. Addition of methylmagnesium iodide (from 1.05 g of magnesium) to 1.9 g of the cis and trans mixture, stirring overnight, and decomposition with ammonium chloride followed by the usual workup gave **1,2,3-trimethyl-1-tetralol**. This was dehydrated with *p*-toluenesulfonic acid[20] to give 1.44 g (76.8% from the ketone), bp 52–56 °C (0.01 mm). Reduction of this dihydronaphthalene in 40 mL of 95% ethanol with 0.35 g of 10% palladium–carbon at slightly above atmospheric pressure gave 1.17 g (80.3%), bp 146–150 °C (29 mm), shown by ^{13}C NMR to contain the isomers **22** and **23** in the ratio 85:15 with ca. 7% olefin present.[31]

1,1,2-Trimethyl-THN (24). Sodio diethyl methylmalonate, from 4.3 mL of diethyl methylmalonate and 1.24 g of sodium hydride (50%) in 60 mL of glyme stirred 30 min, was combined with 5 g of 2-bromoacetophenone in 20 mL of glyme and stirred overnight. The usual workup followed by saponification, acidification, and ether extraction gave 3.92 g (66.4%), mp 175–178 °C dec. A sample from benzene–absolute ethanol melted at 172–178 °C dec. Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.03; H, 5.17. On heating 3.43 g of this under nitrogen for 15 min in a bath at 179–186 °C, **2-methyl-4-oxo-4-phenylbutanoic acid** (2.63 g, 94.5%), mp 129–138 °C, was obtained. From cyclohexane–absolute ethanol the compound melted at 140–144 °C. Anal. Calcd for $C_{11}H_{12}O_5$: C, 68.73; H 6.30. Found: C, 69.35; H, 6.39. Clemmensen reduction of 2.13 g gave 1.5 g (75.9%), bp 97–100 °C (0.01 mm). Esterification of this (methanol–acetyl chloride) gave 1.56 g (96.4%) of methyl ester, bp 62–65 °C (0.01 mm). This in 30 mL of benzene added to 20 mL of ether and 23 mL of 1.3 M methyllithium chilled in an ice–water bath and then refluxed for 3 h followed by stirring overnight gave **3-methyl-5-phenyl-2-pentanol** which was cyclized with 97 g of PPA (2 h, 95 °C) to give 1.08 g of **24** (76.4%), bp 140–141 °C (33 mm). The oil was shown to be 90–95% pure and to be **24** by ^{1}H NMR.

1α,2α,4α- (25) and 1α,2α,4β-Trimethyl-THN (26). To 1,4-Dimethyl-DHN[15] (4.26 g) in 40 mL of methylene chloride was added 6 g of *m*-chloroperbenzoic acid in 80 mL of the same solvent at 23–25 °C. After 30 min at this temperature 10% sodium sulfite was added. The solvent was washed with 8% sodium bicarbonate. The dried solvent (Na_2SO_4) was evaporated and the fraction with bp 147–153 °C (11.5

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(31) The 1α,2β,3α isomer has been reported: Kitahonoki, K.; Takano, Y. *Tetrahedron Lett.* **1963**, 1597.

Table II. Methyl-Substituted 1,2,3,4-Tetrahydroanthracenes[a]

	yield, % [bp (mm) or mp (°C)]	picrate mp (°C)
parent (28)[b]	96.2 (96-105)	
1-CH_3 (29)	81.5 [97-98 (0.02)][d]	129-131.5
2-CH_3 (30)[c]	90.6 (69-74)	110-113
cis-1,3-$(CH_3)_2$ (31)[b,c]	100[e]	121-123
cis-1,4-$(CH_3)_2$ (32)	84.1 [103 (0.02)][f]	122-125
cis-2,3-$(CH_3)_2$ (33)[b,c]	77.7 (68-97)[g]	105-106.5
trans-2,3-$(CH_3)_2$ (34)	. . . (122-125)[h]	
1,1,3 $(CH_3)_3$ (36)	81.7 [114-115 (0.06)][d]	160.5-163

[a] By 10% palladium-carbon catalyzed hydrogenation on the 1,4-dihydroanthracenes reported by footnotes *b* and *c*. [b] Jadot, J.; Roussel, J. *Bull. Soc. R. Sci. Liege* 1954, *23*, 69; *Chem. Abstr.* 1955, *49*, 8897c. [c] Wolthuis, E. *J. Org. Chem.* 1961, *26*, 2215. All picrates gave acceptable values for C, H, and N. [d] Pure by ^1H NMR. [e] 85:15 cis:trans by ^{13}C NMR. [f] 90+% cis. [g] 55:45 cis:trans. [h] 90% trans; **33** crystallized from methanol.

mm) was combined with 200 mL of 30% sulfuric acid and refluxed for 6 h. The ether extract was washed with sodium bicarbonate and water, dried (Na_2SO_4), and distilled to give 1.63 g (49.1%) of **1,4-dimethyl-2-tetralone** bp 146–153 °C (13 mm), shown to be pure and to have the correct structure by ^1H NMR. Addition of 1.57 g of this ketone to methylmagnesium iodide (from 0.4 g of magnesium) gave on workup and distillation an oil containing water. On drying and redistillation 1.15 g (74.2%), bp 132–134 °C (10 mm), was obtained, shown to be 80% pure and to contain two other olefins by ^{13}C NMR. Reduction of 1.11 g of this mixture in 40 mL of absolute ethanol over 0.3 g of 10% palladium–carbon at slightly above atmospheric pressure gave 0.78 g (69.5%), bp 126–130 °C (14 mm). This by ^1H NMR was an 80:20 mixture of **25** and **26**.[32]

***cis*-5,8-Dimethyl-5,6,7,8-tetrahydro-2-naphthoic Acid (27).** A suspension of 3.46 g of aluminum chloride in 16 mL of carbon disulfide at 5 °C was combined with 2.3 mL of oxalyl chloride and stirred for 15 min. In 15 min 3.75 g of **8** and **9** (80:20) was added with the aid of 10 mL of carbon disulfide. The mixture was refluxed for 15 min and then poured onto ice and hydrochloric acid; the product was collected with carbon tetrachloride. Distillation gave 4.22 g (81.2%) of the **acid chloride of 27**, bp 114–115 °C (0.4 mm). Hydrolysis of 1.55 g of this with 35 mL of 3 N sodium hydroxide on the steam bath for 1 h gave 1.36 g (95.3%), mp 114–126 °C, which by ^1H NMR was an 80:20 mixture of the cis:trans acids (**27**). A sample from hexanes melted at 127–132 °C. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.80; H, 7.88.

Tetrahydroanthracenes (THA). Several THA analogues to the corresponding tetralins were also prepared in this study. The summary of yields and boiling points or melting points is given in Table II for **28–34** and **36**.

1,1-Dimethyl-1,2,3,4-tetrahydroanthracene (35). Methyl 4-(2-naphthyl)butanoate[33] (3.89 g) with ethereal methylmagnesium iodide (from 0.82 g of magnesium) gave 3.55 g (90%) of **2-methyl-5-(2-naphthyl)-2-pentanol**, mp 60–64 °C. From petroleum ether (30–60 °C) it melted at 60–63.5 °C. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.52; H, 8.89. Cyclization of 1.99 g of the above pentanol in 104 g of PPA on the steam bath for 2 h gave 1.61 g (87.8%), bp 157–157.5 °C (0.3 mm). It was shown to be an 80:20 mixture of two compounds by ^1H NMR. The larger part was **35**, and the second compound was **4,4-dimethyl-1,2,3,4-tetrahydrophenanthrene**.[34] The picrate of **35** after purification from methanol melted at 149–152 °C. Anal. Calcd for $C_{22}H_{21}N_3O_7$: C, 60.13; H, 4.82. Found: C, 59.75; H, 4.88. A sample of **35**, recovered from the picrate, mp 146–152 °C, was distilled, bp 135 °C (0.75 mm). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.80; H, 8.33.

***cis*-1,4-Dimethyl-1,4-DHA.** The addition of 3.29 g of *trans,trans*-2,4-hexadiene (Fluka) to 1.63 g of 1,4-naphthoquinone as described for other similar Diels–Alder reactions[35] gave 1.84 g (74.5%) of **1,4-dimethyl-1,4,4a10a-tetrahydroanthraquinone**, mp 57.5–60 °C. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.19; H, 6.93.

This product (1.80 g) in 25 mL of THF was reduced with 0.60 g of lithium aluminum hydride in 16 mL of THF with 1 h refluxing. The usual treatment gave 1.78 g (97.3%), mp 146–179 °C. The isomer mixture was cooled to −5 to 0 °C in pyridine, treated with 2 mL of phosphorus oxychloride, and stirred overnight at room temperature. After 1.5 h on the steam bath the usual workup gave 1.4 g (92.2%), mp 80–84 °C. A sample from hexanes, mp 82–85.5 °C, proved to be pure ***cis*-1,4-dimethyl-1,4-DHA** by ^{13}C NMR. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.93; H, 7.87.

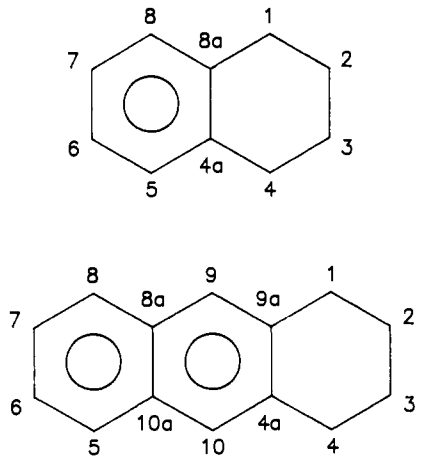

Figure 1. Numbering schemes used for the molecules in this study.

1-Methyl-1,4-DHA. In like manner 1.63 g of 1,4-naphthoquinone and 2.72 g of *trans*-1,3-pentadiene (Fluka) gave 2.31 g (97%), mp 58–62 °C. Reduction of 1.71 g of this diketone gave an oil which was dehydrated to **1-methyl-1,4-DHA** (0.96 g, 65.1% from the diketone), mp 52–55 °C. This from methanol melted at 54–57.5 °C. Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.45; H, 7.48.

1,1,3-Trimethyl-1,4-DHA. Crude 1,1,3-trimethyl-1,4,4a,10a-tetrahydroanthraquinone (1.67 g), mp 82–108 °C (lit.[35] 119 °C), was reduced to the corresponding diol with lithium aluminum hydride as described above. The thick oil, dehydrated by phosphorus oxychloride, gave 0.53 g (36.4% from the diketone), bp 110 °C (0.10 mm). On standing colorless crystals formed, mp 40–45 °C, which from methanol melted at 46–48 °C and were shown by ^1H NMR to be **1,1,3-trimethyl-1,4-DHA**. The compound decomposed on standing overnight in air.

Results

^{13}C and ^1H NMR data have been acquired for the parent tetralin, the 1-, 2-, and 5-methyl derivatives, all possible aliphatically substituted dimethyl compounds, as well as 1,8-dimethyltetralin, nine trimethyltetralins, and a number of analogous tetrahydroanthracenes. ^{13}C chemical shifts are provided in Table I and III. Assignments were made using standards off-resonance and selective decoupling techniques. Aromatic carbons were often assigned by their appearance in a coupled spectrum.[36] In several cases it was not possible to distinguish between C-5 and C-8 or C-6 and C-7 because the chemical shifts of the respective protons were not sufficiently separated to allow the use of selective decoupling.

The regression analysis was carried out on those molecules which either (a) exist primarily in a single conformation because of unfavorable steric interactions in the alternative conformation (**3, 4, 6, 7, 15, 17, 20, 22, 25, 26, 30, 31, 36**) or (b) are undergoing rapid interconversion between identical conformers of equal energy (**1, 8, 10, 12–14, 28, 32, 33, 35**). Thus compounds **2, 5, 9, 18, 19, 21, 24, 27**, and **29** were excluded from the fit as they may exist in more than one form of differing energies or are so highly strained owing to the nature or extent of substitution that it would be expected that the fitting procedure could not adequately predict the chemical shifts. Contributions from boat conformers, which are substantially higher in energy, were assumed to be negligible.[37] A rather large set of parameters was needed in order to account for possible differences in C-1 vs. C-2 substitution, and a preliminary determination of the best-fit values was made using all possible parameters in the calculation. Substituent effects which were negligible in size were removed and the calculation was redone. These results are given in Table IV. The exclusion of

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(33) Huisgen, R.; Rietz, U. *Chem. Ber.* **1957**, *90*, 2768.
(34) This phenanthrene was also prepared by conjugate addition of 1-naphthalmagnesium bromide to diethyl isopropylidenemalonate and subsequent steps as under **16** above. The two samples had identical ^{13}C NMR spectra.
(35) Diels, O.; Alder, K. *Ber.* **1929**, *62*, 2337.
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Table III. Carbon-13 Chemical Shifts of 1,2,3,4-Tetrahydroanthracene and Its Methylated Derivatives[a]

compound	1	2	3	4	5	6	7	8	9	10	4a	10a	8a	9a	CH_3 (position)
parent (28)	29.8	23.5			127.3	125.1			127.0		136.3	132.5			
	(30.0)	(23.3)													
1-methyl (29)	32.8	31.8	21.0	30.2	127.6[b]	125.1[b]	125.3[b]	127.2[b]	126.0	126.8	136.2	132.7[b]	132.4[b]	141.5	22.7
2-methyl (30)	38.6	29.5	31.8	29.6	127.2	125.1	125.1	127.2	126.9[b]	126.7[b]	136.2[b]	132.5[b]	132.4[b]	135.9[b]	22.1
	(38.6)	(29.3)	(32.0)	(30.0)											
cis-1,3- (31)	33.8	42.2	29.6	39.6	127.7[b]	125.2[b]	125.4[b]	127.2[b]	125.2	126.8	136.5	132.3[b]	132.7[b]	141.1	21.9 (1)
	(33.5)	(41.9)	(29.3)	(39.6)											22.7 (3)
cis-1,4- (32)	32.7	29.1			127.5	125.2			125.2		141.6	132.5			22.0
	(33.4)	(28.9)													
cis-2,3- (33)	35.8	32.3			127.3	125.0			127.2		135.1	132.4			15.8
	(35.5)	(32.8)													
trans-2,3- (34)	38.7	35.8			127.3	125.0			126.3		136.4	132.4			19.9
1,1- (35)	34.1	39.5	19.9	31.1	127.0	124.9[b]	125.1[b]	127.5	125.2	127.0	135.1	132.8[b]	132.1[b]	145.0	32.4
	(34.6)	(39.9)	(19.9)	(31.0)											
1,1,3- (36)	35.3	48.6	25.9	40.1	127.7[b]	125.3[b]	125.0[b]	127.0[b]	125.2	126.7	135.5	132.7[b]	132.1[b]	144.8	32.3 (1e)
	(34.6)	(48.5)	(25.8)	(39.6)											33.6 (1a)
															22.5 (3)

[a] Parentheses indicate calculated shifts using parameters of Table IV. [b] Ambiguous assignments.

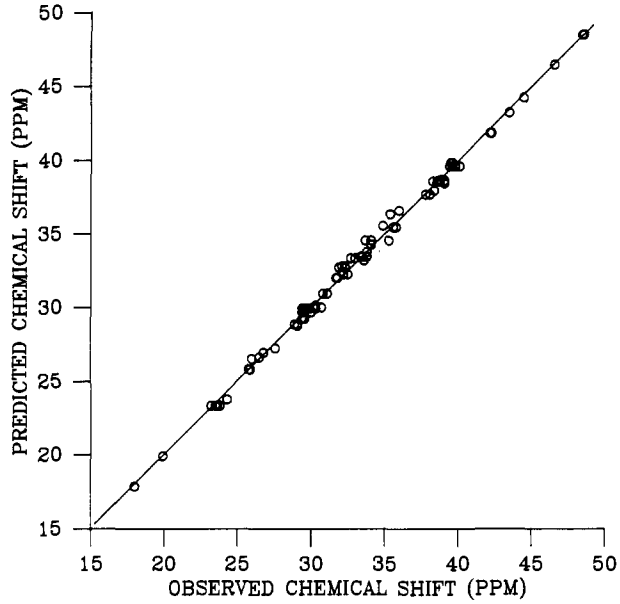


Figure 2. Comparison of predicted and observed carbon-13 chemical shifts for the ring carbons of the tetralins and tetrahydroanthracenes of this study.

the insignificant parameters left the results essentially unchanged except for a lowering of the marginal standard errors. A graphical comparison of the predicted and observed shifts is shown in Figure 2. The line plotted is a least-squares line with slope = 0.997, intercept = 0.11, and correlation coefficient squared = 0.9967. The agreement between predicted and observed shifts indicates that the structural features of unstrained compounds of unequivocal conformation are quite well described by the set of parameters used in the fitting procedure.

Discussion

A. Ring Carbons. Examination of molecular models allows some predictions concerning the significant substituent effects to be expected in Table IV. The environment of an equatorial methyl group at C-2 appears to be very much the same as that of a methyl on a cyclohexane ring, and the α_{2e} (+5.91 ppm) and β_{2e} (+8.67 ppm) effects are found to be virtually identical with the α and β effects, +6.0 and +9.0 ppm, respectively, for methylcyclohexanes.[9] On the other hand, a pseudoequatorial methyl at C-1 experiences a quite different situation by sterically interacting with the peri proton of the aromatic ring, and the α_{1e} parameter (+3.4 ppm) has been determined to be significantly smaller than that found in the cyclohexane derivatives (+6.0 ppm). Models also reveal that a pseudoaxial or axial methyl at C-1 or C-2 is situated approximately the same distance from an axial ring proton and

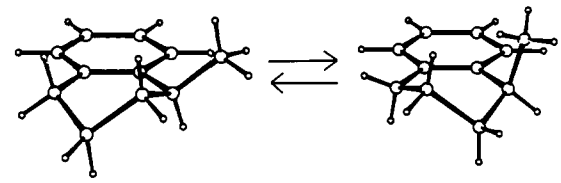


Figure 3. Illustration of the steric interactions involving a pseudoaxial or pseudoequatorial methyl group at C-1.

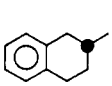
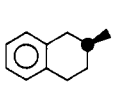
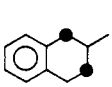
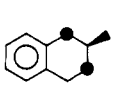
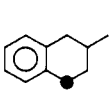
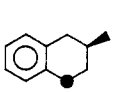
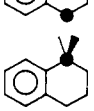
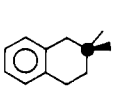
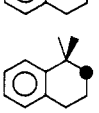
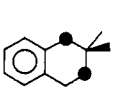
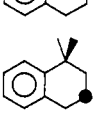
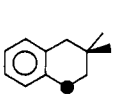
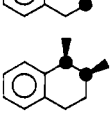
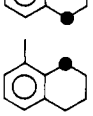
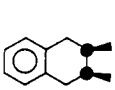
would therefore cause nearly the same amount of shielding at C-3 or C-4, respectively. Table IV shows that γ_{1a} (−5.48 ppm) and γ_{2a} (−5.32 ppm) are the same within experimental error, as are also the geminal correction terms $G_{1\gamma}$ (+2.05 ppm) and $G_{2\gamma}$ (+2.01 ppm).

Perhaps the most interesting entry in Table IV is that for δ_{1e} (+1.0 ppm). That the presence of a pseudoequatorial methyl would bring about a shift of this magnitude at C-4 apparently indicates ring deformation is taking place owing to the steric congestion involving the C-1e methyl group and the C-8 proton. Exclusion of this parameter led to fits which were highly unsatisfactory. Further evidence for flexible ring deformations in these systems is presented later in the Discussion.

The good agreement between experimental and calculated shifts shown in Figure 2 confirms that each compound used in the calculation exists almost exclusively in a single conformation or in two equally energetic forms. The substituent effects may now be used to predict the chemical shifts of the compounds not included, e.g., compound **2**. For the C-2 carbon we may predict a shift of 30.13 ± 0.22 ppm for a pseudoaxial methyl and 33.14 ± 0.24 ppm for a pseudoequatorial methyl. From the observed shift of 31.8 ppm we estimate that this molecule exists as 56 ± 7% pseudoequatorial methyl. Similarly, the respective effect of a 1-methyl in a pseudoequtorial or pseudoaxial conformation upon C-3 is zero or −5.5 ppm. Thus the observed shift of 20.8 ppm indicates that the molecule exists in a pseudoequatorial form 53 ± 4% of the time. The uncertainties are obtained from the error limits of the best-fit parameters. The predicted values for either C-1 or C-4 for the alternative conformations are so close together that the errors prevent one from determining conformational preference with any degree of reliability. These results suggest that the methyl group in **2** only slightly prefers a pseudoaxial position at C-1 and that both conformers contribute significantly at ambient temperatures. The steric interactions involving a C-1 methyl are illustrated in Figure 3. It is important to note the similarity in the positions of the methyl groups in the two conformations vis-à-vis the interaction with a proton, which corroborates the conclusion that neither conformation is highly preferred.

Based on the 1-methyltetralin results, one might also expect *trans*-1,4-dimethyltetralin (**9**) to have almost equally populated conformers. The predicted shifts for C-2 are 24.54 ± 0.37 and 33.20 ± 0.19 ppm, respectively, for the dipseudoaxial and dip-

Table IV. Carbon-13 Chemical Shift Parameters[a] Indicating the Effects of Methyl Substitution on Tetralin As Determined by Least-Squares Analysis of 82 Chemical Shifts

 C-2 = 6.61 ± 0.17	 base value (C-1) = 23.4 ppm
 α_{1e} = 3.51 ± 0.20	 α_{1a} = 2.30 ± 0.20
 β_{1e} = 9.85 ± 0.19	 β_{1a} = 6.67 ± 0.18
 γ_{1e} = negligible	 γ_{1a} = −5.48 ± 0.19
 δ_{1e} = 1.00 ± 0.17	 δ_{1a} = negligible
 α_{2e} = 5.91 ± 0.19	 α_{2a} = 3.00 ± 0.55
 β_{2e} = 8.67 ± 0.13	 β_{2a} = 7.73 ± 0.32
 γ_{2e} = negligible	 γ_{2a} = −5.32 ± 0.38
 $G_{1\alpha}$ = −1.19 ± 0.26	 $G_{2\alpha}$ = −2.57 ± 0.65
 $G_{1\beta}$ = negligible	 $G_{2\beta}$ = −3.11 ± 0.39
 $G_{1\gamma}$ = 2.05 ± 0.27	 $G_{2\gamma}$ = 2.01 ± 0.49
	 γ_5 = −3.01 ± 0.32
V_{ea} = −3.19 ± 0.22	
	

[a] Including data for tetrahydroanthracenes. In ppm ± standard error. Standard error of the fit = 0.41 ppm; multiple correlation coefficient squared = 0.9967.

seudoequatorial conformers. The amount of *dipseudoaxial* conformer determined from these predicted shifts and the observed shift of 28.4 ppm therefore is 55 ± 4%. Again, this estimate is close enough to 50% that a preferential conformation does not appear to obtain for **9**.

Similar calculations on C-3 and C-4 in compound **5** (*trans*-1,2-dimethyltetralin) give respectively 51 ± 6 and 56 ± 6% diequatorial conformation. Thus, a very substantial amount of the time this molecule exists with diaxial methyl groups and the interaction of the C-1 methyl group with the peri hydrogen must be sizable (cf. *trans*-2,3-dimethyltetralin which is predominantly in a diequatorial conformation).

Unfortunately, as the number of methyls on the ring increases, the accumulated errors in the predicted shifts limit the reliability of the estimates of the conformational populations. For this reason only general statements are made about the remaining tetralins. Applying the substituent parameters to the 1,1,8-trimethyl derivative produces calculated shifts which typically differ by >3 ppm from the observed shifts. Severe crowding of methyls at C-1 from substituents in the aromatic ring obviously may cause distortion of the hydrogenated ring, and the fitting parameter set would not be expected to address such structural features. This lack of agreement reflects both the weakness and the strength of parametric fitting techniques. The lack of aggreement in the sterically strained systems indicates that one cannot totally characterize all of the structural deformations which might be expected to arise. Conversely, where agreement is good on less strained molecules, one may make strong arguments for the reliability of the structural assignments.

Predicted shifts for 1,1,4-trimethyltetralin, (**19**) have sufficient error to prevent them from being used in calculating conformational preferences. However, it has been demonstrated in **2** and **9** that an isolated methyl at C-1 or C-4 has no significantly preferred orientation, and one might also expect nearly equally populated conformations for **19**.

The three tetralins, 1,1,2, 1,2,2, and 2,2,3, may all be expected to have significant contribution from the conformer where the nongeminal methyl group is axial since this removes a gauche interaction between equatorial methyls. For instance, the C-3 shift of **18** is 3.6 ppm upfield of the same carbon of **13**, indicating a significant contribution from the conformation. When **21** or **23** was included in the fit, the observed shifts were not well reproduced, in particular, C-1 of **21** and C-4 of **22**, which would be most affected by an axial methyl group.

B. Methyl Carbons. Attempts to apply the same regression analysis technique to the methyl chemical shifts were considerably less successful, as it was not possible to find a relatively small parameter set which would adequately reproduce the observed shifts. Several observations from the data provide an explanation for this dilemma. A reliable estimate of the shift of a pseudoequatorial methyl at C-1 may be obtained from **6** (21.8 ppm), **20** (21.9 ppm), and **24** (22.1 ppm), while the methyl shifts from **7** (24.4 ppm) and **25** (24.8 ppm) provide a value for the pseudoaxial methyl shift. We may predict, then, that an isolated C-1 methyl undergoing rapid interconversion between the two possible orientations in **8** (*cis*-1,4-dimethyltetralin) has an average shift of 23.2 ppm. The observed shift (22.7 ppm) is beyond experimental error, and although this molecule was included in the fitted shifts, it represents one of the larger deviations. Without a "locking" methyl group at the C-2 (or C-3) position, it may well be that the aliphatic ring in *cis*-1,4-dimethyltetralin distorts to relieve the steric strain between the pseudoequatorial methyl and either the C-5 or C-8 protons with only minor costs in energy, whereas a similar distortion in compound **6** (*cis*-1,3-dimethyl) would result in too large an energy increase due to the presence of the C-3 methyl and is thereby decreased in importance. Therefore, the pseudoequatorial methyl at C-1 in **8** probably experiences a slightly different environment and consequently chemical shift than the similar methyl in **6**. Such distortions will, of course, degenerate the success of the parametric fit. Numerous attempts were made, but none could simultaneously predict with reasonable accuracy the methyl chemical shifts of **8** and the other conformationally characterizable compounds at the same time. The flexible nature of the saturated ring, in particular for groups in the C-1 position, is again indicated. The unusual magnitude of δ_{1e} reported in Table IV and discussed briefly above probably also finds its origin in this type of ring deformation. As noted before, Figure 3 demonstrates that the environments of a pseudoaxial or pseudoequatorial methyl group are quite similar, and this is reflected in the small difference in their chemical shifts (ca. 2.5 ppm). This results in an inability to clearly characterize the system and undoubtedly is another factor in the failure to fit parametrically the methyl shifts.

In contrast to the variation in chemical shifts of methyl groups at C-1, those compounds which possess an isolated equatorial methyl at C-2, i.e., **3**, **6**, **7**, etc., display a methyl chemical shift of 22.3 ± 0.2 ppm, not very different from that of methylcyclohexanes.[9,38] Several interesting results are apparent in the methyl chemical shifts of tetrahydroanthracenes in Table III. Whereas

(38) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.*, **1967**, *89*, 6612.

the chemical shifts of C-2 methyls show little deviation from the analogous tetralins, C-1 methyls shift downfield by ca. 0.5 ppm when part of a geminal dimethyl moiety and upfield by as much as 0.7 ppm when isolated as in the case of the *cis*-1,4-dimethyl derivative **31**. The extra benzene ring may increase the rigidity of the molecule which is manifested most strongly at the C-1 position where the saturated ring is likely to be most susceptible to structural deformations. Alternatively these shifts may be produced by ring current effects.

C. **Aromatic Carbon Shifts.** Aromatic carbons 5 and 8 display chemical shifts which are dependent only on the presence or absence of a pseudoequatorial methyl at C-1 or C-4. When C-1 is unsubstituted or substituted with a pseudoaxial methyl, the aromatic carbon (i.e., C-5) chemical shift is 129.1 ± 0.2 ppm, while a pseudoequatorial methyl induces an upfield shift to 126.9 ± 0.2 ppm. Furthermore, a geminal dimethyl moiety at C-1 produces essentially the same chemical shift at C-5 as a single pseudoequatorial methyl, indicating again that only the pseudoequatorial and not the pseudoaxial methyl produces a shift at C-8 or that considerable ring distortion at C-1 exists to make the dimethyl interaction comparable to a monomethyl pseudoequatorial interacton.

D. NMR Spectra in the Solid State. NMR studies of the solid state, where many motional processes will cease, have been informative in a previous study.[1] Since all the tetralins of Table II are liquids at room temperature, we synthesized a solid carboxylic acid derivative of **8**, namely, 5,8-dimethyl-5,6,7,8-tetrahydro–2-naphthoic acid (**27**). However, the aliphatic portion of the NMR spectrum of this molecule in the solid state was identical within experimental error with that of the solution spectrum, suggesting that the interconversion between conformers is not stopped in the solid at ambient termperatures and that these motions continue to average the chemical shifts of the aliphatic carbons. Similar results may be expected for other compounds in this study. This result on a solid compound provides further corroborative evidence for the highly flexible nature of the saturated ring of the tetralin molecule. Obviously, variable-temperature, solid-state NMR possibly would be of value in elucidating the dynamical features of this and many other systems, providing one can lower the temperature below the point where effective molecular motion exists in the solid state.

Conclusion

This study has shown that the aliphatic ring of tetralin and related tetrahydroanthracenes displays structural and conformational properties both similar to and quite different from those of cyclohexane itself. Whereas 2-methyltetralin exists almost entirely in the equatorial conformation, 1-methyltetralin has essentially equally populated conformations due to the interaction of a pseudoequatorial methyl group with the peri proton on the aromatic ring. Similarly, this interaction in *cis*-1,2-dimethyltetralin is large enough to populate substantially the diaxial conformation of this molecule, while the diequatorial conformation strongly dominates in *cis*-2,3-dimethyltetralin.

A least-squares regression analysis of the ^{13}C chemical shifts of the ring carbons resulted in methyl substituent parameters which were nearly identical with those found for cyclohexane for methyls at C-2 whereas those determined for C-1 methyl groups were considerably different. A surprisingly large effect of 1 ppm at C-4 was also found when a pseudoequatorial at C-1 was present. This is presumably due to the high flexibility of the aliphatic ring, which also led to a failure to predict adequately the chemical shifts of highly substituted compounds, as well as a failure to fit parametrically the methyl shifts themselves. However, in less strained molecules, the structural similarities among the compounds has resulted in a high predictability of the chemical shifts and a better understanding of the conformational characteristics of this system.

Acknowledgment. This work was supported by the Department of Energy under Grant No. DE-AC02-78ER05006.

Registry No. 1, 119-64-2; **2**, 1559-81-5; **3**, 3877-19-8; **4**, 36736-25-1; **5**, 36736-26-2; 6, 39172-85-5; **7**, 39172-86-6; **8**, 14109-26-3; **9**, 32151-17-0; **10**, 10074-96-1; **11**, 10074-97-2; **12**, 1985-59-7; **13**, 13556-55-3; **14**, 2809-64-5; **15**, 25419-33-4; **16**, 85268-65-1; **17**, 85268-66-2; **18**, 1077-80-1; **19**, 40463-15-8; **20**, 85268-67-3; **21**, 85268-68-4; **22**, 85268-69-5; **23**, 85268-70-8; **24**, 85268-71-9; **25**, 39172-87-7; **26**, 51193-68-1; *cis*-**27**, 85268-72-0; *trans*-**27**, 85269-05-2; **27** acid chloride, 85269-04-1; **28**, 2141-42-6; **29**, 85268-73-1; **29**·picrate, 85268-80-0; **30**, 85268-79-7; **30**·picrate, 85268-81-1; **31**, 85268-74-2; **31**·picrate, 85268-82-2; **32**, 85268-75-3; **32**·picrate, 85268-83-3; **33**, 85268-76-4; **33**·picrate, 85268-84-4; **34**, 85268-77-5; **35**·picrate, 85269-09-6; **36**, 85268-78-6; **36**·picrate, 85268-85-5; 3,4-dimethyl-DHN, 5195-39-1; 1-hydroxy-1,3-dimethyl-THN, 34599-66-1; 1,4-dimethyl-DHN, 5195-36-8; 2,3-dimethyl-DHN, 21564-83-0; *trans*-1,2-dimethyl-1-tetralol, 85317-27-7; *cis*-1,2-dimethyl-1-tetralol, 85317-28-8; ethyl 2-methyl-3-phenyl-3-pentenoate, 85268-86-6; 2-methyl-3-phenyl-3-pentenoic acid, 85282-20-8; *cis*-2,3-dimethyltetralone, 10074-95-0; 2,3-dimethyl-1-tetralol, 34599-64-9; 2-methyl-1-tetralone, 1590-08-5; 2,2-dimethyl-1-tetralone, 2977-45-9; 4-(2-methylphenyl)butanoic acid, 6943-79-9; 5-methyl-1-tetralone, 6939-35-1; diethyl 2-methylbenzalmalonate, 24331-75-7; 2-(1-(2-methylphenyl)ethyl)malonic acid, 85268-87-7; 3-(2-methylphenyl)pentanoic acid, 72851-31-1; 4-(2-methylphenyl)pentanoic acid, 26232-96-2; 4,5-dimethyl-1-tetralone, 85268-88-8; 4,5-dimethyl-1-tetralol, 85268-89-9; 2-(2-(2-methylphenyl)-2-propyl)malonic acid, 85268-90-2; 3-methyl-3-(2-methylphenyl)butanoic acid, 85268-91-3; methyl 4,4-dimethyl-4-(2-methylphenyl)butanoate, 85268-92-4; 4,4-dimethyl-4-(2-methylphenyl)-butanoic acid, 85268-93-5; 4,4,5-trimethyl-1-tetralone, 85268-94-6; 4,4,5-trimethyl-1-tetralol, 85268-95-7; 1,1,8-trimethyl-DHN, 85268-96-8; 3-methyl-4-phenylbutanoic acid, 7315-68-6; methyl 3-methyl-4-phenylbutanoate, 69573-51-9; 2,4-dimethyl-5-phenyl-2-pentanol, 85268-97-9; 1,2,2-trimethyl-1-tetralol, 18059-84-2; 1-methylene-2,2-dimethyltetralin, 2977-47-1; methyl 4-phenylpentanoate, 20881-29-2; 1,1-dimethyl-4-phenylpentanol, 51193-79-4; 2,2,4-trimethyl-1-tetralone, 85268-98-0; 2,2,3-trimethyl-1-tetralone, 4384-37-6; *cis*-2,2,3-trimethyl-1-tetralol, 62082-78-4; *trans*-2,3-dimethyl-1-tetralone, 10294-74-3; 1,2,3-trimethyl-1-tetralol, 85268-99-1; 2,3,4-trimethyl-1,2-dihydronaphthalene, 85269-00-7; sodium diethyl methylmalonate, 62116-54-5; 2-(2-oxo-2-phenylethyl)-2-methylpropanedioic acid, 85269-01-8; 2-methyl-4-oxo-4-phenylbutanoic acid, 1771-65-9; 2-methyl-4-phenylbutanoic acid, 1949-41-3; methyl 2-methyl-4-phenylbutanoate, 38795-58-3; 3-methyl-5-phenyl-2-pentanol, 36748-82-0; 1,4-dimethyl-2-tetralone, 85269-02-9; 2-methylene-1,4-dimethyltetralin, 85269-03-0; methyl 2-naphthalenebutanoate, 785-19-3; 2-methyl-5-(2-naphthyl)-2-pentanol, 85269-06-3; 4,4-dimethyl-1,2,3,4-tetrahydrophenanthrene, 85269-07-4; 1,4-dimethyl-1,4,4a,9a-tetrahydroanthraquinone, 85269-10-9; 1,4-dimethyl-1,4,4a,9,9a,10-hexahydroanthraquinol, 85269-11-0; 1,1,3-trimethyl-1,4,4a,9a-tetrahydroanthraquinone, 85269-12-1; 1,1,3-trimethyl-1,4,4a,9,9a,10-hexahydroanthraquinol, 85282-21-9; 1,1,3-trimethyl-1,4-DHA, 85269-13-2; 1-methyl-1,4-DHA, 85269-14-3; 1,4-dimethyl-1,4-DHA, 54271-78-2; 3-methyl-1-tetralone, 14944-23-1; methyl iodide, 74-88-4; 1-phenyl-2-propanone, 103-79-7; ethyl 2-bromopropionate, 535-11-5; 2-bromotoluene, 95-46-5; diethyl isopropylidenemalonate, 6802-75-1; 4-phenylpentanoic acid, 16433-43-5; 4-methyl-1-tetralone, 19832-98-5; diethyl methylmalonate, 609-08-5; 2-bromoacetophenone, 70-11-1; oxalyl chloride, 79-37-8; *trans,trans*-2,4-hexadiene, 5194-51-4; *trans*-1,3-pentadiene, 2004-70-8.