

mmol) in ethanol (7.6 mL) was added a mixture of Zn(Cu) (329 mg, 2.55 mmol) and ammonium chloride (68 mg, 1.28 mmol) in water (0.2 mL), which was well agitated by a spatula in advance at room temperature. The mixture was then refluxed for 3 h. The cooled reaction mixture was diluted with *n*-hexane (20 mL) and inorganic precipitates were filtered off. After evaporation of the solvent the residual oil was purified by TLC [*n*-hexane-ethyl acetate (5:1) as solvent] to afford 13 (71 mg, 83%) as colorless crystals: mp 52.5 °C (recrystallized from *n*-hexane); IR (CHCl<sub>3</sub>) 3585, 3430, 3060, 1645, 1047, 902, 820 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)<sup>17</sup> 1.28 (d, 3 H, *J* = 7), 1.2-2.0 (m, 7 H), 2.62 (dd, 1 H, *J* = 12.5, 5.7), 3.05 (d, 1 H, *J* = 3.5), 3.14 (dd, 1 H, *J* = 3.5, 1.8), 3.42 (ddd, 1 H, *J* = 11.5, 9, 3.6, CHOH), 4.86 (br s, 2 H). Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.39; H, 9.59. Found: C, 71.14; H, 9.35.

**Conversion of 13 to (+)-1.** To a solution of 13 (91 mg, 0.54 mmol) in acetone (5 mL) was added dropwise Jones reagent (0.35 mL) at 0 °C, and the resulting mixture was further stirred for 15 min at the same temperature. The reaction mixture was poured into cold water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was washed with water and saturated brine. Evaporation of the solvent left crude epoxy ketone, which was adsorbed on a column of neutral alumina (Woelm activity III). Elution with ether gave 87 mg of an oil, which was purified by TLC [*n*-hexane-ether (1:1) as solvent] to afford 67 mg (74.5% of 1 as colorless crystals.

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## Carbon-13 Magnetic Resonance of Hydroaromatics. 3. Conformation of 1,2,3,4-Tetrahydrophenanthrene and 9,10-Dihydrophenanthrene and Their Methyl Derivatives<sup>1,2</sup>

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<sup>13</sup>C chemical shift data have been obtained for 27 methylated 1,2,3,4-tetrahydro- and 9,10-dihydrophenanthrenes. It has been found that methyl-substituent parameters previously determined for the saturated ring of tetralin and 1,2,3,4-tetrahydroanthracene show a remarkable ability to predict the chemical shifts in spite of the significant structural differences in the basic structure of the hydrophenanthrenes, exemplified by the proximity of the C-4 and C-5 positions. Analogous to the tetralins, 1-methyltetrahydrophenanthrene was determined to prefer slightly the conformer with a pseudoaxial methyl, while, in contrast to the tetralins, the C-4 methyl derivatives were forced to exist entirely with the C-4 methyl pseudoaxial. The conformation of the *cis*-2,4 compound is ambiguous. Variable-temperature <sup>13</sup>C and <sup>1</sup>H NMR has provided  $\Delta H^*$  and  $\Delta S^*$  of 10.3 kcal mol<sup>-1</sup> and -3.3 cal K<sup>-1</sup> mol<sup>-1</sup>, respectively, for the conformational inversion of *cis*-9,10-dimethyl-9,10-dihydrophenanthrene. It is hypothesized that significantly slower methyl group rotation in the transition state compared to the ground state is responsible for the negative  $\Delta S^*$ . The *trans*-9,10 compound is shown to exist exclusively as the diaxial conformer, and 9,9,10-trimethyldihydrophenanthrene is present as an equilibrium mixture where the conformer with the C-10 methyl axial dominates to better than 95%.

### Introduction

The process of coal liquifaction requires the use of hydroaromatics as hydrogen donors.<sup>3,4</sup> As part of a continuing investigation<sup>1,2</sup> of hydroaromatic compounds, we recently analyzed<sup>2</sup> the <sup>13</sup>C chemical shifts of methylated tetralins and 1,2,3,4-tetrahydroanthracenes in terms of methyl substituent parameters, determined from a linear least-squares regression, to gain insight into the conformational characteristics of that ring system. It was found that substituent parameters for methyl groups at C-2 (or C-3) were nearly identical with those found for cyclohexane,<sup>5</sup> but C-1 (or C-4) methyls resulted in quite different substituent effects. In particular, it was shown that a large  $\delta$  effect at C-4 of +1.0 ppm resulted from placement of a pseudoequatorial methyl at C-1. It was hypothesized that this was due to the high flexibility of the saturated ring, which also led to an inability to accurately predict the chemical shifts of the highly substituted derivatives.

The interaction of an equatorial C-1 methyl with the peri proton of the aromatic ring was also found to be severe enough to result in essentially equal populations of the pseudoequatorial and pseudoaxial conformers of 1-methyltetralin whereas 2-methyltetralin exists almost entirely in the equatorial conformation, similar to methylcyclohexane.

The tetrahydrophenanthrene system, while possessing a saturated six-membered ring fused to an aromatic ring, differs from tetrahydroanthracene through the severe steric congestion involving the C-4 and C-5 positions. This feature is anticipated to render those compounds with C-4 methyl groups conformationally immobile (i.e., the mole-

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cule will become "locked" into the conformation with a pseudoaxial methyl group) and provide an interesting contrast to our study of tetralins.<sup>2</sup> Although the chemical shifts of the parent compound have been reported<sup>6</sup> and an X-ray determination of 1,1-dimethyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene has been made,<sup>7</sup> an extensive investigation of the conformational properties of this ring system has not been undertaken.

In addition, we have synthesized and studied, via <sup>13</sup>C chemical shifts, a set of 9,10-methylated 9,10-dihydrophenanthrenes. Previous investigators have used variable-temperature <sup>1</sup>H NMR to determine the free energy barrier to inversion of the central ring of the parent<sup>8</sup> to be <9 kcal mol<sup>-1</sup> and of the *cis*-9,10-dimethyl derivative<sup>9</sup> to be 10.9 kcal mol<sup>-1</sup> at 250 K. Others<sup>10</sup> have measured <sup>1</sup>H-<sup>1</sup>H coupling constants to calculate that the 9-methyl derivative exists in the axial conformer 77% of the time. Our studies have attempted to confirm these findings.

### Experimental Section

<sup>13</sup>C spectra were obtained on a Varian SC-300 spectrometer at 75.5 MHz. A 12-kHz spectral window and 16K data table were employed. Samples were run as ~50% solutions in CDCl<sub>3</sub> with tetramethylsilane as the internal reference. Proton spectra were obtained at 300 MHz on the same instrument.

**Synthesis.** Previously known compounds displayed the correct physical properties and the expected <sup>1</sup>H NMR spectra. The synthetic routes to those compounds which were previously unknown, or whose stereochemistry was unknown, are given below.

**Tetrahydrophenanthrenes.** Table I contains the names and numbers of the tetrahydrophenanthrenes used in this study.

The attempt to prepare 4,4-dimethyl-THP (19) by cyclization of 2-methyl-5-(2-naphthyl)-2-pentanol in polyphosphoric acid (analogous to the method used to obtain 1,1-dimethyl-THP (16)<sup>11</sup>) gave instead the tetrahydroanthracene in 85% yield. The successful synthesis of 19 involved the conjugate addition of 1-naphthylmagnesium bromide to diethyl isopropylidenemalonate and conversion of the product to 4-methyl-4-(1-naphthyl)pentanoic acid. Cyclization of this acid followed by reduction gave 19.

***cis*- and *trans*-1,2-Dimethyl-THP (6 and 7).** To the sodio derivative of diethyl methylmalonate (prepared at 0 °C from 6.1 mL of the ester and 1.81 g of 50% sodium hydride) in 115 mL of glyme was added (0 °C) 8.62 g (34.6 mmol) of 2-bromo-1'-acetonephthone (prepared by the copper(II) bromide procedure<sup>12</sup>) in 33 mL of glyme, and the mixture was stirred at room temperature overnight. After addition of 350 mL of cold water, acidification, and ether extraction, the ether was washed with saturated brine and evaporated. The residue was saponified by the addition of 170 mL of methanol, 43 mL of water, and 47 mL of 6 N sodium hydroxide with heating for 45 min on the steam bath during the addition of 250 mL of water. After distillation of the methanol the cooled solution was filtered (norite) through Filtercel and acidified. The snow white diacid (7.40 g, 25.9 mmol, 74.9%) melted at 181–188 °C (gas evolution). Anal. Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>: C, 67.13; H, 4.93. Found: C, 67.66; H, 4.96. This gave acid (6.13 g, 25.3 mmol, 97%), mp 110–121 °C, when heated under argon in a bath at 192–210 °C. The Clemmensen reduction<sup>13</sup> of 3.74 g (15.5 mmol) of this keto acid gave an oil which was cyclized as the acid chloride with stannic chloride<sup>14</sup> to 1-keto-2-methyl-THP (1.62 g, 7.71 mmol, 46.7%), bp 150–153 °C (0.012 mm), mp

53–68 °C [lit.<sup>15</sup> 75–76 °C]. The addition of this ketone in 22 mL of benzene to ethereal methylmagnesium iodide (from 0.75 g of magnesium) and stirring overnight gave, after addition of 28 g of ammonium chloride in 70 mL water, an oil shown by <sup>1</sup>H NMR to consist of the two expected carbinols and no impurities. The oil was dehydrated<sup>16</sup> to 1,2-dimethyl-3,4-dihydrophenanthrene (1.44 g, 6.92 mmol, 89.8% from the ketone), bp 128 °C (0.013 mm), mp 78–92 °C. Crystallization from aqueous methanol brought the melting point to 99–101 °C. Reduction of 0.84 g (4.04 mmol) of the olefin in 45 mL of absolute ethanol over 0.4 g of 10% palladium/carbon and hydrogen at slightly above atmospheric pressure gave 0.82 g (3.90 mmol, 96.5%), bp 105–106 °C (0.03 mm). This was shown by <sup>1</sup>H NMR to be the *cis* form of the expected structure with no trace of the *trans* compound. From methanol, the material melted at 34–35.5 °C.

Catalytic reduction of 1.89 g (8.36 mmol) of the carbinol mixture described in the synthesis of 6 above in 180 mL of methanol plus 1.8 mL of perchloric acid with 10% palladium/carbon and hydrogen at 33 psig gave 1.24 g (5.9 mmol) containing some over-reduced product. This (1.09 g) gave 1.3 g of mixed picrates, mp 72–89 °C. The hydrocarbon recovered from the picrates proved to consist of 70% *cis*- and 30% *trans*-1,2-dimethyl-THP as shown by <sup>1</sup>H NMR.

***cis*- and *trans*-1,3-Dimethyl-THP (8 and 9).** 3-Methyl-1,2,3,4-tetrahydro-1-phenanthrone<sup>17,18</sup> (0.99 g, 4.71 mmol) in 1 mL of benzene was added to methylmagnesium iodide prepared in ether from 0.23 g of magnesium, and the reaction was stirred at room temperature overnight. After decomposition with aqueous ammonium chloride and the usual workup, the residual pale yellow oil was dehydrated with 3 mL of 95–97% formic acid and standing overnight. After dilution with water and benzene extraction, the olefin distilled at 128–133 °C (0.05 mm) (0.75 g, 3.6 mmol, 76.4% from the ketone). This in 40 mL of ethyl acetate and 0.3 g of 10% palladium/carbon was shaken under hydrogen at slightly above atmospheric pressure to give 0.68 g of *cis*-1,3-dimethyl-THP, mp 37–57 °C. The material contained about 10–15% of its geometrical isomer. Crystallization from cold methanol gave 0.54 g (2.57 mmol, 71.4%), mp 63–66.5 °C [lit.<sup>19</sup> (geometry not given) 64–65 °C]. The material is pure *cis* compound by <sup>1</sup>H NMR. The picrate, crystallized from methanol, melted at 136.5–139 °C [lit.<sup>19</sup> 133–135 °C]. Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>: C, 60.13; H, 4.82; N, 9.56. Found: C, 60.36; H, 4.72; N, 9.54.

1,3-Dimethyl-1,2,3,4-tetrahydro-1-phenanthrol, obtained from 1.43 g (6.81 mmol) of 3-methyl-1,2,3,4-tetrahydro-1-phenanthrone by addition of methylmagnesium iodide, was reduced in 150 mL of methanol containing 1.5 mL of 70% perchloric acid and 1.0 g of 10% palladium/carbon at room temperature and 33 psig of hydrogen for 4 h. After addition of 1.7 g of powdered potassium carbonate and filtration, the methanol was evaporated. Distillation gave 1.12 g (5.33 mmol, 78.3% from the ketone), bp 101–102 °C (0.01 mm), mp 47–62 °C. This by <sup>1</sup>H NMR was shown to be an approximately 55:45 *cis*:*trans* mixture of the expected dimethyltetrahydrophenanthrenes and 10–15% of an unknown impurity.

***cis*- and *trans*-1,4-Dimethyl-THP (10 and 11).** 1-Methyl-1,2,3,4-tetrahydro-4-phenanthrone<sup>20–22</sup> (1.62 g, 7.71 mmol) in 26 mL of ether was added to methylmagnesium iodide in 8.5 mL of ether (from 0.36 g of magnesium), and the reaction was refluxed for 1 h. After the usual workup the carbinol crystallized at once, giving 1.69 g (7.48 mmol, 97%), mp 95–121 °C. The material was 70:30 *cis*:*trans* mixture by <sup>1</sup>H NMR. Dehydration<sup>16</sup> of 1.62 g (7.17 mmol) gave 1.26 g (6.06 mmol, 84.5%), bp 104–107 °C (0.03 mm) [lit.<sup>22</sup> 144–146 °C (3 mm)], of an 85:15 mixture of exocyclic to endocyclic olefin mixture containing no other compounds as shown by <sup>1</sup>H NMR. This (1.04 g, 5 mmol) in 60 mL of absolute ethanol

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Table I. Carbon-13 Chemical Shifts of 1,2,3,4-Tetrahydrophenanthrene and Its Methylated Derivatives<sup>c</sup>

compound	1	2	3	4	4a	4b	5	6	7	8	8a	9	10	10a	CH <sub>3</sub> (position)
parent (1)	30.4	23.2 <sup>b</sup>	23.0 <sup>b</sup>	25.5	132.5 <sup>b</sup>	131.5	123.0	125.8	124.7	128.6	132.9 <sup>b</sup>	125.9	128.3	134.2	
1-methyl (2)	33.2	30.8	19.7	26.1	132.3 <sup>b</sup>	131.4	123.3	126.0	125.0	128.6	132.8 <sup>b</sup>	126.1	127.5	139.4	22.9
2-methyl (3)	38.8	28.7	31.2	25.5	132.4 <sup>b</sup>	131.0	123.0	125.8	124.7	128.5	132.7 <sup>b</sup>	125.9	128.2	133.9	21.7
	(39.1)	(29.1)	(31.7)	(25.5)											
3-methyl (4)	30.4	31.1	29.2	34.3	132.4 <sup>b</sup>	131.4	123.0	125.8	124.8	128.6	132.7 <sup>b</sup>	125.8	128.1	133.9	22.2
	(30.4)	(31.9)	(28.9)	(34.2)											
4-methyl (5)	30.3	17.8	30.2	28.2	136.8	132.4 <sup>b</sup>	123.5	125.8	124.6	129.0	133.1 <sup>b</sup>	126.3	128.5	133.2	22.0
	(30.4)	(17.7)	(29.7)	(27.8)											
cis-1,2-dimethyl (6)	38.6	31.8	25.5	25.9	132.4 <sup>c</sup>	130.6	123.3	125.9	125.0	128.6	132.7 <sup>b</sup>	126.1	128.4	140.7	16.8 (1)
	(38.2)	(32.6)	(26.2)	(25.5)											18.7 (2)
trans-1,2-dimethyl (7)	40.7	34.5	27.2	23.5	132.2 <sup>b</sup>	131.1	123.3	126.2	125.0	128.6	132.6 <sup>b</sup>	126.2	128.2	138.6	22.7 (1)
															19.8 (2)
cis-1,3-dimethyl (8)	34.1	41.8	29.2	35.4	132.1 <sup>b</sup>	131.7	123.5	125.9	124.9	128.5	132.5 <sup>b</sup>	125.8	126.1	138.7	22.2 (1)
	(33.9)	(41.7)	(28.9)	(35.2)											22.6 (3)
trans-1,3-dimethyl (9)	33.6	38.2	23.8	34.6	132.4 <sup>b</sup>	130.8	123.2	125.9	124.9	128.5	132.6 <sup>b</sup>	126.1	127.9	138.9	23.8 (1)
	(32.7)	(38.5)	(23.4)	(34.2)											22.5 (3)
cis-1,4-dimethyl (10)	33.6	27.5	29.8	28.8	137.2	132.1 <sup>b</sup>	123.9	126.0	124.9	128.8	132.6 <sup>b</sup>	126.5	126.6	138.4	22.1 (1)
	(33.9)	(27.6)	(29.7)	(28.8)											23.0 (4)
trans-1,4-dimethyl (11)	33.0	25.1 <sup>b</sup>	24.4 <sup>b</sup>	28.3	136.4	133.0 <sup>b</sup>	123.9	126.0	124.9	128.7	132.7 <sup>b</sup>	126.4	128.9	138.7	24.1 (1)
	(32.7)	(24.4)	(24.2)	(27.8)											22.0 (4)
cis-2,3-dimethyl (12)	36.8	31.8 <sup>b</sup>	32.1 <sup>b</sup>	31.8	132.7	130.6	123.2	126.0	124.9	128.7	132.7	126.1	128.0	134.3	15.0 <sup>b</sup>
	(35.9)	(32.7)	(32.5)	(31.0)											16.7 <sup>b</sup>
trans-2,3-dimethyl (13)	39.5	35.0 <sup>b</sup>	35.4 <sup>b</sup>	35.0	132.7	131.5	123.2	126.0	124.9	128.7	132.7	126.0	128.0	134.3	19.4 <sup>b</sup>
															19.8 <sup>b</sup>
cis-2,4-dimethyl (14)	40.2	29.2	42.3	29.8	136.6	132.1	124.3	125.3	124.4	128.8	133.3	126.0	128.1	135.3	21.9 (2)
															25.2 (4)
trans-2,4-dimethyl (15)	39.0	23.3	38.9	29.1	136.3	133.2	123.5	125.7	124.5	128.8	132.9 <sup>b</sup>	126.2	128.2	132.0	22.4 <sub>9</sub> (2)
	(39.1)	(23.6)	(38.3)	(27.8)											22.5 <sub>3</sub> (4)
1,1-dimethyl (16)	34.0	38.8	19.4	26.6	130.5	132.0 <sup>b</sup>	123.5	125.8	124.9	128.4	132.7 <sup>b</sup>	126.4	125.1	142.4	31.3
	(35.0)	(39.7)	(19.6)	(26.5)											
2,2-dimethyl (17)	44.4	29.3	35.9	23.4	132.4 <sup>b</sup>	130.5 <sup>b</sup>	123.2	126.0	124.9	128.7	132.6 <sup>b</sup>	126.1	128.9	133.8 <sup>b</sup>	28.0
	(43.7)	(29.5)	(36.3)	(22.2)											
3,3-dimethyl (18)	27.5	35.5	29.3	39.5	130.9	132.9 <sup>b</sup>	123.0	125.9	124.8	128.7	132.6 <sup>b</sup>	125.8	128.1	133.1 <sup>b</sup>	28.5
	(27.1)	(36.5)	(29.3)	(38.8)											
4,4-dimethyl (19)	32.9	19.1	44.6	34.7	139.9	132.5 <sup>b</sup>	126.8	124.6	124.0	129.5	134.1 <sup>b</sup>	126.8	128.7	134.8 <sup>b</sup>	30.3
															19.6 (3)
cis-3,4-dimethyl (20)	30.6	24.8	32.4	33.7	138.4	132.8 <sup>b</sup>	123.3	125.9	124.6	128.9	131.6 <sup>b</sup>	126.2	128.4	132.8 <sup>b</sup>	15.2 (4)
	(30.4)	(26.4)	(32.4)	(33.3)											

<sup>a</sup> Parentheses indicate calculated shifts. <sup>b</sup> Ambiguous assignments.

containing 1 g of 10% palladium/carbon was shaken under hydrogen at slightly above atmospheric pressure to give 0.90 g (4.29 mmol, 85.8%) of colorless oil, bp 101–102 °C (0.04 mm) [lit.<sup>21</sup> 150 °C (4 mm) (stereoisomer not stated)]. This on examination by <sup>1</sup>H NMR was a 75:25 *cis*:*trans* mixture of isomers and contained ~5% of an unknown impurity. The mixture crystallized in the freezing chamber but melted at room temperature. From methanol in the freezer 0.27 g of presumably *cis* compound, mp 44–48 °C, was obtained. The picrate from methanol melted at 113.5–116.5 °C [lit.<sup>21</sup> 116 °C].

***cis*- and *trans*-2,3-Dimethyl-THP (12 and 13).** The Reformatsky reaction using the Bachmann procedure<sup>14</sup> on 1-(1-naphthyl)-2-propanone (3.68 g, 20 mmol) with 4.12 mL of ethyl 2-bromopropionate gave 5.07 g (17.7 mmol, 88.6%) of a yellow oil, bp 144–148 °C (0.03 mm). Dehydration of this mixture with phosphorus pentachloride<sup>23</sup> gave 4.61 g (17.2 mmol, 97.2%), bp 127–131 °C (0.08 mm), which was hydrogenated over platinum oxide and saponified to give an oil (1.57 g, 6.49 mmol, 43.3% from the olefinic ester). Cyclization of the acid chloride (from 4.79 g of acid, 19.8 mmol) with stannic chloride<sup>14</sup> gave 3.27 g (14.6 mmol, 73.7%), bp 144–147 °C (0.05 mm) [lit.<sup>17</sup> 182–187 °C (3 mm), mp 99 °C]. This (3.27 g, 14.6 mmol) on reduction with lithium aluminum hydride gave 2.3 g (10.2 mmol, 69.9%), mp 107–128 °C. By <sup>1</sup>H NMR the mixture consisted of only two isomeric compounds in a ratio of 80:20, the 80% portion having equatorial methyl groups and an axial OH. Dehydration of the isomer mixture (2.22 g, 9.82 mmol) with *p*-toluenesulfonic acid monohydrate<sup>16</sup> gave 1.91 g (9.18 mmol, 93.5%), bp 106–108 °C (0.03 mm). On hydrogenation of 1.04 g (5 mmol) over 1 g of 10% palladium/carbon in 60 mL of absolute ethanol the resultant light yellow oil (0.87 g, 4.14 mmol, 82.8%) boiled at 100–101 °C (0.03 mm) [lit.<sup>17</sup> 165 °C (3 mm) (geometrical isomer(s) not stated)] and consisted of a 2:1 mixture of *cis*:*trans* isomers with an approximately 10% impurity. Repeated crystallizations of the picrate gave a solid, mp 94–96 °C. Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>: C, 60.13; H, 4.82; N, 9.56. Found: C, 60.08; H, 4.72; N, 9.54.

***cis*- and *trans*-2,4-Dimethyl-THP (14 and 15).** 2-Methyl-1,2,3,4-tetrahydro-4-phenanthrone (1.07 g, 5.1 mmol) added to methylmagnesium iodide (from 0.23 g of magnesium) gave an oil which was dehydrated<sup>16</sup> to the olefin, bp 114–115 °C (0.09 mm) [lit.<sup>24</sup> 185–190 °C (10 mm)]. Reduction in 40 mL of ethyl acetate over 0.3 g of 10% palladium/carbon gave 0.82 g (3 mmol, 92.2%), bp 98–103 °C (0.01 mm) [lit.<sup>22</sup> 151–153 °C (4 mm)]. The compound solidified in the freezer, mp 35–54 °C [lit.<sup>22</sup> 67 °C (geometrical isomer not stated)]. By <sup>1</sup>H NMR the material contained 20–30% of the *trans* compound. The picrate from repeated crystallizations from methanol melted at 107–111 °C [lit.<sup>22</sup> 113 °C].

**2,2-Dimethyl-THP (17).** To 2.58 g (53.8 mmol) of 50% sodium hydride in oil (washed twice with light petroleum ether) was added 20 mL of glyme and 2.66 g (13.6 mmol) of 1,2,3,4-tetrahydro-1-phenanthrone in 25 mL of glyme. After refluxing for 30 min, the mixture was chilled to 0 °C and 3.34 mL (53.7 mmol) of methyl iodide was added, followed by stirring overnight at room temperature. The product, after workup (2.75 g, 12.3 mmol, 90.4%) bp 130–133 °C (0.05 mm), was pure 2,2-dimethyltetrahydrophenanthrone by <sup>1</sup>H NMR. This 2.75 g, by Clemmensen reduction<sup>13</sup> with refluxing for 46 h, gave 2.36 g, bp 110–114 °C (0.09 mm), which was shown by <sup>1</sup>H NMR to be only half converted to hydrocarbon. The reduction was repeated on 1.08 g (48 h). The colorless hydrocarbon crystallized in the freezer and was found to be pure by <sup>1</sup>H NMR. The reported<sup>25</sup> melting point is 45–46 °C.

**3,3-Dimethyl-THP (18).** In a sodium hydride–methyl iodide methylation similar to the above, 2.71 g (13.8 mmol) of the 1,2,3,4-tetrahydro-4-phenanthrone gave 2.85 g (12.7 mmol, 92%) of the dimethyl ketone, bp 132–136 °C (0.02 mm). The compound was shown to be >95% pure and to have the expected structure by <sup>1</sup>H NMR. Reaction of 2.46 g (11 mmol) of the dimethyl ketone with 1.51 g of lithium aluminum hydride gave 1.85 g (8.19 mmol,

74.5%), mp 90–95 °C. After crystallization from hexanes the 3,3-dimethyl-1,2,3,4-tetrahydro-4-phenanthrol melted at 96–97.5 °C. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O: C, 84.91; H, 8.02. Found: C, 85.12; H, 8.08. Hydrogenation of 1.07 g (4.78 mmol) of the carbinol in 200 mL of methanol containing 1 mL of 70% perchloric acid and 1 g of 10% palladium/carbon for 1 h at 33 psig of hydrogen gave 0.81 g (3.86 mmol, 80.8%) of pale yellow oil, bp 97–98 °C (0.04 mm). The product was 85% pure and contained overhydrogenated material as indicated by <sup>1</sup>H NMR. The picrate melted at 147–149 °C after several recrystallizations from methanol. Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>: C, 60.13; H, 4.82; N, 9.56. Found: C, 60.17; H, 4.79; N, 9.21.

**4,4-Dimethyl-THP (19).** To 1-naphthylmagnesium bromide (from 1.83 g, 75 mmol of magnesium and 16.56 g, 80 mmol of 1-bromonaphthalene) was added (0 °C) 0.1 g of copper(I) chloride and then (–5 to 0 °C) 10 g (50 mmol) of diethyl isopropylidene-malonate.<sup>26</sup> After workup, the oil obtained was saponified and acidified to obtain 12.14 g (44.6 mmol, 89.2%) of the malonic acid, mp 148–160 °C (gas evolution). From benzene–absolute ethanol it melted at 163–167 °C (gas evolution). Anal. Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>: C, 70.57; H, 5.92. Found: C, 71.11; H, 5.97. The malonic acid, on heating for 10 min at 183–194 °C, gave (77%) 3-methyl-3-(1-naphthyl)butanoic acid, mp 92–95 °C after crystallizations from hexanes and sublimation at 180 °C (bath) (1.5 mm). Anal. Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>: C, 78.92; H, 7.07. Found: C, 79.29; H, 7.21. The butanoic acid (1.97 g, 8.64 mmol) was converted by the Arndt–Eistert reaction<sup>14</sup> to 4-methyl-4-(1-naphthyl)pentanoic acid (1.56 g, 64.5 mmol, 74.7%), which was collected as a pale yellow glass by sublimation at 155–185 °C (bath) (0.09 mm). This was cyclized via the acid chloride and stannic chloride to an oil, 4,4-dimethyl-1,2,3,4-tetrahydro-1-phenanthrone (1.23 g, 5.49 mmol, 85%). The material, distilled onto a cold finger condenser at 140–144 °C (0.25–0.35 mm), also failed to crystallize. It was shown to have the correct structure and to contain some impurity by <sup>1</sup>H NMR. Reduction of 2.10 g (9.38 mmol) of the ketone with 1.28 g of lithium aluminum hydride gave an oil which was dehydrated with 90 mg of *p*-toluenesulfonic acid<sup>16</sup> to olefin 1.7 g (8.17 mmol, 87.1%), bp 114–115 °C (0.01 mm), having the expected structure and minor impurities by <sup>1</sup>H NMR. Reduction of 1.47 g (7.07 mmol) in 160 mL of ethyl acetate over 0.5 g of 10% palladium/carbon and hydrogen at atmospheric pressure gave 1.37 g (6.52 mmol, 92.2%) of colorless oil, bp 104–107 °C (0.01 mm). This proved to be pure and to have the correct structure by <sup>1</sup>H NMR. It formed a golden yellow picrate, mp 135–137 °C from 95% ethanol. Anal. Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>: C, 60.13; H, 4.82; N, 9.56. Found: C, 60.32; H, 4.88; N, 9.54.

***cis*-3,4-Dimethyl-THP (20).** Similar to the procedure under 1,2-dimethyl-THP above, addition of 8.62 g (34.5 mmol) of 2-bromo-2'-acetonaphthone to the sodio salt of diethyl methylmalonate (6.1 mL) followed by saponification gave 8.67 g (30.3 mmol, 87.6%) of the malonic acid, mp 182–184 °C dec. A sample from acetone melted at 176–178 °C dec. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>: C, 67.13; H, 4.93. Found: C, 67.72; H, 5.20. The acid (7.65 g, 26.7 mmol) at 192–200 °C for 15 min gave 5.34 g (22.1 mmol, 82.8%), mp 161–168 °C [lit.<sup>15</sup> 165–166 °C]. Ketone reduction by the Huang-Minlon method<sup>27</sup> on 3.0 g (12.4 mmol) gave 2.34 g (10.3 mmol, 83.3%), mp 63–87 °C [lit.<sup>15</sup> 85–86 °C]. This acid was cyclized as the acid chloride with stannic chloride to give 0.98 g (4.67 mmol, 72%), mp 55–59 °C [lit.<sup>15</sup> 64–65 °C]. The ketone (1.22 g, 5.81 mmol) with methylmagnesium iodide (from 0.27 g magnesium) gave the carbinol, which was dehydrated<sup>16</sup> directly to yield 1.14 g (5.48 mmol, 94.3%), bp 131–132 °C (0.35 mm) [lit.<sup>24</sup> 192–194 °C (10 mm)]. The olefin, by <sup>1</sup>H NMR, was 95% pure with other olefins as impurities. Hydrogenation with 0.3 g of platinum oxide in methanol containing 1.2 mL of 70% perchloric acid and hydrogen at nearly atmospheric pressure gave 1.01 g (4.81 mmol, 87.8%), bp 106–107 °C (0.15 mm), shown to be *cis*-3,4-dimethyl-THP and to contain a trace of olefin by <sup>1</sup>H NMR.

**Dihydrophenanthrenes.** Table II contains the names and numbers of the dihydrophenanthrenes used in this study.

The ring closure of 2,2'-bis(bromomethyl)biphenyls with phenyllithium has been reported many times as an avenue to

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Table II. Carbon-13 Chemical Shifts of 9,10-Dihydrophenanthrene and Its Methylated Derivatives

compound	1	2	3	4	4a	4b	5	6	7	8	8a	9	10	10a	CH <sub>3</sub> (position)
parent (21)	128.3	127.5	127.1	123.9	134.7						137.4	29.0			
9-methyl (22)	128.9	127.7 <sup>a</sup>	127.1 <sup>a</sup>	123.7	134.3 <sup>a</sup>	133.9 <sup>a</sup>	124.1	127.0 <sup>a</sup>	129.9 <sup>a</sup>	126.8	142.2	33.0	36.7	136.1	19.6
cis-9,10-dimethyl (23)	126.8	127.9	126.9	124.0	134.0						141.8	37.8			14.6
trans-9,10-dimethyl (24)	129.3	128.0	127.0	123.9	132.5						140.7	40.9			21.8
9,9-dimethyl (25)	128.8	127.6	127.1 <sup>a</sup>	123.7	134.4 <sup>a</sup>	133.4 <sup>a</sup>	124.3	126.7 <sup>a</sup>	128.1	124.4	145.5	34.0	44.1	136.1	27.9
9,9,10-trimethyl (26)	128.2	127.9 <sup>a</sup>	126.9 <sup>a</sup>	123.9	132.8 <sup>a</sup>	133.0	124.0	126.6 <sup>a</sup>	128.2 <sup>a</sup>	125.3	143.7	37.1	46.4	142.3	24.6 (9e) 29.8 (9a) 17.1 (10)

<sup>a</sup> Ambiguous assignments.

9,10-dihydrophenanthrenes. We have extended the reaction (using Li<sup>0</sup>/THF) to the formation of 24. The product formed was exclusively the trans isomer thus neatly complementing the Harvey reduction<sup>28</sup> (Li<sup>0</sup>/NH<sub>3</sub>) which gives exclusively the cis isomer.

**trans-9,10-Dimethyl-DHP (24).** By lithium aluminum hydride reduction of 2.39 g (10 mmol) of 2,2'-diacetylbi-phenyl (mp 80–86 °C) a mixture of diastereomeric diols (2.26 g, 9.34 mmol, 93.4%) was obtained, mp 103–117 °C [lit.<sup>29</sup> diol A 147.5–149 °C and diol B 153–155 °C]. This mixture in 25 mL of 48% aqueous hydrobromic acid was refluxed for 15 min and then poured into water. The dibromide (1.52 g, 4.13 mmol, 44.2%) melted at 73–84 °C [lit.<sup>29</sup> 88–92 °C]. This dibromide in 150 mL of ether at 0 °C was treated with 0.1 g of lithium in small pieces. After the mixture had been stirred for 2 h at 0 °C and 96 h at room temperature, the excess lithium was filtered on a sintered glass funnel and washed with ether. The ether solution was washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Distillation gave 0.75 g (3.6 mmol, 87.2%), bp 89 °C (0.01 mm). The <sup>1</sup>H NMR showed that the material was 90% 24, 10% starting material, and free of the cis isomer.

**9,9,10-Trimethyl-DHP (26).** A suspension of 0.95 g (4.28 mmol) of 10,10-dimethyl-9-phenanthrene,<sup>30</sup> mp 54–58 °C [lit.<sup>30</sup> 61 °C], in 25 mL of ether was treated (0 °C) with 8 mL of 1.4 M methylolithium in ether and stirred overnight at room temperature. The usual workup gave 0.99 g (4.16 mmol, 97.2%) of a golden yellow oil. The oil, with 150 mL of methanol, 1 mL of 70% perchloric acid, and 1 g of 10% palladium/carbon, was shaken for 4 h under hydrogen at 33 psig. Workup gave 0.72 g (3.24 mmol, 77.9%) of practically colorless oil shown to be pure 26 by <sup>1</sup>H NMR. A sample boiled at 88–90 °C (0.015 mm). Anal. Calcd for C<sub>17</sub>H<sub>18</sub>: C, 91.84; H, 8.16. Found: C, 92.10; H, 7.72.

## Results

<sup>13</sup>C and <sup>1</sup>H NMR data have been obtained for twenty 1,2,3,4-tetrahydrophenanthrenes and seven 9,10-dihydrophenanthrenes. <sup>13</sup>C shifts are reported in Tables I and II. Assignments were made by using standard off-resonance and selective decoupling techniques. Aromatic carbons were occasionally assigned by their appearance in a coupled spectrum.<sup>31</sup> Computer calculations were performed on a DEC VAX-11/750 or 11/780.

**A. Tetrahydrophenanthrenes.** Initially, it had been our intent to carry out a regression analysis of the shifts of the tetrahydrophenanthrenes as was done in the previous studies.<sup>2,5</sup> This, however, was not possible due to the relatively small size of the data set; in particular, trimethyl derivatives were lacking. The small number of chemical shifts available, relative to the number of parameters required, made it impossible to perform the calculation with a parameter set whose members were sufficiently linearly independent of each other. As a result of the aforementioned structural difficulties, it was decided to apply the methyl substituent parameters from the tetralin work<sup>2</sup> in

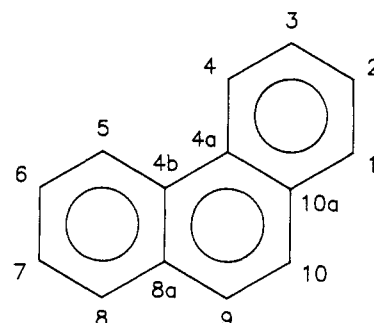


Figure 1. Numbering scheme for phenanthrene.

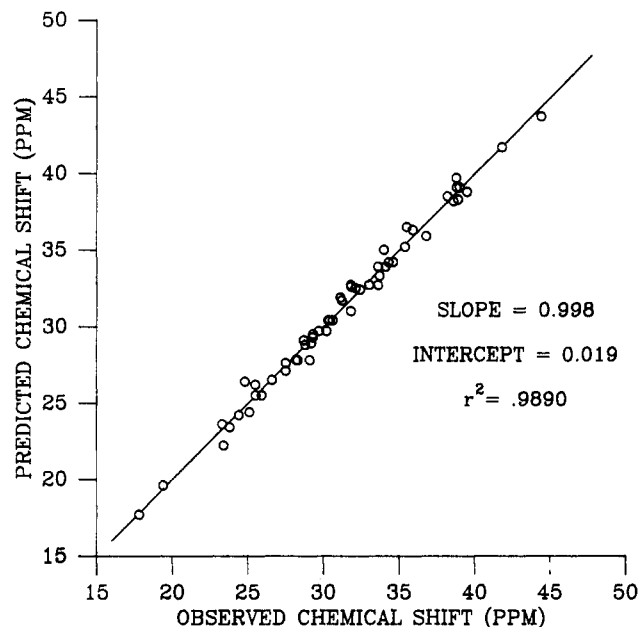


Figure 2. Comparison of predicted and observed carbon-13 chemical shifts for the ring carbons of the tetrahydrophenanthrenes of this study.

Table III. Carbon-13 Chemical Shift Parameters Indicating the Effects of Methyl Substitution<sup>a</sup>

$\alpha_{1e} = 3.51$	$\beta_{1e} = 9.85$	$\delta_{1e} = 1.00$
$\alpha_{1a} = 2.30$	$\beta_{1a} = 6.67$	$\gamma_{1a} = -5.48$
$\alpha_{2e} = 5.91$	$\beta_{2e} = 8.67$	$\gamma_{2a} = -5.32$
$\alpha_{2a} = 3.00$	$\beta_{2a} = 7.73$	$V_{ea} = -3.19$

<sup>a</sup> In ppm. See ref 2 for definition of the parameters.

an attempt to predict the observed shifts of the ring carbons of the 1,2,3,4-tetrahydrophenanthrenes. This was done in the following manner. The shifts of the saturated ring of the parent (1) (see Figure 1 for numbering) were used for base values, to which were added the appropriate substituent parameters. In this treatment the C-4 position is equivalent to C-1 and C-3 equivalent to C-2. Equating the C-1 and C-4 carbons, while rather unusual, was sub-

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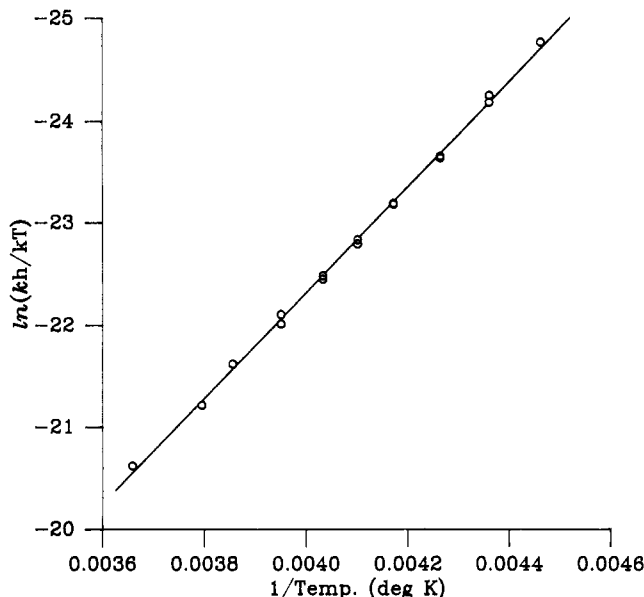


Figure 3. Eyring plot of the conformational inversion rate of 23.

sequently shown to be justified. Using the relevant parameters<sup>2</sup> in Table III an example calculation for the *trans*-2,4 compound (14) is given as follows:

$$C-1 = 30.4 + \beta_{2e} = 30.4 + 8.67 = 39.07 \text{ ppm}$$

$$C-2 = 23.2 + \alpha_{2e} + \gamma_{1a} = 23.2 + 5.91 - 5.48 = 23.63 \text{ ppm}$$

$$C-3 = 23.0 + \beta_{2e} + \beta_{1a} = 23.0 + 8.67 + 6.67 = 38.34 \text{ ppm}$$

$$C-4 = 25.5 + \alpha_{1a} = 25.5 + 2.30 = 27.80 \text{ ppm}$$

A graphical comparison of the predicted and observed shifts is given in Figure 2 as well as the results of a linear least-squares fit. The line plotted is the linear least-squares line. Included in the fit were all molecules expected to exist essentially in one half-chair conformer due to unfavorable steric interactions in the alternative one. Molecules not included were 1, 2, 7, 13, 14 and 19. The shifts of compound 1 were used as base values for the calculation. 2 and 7 are expected to be conformationally mobile, and 13 possesses diequatorial vicinal methyl groups for which no parameter has been previously calculated. A single preferred conformation for the *cis*-2,4 derivative, 14, is not obvious. The two possible half-chair conformers require either a pseudoequatorial C-4 methyl or a 1,3-diaxial methyl interaction. Neither situation is particularly favorable, and due to this uncertainty this molecule was omitted from the fit. Compound 19 was excluded owing to the considerable steric crowding present.

**B. Dihydrophenanthrenes.** An investigation of *cis*-9,10-dimethyl-9,10-dihydrophenanthrene revealed a temperature dependence to the <sup>13</sup>C NMR spectrum as the exchange between the two identical conformers became slow on the NMR time scale. At low temperatures (ca. -60 °C) the chemical shift difference between the axial and equatorial methyls was 1.6 ppm and between the correspondingly substituted methines 4.8 ppm. The line shapes of the methyl and the aliphatic methine carbons were simulated as a function of temperature by using a program written by Solum<sup>32</sup> modified for two site exchange in iso-

tropic medium, to obtain  $k_r$ , the exchange rate.<sup>33</sup> A plot<sup>34</sup> of  $\ln(k_r h/kT)$  vs.  $T^{-1}$  is given in Figure 3 with a least-squares line indicated. The enthalpy and entropy of activations were found to be  $10.3 \pm 0.1 \text{ kcal mol}^{-1}$  and  $-3.3 \pm 0.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ , resp. The errors are one marginal standard deviation of the fit and the correlation coefficient,  $r^2$ , was 0.9985. The calculated  $\Delta G^\ddagger$  is  $11.1 \text{ kcal mol}^{-1}$  at 250 K.

## Discussion

**A. Tetrahydrophenanthrenes. Ring Carbons.** The excellent agreement between the predicted and observed <sup>13</sup>C chemical shifts is quite remarkable in light of our anticipation that the strong steric interaction involving C-4 and C-5 of the tetrahydrophenanthrenes would result in significant changes in the substituent parameters. Indeed the X-ray study<sup>7</sup> provides an H-4 to H-5 distance of just 2.1 Å, well within two van der Waal's radii, and as a consequence, the C-4 shift of 1 (25.5 ppm) is 4.1 ppm upfield of that of tetralin itself (29.6 ppm), and a concomitant upfield shift of 4.3 ppm, from 127.3 ppm to 123.0 ppm, occurs for C-5. It is evident, however, that such changes in the methyl substituent parameters are minor and beyond the realm of experimental determination. The success of the fit ( $r^2 = 0.9890$ , standard deviation of the points,  $\sigma = 0.58 \text{ ppm}$ ) is only slightly poorer than for the tetralins themselves ( $r^2 = 0.9967$ ,  $\sigma = 0.41 \text{ ppm}$ ). It may tentatively be concluded that the parameters are generally suitable to molecules containing the cyclohexene ring moiety provided caution is used in the event of serious steric congestion.

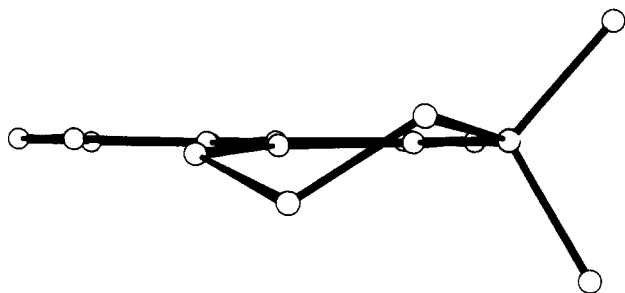
The results also demonstrate the validity of the assumption of a single conformation for each of the compounds used in the fit. Those with a C-4 methyl (5, 10, 15 and 20) have, without doubt, been forced into a single conformation because of the proximity of the C-5 position. The 4-methyl derivative, 5, clearly populates the pseudoaxial conformer only. The shifts of *cis*-1,4 (10) and *trans*-1,4 (11) were calculated on the assumption that they occur solely as the C-1e,C-4a and C-1a,C-4a conformers, respectively, and the success of the calculations indicates these assumptions are correct. In contrast, the analogous tetralins had nearly equally populated conformations in both cases.<sup>2</sup> It is important to note that it was imperative to include the  $\delta_{1e}$  effect of +1.0 ppm mentioned in the Introduction to calculate the shifts of C-4 of the tetrahydrophenanthrenes accurately.

On the other hand, curious results have been obtained for the two 2,4-dimethyl compounds. The shift of the C-4 carbon of the *trans* isomer (15) is very poorly reproduced, about three standard deviations from the observed value. At this point the reason for this discrepancy is not clear. (Exclusion of this datum from Figure 2 resulted in a least-squares fit with  $m = 0.999$ ,  $b = -0.0005$ ,  $\sigma = 0.52$ , and  $r^2 = 0.9914$ ) Another interesting result is found for the *cis* isomer (14) which was not included in Figure 2 but is, perhaps fortuitously, well reproduced by the tetralin substituent parameters under the assumption of a C-2e,-C-4e conformation. The observed and calculated shifts for C-1 through C-4 are 40.2 (40.1), 29.2 (29.1), 42.3 (41.6), and 29.8 (29.0) ppm. The deviations increase as one moves toward the C-4 position of the ring but are still reasonable given the overall standard deviation of the least squares

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**Figure 4.** Illustration of the similarity of environments for the two methyl groups of 16. Figure constructed from data in ref 7.

fit. Alternatively, the conformer with diaxial methyl groups would be predicted to have the following shifts: 38.1, 20.7, 37.4, and 22.5 ppm. Obviously, neither C-2 nor C-4 is as shielded as these values predict. If 14 does, in fact, exist as a diequatorial conformer with little contribution from the diaxial, then the methyl substituent parameters must be nearly independent of the environment of the methyls themselves, an assumption implicit in the calculations above. A somewhat anomalous chemical shift for C-5, described below, is evidence that the C-4 methyl is not pseudoequatorial. However, the ambiguity in the molecular conformation makes it difficult to make definitive statements.

It should be recalled that the calculated shifts of the *gem*-dimethyl derivatives in the tetralin series resulted in some of the larger deviations. Therefore it is not surprising that the same parameters again predict some of the more poorly predicted chemical shifts. Using data from the previously performed X-ray analysis<sup>7</sup> to construct Figure 4, one can see that the geminal dimethyl portion of 1,1-dimethyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene apparently flattens out the ring, resulting in very similar environments for the two methyl groups rather than producing distinctly pseudoaxial or pseudoequatorial positions. This is a clear indication that the high flexibility of the saturated ring allows for significant distortions in the solid state and demonstrates the care with which solid-state NMR data should be used to examine such systems.<sup>2</sup> Alternatively, this more symmetric conformation may represent another minimum on the reaction coordinate between the two conformations and give rise to the higher errors obtained for the calculated shifts of 16, having assumed the molecule exists only in the half-chair type conformations.

Using the substituent parameters provided by the molecules of unambiguous conformation, one may make approximate determinations of the conformational preferences of the compounds that were not included in the fit. In the earlier study of methylated tetralins and tetrahydroanthracenes,<sup>2</sup> it was shown that the 1-methyl derivative populated the pseudoaxial conformer to only a slight extent over the pseudoequatorial conformer. If one assumes a 60:40 ratio for 1-methyl-1,2,3,4-tetrahydrophenanthrene (2) and uses the substituent parameters from the tetralin paper,<sup>2</sup> the observed shifts compare with the calculated shifts (in parentheses): 33.2 (33.2), 30.8 (31.1), 19.7 (19.7), 26.0 (26.4) ppm for C-1 through C-4. A small change in the ratio will still give reasonable results, but the supposition of a slight preference for the pseudoaxial conformation is justified, in complete analogy with 1-methyltetralin. A similar calculation for the trans-1,2 derivative, 7, provides an estimate of 55% dipseudoequatorial conformer in the equilibrium, also essentially unchanged from the tetralin analogue, confirming the discovery that the tetrahydrophenanthrene ring system is

very similar to the tetrahydroanthracenes for methyl substitution at C-1, C-2, or C-3.

**Aromatic Carbons.** The aromatic chemical shifts show little variation except for C-5 and C-10 which are the sole carbons that will sterically interact to a measurable and variable extent with the methyl groups. The shift of C-5 is  $123.3 \pm 0.3$  ppm in the absence of a pseudoequatorial methyl at C-4 but is moved downfield to 126.8 ppm in the 4,4 compound (19), where a severe interaction with at least one of the methyl groups is unavoidable. This downfield shift, opposite in direction to that normally encountered for nuclei involved in a  $\gamma$  interaction, is typical when the nuclei are situated in this  $\delta$  (i.e., 1,4) conformation. Others have discovered,<sup>35</sup> in a series of substituted cyclohexanes, norbornanes, and steroids, downfield shifts of 2.0–3.5 ppm when a  $\delta$  steric interaction takes place. An even larger effect was demonstrated by the determination<sup>36</sup> that the methyl group of 1,8-dimethylnaphthalene resonates 6.7 ppm downfield of the methyl of 1-methylnaphthalene. An intermediate value of 124.3 ppm is found for the cis-2,4 derivative (14), indicating that the C-4 methyl is not occupying the pseudoequatorial position exclusively or that the molecule, rather than switching to the alternative half-chair conformation with 1,3-diaxial methyls, has distorted to some other, undefined conformation. This is more evidence that the conformation of this molecule is ill-defined and that the surprisingly good agreement between predicted and observed shifts for the aliphatic carbons does not result from suitable conformational effects.

Conversely, C-10 resonates at  $128.3 \pm 0.4$  ppm when C-1 is unsubstituted or substituted with a pseudoaxial methyl but is shifted upfield  $\sim 2$  ppm to 126.1 or 126.6 ppm for compounds 8 and 10 which possess a pseudoequatorial methyl group and a further 1 ppm to 125.1 ppm for 1,1-dimethyl-1,2,3,4-tetrahydrophenanthrene (16).

**Methyl Carbons.** In the previous study of the tetralins<sup>2</sup> a similar linear regression analysis on the methyl carbon shifts was unsuccessful. The chemical shift range over which the methyls appeared was too small to give significant structural parameters, and the same deficiency is manifested here. However, the salient features of Table I will be indicated. First, an isolated equatorial methyl group at C-2 (or C-3) (cf. 3, 4, 8, 14) is found at  $22.1 \pm 0.1$  ppm, essentially the same as that found for a similar methyl on a cyclohexane ring.<sup>37</sup> Most of the remaining shifts are unchanged from those determined in the tetralin work, with minor deviations up to  $\sim 0.6$  ppm. Those methyls which are oriented pseudoaxially, e.g., 9 (23.8 ppm) and 11 (24.1 ppm), or pseudoequatorially, e.g., 8 (22.2 ppm) and 10 (22.1 ppm), at C-1 are unchanged in their chemical shifts from the tetralins.

The most interesting data are provided by the two 2,3-dimethyl derivatives. Here the trans isomer (13) undoubtedly exists in the diequatorial conformation,<sup>2,38</sup> but the methyl groups are nonequivalent to the extent of  $\Delta\delta = 0.4$  ppm. The chemical shift difference between the equatorial methyls of 2-methyl- and 3-methyl-THP is also only 0.5 ppm (21.7 vs. 22.2 ppm) while the cis isomer (12), believed to be two rapidly interconverting conformations that should result in comparable time-averaged environ-

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ments for the two methyl groups, has  $\Delta\delta = 1.7$  ppm. As the difference between the chemical shifts of equatorial methyls at the two sites is small, one might attribute the difference in the shifts of 12 to differences in the environments of the axial methyls at the C-2 vs. C-3 sites, although examination of molecular models does not support this conclusion.

**B. Dihydrophenanthrenes.** The most valuable results for this series have been provided by the *cis*-9,10-dimethyl derivative (**23**). The negative  $\Delta S^\ddagger$  obtained may be ascribed to a change in rotational mobility of the methyl groups as the central ring becomes planar in the transition state where the hindrance to rotation is somewhat greater than in the ground state. Although it is well-known<sup>39,40</sup> that precautions must be taken when the results of an analysis of NMR line shapes are interpreted, a similar <sup>13</sup>C NMR investigation of the conformational inversion rate of *cis*-1,2-dimethylcyclohexane<sup>41</sup> found  $\Delta H^\ddagger = 9.3$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -3.5$  cal K<sup>-1</sup> mol<sup>-1</sup> ( $\Delta G^\ddagger = 10.2$  kcal mol<sup>-1</sup> at 250 K). The similarity of the  $\Delta S^\ddagger$  found for **23**, which closely resembles the dimethylcyclohexane in the vicinity of the methyl groups, lends further credence to the belief that the presence of the vicinal dimethyls is the source of the decreased entropy in the transition state.

The low-temperature chemical shifts of **23** are themselves interesting. While the methine shifts differ by 4.8 ppm, the methyl carbons differ in shift by just 1.6 ppm. While one might expect that the equatorial methyl would be considerably shielded because of the interaction with the peri proton at C-1 (or C-8) compared with the lack of steric encumbrances in the axial position, molecular models demonstrate that an axial methyl is situated over the biphenyl ring moiety of the molecule, a region which is known to exert a relative shielding effect on a nucleus positioned there.<sup>42</sup> As a consequence, the closeness of the shifts makes it difficult to assign peaks to a particular conformer at low temperatures.

Variable-temperature measurements were also taken on the trimethyl compound, **26**. Although broadening of the resonances due to slowing of the exchange between two conformations (those with the C-10 methyl axial or equatorial) took place in the region -20 °C to -40 °C, in the slow exchange limit (-60 °C) the peaks due only to one conformer were observed. This indicates that the equilibrium is strongly biased toward one of the conformers. It has previously been determined<sup>43</sup> that the conformational equilibrium of 1,1,2-trimethylcyclohexane favors the conformation with an equatorial 2-methyl group. Several important differences exist between that molecule and **26**, however. The equatorial 2-methyl group of 1,1,2-trimethylcyclohexane is in a rather unhindered position relative to the other ring protons of the molecule, whereas the analogous methyl in **26** sterically interacts with the C-1 peri proton. Also, the destabilization of the conformer of 1,1,2-trimethylcyclohexane with the C-2 methyl axial is due to the  $\gamma$  interactions of the methyl with the axial ring protons at the C-4 and C-6 positions. These protons are absent in **26**. In summary, the conformer of **26** with an equatorial C-10 methyl experiences one more gauche methyl interaction as well as an interaction with a peri

proton when compared to the alternative conformation. This results in a substantial preference for the axial conformation in direct contrast to 1,1,2-trimethylcyclohexane. This is confirmed by the observation that the chemical shift of C-1 of **26** is the same as the parent, indicating that the methyl at C-10 is axial and not equatorial. An upper limit of ~5% can be placed on the population of the minor conformer corresponding to a free energy difference  $\Delta G^\circ > 1.5$  kcal mol<sup>-1</sup>.

Insights into the conformational preference of 9-methyl-9,10-dihydrophenanthrene (**22**) may be obtained by comparing the <sup>13</sup>C chemical shift of the methyl group (19.6 ppm) to that of the *trans*-9,10-dimethyl derivative **24** (21.8 ppm). If the methyl group of the former was essentially axial, one would expect the addition of another methyl *trans* to it to have a negligible effect on the chemical shift. The actual effect of 2.2 ppm may indicate that **22** has some contribution from the equatorial conformer. This would presumably result in some shielding due to the presence of the C-8 position which is removed in **24** when the methyl group is axial. Furthermore, a comparison of the shift of C-8 of the *cis*-9,10 derivative **23**, which has an equatorial methyl at C-9 precisely one-half of the time, is found to be identical to C-8 of **22**. While it is unlikely that **22** also has an equatorial methyl 50% of the time, this observation corroborates the assertion that there is indeed a significant contribution from that conformer to the equilibrium.

### Conclusion

This study has shown that the methyl substituent parameters previously determined for tetralin and tetrahydroanthracene also demonstrate a remarkable ability to predict the <sup>13</sup>C chemical shifts of the methyl-substituted tetrahydrophenanthrenes in spite of major structural differences in the two types of ring systems, e.g., the proximity of the C-4 and C-5 positions in the latter. While 1-methyl-1,2,3,4-tetrahydrophenanthrene is found to have conformational properties similar to those of the analogous tetralin, those derivatives with a C-4 methyl are "locked" into the conformation which has that methyl in the pseudoaxial position.

Variable-temperature NMR measurements on a series of 9,10-dihydrophenanthrenes have proven the predominance of a single conformation for both the *trans*-9,10-dimethyl and 9,9,10-trimethyl derivatives. The enthalpy and entropy of activation for the conformational inversion of the *cis*-9,10-dimethyl compound has been determined to be 10.3 kcal mol<sup>-1</sup> and -3.3 cal mol<sup>-1</sup> K<sup>-1</sup>, respectively, a substantially reduced methyl group rotation rate in the transition state being responsible for the negative  $\Delta S^\ddagger$ .

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**Registry No.** 1, 1013-08-7; 2, 17058-00-3; 3, 97277-81-1; 4, 17058-01-4; 5, 78396-23-3; 6, 97277-82-2; 7, 97277-83-3; 8, 97277-84-4; 9, 97277-85-5; 10, 97277-86-6; 11, 97277-87-7; 12, 97277-88-8; 13, 97277-89-9; 14, 97277-90-2; 15, 97277-91-3; 16, 97277-92-4; 17, 97277-93-5; 18, 97277-94-6; 18-picrate, 97278-37-0; 19, 85269-07-4; 19-picrate, 97278-38-1; 20, 97277-95-7; 21, 776-35-2; 22, 52978-94-6; 23, 22140-64-3; 24, 22140-65-4; 25, 27094-32-2; 26, 97278-32-5; CH<sub>3</sub>CNa(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, 18424-77-6; CH<sub>3</sub>CHBrCOOC<sub>2</sub>H<sub>5</sub>, 535-11-5; (CH<sub>3</sub>)<sub>2</sub>C=(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, 6802-75-1; 2-bromo-1'-acetophenone, 13686-51-6; 2-methyl-2-(1-naphthylmethyl)malonic acid, 97277-96-8; 2-methyl-3-(1-naphthyl)propanoic acid, 75381-40-7; 2-methyl-4-(1-naphthyl)butanoic acid, 7498-80-8; 2-methyl-4-(1-naphthyl)butanoyl chloride, 87883-48-5; 1-keto-2-methyl-THP, 3580-60-7; *cis*-1,2-dimethyl-1-hydroxy-THP, 97277-97-9; *trans*-1,2-dimethyl-1-hydroxy-THP, 97277-99-1; 1,2-

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naphthyl)-2-propyl]malonate, 97278-29-0; [2-(1-naphthyl)-2-propyl]malonic acid, 97278-16-5; 3-methyl-3-(1-naphthyl)butanoic acid, 63253-34-9; 4-methyl-4-(1-naphthyl)butanoic acid, 63253-37-2; 4-methyl-4-(1-naphthyl)butanoyl chloride, 97278-17-6; 4,4-dimethyl-1-keto-THP, 97278-18-7; 4,4-dimethyl-1-hydroxy-THP, 97278-30-3; 4,4-dimethyl-3,4-dihydrophenanthrene, 97278-19-8; 2-bromo-2'-acetonephthone, 613-54-7; 2-methyl-2-(2-naphthoyl-methyl)malonic acid, 97278-20-1; 2-methyl-3-(2-naphthoyl)propanoic acid, 16206-42-1; 2-methyl-4-(2-naphthyl)butanoic acid, 97278-21-2; 2-methyl-4-(2-naphthyl)butanoyl chloride, 97278-22-3; 3-methyl-4-keto-THP, 40154-19-6; 3,4-dimethyl-4-hydroxy-THP, 97278-23-4; 3,4-dimethyl-1,2-dihydrophenanthrene, 97278-24-5; 2,2'-diacetyl biphenyl, 24017-95-6; (*R*\*,*R*\*)-2,2'-bis(1-hydroxyethyl)biphenyl, 18152-34-6; (*R*\*,*R*\*)-2,2'-bis(1-hydroxyethyl)biphenyl, 18152-33-5; 2,2'-bis(1-bromoethyl)biphenyl, 97278-25-6; 10,10-dimethyl-9-keto-DHP, 6948-59-0; 9,10,10-trimethyl-9-hydroxy-DHP, 97278-31-4; 2,3-dimethyl-THP picrate, 97278-34-7; 2,4-dimethyl-THP picrate, 97278-36-9.

## Electrogenerated Bases: The Role of Weak Electroinactive Proton Donors and the Effect of Electrocatalysis on the Redox Behavior of Azobenzene

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The stepwise electrochemical reduction of PhN=NPh in DMF-0.1 M (CH<sub>3</sub>)<sub>4</sub>NPF<sub>6</sub> can give, depending upon proton availability, three anionic reduction products. The basicities of these electrogenerated bases increase in the order PhN=NPh<sup>-</sup> < PhNHN<sup>-</sup>Ph < PhN<sup>-</sup>N<sup>-</sup>Ph. Water (pK<sub>a</sub><sup>Me<sub>2</sub>SO</sup> = 31.6), which is capable only of protonating PhN<sup>-</sup>N<sup>-</sup>Ph, causes the reversible PhN=NPh<sup>-</sup>/PhN<sup>-</sup>N<sup>-</sup>Ph redox couple to shift to more positive potential. From the magnitude of the potential shift and the reported value of pK<sub>a</sub><sup>DMF</sup>(H<sub>2</sub>O) = 34.7, pK<sub>a</sub><sup>DMF</sup>(PhNHN<sup>-</sup>Ph) is estimated to be 38.1. Ph<sub>2</sub>C=NNH<sub>2</sub> and PhNHNHPh both protonate PhN<sup>-</sup>N<sup>-</sup>Ph irreversibly. The PhNHN<sup>-</sup>Ph that is produced in this reaction is subsequently consumed in an electrocatalytic cycle which involves PhN=NPh as the oxidant, the less easily oxidized PhNHN<sup>-</sup>Ph as the reductant, and proton transfer from PhNHN<sup>-</sup>Ph to the conjugate base of the added proton donor as the rapid, irreversible follow-up reaction. The anodic peak for the irreversible oxidation of PhNHN<sup>-</sup>Ph is discernible only at scan rates in excess of about 1 V/s at -51 °C. Protonation of PhNHN<sup>-</sup>Ph by both diethyl malonate (pK<sub>a</sub><sup>Me<sub>2</sub>SO</sup> = 16.4) and fluorene (pK<sub>a</sub><sup>Me<sub>2</sub>SO</sup> = 22.6) and of PhN=NPh<sup>-</sup> by diethyl malonate is irreversible and affords PhNHNHPh and the conjugate base of the added proton donor as the principal electroactive products.

The electrochemical reduction of azobenzene (PhN=NPh) in aprotic media is reported to occur in two successive one-electron steps.<sup>1-6</sup> Although PhN=NPh<sup>-</sup> is quite stable in the absence of added proton donors and can be reoxidized quantitatively on the cyclic voltammetric time scale, the lifetime of the corresponding dianion is sufficiently short in most solvent-electrolyte systems so as to preclude a cyclic voltammetric anodic peak for its re-oxidation. Rapid reaction of the dianion involves its protonation by acidic impurities such as water and is generally believed to afford hydrazobenzene (PhNHNHPh) or its conjugate base as the principal product.<sup>4</sup>

Because of the basicity of PhN<sup>-</sup>N<sup>-</sup>Ph and the ease with which it can be prepared in known amount, electrogenerated PhN<sup>-</sup>N<sup>-</sup>Ph has been used widely as a strong base in electroorganic synthesis<sup>7-10</sup> and diagnostic electrochem-

ical studies.<sup>11,12</sup> Our current interest in PhN<sup>-</sup>N<sup>-</sup>Ph as an electrogenerated base was created by our need to prepare certain carbanions and nitranions in *N,N*-dimethylformamide (DMF) in order to measure their oxidation potentials and to determine their reactivities with selected substrates. Although evidence indicated that electrogenerated PhN<sup>-</sup>N<sup>-</sup>Ph reacted rapidly with the added proton donor, a cyclic voltammetric anodic wave for the oxidation of the conjugate base of the proton donor frequently could not be found on the reverse, positive-going sweep. The studies that are described here examine the chemical and electrochemical reactions that cause this behavior.

### Results and Discussion

The basicity of the electrogenerated bases in the azobenzene series increases in the order PhN=NPh<sup>-</sup> <

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