CONFORMATIONAL ANALYSIS OF THE 4a-METHYL
OCTAHYDROPHENANTHRENE SYSTEM. A SPECTROSCOPIC
AND THEORETICAL APPROACH.

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Abstract: Solution low temperature ^{1}H and ^{13}C NMR experiments
were run for the cis 4a-Methyl Octahydrophenanthrene hydrocarbon
1b, together with force-field and semiempirical MO calculations,
which allow to predict its conformational preferences, and to
calculate the kinetic parameters for this equilibrium. The synthesis
and spectroscopic analysis of related rigid models (1a and 7) and
of a series of configurationally defined 4a-Methyl Octahydro-
phenanthrols (9a to 13c) confirmed those findings and allowed
some empirical rules to be drawn for predicting the stereo-
chemistry, as well as the preferred conformation adopted by
substituted 4a-Methyl octahydrophenanthrenes.

Octahydrophenanthrenes and their 4a-Methyl derivatives have been of interest for many years,[1] as shown by several studies related to their conformational preferences[2,3] and A/B ring junction stereochemistry. Wenkert and coworkers[2d] have demonstrated that the 4a-Methyl ^{1}H NMR shift is extremely sensitive to conformational changes, and this approach has been used[2e,f] in the analysis of the conformational effects of substituents in this system. More recently, Davis et al, when dealing with the synthesis of some octahydrophenanthrenes,[4] reported the splitting of the 4a-Methyl signal in the low temperature ^{13}C NMR spectrum of the cis 4a-Methyl Octahydrophenanthrene hydrocarbon.

In addition, hydroaromatic compounds have been the subject of renewed interest in recent years, since such compounds appear to serve as hydrogenation agents in coal liquefaction and gasification processes. This fact has led to a systematic survey of their conformational properties by solution and solid ^{13}C NMR spectroscopy.[5] Nonetheless, a fully comprehensive investigation has been lacking for the 4a-Methyl Octahydrophenanthrene system.

In the present work, a series of low temperature ^{1}H and ^{13}C NMR measurements, together with MNDO and Molecular Mechanics calculations, and the comparative analysis of synthetic conformationally rigid models have been undertaken in an attempt to clarify the dynamic conformational behaviour of this system. In addition, the ^{13}C NMR spectra of a series of structurally defined 4a-Methyl octahydrophenanthrols are reported and analyzed, providing the necessary information to draw some empirical rules for predicting the ring junction stereochemistry and the conformational preferences of derivatives of this series.

<div align="center">RESULTS AND DISCUSSION</div>

The trans-fused (10aαH) 4a-Methyl Octahydrophenanthrenes adopt the rigid conformation I (Figure 1), while the cis-fused ones (10aβH) may exist either in conformation II or III (Figure 1), or in an equilibrium mixture of both.

Figure 1:
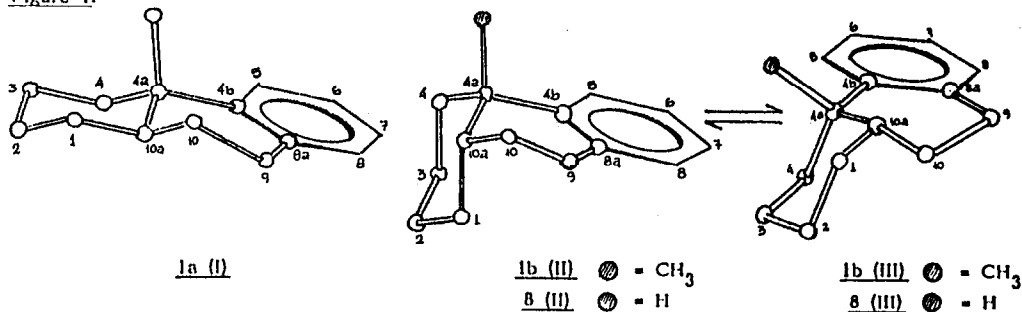
From extensive studies on natural products containing this skeleton, it has been proposed a correlation of the $\delta_{(4a-Me)}$ as a function of the dihedral angle subtended by the plane of the aromatic ring and that defined by carbons 4a, 4b and 4a-Me.[2e] In this approach, the anisotropic ring current effect was considered to be the major contributing factor to the observed shift. Taking into account this assumption, it was predicted that the methyl signal of conformer II for the cis hydrocarbon 1b would be very close to that observed in a rigid model, its trans isomer 1a (δ1.07). On the other hand, in conformation III it should experience a severe deshielding. Therefore, the chemical shift value found for 1b at room temperature (δ1.24) would correspond to an almost 1:1 equilibrium mixture of both conformers.

Variable temperature ^{1}H NMR experiments: The averaged 4a-Methyl signal at δ1.24 began to broaden as the temperature was lowered (250oK), and finally split into two peaks. The upfield peak appeared clearly at δ1.19, but unfortunately the downfield signal was obscured by the methylene absorptions. Nevertheless, it is interesting to note that the extreme upfield peak, which we assign to conformation II, is deshielded by 0.12 ppm with respect to the value found for the trans hydrocarbon 1a. This discrepancy cannot be ascribed to different ring current effects because the methyl group's position respect to

the aromatic ring is quite similar in both structures (trans I and cis II). Therefore, it could be attributed to two extra Methyl/Hydrogen 1,3 diaxial interactions which occur in the trans-fused hydrocarbon.

The calculated $\Delta\delta$ for the methyl group between conformations II and III induced by ring current effects using McConnell's dipole approximation[6] is 0.12 ppm. If we add this effect to the observed signal for conformation II, the low field absorption for conformation III should be around δ 1.31, and would represent an approximate 60:40 population ratio. Nevertheless, we feel that this simple approach oversimplifies the problem since the methyl's chemical shift cannot be predicted accurately considering only ring current effects, and it should also reflect the 1,3 Methyl/Hydrogen interactions with ring A and the peri interaction[3a] with the proton bonded to carbon 5.

Variable temperature ^{13}C NMR experiments: Since the ^{1}H NMR experiments left the problem unsolved, we turned to ^{13}C NMR spectroscopy at low temperatures. When the interconversion was frozen out in the NMR time scale, several splittings were observed. Among them, the 4a-Methyl signal (31.6 ppm at 308°K) separated into two peaks at 34.4 and 26.3 ppm (below 240°K). From these observed splittings, we could establish a 65:35 population ratio. By considering the well-known γ-gauche interactions acting on II and III, the more deshielded signal (34.4 ppm) might be assigned to the conformer in which the methyl group adopts an equatorial position, i.e., conformation II. Therefore, we could assume the latter to be the preferred conformation.
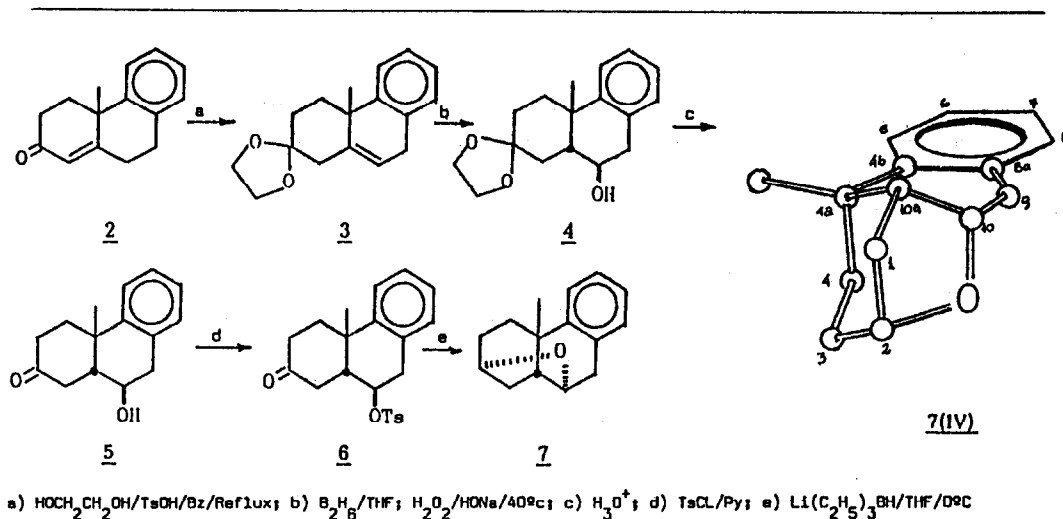
An unexpectedly large splitting was also observed at extreme low field in the spectrum. When the temperature was lowered under 220°K, a signal which averaged at 144.2 ppm (308°K) and corresponded to the 4b-carbon, was split into two peaks at 142.4 (major) and 147.5 (minor) ppm. Relying on our previous assumption, the shielded signal should be assigned to structure II. The $\Delta\delta$ observed between both conformations (5.1 ppm) might be ascribed to the γ-gauche interactions affecting carbon 4b. However, it is rather surprising to observe such a large non bonding effect over a non-bearing proton sp^2 carbon. Therefore, we tried to confirm this fact analyzing the electron density upon carbon 4b as calculated by MNDO. However, the computed results predicted only a slight difference on electron density between conformations II and III.

In order to confirm the assignment of the 4b carbon signals, we decided to synthesize a cis fused 4a-Methyl octahydrophenanthrene derivative frozen in one of the extreme conformations (either II or III). We must assure that any additional substituent in our model conformer must not affect carbon 4b's shift. This condition led us to envisage the synthesis of the tetracyclic ether 7, which adopts a III-like conformation (see Scheme 1).

The key step in this synthesis was the highly chemi and stereoselective action of Super Hydride, which reduced exclusively the carbonyl function in 6 yielding only the α-alcoxy group which promotes the intramolecular displacement of the tosylate at carbon 10. The ^{1}H NMR of 7 exhibits a singlet at δ 1.50, characteristic of a 4a-Methyl almost coplanar to the aromatic ring. The observed ^{13}C NMR signal at 146.9

ppm is very close to the extreme shift observed in the low temperature spectra (147.5 ppm, minor component) of hydrocarbon **1b**, which was assigned to conformer III.

<u>Scheme 1</u>

a) $HOCH_2CH_2OH/TsOH/Bz/Reflux$; b) B_2H_6/THF; $H_2O_2/HONa/40^{\circ}c$; c) H_3O^+; d) $TsCL/Py$; e) $Li(C_2H_5)_3BH/THF/0^{\circ}C$

With the assignment of these split signals on safe grounds, we decided to perform a kinetic and thermodynamic study of the conformational equilibrium of the 4a-Methyl octahydrophenanthrene system. Hence, spectra of **1b** were acquired over the range 35 to -65°C with this purpose. The temperature dependence of carbon 4b's resonances were measured relative to Me_4Si and corrected by removing the temperature variation already known[5a] for the Me_4Si shifts (cf. Experimental). It may be noted that the 4b carbon chemical shift is almost temperature independent, indicating that the population ratio II:III does not change drastically when the equilibrium mixture is cooled. Therefore, the energy gap between both conformers might be small.

After measuring the averaged shift of carbon 4b at eleven different temperatures ranging from 307°K to 233°K, we performed a non-linear least-squares regresion analysis on equation **1** :[5a]

$$(1) \qquad \delta = \frac{\delta_{II} + \delta_{III}\, e^{-\Delta H/RT}\, e^{\Delta S/R}}{1 + e^{-\Delta H/RT}\, e^{\Delta S/R}}$$

where δ_{II} and δ_{III} are the extreme observed shifts for conformations II and III. This correlation yielded the following thermodynamic data for the equilibrium II $\rightleftharpoons$ III: ΔH= 0.736±0.06 Kcal/mol; ΔS=1.21±0.2 cal/mol.K, and $\Delta G_{(300^\circ K)}$=0.373 Kcal/mol (calculated from ΔH and ΔS).

Taking advantage on the fact that the carbon 4b's signal appears clearly isolated in the spectra, a total lineshape analysis was performed. At temperatures remote from coalescence, the rate constant was obtained from the exchange linewidth contribution after substraction of non-exchanging contributing factors. In the neighbourhood of coalescence, the observed lineshape was fitted with the full lineshape expression for two-site exchange[8] incorporating a non-exchange broadening term. Then, ten calculated rate constants were fitted into an Arrhenius equation, which yielded an E_{act} = 15.5 Kcal/mol. $\Delta G^{\neq}$ = 12.35 Kcal/mol at coalescence temperature (226°K).

Molecular Mechanics calculations: The experimental data pertaining to the conformational equilibrium of 1b offer a good picture of its behaviour. However, in order to give further support to it, a theoretical analysis was performed for this hydrocarbon and some related compounds (7 and 8) in their different posible conformations. The method of choice was MMP2, which incoporates the latest Allinger MM2 force field together with a π-system treatment.[9] The most significant force field results are summarized in Table 1.

Table 1: Some significative force field results.

Compound (Conformation)	1b		7	8	
	(II)[a]	(III)[a]	(IV)[a]	(II)[b]	(III)[b]
ΔH_f (Kcal/mol)	−12.13	−12.23	−30.98	−5.97	−7.61
Steric Energy	12.19	12.09	24.97	9.64	7.08
ψ (8a−4b−4a−R)	97	129	160	94	135
ω (4b−8a−9−10)	9	−21.5	18.6	10.5	−16.5
γ (10−10a−4a−R)	65	161	176	62	166
ζ (9−10−10a−4a)	61	−64	−45	63	−63
$E^{VDW}_{(4a-Me)}$	0.73	1.06	1.29	−	−

[a]R= Me; [b]R= H

As expected, the calculated $\Delta H_{III/II}$ is rather small:-0.1 Kcal/mol, against an experimental value of 0.763 Kcal/mol (It has to be kept on mind that the accuracy of MMP2 for heats of formation is about 0.84 Kcal/mol[9]). It is interesting to point out that this calculated value is significantly smaller than that obtained for its 4a-nor methyl homologue 8 ($\Delta H_{III/II}$ =-1.64 Kcal/mol), for which the existence of only one conformer in a III-like geometry has been predicted.[3b]
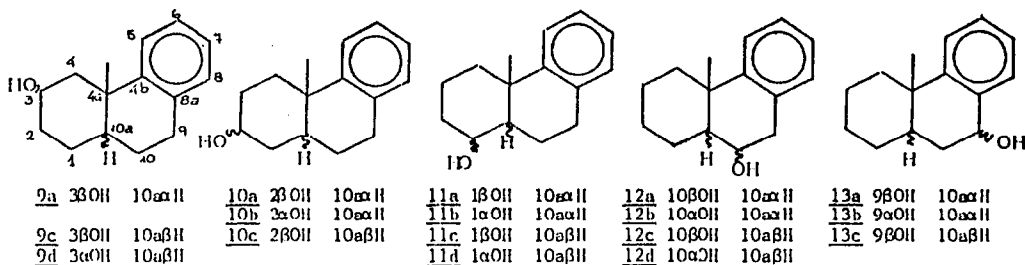
The relatively large, positive entropy (1.2 cal/mol.K) found for conformation III may result from differences in mobility in the internal rotational characteristics of the 4a-Methyl group, since other entropy-producing factors appear to be similar in both

conformers. This fact was confirmed by MMP2 results, which showed a total van der Waals energy for the methyl group of 0.73 Kcal/mol in II and 1.06 Kcal/mol in III. Such a difference implies a more restricted rotation for the 4a-Methyl group in conformation III, which might be ascribed to its axial position with respect to ring A and also to the interaction with the peri hydrogen of the aromatic ring.

The dihedral angles listed in Table 1 describe the changes on ring B's geometry through the different compounds analyzed. Since ring B adopts a half-chair conformation, its flexibility allows some small distortions in order to minimize steric interactions. Thus, a comparison of the dihedral angle ψ between $\underline{1b}_{III}$ and $\underline{8}_{III}$ shows that the replacement of the 4a-hydrogen in $\underline{8}$ by the bulkier methyl group pulls the 4a-substituent away from the plane of the aromatic ring, releasing the steric compression due to the peri interaction.

On the other hand, a similar comparison between $\underline{1b}_{III}$ and the rigid tetracyclic ether $\underline{7}$ shows a $\Delta\psi$ of 31°, i.e., in $\underline{7}$, the methyl group is forced to lie almost coplanar to the aromatic ring, as can be seen by the highly deshielded shift of the ^{1}H methyl resonance at δ 1.50. The additional tetrahydrofuran ring also forces a distortion on ring A's geometry, affecting the 4a-Methyl chemical shift (29.3 ppm).

[13]C chemical shift dependence upon structural changes: The availability of cis and trans C-1, C-2, C-3, C-9 and C-10 4a-Methyl Octahydrophenanthrols as a result of synthetic studies in our laboratories[2e,f] gave us the opportunity to study their ^{13}C NMR spectra. We examined seventeen synthetic Octahydrophenanthrols and their parent hydrocarbons $\underline{1a}$ and $\underline{1b}$, which ^{13}C chemical shifts are listed in Tables 1 and 2. A perusal of these tables renders some interesting conclusions upon ^{13}C shifts and conformational preferences.

$\underline{9a}$ 3βOH	10αII	$\underline{10a}$ 2βOH	10αII	$\underline{11a}$ 1βOH	10αII	$\underline{12a}$ 10βOH	10αII	$\underline{13a}$ 9βOH	10αII
		$\underline{10b}$ 2αOH	10αII	$\underline{11b}$ 1αOH	10ααII	$\underline{12b}$ 10αOH	10αII	$\underline{13b}$ 9αOH	10αII
$\underline{9c}$ 3βOH	10αβII	$\underline{10c}$ 2βOH	10αβII	$\underline{11c}$ 1βOH	10αβII	$\underline{12c}$ 10βOH	10αβII	$\underline{13c}$ 9βOH	10αβII
$\underline{9d}$ 3αOH	10αβII			$\underline{11d}$ 1αOH	10αβII	$\underline{12d}$ 10αOH	10αβII		

In the trans-fused series, the 4a-Methyl signal is observed at 20.2 to 22.8 ppm, for all but three alcohols. Considering the rigid nature of the trans ring juncture, the expected influence of conformational changes upon its chemical shift would be minimal. Therefore, any major variation must be accounted for by direct interactions with the substituents. In fact, extreme downfield shifts are observed when there is an axial substituent capable of a 1,3 interaction with the methyl group, i.e. compounds $\underline{9a}$, $\underline{11a}$ and $\underline{12a}$ (Table 2).

Table 2: ^{13}C NMR Chemical shifts of the 10aαH (trans) series.

Compound (Conformation)

Carbon shifts	1a(I)	9a(I)	10a(I)	10b(I)	11a(I)	11b(I)	12a(I)	12b(I)	13a(I)	13b(I)
1	29.0[a]	23.9	37.9	36.0	71.7	70.0	25.6[a]	22.7	28.5	28.5
2	26.4	33.4	70.6	66.1	33.4	35.8	26.4[a]	25.7	26.2	26.2
3	22.3	67.8	31.4	29.3	17.1	19.4	22.1	21.8	22.1	22.2
4	37.7	43.6	35.8	31.4	37.6	37.0	38.5	37.9	37.7	37.3
4a	36.8	36.5	36.0	36.4	36.6	38.1	36.2	38.2	37.3	37.0
4b	148.0	148.3	147.0	147.5	148.6	147.1	147.3	146.9	147.9	148.2
5	124.3[b]	124.2	124.5	124.4	123.7	124.3	124.2[b]	124.2	124.3	124.3
6	125.1[b]	125.2[a]	124.4[a]	125.3[a]	125.0[a]	125.2[a]	125.3[b]	125.7[a]	125.8	125.9
7	125.3[b]	125.4[a]	125.4[a]	125.4[a]	125.4[a]	125.4[a]	125.7[b]	125.9[a]	127.1[a]	127.0
8	129.1	129.3	120.1	129.2	128.9	129.0	129.1	129.0	127.4[a]	130.3
8a	135.3	134.8	135.2	135.4	134.6	135.0	132.2	133.3	138.3	136.3
9	29.3	28.9	29.1	29.2	29.2	29.0	39.0	39.6	69.6	67.5
10	25.7	25.4	25.3	25.2	22.7	20.5	70.3	67.7	36.4	34.7
10a	42.2	42.3	40.1	34.5	49.6	49.5	45.9	49.1	41.2	36.4
4a-Me	21.6	24.6	21.6	20.7	25.1	22.8	23.2	22.7	20.2	20.9

[a,b]Assignments may be interchanged in each vertical row

On the other hand, substituted cis 4a-Methyl Octahydrophenanthrenes are known to adopt only that conformation which minimizes the steric interactions.[3e,f] Low temperature ^{1}H experiments on these alcohols showed no splitting of the 4a-Methyl resonance but a slight broadening, that could be due to the existence of a largely predominant conformer in the equilibrium mixture. Careful spectral inspection and conformational analysis have led us[3e,f] to the conclusion that epimeric pairs of this series are likely to exist in different ring conformations, favouring the placement of the hydroxyl group in an equatorial position. MMP2 calculations predict an energy difference between the axial and the equatorial conformers higher than 1 Kcal/mol in this series of alcohols. Thus, alcohols 9b, 10c, 11c, 12d and 13c must exist mainly in conformation II, whereas 9c, 11d and 12c adopt conformation III.

Table 3: ^{13}C NMR Chemical shifts of the 10aβH (cis) series.

Compound (Conformation)

Carbon shifts	1b	9c(II)	9d(III)	10c(II)	11c(II)	11d(III)	12c(II)	12d(III)	13c(III)
1	28.0	26.1[a]	30.1[a]	35.9	68.4	69.0	21.7	20.7	28.5
2	25.0[a]	35.7	30.2[a]	70.3	35.8	29.7	21.0	25.8	22.5[a]
3	22.8	67.4	67.3	31.8	20.6	21.1	22.7	22.6	21.8[a]
4	38.0	47.1	45.5	36.8	37.8	35.9	38.4	38.7	37.1
4a	37.3	38.5	38.1	36.7	38.6	38.7	38.7	40.1	36.9
4b	144.2	142.2	145.8	141.9	142.5	146.6	146.1	141.8	146.1
5	124.9[b]	126.0[b]	126.1[b]	125.8	124.9[a]	126.2	126.1	126.1[b]	126.4[b]
6	125.7[b]	125.3[b]	124.8[b]	125.2	125.2[a]	125.7	125.4	125.4[a]	125.7[b]
7	125.9[b]	125.1[b]	125.5[b]	125.2	125.8[a]	125.1	126.1	125.3[a]	125.3[b]
8	129.1	129.4	128.5	129.4	129.4	128.8	128.8	129.4	127.0
8a	135.7	131.1	134.7	135.4	136.1	135.7	132.8	134.7	138.4
9	27.0[a]	25.0[a]	26.6	25.1	25.0	30.6	38.9	35.3	69.0
10	24.3[a]	23.9	24.9	23.5	18.2	17.3	65.7	65.9	35.3
10a	41.1	40.5	39.0	39.7	48.9	47.1	47.3	48.4	38.1
4a-Me	31.6	34.1	25.8	33.0	34.1	25.6	26.9	34.1	26.8

[a,b]Assignments may be interchanged in each vertical row.

As we have already shown, such situation must be evidenced through the ^{13}C chemical

shift variation (see Table 3). Thus, compounds in conformation III present methyl shifts of 33.0 to 34.1 ppm, while in those adopting conformation III the signal falls between 25.6 and 29.3 ppm.

Similarly, a strong conformational dependence has been observed for the 4b carbon's chemical shift and, moreover, being a quaternary carbon, we expected that its chemical shift should remain mostly unaffected by substitution in rings A and B. The following 4b chemical shift ranges characterize different conformations: 146.9-148.6 ppm for the trans isomer I, 141.8-142.5 ppm for the cis isomer II, and 145.4-146.6 ppm for the cis isomer III. Table 4 summarizes its extreme chemical shifts values for each conformation.

Table 4. ^{13}C Chemical shift ranges of 4a-Methyl and
C-4b in different ring junctions.

A/B Ring Junction	4a-Me	C-4b
trans(I)	20.2-22.8	146.9-148.6
cis (II)	33.0-34.1	141.8-142.5
cis (III)	25.6-29.3	145.4-146.6

These empirical observations of the behaviour of the 4a-Methyl and 4b-carbon chemical shifts may be used safely for the assignment of the A/B ring junction stereochemistry and conformational preferences of any compound in the cis series. When dealing with compounds of the trans series, one must be aware that if any syn-diaxial Methyl/OH interaction is present, the 4a-Methyl shift might behave abnormally.

CONCLUSION

This study analyzed the dynamic conformational behaviour of the cis 4a-Methyl Octahydrophenanthrene hydrocarbon 1b. By means of low temperature NMR, the kinetic and thermodynamic parameters of the equilibrium between conformation II and III were calculated. The experimental results indicate that there is a slight preference towards conformation II. The small energy difference between both conformers (less than one Kcal/mol) makes it difficult to explain the preference. A comparison with the 4a-nor Methyl system 8 and the tetralins[15] seems to indicate that the equalization of the peri interactions in the 4a-Methyl system reduces the energy difference between the conformers. Even though the overall conformations for the compounds analyzed are very similar, the degree of puckering of ring B does vary considerably between the members of this series. This conformational flexibility is undoubtedly an unique feature of the octahydrophenanthrene system.

Low temperature measurements also allowed the identification of conformationally dependent ^{13}C shifts; i.e., the 4a-Methyl and 4b-quaternary carbon. These signals can be used as conformational markers, as it has been shown for a series of 4a-Methyl Octahydrophenanthrols.

EXPERIMENTAL

<u>General Methods</u>: Melting points were determined on an Ernst Leitz hot-stage microscope and are uncorrected. IR spectra were measured with a Beckman Acculab 8 spectrophotometer as specified in each case. The ^{13}C and ^{1}H NMR spectra were measured on a Bruker WP 80 SY-FT spectrometer at 80.13 and 20.15 MHz, respectively. 2D spectra were measured in a Bruker AM-400 using standard Bruker software. The chemical shifts are in part per million down from Me_4Si, and the J are in Hertz. The samples were examined as 0.1-0.3 M solutions in $CDCl_3$ in standard 5 mm tubes. All ^{13}C NMR data are included in Tables 2 and 3. ^{13}C signal assignments were normally based upon signal multiplicities, APT spectra,[10] a combination of hetero- and homonuclear correlated 2D spectra,[11] known chemical shifts rules,[12] comparison with data from the literature,[8] and substituent parameters.[13] All solvents were purified and dried by standard techniques. All reactions were performed under dry nitrogen. Column cromathography was performed on silica gel 60H, slurry-packed, run under a low pressure of nitrogen, with increasing amounts of ethyl acetate in hexane as solvent. All reactions were monitored by TLC on Merck aluminium plates pre-coated with 0.2mm of silica gel."Ether" refers to diethyl ether. MMP2 and MNDO calculations were performed on an IBM 3031.

<u>Low temperature NMR measurements</u>: All variable-temperature NMR spectra were measured in the Bruker WP 80 SY-FT spectrometer using the variable temperature unit B-VT 1000 with simultaneous temperature measurement using an internal chemical thermometer ($TMS:CH_3I$, 1:3, v:v) as described in reference 14. All data were obtained from the broad band decoupled spectra using data tables of 16K words with a 5-KHz spectral window. Deuterochloroform was used as solvent, with tetramethylsilane as internal reference. All chemical shifts were referenced to Me_4Si at 0°C by adjusting[5a] for the temperature dependence of Me_4Si according to the equation $\delta_{corr} = \delta_{obs} - 0.009751T - 0.00002159T^2$, T in degrees Celsius.

<u>4a-Methyl-1,2,3,4,9,10,10aα and 10aβ-Octahydrophenanthrenes 1a and 1b</u>: were obtained according to the procedure described in reference 16, as colorless oils. All the spectral data were in agreement with those reported in the literature.

<u>2-Ethylenedioxy-4a-Methyl-1,2,3,4,4a,9-hexahydrophenanthrene (3)</u>: 3.5 gs (16.5 mmol) of 2 (Ketone 2 was prepared according reference 16, mp 89.0-90°C; Lit 89.5-90°C) were dissolved in 150 ml of benzene, and 8 ml of ethyleneglycol and 0.35 gs (1.8 mmol) of p-toluenesulphonic acid were added. The suspension was refluxed, while the formed water was azeotropically distilled and collected in a Dean-Stark trap. The reaction was cooled, poured over a cold saturated $NaHCO_3$ solution, and extracted with ether (3x70 ml). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue (4.04 gs, 95%) was recrystallized from MeOH, mp 71-72°C; ^1H NMR 1.42 (s, 3H, CH_3), 1.7-3.0 (m, 6H, aliphatic), 3.41 (t, 2H, bencylic), 3.95 (s, 4H, $-OCH_2CH_2O-$), 5.53 (m,1H, vinylic), 6.9-7.3 (m, 4H, aromatic). MS, m/z: 256(M^+ 0.87), 197 (1.4), 167 (1.6), 156 (2.14), 155 (5.5), 141 (9), 128 (3.8), 100 (13), 99 (100), 77 (2.9), 55 (14).

<u>2-Ethylenedioxy-4a-Methyl-1,2,3,4,4a,9,10,10aβoctahydro-10βphenanthrol (4)</u>: Compound 3 (0.256 gs, 1mmol) was dissolved in THF (10 ml) under an inert atmosphere and treated with borane (4 mmol) at 25°C for 24 h . The reaction was cooled (0°C), the excess of borane was destroyed by careful addition of water, then 3N NaOH (2 ml) and 30% H_2O_2 (2 ml) were simultaneously added dropwise, with a vigorous stirring. After 1 h at 35-40°C, brine (40 ml) was added, the solution was extracted with ether (3x15 ml) and the combined organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. After column cromathography, compound 4 was obtained in pure form 0.160 g (58%), which was recrystallized from MeOH, mp 109-110 C; IR (KBr) 3300, 1100, 1080, 1050, 1030, 820, 750, 730 cm^{-1}. ^1H NMR 1.50 (s, 3H, CH_3), 1.60-2.30 (m, 7H, aliphatic), 2.78 (dd, 1H, J=15.7,10.1, C9-H), 3.04 (dd, 1H, J=15.7, 5.27, C9- H), 4.0 (s, 4H, $-OCH_2CH_2O-$), 4.16 (m, 1H, $W_{1/2}$=21.2, C10-H), 6.9-7.16 (m, 4H, aromatic). MS, m/z: 274 (M^+, 3.6), 256 (2), 158 (1.6), 155 (2.8), 141 (4), 131 (2), 129 (4), 128 (8), 115 (5), 100 (7.2), 99 (100), 91 (5), 86 (10), 77 (3), 57 (2.6), 55 (10).

<u>2-oxo-4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-10β-phenanthrol (5)</u>: A solution of 4 (0.274 g, 1 mmol) in THF (25 ml), and 1N HCl (2.5 ml) was stirred at 25°C for 5h. The reaction was poured over a cold saturated solution of $NaHCO_3$ (50 ml) and then extracted with ether (3x30 ml). The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure, yielding 0.210 g (91%) of a yellowish glass. IR(neat) 3500, 3300, 3980-2800, 1700, 1500, 1450, 1050, 1030, 760 cm^{-1}. ^1H NMR 1.68 (s, 3H, CH_3), 1.98-2.3 (m, 7H, aliphatic), 2.61 (dd, 1H, J=16.0, 9.6, C9- H), 3.16(dd, 1H, J=16.0, 5.8, C9- H), 3.88 (m, 1H, $W_{1/2}$=24 Hz, C10-H), 6.96-7.20 (m, 4H, aromatic). MS, m/z:262(M^+, 3), 230(22), 212(10), 197(19), 169(21), 157(28), 156(24), 155(100), 154(12), 153(10), 145(56), 143(34), 142(37), 141(90), 129(53), 128(80), 127(26), 115(67), 114(14), 105(11), 95(50), 83(19), 81(10), 77(29).

<u>2-oxo-4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-10β-phenanthrol Tosylate(6)</u> : To keto-alcohol 5 (0.34 g, 1.48 mmol) in anhydrous pyridine (5 ml) cooled to 0°C was added p-toluenesulfonyl chloride (0.56 g, 2.96 mmol). After

solution was complete, the mixture was stored in the refrigerator (-5°C) overnight. The mixture was allowed to warm to 25°C while being stirred, then poured onto ice an stirred for 30 min. The resulting mixture was then extracted with ether (3x15ml). The ethereal extracts were combined and washed twice with cold aqueous HCl (1:1), and then with water (2x10 ml) affording 0.53 g (93%) of **6** as a clear oil. ^{1}H NMR : 1.2-1.4 (m,2H, aliphatic), 1.52 (s, 3H CH$_3$), 1.6-2.3 (m, 4H, aliphatic), 2.46 (s, 3H, tosylate CH$_3$), 3.17 (dd, 2H, J=15, 6 Hz, C9-H), 4.70 (m, W$_{1/2}$=24 Hz, 1H, C10-H), 6.9-7.4 (m, 6H, aromatic), 7.6-7.9 (m,2H, tosylate ortho H).

2α,10α-Oxy-4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (7): Compound **6** (0.41 g, 1.1 mmol) was dissolved in anhydrous THF (10 ml) in a 50-ml round flask equipped with a reflux condenser, under an inert atmosphere. The mixture was cooled to 0°C, and to this stirred solution, lithium triethylborohydride, 1.3 ml (1.3 mmol) of a 1M solution in THF was added and the ice bath removed. The mixture was refluxed for 3h. Excess hydride was decomposed with water, and the organoborane was oxidized with 2ml of 3N NaOH and 2 ml of 30% H$_2$O$_2$. Then the THF layer was separated, and the aqueous layer was extracted with ether (3x20 ml). The combined organic extracts were washed with brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure, yielding compound **7** as the only product (0.17 g, 72%), recristallized from ethyl acetate, mp 66-67°C. IR(KBr): 2920, 1720, 1470, 1440, 1250, 1160, 1040, 1010, 930, 880, 810, 760, 740 cm^{-1}. ^{1}H NMR : 1.5(s, 3H, CH$_3$), 1.61-1.8 (m, 7H, aliphatic), 1.93-2.1 (dd, 2H, C9-H), 3.3 (m, 1H, W$_{1/2}$= 7Hz, C10-H), 4.42 (m, 1H, W$_{1/2}$=15 Hz, C2-H), 6.9-7.2 (m, 4H aromatic). MS:214 (M$^+$,83.8), 199 (53.1), 181 (74.4), 167 (22.1), 158 (68.1), 143 (100), 128 (73.7), 115 (56.3), 105 (7.4), 91 (23.9), 77 (13.3), 65 (6.2). Anal. Calcd. for C$_{15}$H$_{18}$O: C, 84.11; H, 8.41 Found: C, 84.00 H,8.48.

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