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Stereochemistry of 1,3-Cyclohexadienes. Conformational Preferences in 9-Substituted 9,10-Dihydrophenanthrenes

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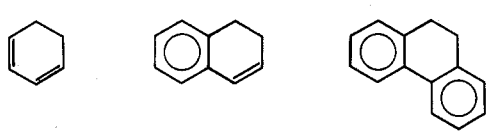
Received May 4, 1976

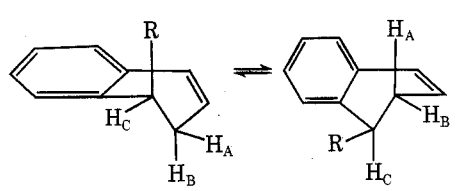
A series of 9-R-9,10-dihydrophenanthrenes [R = CH_3, CN, $C(CH_3)_3$, $COCH_3$, CO_2CH_3, $CO_2CH_2CH_3$, OH, $Si(CH_3)_3$] as well as two related 5,6-dihydrochrysenes, are studied by NMR analysis of the three spin H_9, H_{10}, $H_{10'}$ system. The coupling constants thus obtained are then used to determine the conformational preferences of these mobile ring systems with regard to the location of substituents in pseudoaxial or pseudoequatorial positions. All substitutes except cyano were found to preferentially adopt the pseudoaxial conformation.

The majority of studies concerned with the stereochemistry of 1,3-cyclohexadiene ring systems (**1–3**) have dealt with



1 **2** **3**

derivatives of 1,2-dihydronaphthalene (**2**).[1-5] In the case of 1-substituted 1,2-dihydronaphthalenes, NMR investigations into the equilibrium between **4a′** and **4e′** were carried out by computer analysis of the ABC spectra resulting from the benzylic and allylic protons.[2-4] In both **4a′** and **4e′** the protons



4a′ **4e′**

H_B and H_C interact in a pseudoaxial/pseudoequatorial relationship and the spin interactions are equivalent, leading to a J_{ae} coupling constant which is independent of the position of equilibrium, and values of 6.8 Hz have been determined.[2] On the other hand, protons H_A and H_C interact as pseudoequatorial/pseudoequatorial in **4a′** and pseudoaxial/pseudoaxial in **4e′**, and the time average value of this coupling constant is directly related to the conformational populations. Thus, using values of J_{aa} = 16 and J_{ee} = 2 Hz, and the relationship

$$J_{AC} = xJ_{ee} + (1 - x)J_{aa} \quad (1)$$

the fraction (x) of the conformations with the group in the pseudoaxial position was calculated for a number of R groups.[4]

Although the 9,10-dihydrophenanthrene system (**3**) would appear to be closely related, discrepancies have been noted in comparing coupling constant data with the dihydronaphthalenes. Thus, one report[1] based on ^{13}C satellite resonances provides values of 8.3 and 5.8 Hz for **3**, presumably corresponding to the average $\frac{1}{2}(J_{aa} + J_{ee})$ value (9.4 in **2**) and to J_{ae} (7.0 in **2**), respectively. Furthermore, 9,10-dihydro-4,5-dimethylphenanthrene shows $\frac{1}{2}(J_{aa} + J_{ee})$ = 10.59 and J_{ae} = 3.97 Hz,[6] whereas the values for 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene are $\frac{1}{2}(J_{aa} + J_{ee})$ = 7.92 and J_{ae} = 3.5 Hz.[7] Katritzky et al.[2] have suggested that the contrast between 1,2-dihydronaphthalene and 9,10-dihydrophenanthrene may be due to differences in dihedral angles, although de la Mare et al.[5] have presumed approximately equal dihedral angles for both systems in a more recent NMR study. Furthermore, these latter workers have suggested that their coupling constant data for *cis*- and *trans*-9-acetoxy-10-chloro-9,10-dihydrophenanthrene compare favorably with the corresponding values for 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene when electronegativities are taken into account. However, a recent NMR investigation[6] on 9,10-dihydro-4,5-dimethylphenanthrene itself has suggested a much larger dihedral angle between the benzene rings in this system as a result of 4- and 5-methyl steric interaction.

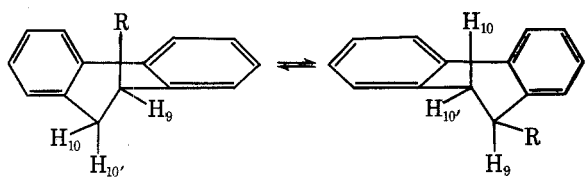
We now report NMR special analysis of a series of 9-substituted 9,10-dihydrophenanthrenes (**5a′** ⇌ **5e′**). These studies were conducted in order to obtain accurate coupling constant data for comparison with the 1,2-dihydronaphthalene ring system and to determine the conformational preferences of the 9 substituents.

Since H_9 and H_{10} are dipseudoequatorial in **5a′** and dipseudoaxial in **5e′**, $J_{9,10}$ is expected to reflect the relative contributions from each conformation. On the other hand, H_9

Table I. NMR Data for 9-R-9,10-Dihydrophenanthrenes [a]

Registry no.	R (solvent) [b]	$J_{9,10}$	$J_{9,10'}$	$J_{10,10'}$	δ_9	δ_{10}	$\delta_{10'}$	Rms error	δ_{arom}, ppm	% pseudo-axial [c]
56666-55-8	CN (CCl_4)	9.89	6.37	−14.57	223.66	175.25	178.90	0.026	7.3, 7.8	44
52978-94-6	CH_3 (CS_2)	5.24	6.70	−14.73	213.71	213.01	247.47		7.1, 7.6	77
60084-36-8	$C(CH_3)_3$ (CD_3CN)	1.50	7.11	−16.57	160.93	190.93	182.10	0.100	7.2	100
60084-37-9	$COCH_3$ (CCl_4)	3.81	6.02	−15.38	223.63	199.19	188.06	0.095	7.25, 7.7	86
32892-19-6	CO_2CH_3 (CCl_4)	5.76	6.64	−15.40	223.00	177.95	192.28	0.023	7.05, 7.5	73
60084-38-0	$CO_2CH_2CH_3$ (CCl_4)	5.38	6.86	−14.57	216.25	174.64	186.08	0.022	7.05, 7.5	75
60084-39-1	OH [e] ($CDCl_3$)	2.9	5.9	−15.2	287.0	183.0	183.0		7.3, 7.8	94
56465-93-1	$Si(CH_3)_3$ ($CDCl_3$)	1.95	6.79	−15.5	144.0	172.3	196.8		7.3, 7.8	100

[a] 60 MHz unless otherwise indicated. [b] In many cases, δ_{10} and $\delta_{10'}$ were nearly identical, and several solvents were tried to maximize the difference. [c] See ref 4b. [d] 100 MHz, methyl decoupled (this analysis was performed by Professor J. B. Stothers). [e] Chemical shift data provided for $CDCl_3$ solution, J values determined after addition of $Eu(fod)_3$.



5a' **5e'**

R = CH_3, CN, $C(CH_3)_3$, $COCH_3$, CO_2CH_3, $CO_2CH_2CH_3$, OH, $Si(CH_3)_3$

and $H_{10'}$ are related as pseudoequatorial/pseudoaxial in both **5a'** and **5e'**, so that $J_{9,10'}$ should be constant and independent of the position of the equilibrium. The values of $J_{9,10}$ and $J_{9,10'}$ were determined by computer analysis[8] of the three spin (ABC or ABX) system, and in each case the value closest to 6.8 Hz ($J_{pa,pe}$ in 1,2-dihydronaphthalene) was assigned as $J_{9,10'}$. As an example, this region of the NMR spectrum for 9-*tert*-butyl is shown in Figure 1. It is interesting to note the rather striking difference in complexity when CD_3CN was used as solvent (trace b), and this is due (primarily) to an upfield shift of $H_{10'}$ relative to CCl_4 as solvent (trace a). Fortunately, in all cases one of the J values was within 0.9 Hz of 6.8 (and usually closer), and the other value ranged from 1.50 for *tert*-butyl to 9.89 Hz for cyano. The data are summarized in Table I, and it should be noted that in contrast to the cyclohexane ring system, the axial and equatorial protons cannot be distinguished on the basis of chemical shift alone, since there is considerable variation in whether H_{10} or $H_{10'}$ appears at higher field.

In calculating the percent of the conformations with the group pseudoaxial using eq 1, we employed the values of $J_{pa,pa}$ = 16 and $J_{pe,pe}$ = 2 Hz used for the 1,2-dihydronaphthalenes.[2-4] This seemed valid, since the values for $J_{pa,pe}$ correspond so closely between the two systems, and **5** with R = $Si(CH_3)_3$ shows $J_{pe,pe}$ = 1.95. Although we classify both the trimethylsilyl and *tert*-butyl derivatives as 100% axial, we prefer to use the trimethylsilyl $J_{pe,pe}$ value since the *tert*-butyl group may be causing some distortion (e.g., the larger $J_{10,10'}$ value). It is interesting to note that the value of 73% pseudoaxial for R = CO_2CH_3 compares very favorably with a value of 74% determined previously for 1,4-dicarbomethoxy-1,4-dihydronaphthalene.[4]

The observed pseudoaxial preference of benzylic substituents in **5** can be attributed to destabilization of the pseudoequatorial position by the adjacent aryl proton (i.e., peri interaction) and the absence of additional steric effects (cf. 1,3 interactions in cyclohexanes). Similar factors appear to govern the conformational properties of the related 1,2- and 1,4-dihydronaphthalene and the 9,10-dihydroanthracene[9,10] ring systems. As compared to the other substituents, the cyano group (**5**, R = CN) provides significantly different results, and seems to show a slight pseudoequatorial preference. However, when one takes into account the very small conformational free-energy difference (A value = 0.2)[11] for cyano, it is apparent that the aforementioned peri interaction will be greatly reduced. In fact, 2-substituted 1,2-dihydronaphthalenes, in which peri interactions are absent, show pseudoequatorial group preference,[4] and it may be inferred that this will be the general conformational preference in the absence of additional, important steric effects. In this regard, it should be noted that vicinal coupling constants are dependent on group electronegativities as well as bond angle.[12,13] On the other hand, such corrections are not expected to cause significant changes in these results, because the effects of electronegativities on values of $J_{pa,pa}$ and $J_{pe,pe}$ used in the calculation must be small since the variation in $J_{pa,pe}$ is less than 1.0 Hz.[4b]

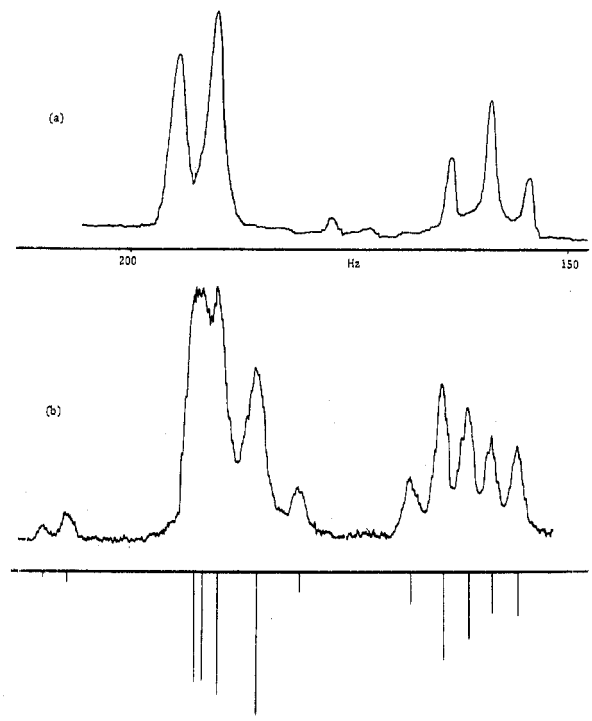
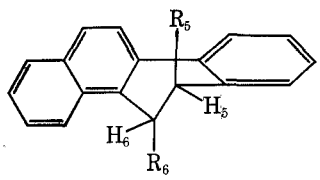


Figure 1. Partial NMR spectrum (benzylic protons; H_9, H_{10}, $H_{10'}$) of 9-*tert*-butyl-9,10-dihydrophenanthrene: (a) in CCl_4; (b) in CD_3CN (lower trace is theoretical).

The 9-hydroxyl compound (**5**, R = OH) exhibits a pseudoaxial preference (94%) unexpectedly high in comparison to the conformational free-energy differences usually found for hydroxy,[11] and also the $J_{9,10'}$ value of 5.9 Hz represents the largest deviation from the 6.8 Hz value of the compounds studied. It should be noted, however, that the NMR spectrum of this compound showed simply a doublet and triplet for the

benzylic protons (under a variety of solvent conditions) and $Eu(fod)_3$ was added until an ABX pattern resulted; although shift reagents did not affect coupling constants or conformations in 1,4-cyclohexadienes[14] (as determined by certain measurements before and after addition), it cannot be certain in this case whether such effects are taking place.

We also examined the NMR spectra of the related compounds of 6-methyl- and *trans*-5,6-dimethyl-5,6-dihydrochrysene (**6** and **7**). Since the values for $J_{5,6}$ were small in both



6, $R_5 = H$; $R_6 = CH_3$
7, $R_5 = R_6 = CH_3$

cases [**6**, $J_{5,6}$ = 1.91 ($J_{H',6}$ = 6.0); **7**, $J_{5,6}$ = 1.6 Hz] it would appear that the pseudoaxial for **6** and dipseudoaxial for **7** are the exclusive conformations of these systems. This is not surprising, of course, in view of the added steric interaction with the additional benzene ring as compared to 9-methyl-**5**, which itself indicates 77%, pseudoaxial preference.

Since we have been observing time-averaged spectra resulting from a rapid ring inversion process, these spectra may be expected to be temperature dependent. In fact, we have observed a number of these compounds at lowered temperature (CS_2), and there is no significant change until crystallization takes place (e.g., R = OH, −25 °C; R = $CO_2CH_2CH_3$, −50 °C; R = CN, −75°C). However, in view of the fact that the barrier to ring inversion in *cis*-9,10-dialkyl-9,10-dihydrophenanthrenes is not large,[15] it was not unexpected that this process cannot be "frozen out" in temperature ranges which maintain solubility.

Synthesis of the majority of the dihydrophenanthrenes for this study was accomplished through metal–ammonia reduction of the corresponding phenanthrenes. Although the cyano, acetyl, and carboxylate groups are known to be susceptible to reduction by alkali metals in liquid ammonia, competitive reduction was not a serious problem under the conditions employed. The method appears to be quite general, and several 9-R-9,10-dihydrophenanthrenes (R = phenyl, carboxyl, benzyl) not included in Table I (owing to problems in interpretation of the NMR spectra) were also synthesized by this method.

Experimental Section

Material and Methods. 9-Methyl-9,10-dihydrophenanthrene was synthesized through reduction of 9-methylphenanthrene with lithium in ammonia in the presence of colloidal iron.[16] 9,10-Dihydrophenanthrene-9-carboxylic acid was prepared by reduction of phenanthrene-9-carboxylic acid with sodium in ammonia.[17] 9-Acetyl-, 9-cyano-, and 9-bromophenanthrene were purchased from the Aldrich Chemical Co. 9-Phenylphenanthrene was synthesized through photocyclization of triphenylethylene.[18] Microanalyses for C, H, and N where appropriate for all new compounds were obtained and were correct in ±0.3%.

NMR spectra were recorded at 60 MHz on a JEOL C6OHL, and at 270 MHz on a Bruker Hx-270. The 270-MHz spectra were used in certain cases to estimate coupling constants, and the NMR data provided in Table I are from 60-MHz spectra usually coupled with computer simulation. The LAOCN 3 program (QCPE, Indiana University) was used on either a CD6600 or IBM 360 computer. Line positions were determined using a Hewlett-Packard 5301A frequency counter.

Reactions in Liquid Ammonia. The general procedures developed in prior studies[19] for the controlled reduction of polycyclic aromatic compounds were employed. The recommended precautions for the exclusion of moisture, air, peroxides in ethereal solvents, and ferrous metal salts in ammonia were scrupulously observed, and products were isolated rapidly by partition between ether and water.

2-Cyano-9,10-dihydrophenanthrene. A solution of 9-cyanophenanthrene (2.03 g, 10 mmol) in tetrahydrofuran (100 ml) followed by lithium wire (174 mg, 22 mmol) were added to 200 ml of refluxing ammonia, affording a red-purple solution. After 30 min, reaction was quenched with solid NH_4Cl (20 g) and worked up conventionally to yield 9-cyano-9,10-dihydrophenanthrene (1.85 g, 90%) as a yellow oil which crystallized from CCl_4 as a colorless solid, mp 83–84 °C.

9-Acetyl-9,10-dihydrophenanthrene. Reduction of 9-acetylphenanthrene (1.10 g, 5 mmol) with lithium (76 mg, 11 mmol) in ether (100 ml) and ammonia (150 ml) at −33 °C afforded a dark green solution. Reaction was quenched after 4 min by addition of NH_4Cl (20 g) and worked up in the usual manner to yield 1.13 g of a colorless solid. Chromatography on silica gel and elution with benzene–hexane (1:2) gave pure 9-acetyl-9,10-dihydrophenanthrene (578 mg, 52%) as a pale yellow oil, ir (CCl_4) 1705 cm^{-1} (CO). Several minor products also obtained were not identified.

Treatment of the ketone (371 mg) with *p*-toluenesulfonic acid (30 mg) and ethylene glycol (10 ml) in dry benzene (30 ml) at reflux for 6 h furnished after workup the corresponding ketal (436 mg, 97%). Crystallization from methanol afforded pure 9-(1-ethylenedioxyethyl)-9,10-dihydrophenanthrene as white needles (401 mg, 90%), mp 83.5–85 °C. The latter (273 mg) was reconverted quantitatively to 9-acetyl-9,10-dihydrophenanthrene on heating in aqueous acetone (5%) in the presence of *p*-toluensulfonic acid (20 mg) at reflux temperature for 1 h.

Methyl 9,10-Dihydrophenanthrene-9-carboxylate. Methyl phenanthrene-9-carboxylate was synthesized from the parent acid by reaction with thionyl chloride following a conventional procedure. Recrystallization of the crude ester from methanol afforded the pure methyl ester (76%) as white needles: mp 118–119 °C (lit.[20] 118–119 °C); NMR (CCl_4) δ 3.97 (s, 3, CH_3), 7.42–8.0 (m, 6, $H_{1,2,3,6,7,8}$), 8.37 (s, 1, H_{10}), and 8.50–9.2 ppm (m, 2, $H_{4,5}$); GLC on a 5 ft × 0.125 in. column of 1.5% OV 101 at 195 °C gave a single sharp peak.

Reduction of the methyl ester (313 mg, 133 mmol) with lithium (20 mg, 2.9 mmol) in ether (30 ml) and ammonia (80 ml) at −40 °C gave a dark green solution. Reaction was quenched after 15 min by solid NH_4Cl (20 g) and worked up in the usual manner. Chromatography of the solid product (311 mg) on silica gel and elution with benzene–chloroform (1:3) gave pure methyl 9,10-dihydrophenanthrene-9-carboxylate (179 mg, 52−) as a pale yellow oil. The NMR spectrum matched that reported;[21] GLC on 1.5% OV 101 gave a single sharp peak.

Ethyl 9,10-Dihydrophenanthrene-9-carboxylate. Ethyl phenanthrene-9-carboxylate was synthesized by the same method as the methyl ester. Purification was effected by chromatography on silica gel eluted with acetone. The pure ethyl ester (98%) was obtained as an oil: NMR (CCl_4) δ 1.43 (t, 3, J = 7.0 Hz, CH_3), 4.40 (q, 2, J = 7.0 Hz, CH_2), 7.35–7.90 (m, 6, $H_{1,2,3,6,7,8}$), 8.26 (s, 1, H_{10}), and 8.34–8.94 ppm (m, 2, $H_{4,5}$); GLC on 1.5% OV 101 gave a single sharp peak.

Reduction of the ethyl ester (555 mg) by the method employed for the methyl ester gave pure ethyl 9,10-dihydrophenanthrene-9-carboxylate as a colorless oil (188 mg, 34%); GLC analysis showed a single sharp peak.

9-Trimethylsilyl-9,10-dihydrophenanthrene. 9-Trimethylsilylphenanthrene was synthesized from 9-bromophenanthrene (2.57 g, 10 mmol) via reaction with *n*-butyllithium and chlorotrimethylsilane. The method of Eaborn[22] was employed except that reaction with the lithium reagent was conducted at room temperature, rather than reflux, and a larger excess of the silane was employed. The crude product was chromatographed on silica gel eluted with hexane to furnish pure 9-trimethylsilylphenanthrene (82%) as an oil which crystallized on standing: NMR (CCl_4) δ 0.50 (s, 9, CH_3), 7.37–8.20 (m, 6, $H_{1,2,3,6,7,8}$), 7.87 (s, 1, H_{10}), and 8.30–8.67 (m, 2, $H_{4,5}$).

A solution of 9-trimethylsilylphenanthrene (1.33 g, 5.3 mmol) in ether (80 ml) was added to 150 ml of refluxing ammonia, followed by lithium wire (84 mg, 12 mmol). Reaction was quenched after 10 min by addition of NH_4Cl (20 g) to the dark green solution. Chromatography of the product on Florisil furnished pure 9-trimethylsilyl-9,10-dihydrophenanthrene as a colorless oil, mass spectrum (70 eV) *m/e* 252.

9-Hydroxy-9,10-dihydrophenanthrene. Phenanthrene 9,10-oxide[23] (400 mg, 2 mmol) was treated with $LiAlH_4$ (160 mg, 4 mmol) in refluxing ether (30 ml) for 40 min, then 100 ml of water and 1 ml of acetic were added. Conventional workup gave 9-hydroxy-9,10-dihydrophenanthrene (397 mg, 98%) essentially pure by NMR. Recrystallization from benzene–hexane gave the analytical sample as white needles, mp 105–106 °C.

9-Phenyl-9,10-dihydrophenanthrene. Reduction of 9-phenylphenanthrene (200 mg, 0.8 mmol) with lithium in ether and ammonia

at −78 °C by the standard method[19] gave 9-phenyl-9,10-dihydrophenanthrene (200 mg, 99%) as a colorless oil which solidified on standing, mp 80–82 °C. Chromatography on Florisil gave the analytical sample, mp 82–83 °C.

9-Benzyl-9,10-dihydrophenanthrene. 9-Benzylphenanthrene was prepared from 9-bromophenanthrene through reaction of the Grignard derivative with benzyl chloride.[24] Reduction of 9-benzylphenanthrene with lithium in ammonia in the presence of colloidal iron under conditions similar to those employed with the 9-methyl analogue[16] gave 9-benzyl-9,10-dihydrophenanthrene (94%) as oil. Chromatography on silica gel effected removal of residual starting material and furnished the pure title compound.

9-*tert*-Butyl-9,10-dihydrophenanthrene. 9-*tert*-Butylphenanthrene was synthesized through reaction of phenanthrene 9,10-oxide[23] with *tert*-butyllithium followed by acid-catalyzed dehydration. Complete purification required several chromatographies on silica gel impregnated with trinitrofluorenone.[25] The pure 9-*tert*-butylphenanthrene had mp 64–65 °C (lit.[26] 64–65 °C).

Reduction of 9-*tert*-butylphenanthrene (234 mg, 1 mmol) with lithium in ether and ammonia by the standard method have an oil containing 9-*tert*-butyl-9,10-dihydrophenanthrene and recovered starting material (7:3). Chromatography twice on neutral alumina and elution with hexane gave pure 9-*tert*-butyl-9,10-dihydrophenanthrene (86 mg, 35%) free of the parent aromatic hydrocarbon.

5-Methyl- and 5,6-Dimethyl-5,6-dihydrochrysene. The method for the reductive methylation of chrysene previously reported[27] was modified to improve the yield. A solution of chrysene (2.74 g, 12 mmol) in THF (200 ml) was added to 100 ml of refluxing ammonia. Sodium metal (220 mg, 14 mmol) was added, and the resulting deep blue solution was stirred for 4 min, then methyl bromide was bubbled into the solution for 2 min, followed by NH_4Cl (20 g). Conventional workup afforded 2.31 g of a solid. Chromatography on neutral alumina eluted with hexane gave initially 5,6-dimethyl-5,6-dihydrochrysene as a minor product. Recrystallization from chloroform–hexane gave the pure dimethyl compound as a white solid, mp 104–106 °C. Further elution with hexane furnished pure 5-methyl-5,6-dihydrochrysene (1.57 g, 93%) as a colorless solid, mp 132–133 °C.

Acknowledgment. Support of this research by grants from the U.S. Public Health Service CA-11968 (R.G.H.) and the Indiana University Office of Research and Advanced Studies (P.W.R.) is gratefully acknowledged. The Hx-270 Bruker superconducting NMR spectrometer was provided through the University of Chicago Cancer Research Center Grant CA-14599. We also wish to thank Dr. Frederick Beland for synthesis of the sample of pure 9-*tert*-butylphenanthrene, Mr. Walter Flack for modification of the LAOCN 3 program to run on the IBM 360, and Mrs. Sarah Land for testing the program.

Registry No.—9-Cyanophenanthrene, 2510-55-6; 9-acetylphenanthrene, 2039-77-2; 9-(ethylenedioxyethyl)-9,10-dihydrophenanthrene, 60084-40-4; methyl phenanthrene-9-carboxylate, 1217-49-8; phenanthrene-9-carboxylic acid, 837-45-6; ethyl phenanthrene-9-carboxylate, 4895-92-5; 9-trimethylsilylphenanthrene, 18209-95-5; 9-bromophenanthrene, 573-17-1; phenanthrene 9,10-oxide, 585-08-0; 9-*tert*-butylphenanthrene, 17024-05-4; chrysene, 218-01-9; 5,6-dimethyl-5,6-dihydrochrysene, 60084-41-5; 5-methyl-5,6-dihydrochrysene, 34908-52-6; 9-phenyl-9,10-dihydrophenanthrene, 5235-80-3; 9-phenylphenanthrene, 844-20-2; 9-benzyl-9,10-dihydrophenanthrene, 60084-42-6; 9-benzylphenanthrene, 605-05-0.

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Syntheses and Absolute Configurations of Tricyclo[4.3.0.0^{3,7}]nonane ("Brexane"), 3-Oxatricyclo[4.3.0.0^{4,9}]nonane ("3-Oxabrexane"), and Tricyclo[4.2.0.0^{3,7}]octan-2-one ("Norbrexan-2-one")[1]

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Received April 30, 1976

(−)-(1*S*,3*S*,6*R*,7*R*)-Brexane (tricyclo[4.3.0.0^{3,7}]nonane) (**3**) was prepared from (+)-(1*R*,4*R*,7*S*)-7-*syn*-methoxycarbonylbicyclo[2.2.1]heptan-2-one (**12**). Examination of the circular dichroism curve of the intermediate, (−)-brexan-2-one (tricyclo[4.3.0.0^{3,7}]nonan-2-one) (**4**), which exhibited a (−) Cotton effect, confirmed the absolute configuration. Starting from (−)-(1*S*,4*S*,7*R*)-7-*syn*-methoxycarbonylbicyclo[2.2.1]heptan-2-one (**16**), 3-oxabrexane (3-oxatricyclo[4.3.0.0^{4,9}]nonane) (**5**), and norbrexan-2-one (tricyclo[4.2.0.0^{3,7}]octan-2-one) (**6**) were synthesized in optically active forms.

A feature common to tricyclo[4.4.0.0^{3,8}]decane ("twistane")[2] (**1**) and tricyclo[4.3.0.0^{3,8}]nonane ("twist-brendane")[3] (**2**), whose preparations in optically active forms have been recently reported from our laboratory, is the "twist carbon frame" inherent to their gyrochiral[4] cage-shaped molecules (D_2 and C_2 symmetry, respectively). These twisted carbon