We also estimated the twist angle from the hypochromic effect of twisting on the molar absorptivity of the longest wavelength electronic absorption band in β,β-dimethylstyrene using the relation[32]

$$\epsilon/\epsilon_0 = \cos^2 \theta$$

As the reference compound, we chose styrene (ϵ 15,600),[22] generally regarded as planar. From the molar absorptivity of β,β-dimethylstyrene (ϵ 11,750), we calculate a twist angle of about 30°, in reasonable agreement with the data for 2-methylstyrene[22] and 2,5-dichlorostyrene,[27] and with our concusions based on the magnitude of $^9J_{HH}$.

Experimental Section

Nmr spectra were recorded at ambient temperature on a Varian Associates Model HA-60-IL spectrometer, operating in the frequency swept mode. Chemical shifts were measured from spectra run on the 500-Hz scale at a sweep speed of 1 Hz/sec, and are the average of two to three upfield sweeps. Coupling constants were determined from spectra traced on the 50-Hz scale at a sweep speed of 0.1 Hz/sec. Under these conditions, the precision (standard deviation of 20 separate determinations) exceeded ±0.03 Hz. Inaccuracies in chart calibration are less than +0.01 Hz.

Isopropylidenic couplings were determined from spectra from which line broadening due to unresolved long-range couplings had been eliminated by decoupling.

Decoupling experiments were also done in the frequency swept mode, using either a Hewlett-Packard Model 200AB signal generator or a General Radio Model 1304B audio oscillator.

Nmr samples contained approximately 10 vol % of the appropriate β,β-dimethylstyrene in spectroquality carbon disulfide, with about 5 vol % of tetramethylsilane added to serve as both internal reference and lock signal. Samples were degassed by repeated freeze–pump–thaw cycles, and sealed under vacuum to ensure optimum resolution. No degradation of samples was evident over a 3-year period.

Compounds were prepared by the method of Sternhell, et al.,[11] described below for β,β-dimethylstyrene.

A solution of benzaldehyde (0.2 mol in 60 ml of anhydrous ether) was added dropwise to 0.4 mol of isopropylmagnesium bromide in 150 ml of ether. After being heated under reflux for 3 hr, the reaction mixture was cooled and poured onto a mixture of 10% H_2SO_4 and ice. The aqueous layer was extracted with ether, the extracts were combined with the original ether layer and dried (Na_2SO_4), and the solvent was removed *in vacuo*. A mixture of isopropylphenylcarbinol and unreacted benzaldehyde resulted.

The mixture was heated under reflux with 30% H_2SO_4 for 4 hr, yielding a mixture of β,β-dimethylstyrene and benzaldehyde. Chromatography on neutral alumina (activity I) with low-boiling petroleum ether afforded β,β-dimethylstyrene, which was further purified by preparative vapor phase chromatography (Varian Aerograph Model 1700; 6 ft × 0.25 in, column packed with 30% SE-30 on firebrick). Sample purity was checked with refractometry, vpc, ir, and nmr spectroscopy.

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(32) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.

Carbon-13 Magnetic Resonance. XXIV.[1]
The Perhydroanthracenes and Perhydrophenanthrenes

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Abstract: The proton-decoupled, carbon-13 magnetic resonance (cmr) data have been determined for all of the five possible perhydroanthracene structural isomers and for four of the six possible perhydrophenanthrene compounds. The former are of known configuration, but the latter are unidentified in the chemical literature prior to the present work. The data are initially assigned to specific carbon positions using a parameter set derived from the methyldecalins. The calculated spectra are then refined by least-squares, regression analysis. New chemical shift parameters associated with boat and skew pentane conformations are discussed.

The first tetradecahydroanthracene (or perhydroanthracene, abbreviated for convenience to PHA) isomer was synthesized about the turn of the century.[2–4] It was soon recognized that other geometric isomers were possible[5] and as many as 20 were suggested.[6] Fries and Schilling ultimately delineated the correct number as being five,[7] the last of which was synthesized only in recent years.[8] Many workers contributed to the synthesis and characterization of the several isomers.[7,9–14] X-Ray[15] and electron diffraction[16,17] work
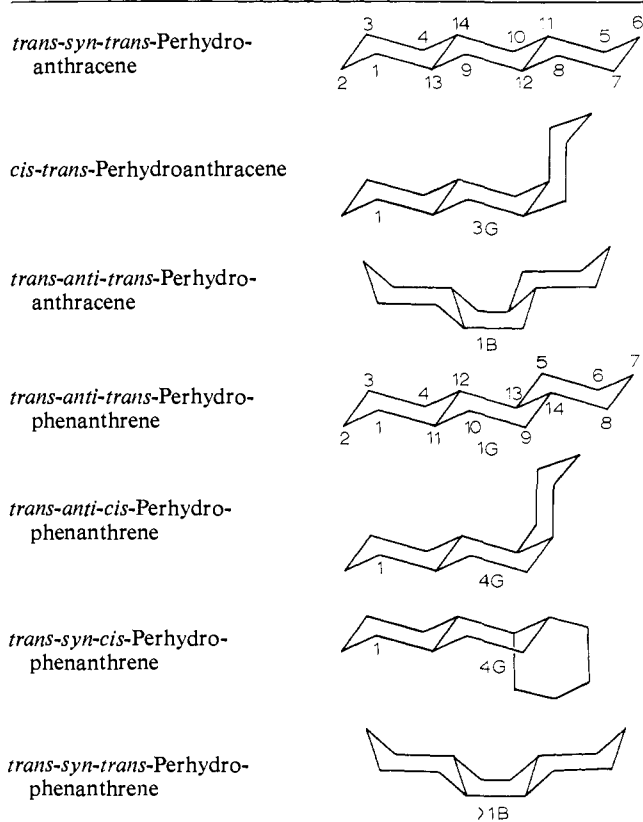
demonstrated that the individual six-member rings in these compounds normally exist as chair forms, with the exception of the center ring of the trans-anti-trans compound, which is locked in a boat conformation.

Table I portrays the compounds which are conformationally locked by at least one trans ring fusion. The isomers which have two cis ring junctions may interconvert between all-chair forms; they are diagrammed in Table II. The nomenclature for the PHA isomers is

(1) Previous paper in the series: D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **95**, 3718 (1973).
(2) M. Godchot, *C. R. Acad. Sci.*, **141**, 1028 (1905).
(3) W. Ipatiew, W. Jakolew, and L. Rakitin, *Ber.*, **41**, 996 (1908).
(4) L. Lucas, *Ber.*, **21**, 2510 (1888).
(5) M. Godchot, *Bull. Soc. Chim. Fr.*, **1**, 724 (1907).
(6) G. Shroeter, *Ber.*, **57**, 1990 (1924).
(7) K. Fries and K. Schilling, *Ber.*, **65**, 1494 (1932).
(8) R. L. Clarke, *J. Amer. Chem. Soc.*, **83**, 965 (1961).
(9) J. H. Brown, H. W. Durand, and C. S. Marvel, *J. Amer. Chem. Soc.*, **58**, 1594 (1936).

(10) J. W. Cook, N. A. McGinnis, and S. Mitchell, *J. Chem. Soc.*, 286 (1944).
(11) R. L. Clark and W. S. Johnson, *J. Amer. Chem. Soc.*, **81**, 5706 (1959).
(12) R. K. Hill and J. G. Martin, *Proc. Chem. Soc., London*, 390 (1959).
(13) N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960).
(14) R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Amer. Chem. Soc.*, **83**, 4006 (1961).
(15) K. E. Hjortaas, *Acta Chem. Scand.*, **14**, 1443 (1960).
(16) S. Bog, O. Hassel, and E. H. Vihovde, *Acta Chem. Scand.*, **7**, 1308 (1953).
(17) M. I. Davis and O. Hassel, *Acta Chem. Scand.*, **18**, 813 (1964).

Table I. Perhydroanthracenes and Perhydrophenanthrenes Which Are Conformationally Locked by Trans Ring Junctions[a]

trans-syn-trans-Perhydro-anthracene

cis-trans-Perhydroanthracene

trans-anti-trans-Perhydro-anthracene

trans-anti-trans-Perhydro-phenanthrene

trans-anti-cis-Perhydro-phenanthrene

trans-syn-cis-Perhydro-phenanthrene

trans-syn-trans-Perhydro-phenanthrene

[a] The number of steric interactions (G ≅ 0.9 kcal/mol, B ≅ 5.4 kcal/mol) is indicated beneath each scheme.

Table II. Perhydroanthracenes and Perhydrophenanthrenes Which Can Conformationally Invert between All-Chair Forms[a]

cis-anti-cis-Perhydro-anthracene

cis-syn-cis-Perhydro-anthracene

cis-anti-cis-Perhydro-phenan-threne[b]

cis-syn-cis-Perhydro-phenan-threne-

[a] The number of γ-gauche (G ≅ 0.9 kcal/mol) and skew pentane (AA ≅ 3.7 kcal/mol) steric interactions is indicated beneath each scheme. [b] The two conformations of this compound are not of equal energy.
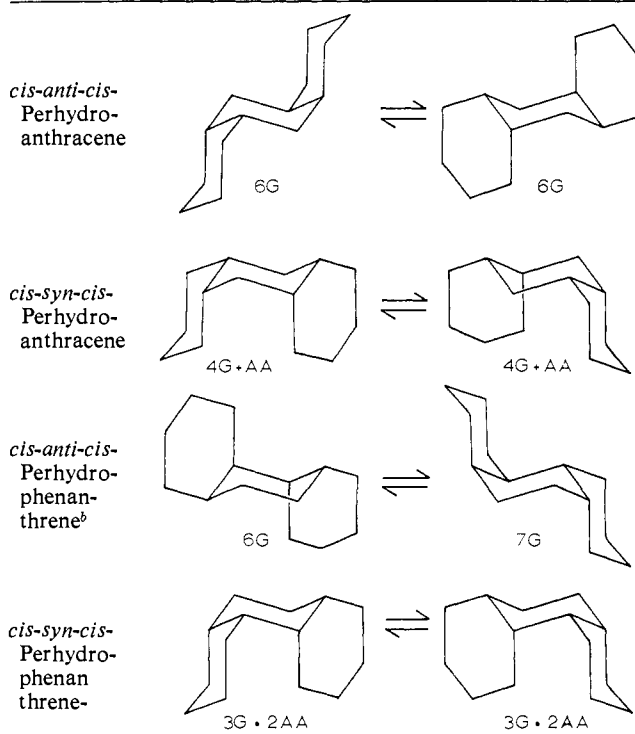
similar to that of decalin in that cis and trans are used to denote the relationship of the hydrogens at the ring fusions; however, syn and anti are now employed in addition to indicate whether the bridgehead hydrogens of one ring junction are respectively cis or trans to the nearest bridgehead hydrogens of the other ring junction. In the case of the isomeride which has one cis and one trans ring fusion, the use of syn or anti is redundant and it is omitted. A 1–14 numbering system has been used, as indicated in Table I; however, in the case of the cis-trans (CT) compound, there is ambiguity, and "1" has been placed on the diagram to indicate where numbering begins.

A cis ring junction normally produces three steric interactions of the type found in the gauche form of *n*-butane, introducing 2.4 to 3.0 kcal/mol of strain energy into the system.[18] When the ring junctions are both cis, and also syn to each other, a skew pentane interaction, such as would be found in the high energy chair conformation of *cis*-1,3-dimethylcyclohexane, is found. This interaction introduces approximately 3.7 kcal/mol[19] of additional steric strain energy into the molecule. It is also necessary to consider the energy increase which results from the center ring of TAT-PHA being locked into a boat conformation, causing steric interactions which are like those of *eclipsed n*-butane, *i.e.*, where four carbons lie in a plane. The energy increment between the TAT and TST isomers, which

differ only because of the center boat in the TAT compound, has been measured as 5.39 ± 0.86 kcal/mol.[20] The numbers of *gauche*-butane (G), skew pentane (AA), and boat (B) interactions occurring in each isomer are indicated below their respective figures.

Aside from the measurements mentioned above, no data have been reported of the energy differences of the several PHA isomers. Several authors[21–23] have estimated the steric energy inherent in the PHA compounds. Although the estimates vary somewhat, the ordering of the compounds from lowest to the highest energy generally follows that which results from application of the parameters listed in Tables I and II.

The two all-chair forms of CAC- and CSC-PHA listed in Table II are of equal energies, so that at room temperature the cmr spectra of these compounds should result from equally weighted averages of the two conformations. Although it is not so obvious without making a model, the TAT isomer can also average by interconverting between two possible orientations of the center boat. Thus, only four lines occur in the proton-decoupled, carbon-13 spectrum of this molecule instead of the seven lines which would result if the center ring were conformationally immobile. The trans ring linkages, however, do not allow all the possible orientations which a boat conformation might be expected to have.

(18) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **94**, 5318 (1972), see ref 5–10 therein.

(19) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **83**, 2145 (1961).

(20) J. L. Margrave, M. A. Frisch, R. G. Bautista, R. L. Clark, and W. S. Johnson, *J. Amer. Chem. Soc.*, **85**, 546 (1963).

(21) W. S. Johnson, *J. Amer. Chem. Soc.*, **75**, 1498 (1953); *Experientia*, **8**, 315 (1951).

(22) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

(23) W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, **82**, 1255 (1960).

The proton magnetic resonance (pmr) spectra of four of the PHA isomers (CT-PHA being the exception) have been reported,[21] but no carbon-13 magnetic resonance data are found in the scientific literature. The pmr spectrum of the cis-trans compound indicates that there is some proton averaging, presumably due to the flipping of the cis joined ring.

Tetradecahydrophenanthrene is abbreviated in the same manner as for the previous series to perhydrophenanthrene or PHP. Scientific papers treating the parent compounds are not numerous, but their derivatives are extensively treated in the chemical literature, since hydrogenated phenanthrene is one of the most commonly encountered backbone structures for natural products of the steroid type. The vast literature concerning these compounds will not be reviewed here.

Liebermann and Spiegel probably prepared the first authentic, unsubstituted perhydrophenanthrene,[24] but later workers were unable to duplicate their results.[2,25] Just a few other references to synthesis of the parent compounds can be found.[3,26–29] The infrared spectra of two unspecified isomers are published in ref 27.

The possible stereochemistry of the perhydrophenanthrenes has been duplicated in some closely related compounds. Linstead and coworkers prepared and characterized the six perhydrodiphenic acids analogous to the six possible PHP isomers, as well as three 9-oxoperhydrophenanthrenes.[30–35] Robins and Walker subsequently prepared all of the 1,4-dioxoperhydrophenanthrenes except the one which must have a center boat.[36]

The six possible perhydrophenanthrene isomers are also portrayed in Tables I and II. The naming of these compounds is similar to that of the PHA isomers, the difference being that the use of syn or anti is applied only to the vicinal bridgehead hydrogens at carbons 12 and 13. The numbering system is indicated in Table I. In this series there are two compounds, TAC- and TSC-PHP, for which the general numbering system is ambiguous, and the carbon with which numbering begins must be specified.

In the TST isomeride, for which the center ring must exist as a boat, carbons 4, 12, 13, and 5 are involved in an "eclipsed n-butane" interaction similar to that found for the planar carbons in the center ring. The interaction is probably not as severe as it might be, however, as manipulation of a model demonstrates that

slight skewing of the center boat relieves the C-4, C-5 interaction substantially. We estimate the steric energy involved in this interaction to be somewhat more than half that of a full boat conformation, i.e., about 3.6 kcal/mol. Unfortunately, this compound is unavailable for study at this time.

The two PHP isomers listed in Table II have only cis ring junctures and hence have two possible all-chair conformations. In CAC-PHP the two conformations do not have the same energy, making one form favored over the other. This compound is also presently unavailable for study.

For the cis-syn-cis isomer, it is possible for averaging to occur between the two all-chair forms of equal energy. Due to the large interaction energy of the all-chair forms (3G + 2AA $\cong$ 10.1 kcal/mol), conformations other than all-chair forms might be expected to contribute to the population distribution. The center boat conformation of lowest energy appears to have four gauche interactions, one boat, and one "half-boat" interaction, which total about 12.6 kcal/mol. This energy is substantially greater than that of the all-chair forms, but if these steric interactions are relaxed somewhat by skewing, then the lowest energy center boat conformation can be expected to influence the carbon-13 spectrum.

No experimental work has been reported comparing the relative energies of the perhydrophenanthrenes since they have not been characterized previously, nor have proton or carbon-13 mr spectra been reported for the PHP series.

Experimental Section

(A) **Instrumentation and Spectral Techniques.** A Varian Associates AFS-60 spectrometer was used to obtain the cmr data. The 10-mm sample tubes were spun in a Varian V-4331A probe, while simultaneous proton decoupling was accomplished as described in previous papers in this series. Some spectra were accumulated in a Varian C1024 time averaging computer. Proton spectra were obtained on a Varian A-56/60 spectrometer.

The perhydrophenanthrenes studied are liquids at room temperature and were run neat with about 10% by volume of tetramethylsilane (TMS) added as an internal standard. In a few cases sample size was insufficient, and it was necessary to add a diluent in order to have adequate sample volume in the probe. The PHA isomers were examined in solution with 1 to 2 ml of CS_2 with TMS added.

Chemical shifts were measured relative to internal TMS. The values have been converted to benzene scale so as to be easily relatable to previous papers in this series. The conversion was made by subtracting the measured chemical shifts from 128.82 ppm.[18]

(B) **Compound Preparation.** Three of the perhydroanthracene isomers (TST-, TAT-, and CAC-PHA) were obtained from R. L. Clark.[37]

Catalytic hydrogenation was a convenient method for preparing a number of other compounds in these series, since some control of the stereochemistry of the products was possible by a suitable choice of catalyst. Weitkamp,[38] in catalytically hydrogenating methylnaphthalenes, found that Ru/C catalyst produced mostly cis addition of hydrogen, while Pd/C catalyst gave the highest percentage of trans addition products, so these were the catalysts of choice.

The reaction conditions and experimental results are summarized in Table III. About 50 g of the material to be hydrogenated was dissolved in 250 ml of cyclohexane, and the solution was put in a stainless steel liner for a 3-l. high-pressure bomb. About 0.5 g of catalyst was added; the catalysts were 5% metal on charcoal. Commercially available perhydrophenanthrene is also listed in Table III. The per cent yields were determined by gas chromatographic and/or cmr analysis.

(24) C. Liebermann and L. Spiegel, *Ber.*, **22**, 779 (1889).

(25) J. Schmidt and R. Mezger, *Ber.*, **40**, 4240 (1907).

(26) P. S. Pinkey, G. A. Nesty, R. H. Wiley, and C. S. Marvel, *J. Amer. Chem. Soc.*, **58**, 972 (1936).

(27) J. W. Cook, C. L. Hewett, and A. M. Robinson, *J. Chem. Soc.*, 168 (1939).

(28) R. P. Linstead and A. L. Walpole, *J. Chem. Soc.*, 842 (1939).

(29) J. D. Brooks, R. A. Durie, and H. Silberman, *Aust. J. Chem.*, **17**, 55 (1964).

(30) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, **64**, 1985 (1942).

(31) R. P. Linstead and W. E. Doering, *J. Amer. Chem. Soc.*, **64**, 1991, 2003 (1942).

(32) R. P. Linstead and S. B. Davis, *J. Amer. Chem. Soc.*, **64**, 2006 (1942).

(33) R. P. Linstead, S. B. Davis, and R. R. Whetstone, *J. Amer. Chem. Soc.*, **64**, 2009 (1942).

(34) R. P. Linstead, R. R. Whetstone, and P. Levine, *J. Amer. Chem. Soc.*, **64**, 2014 (1942).

(35) R. P. Linstead and P. Levine, *J. Amer. Chem. Soc.*, **64**, 2022 (1942).

(36) P. A. Robins and J. Walker, *J. Chem. Soc.*, 3960 (1954); 1789 (1955).

Table III. Results from Hydrogenation of *sym*-Octahydroanthracene and *sym*-Octahydrophenanthrene with Two Different Catalysts

Compd hydrogenated	Catalyst	Initial H$_2$ pressure, psi	Temp,[a] °C	% yield	Products (%)[b]
1,2,3,4,5,6,7,8-Octahydroanthracene	Ru/C[c]	1500	250	99	CSC-PHA (80) Undetermined (20)
	Pd/C[d]	1500	220	99	CT-PHA (49) TST-PHA (40) Cis isomers (11)
1,2,3,4,5,6,7,8-Octahydrophenanthrene	Ru/C	1700	210	86	CSC-PHP (85) Undetermined (15)
	Pd/C	1200	250	91	TAT-PHP (35) TAC-PHP (24) TSC-PHP (36) Undetermined (5)
Commercial PHP[e]					TAT-PHP (13) TAC-PHP (22) TSC-PHP (54) CSC-PHP (9)

[a] The reaction was begun at room temperature but was held at the listed temperature for 12 to 36 hr. [b] As determined by glc and nmr analysis to about ±3%. [c] Purchased from Engelhard Industries, Inc. [d] Purchased from Matheson Coleman and Bell. [e] Purchased from Aldrich Chemical Co.
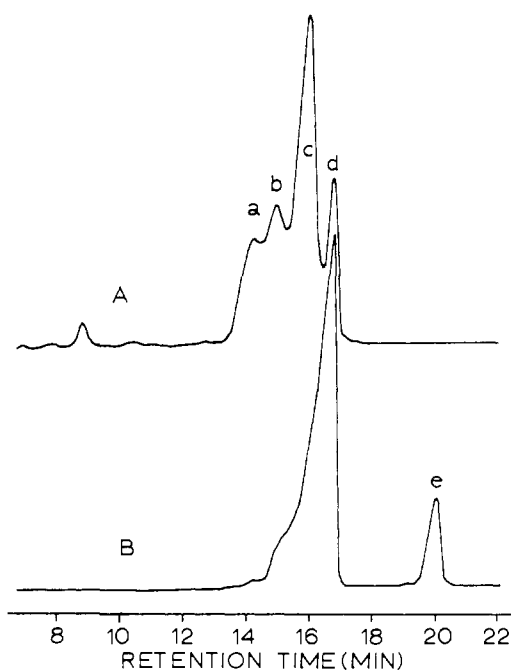
Figure 1. Gas chromatograms of two mixtures of perhydrophenanthrene isomers: (A) commercial sample; (B) hydrogenation product of *sym*-octahydrophenanthrene with Ru/C catalyst. The compounds are a = TAT, b = TAC, c = TSC, d = CSC, and e = starting material.

The isomers produced by hydrogenation are extremely difficult to isolate due to the similarity of their boiling points. Partial purification was affected by use of preparative scale gas chromatography as detailed in the next section. Although the separation was sufficient to allow cmr spectra to be obtained, the incomplete purification did, however, preclude the determination of other physical properties for the previously unknown perhydrophenanthrene isomers.

The compound identifications in Table III were deduced from examination of the proton and carbon-13 spectra of the products. Some of the results depend on parametric evaluation of the product spectra; they are discussed in a later section. Since many of the gas chromatographic peaks for the compounds in the various hydrogenation products overlapped considerably (for example see Figure 1), the percentage yields given in Table III are accurate only to about 3% of the total products.

Spectroscopic Assignments

(A) Identification of the Perhydrophenanthrene Iso-

mers. The chemical shifts for the available alicyclic compounds are listed in Table IV. The previously published values for *cis*- and *trans*-decalin are included for comparison.[1] As previously stated the PHA isomers have been characterized and are of known configuration.

Of the six possible PHP isomers, two are locked in completely unsymmetrical configurations (the TAC and TSC isomers of Table I), and they will have 14 lines in their carbon-13 spectra (barring accidental degeneracy). The TAT and TST compounds are also conformationally locked by trans ring junctions, but they have elements of symmetry which reduce the number of resonance lines in their decoupled carbon-13 spectra to seven.

The two PHP compounds of Table II having all cis ring junctions (CAC and CSC) can interconvert between pairs of all-chair conformers. The two conformers of CAC-PHP differ in energy by one gauche interaction. Due to this small energy difference, it is anticipated that the higher energy conformer would contribute significantly to the ¹³C spectrum of this molecule. The proton spectrum should be quite broadened, compared to that of *cis*-decalin. Both favored and unfavored forms of the CAC isomer have a C$_2$ axis of symmetry, so that even at low temperatures each conformer would produce only seven spectral lines. Even so, if the rapid interconversion was frozen out one should observe two separate seven-line spectra of differing line intensity. The CSC isomer is unsymmetrical, and its cmr spectrum should have 14 lines at low temperatures. However, at normal temperatures the two all-chair conformers, which are enantiomers of equal energy, will be rapidly interconverting, and there will be only seven lines in its decoupled cmr spectrum, representing the averages of the two environments which the pairs of carbons experience. The lowest energy center boat conformation, which may influence the spectrum, contains a reflection plane so that its cmr spectrum has only seven lines at all temperatures.

Preparative scale gas chromatography utilizing a ³/₈ in. by 10 ft column packed with 20% SE 30 on Chromsorb W was used to substantially purify four perhydrophenanthrene isomers from the commercially

Table IV. Carbon-13 Chemical Shift Data for Some Alicyclic Hydrocarbons

Compd[a]	Item	Experimental From TMS	Experimental From benzene[b]	Predicted from Table V[e] Carbon	Value[b]
trans-Decalin	1	44.22	84.60	9, 10	85.60
	2	34.74	94.08	1, 4, 5, 8	93.58
	3	27.17	101.65	2, 3, 6, 7	101.60
cis-Decalin	4	36.93	91.89	9, 10	91.13
	5	29.78	99.04	1, 4, 5, 8	99.15
	6	24.62	104.20	2, 3, 6, 7	104.06
trans-syn-trans-Perhydroanthracene	7	43.82	85.00	11, 12, 13, 14	85.60
	8	42.14	86.68	9, 10	85.56
	9	34.38	94.44	1, 4, 5, 8	93.58
	10	27.10	101.72	2, 3, 6, 7	101.60
cis-trans-Perhydroanthracene	11	44.18	84.64	13	85.60
	12	40.78	88.04	10	88.16
	13	37.50	91.32	12	90.79
	14	37.09	91.73	11	90.79
	15	36.60	92.22	14	91.13
	16	34.43	94.39	1	93.58
	17	34.35	94.47	4	93.58
	18	33.88	94.94	9	94.10
	19	32.62	96.20	8	96.18
	20	27.57	101.25	6	101.60
	21	27.16	101.66	2	101.60
	22	27.16	101.66	3	101.60
	23	27.07	101.75	5	102.12
	24	21.37	107.45	7	107.12
cis-anti-cis-Perhydroanthracene[c]	25	33.9	94.9	11, 12, 13, 14	93.56
	26	32.4	96.4	9, 10	96.70
	27	29.7	99.1	1, 4, 5, 8	99.15
	28	24.3	104.5	2, 3, 6, 7	104.06
trans-anti-trans-Perhydroanthracene	29	38.45	90.37	9, 10	90.37
	30	36.44	92.38	11, 12, 13, 14	92.38
	31	35.47	93.35	1, 4, 5, 8	93.58
	32	26.81	102.01	2, 3, 6, 7	101.60
cis-syn-cis-Perhydroanthracene	33	37.59	91.23	11, 12, 13, 14	90.79
	34	33.26	95.56	9, 10	96.70
	35	32.28	96.54	1, 4, 5, 8	96.09
	36	25.30	103.52	2, 3, 6, 7	104.37
trans-anti-trans-Perhydrophenanthrene	37	48.21	80.61	12, 13	80.96
	38	43.61	85.21	11, 14	85.60
	39	35.02	93.80	9, 10	93.58
	40	34.59	94.23	1, 8	93.58
	41	30.13	98.69	4, 5	99.11
	42	27.14	101.68	3, 6	101.60
	43	26.84	101.98	2, 7	101.60
trans-anti-cis-Perhydrophenanthrene[d]	44	44.20	84.62	11	85.60
	45	42.27	86.55	13	86.16
	46	38.47	90.35	12	89.50
	47	37.96	90.86	14	90.79
	48	34.99	93.83	1	93.58
	49	32.86	95.96	9	96.18
	50	30.44	98.38	4	99.11
	51	29.84	98.98	10	99.11
	52	28.18	100.64	3	101.60
	53	27.61	101.21	7	101.60
	54	27.21	101.61	2	101.60
	55	27.21	101.61	5	101.71
	56	26.98	101.84	8	102.12
	57	20.74	108.08	6	107.13
trans-syn-cis-Perhydrophenanthrene	58	47.70	81.12	12	83.56
	59	42.35	86.47	13	86.17
	60	38.38	90.44	14	90.79
	61	36.47	92.35	11	91.13
	62	35.40	93.42	10	93.58
	63	35.33	93.49	1	93.58
	64	33.05	95.77	8	96.18
	65	31.03	97.79	4	99.11
	66	27.48	101.34	2	101.60
	67	27.48	101.34	3	101.60
	68	27.08	101.74	6	101.60
	69	26.08	102.74	9	102.12
	70	21.81	107.01	7	107.13
	71	21.81	107.01	5	107.65
cis-syn-cis-Perhydrophenanthrene	72	41.68	87.14	12, 13	87.45
	73	38.06	90.76	11, 14	90.79
	74	32.42	96.40	1, 8	96.71
	75	29.95	98.87	4, 5	98.54
	76	28.38	100.44	9, 10	100.65
	77	26.22	102.60	3, 6	103.43
	78	24.61	104.21	2, 7	104.37

[a] The perhydrophenanthrenes were run as neat liquids, while perhydroanthracenes were dissolved in CS_2. About 10% TMS was added as an internal standard. [b] In parts per million. [c] The chemical shifts of this compound have been determined with less precision (± 0.5 ppm) than those of other compounds in this series because the resonance lines are substantially broadened by kinetic processes at the ambient temperature of the spectrometer and the concentration was very low. [d] It was necessary to add a small amount of CS_2 to this compound, because the volume available was inadequate for carbon-13 spectroscopic work. [e] The determination of calculated values by use of the parameters of Table V may be profitably illustrated by an example. Consider C-9,10 of trans-decalin (item 1); there are three carbons α to C-9 and four carbons β to C-9. It is a tertiary carbon and is involved in four V_g and four V_t interactions. Hence the predicted value is given by $131.31 + 3\alpha + 4\beta + T + 4V_g + 4V_t = 85.59$ ppm. This differs by 0.01 ppm from the tabulated value as a result of computer processing involving more significant figures.

available mixture (see Table III). The upper chromatogram of Figure 1 is that of the commercial PHP from which four isomers were obtained with 70 to 90% purity. Isomers labeled a and d were found to have seven lines in their carbon-13 spectra, while the spectra of isomers b and c had 14 lines each.

The lower chromatogram of Figure 1 is that of products which result from hydrogenation of 1,2,3,4,-5,6,7,8-octahydrophenanthrene using Ru/C as catalyst; as discussed in the Experimental Section, the principal product of hydrogenation using Ru/C catalyst should be the CSC isomer. The retention time of the hydrogenation product corresponds to that of isomer d of the upper chromatogram, and the carbon-13 spectra of these two fractions proved to be identical.

The proton spectrum of this compound is similar to that of cis-decalin, which indicates rapid conformational averaging. It is thus concluded that isomer d of Figure 1 is cis-syn-cis-perhydrophenanthrene.

The spectra of isomers b and c of Figure 1, having 14 lines each, must result from the two, unsymmetric TSC- and TAC-PHP isomerides. Further, characterization of these two compounds was made solely on the basis of comparison of their cmr spectra with those predicted by use of previously published parameters[1] and the chemical shift factor analysis given in a later section.

The proton spectrum of isomer a is a broad band similar to that of trans-decalin, indicating it has an all-trans, nonaveraging conformation. On that basis,
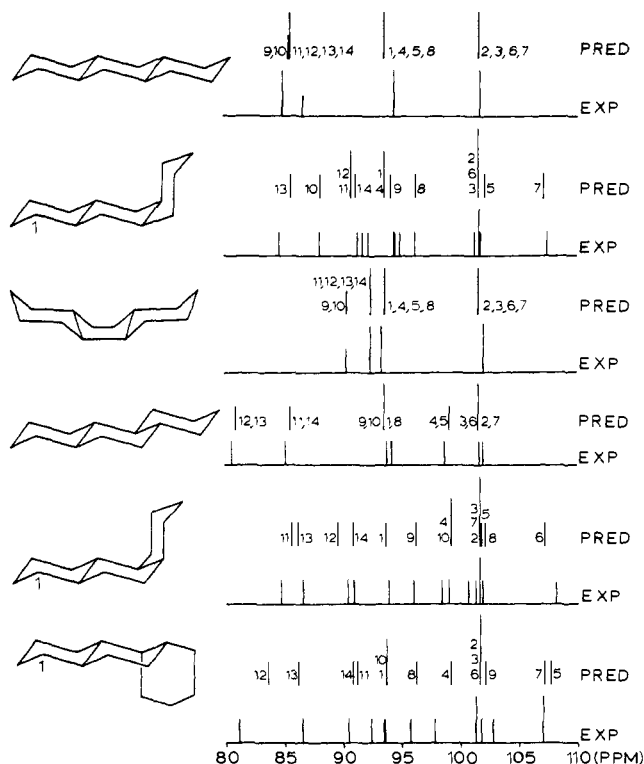
Figure 2. A comparison of predicted and experimental spectra for the compounds of Table I which were available for study. The parameters of Table V were used to calculate the values listed in Table IV.

Figure 3. A comparison of predicted and experimental spectra for the compounds of Table II which were available for study; cf. Figure 2.

Discussion

(A) Parametric Factor Analysis of the Carbon-13 Chemical Shifts of the Paraffin Polycyclics. After initial assignments of the chemical shifts in Table IV were made using parameters derived from the methyldecalins,[1] a stepwise, multiple, linear regression analysis was executed on the carbon-13 data for the purpose of refining the assignments and calculated spectra. Added to the data were the chemical shifts of methane, ethane, propane, and isobutane.[39] The regression analysis was repeated several times, changing assignments as necessary and eliminating less significant parameters, until self-consistent values were obtained. The factor analysis results are presented in Table V.

The parametric values of Table V are quite consistent with those obtained for the methyldecalins in Table IV of ref 1. There is somewhat less variance between predicted and experimental spectra in the present case, because the wide range of chemical shifts resulting from γ-gauche interactions with methyls are not encountered.[18] Also no quaternary carbons occur in these molecules, so the Q parameter of ref 1 was not present. The $\beta_g\gamma_t$ parameter, because of the uncertainty of its nature and significance, has not been used in this study. A vicinal trans (V_t) parameter was added, together with three parameters used to characterize molecular features not found in the methyldecalins, i.e., skew pentane (δ_{sp}), γ prow (γ_p), and vicinal eclipsed (V_e) interactions.

Since smaller parameters were eliminated from the regression analysis, the predicted spectra exhibit more accidentally degenerate resonance lines than do the experimental ones; hence, it is not possible to make all assignments unambiguously by comparing predicted and experimental spectra; however, it is relatively simple to distinguish between the various isomers of a related series. As previously stated, the TAC and TSC isomers of perhydrophenanthrene were identified on that basis. Carbon-13 spectroscopic techniques provide perhaps the simplest possible method for identifying compounds of the class treated herein, which otherwise would have to be synthesized individually by routes of known stereospecificity.

(B) The Effects of Skew Pentane Interactions and

isomer a might be *trans-anti-trans*-PHP (all-chair) or *trans-syn-trans*-PHP (center boat). However, Weitkamp[38] observed that in a series of geometrically isomeric hydrocarbons the gas chromatographic retention times, with few exceptions, followed the same order as the relative steric interaction energies; i.e., the lowest energy isomer came off the column first, etc. Since TAT-PHP is much lower in steric energy than is the TST isomeride, it may be argued that isomer a is the all-chair trans-anti-trans compound. This assertion is corroborated by the close agreement found between the experimental and predicted spectra of this isomer (cf. Table IV).

(B) Assignment of the Carbon Resonance Lines. The decalin resonances have been assigned previously.[1] Items 8, 26, 29, and 34 of Table IV may be incontrovertibly assigned on the basis of intensity; they result from center ring methylenes in the symmetric PHA compounds. All other assignments were made parametrically. Initial designations were made using the parameters of ref 1. The assignments were made with a high degree of confidence except for a number of ambiguities which occurred in the less symmetric compounds, which have many more lines to assign. A new factor analysis was undertaken, applying the technique suggested in ref 1 of deleting unnecessary parameters while adding those needed to characterize interactions which had not been previously encountered. The best calculated values are included in Table IV. The success of the fit is seen in Figures 2 and 3, where the experimental and calculated spectra are compared. The assignments which cannot be made with a reasonable level of confidence are bracketed in Table IV.
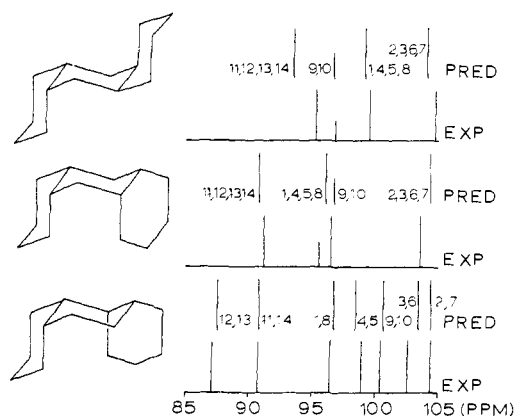
(39) See D. M. Grant and E. G. Paul, J. Amer. Chem. Soc., **86**, 2984 (1964), for these data.

Table V. Factor Analysis Results for the Carbon-13 Chemical Shifts of the Perhydroanthracenes and Perhydrophenanthrenes[a]

Symbol	Parameter	Value[b]	No. of occurrences	F value
α		-9.43 ± 0.32	77	842.8
β		-8.81 ± 0.26	74	1141.5
T		1.13 ± 0.73	20	2.4
V_g		3.38 ± 0.17	72	984.5
V_t		0.79 ± 0.20	48	89.9
γ_{HH}		5.53 ± 0.23	25	586.4
γ_{2HH}		3.01 ± 0.33	10	82.6
δ_{sp}		3.65 ± 0.57^c	4	41.3
γ_p		11.01 ± 2.21^c	1	24.9
V_e		8.19 ± 0.80^c	2	104.7

[a] Included in the analysis were the chemical shifts of methane, ethane, propane, and isobutane. [b] In ppm. The analysis was characterized by the following parameters: constant term = 131.31 ppm, standard error of the estimate = 0.71 ppm, correlation coefficient = 0.9969. [c] This parameter may not be characterized as well as the error limits indicate because of its limited occurrence in the data set.

Center Boat Configurations. In the case of idealized geometry, the skew pentane configuration involves a very close approach of hydrogens. Analogous to γ_{HH} interactions, it might be anticipated that very large upfield ^{13}C chemical shifts would be associated with the skew pentane geometry. However, the regression analysis resulted in a value of only $+3.65$ ppm for this parameter. Although this value is probably somewhat inaccurate due to the small number of occurrences of this geometric feature, the indication is that the skew pentane interaction has not produced the large, upfield chemical shifts anticipated.

We suggest that the surprisingly small value determined for δ_{sp} may be attributable to several factors. Manipulation of models indicates that relaxation of the high energy steric interactions by molecular distortion is possible, consistent with the geometry found for CSC-PHA in the solid state as determined by electron diffraction.[17] Extensive molecular distortion will probably reduce significantly the upfield chemical shifts associated with the δ_{sp} conformation and also those due to γ-gauche interactions, in accordance with the results presented in ref 18 for the methylcyclohexanes and other compounds. Moreover, the use of the full

γ_{HH} parameters of Table V in calculating the chemical shifts of carbons involved in δ_{sp} interactions will overestimate the true upfield shift resulting from the γ_{HH} configuration, and the regression analysis must then produce a value for δ_{sp} which is too small.

Also it has been proposed[40] that the γ-gauche chemical shift involves a cosine dependence of the $C-H\cdots H$ angle of the interacting moieties. If that cosine relationship is applicable in the δ_{sp} case, it is possible that molecular distortion has produced unfavorable angles near $\pi/2$, causing the chemical shift associated with δ_{sp} to be small. Complete characterization of the δ_{sp} parameter will require further investigation.

Although the center ring of TAT-PHA exists in a boat form, the presence of two trans ring junctions limits the flexibility of the system. If the two outside rings exist primarily as chair forms, which is very probable, the center boat cannot skew but is limited to interconversion between two "true boat" orientations of equal energy. The contention that conformational averaging occurs is confirmed by the fact that the carbon-13 spectrum of this compound has four lines instead of seven.

The fact that only two conformations are important is advantageous, because it allows a calculation to be made of the chemical shift parameters associated with the conformational features peculiar to boat forms. A comparison of the chemical shifts of the carbons in the center ring with those of the analogous carbons of the TST compound, which has a center chair form, reveals that the carbons of the center boat have resonance signals which are considerably upfield from those of the all-chair compound, while the remaining two lines compare rather well. The center-ring carbons are involved in two important interactions which have not been characterized previously. Both result from an "eclipsed n-butane" type of conformation. One may be described by a vicinal eclipsed (V_e) parameter, while the second results from a rather close approach of hydrogens on 1,4-carbons and is termed a γ_p (γ prow) interaction.

The linear regression produced values of $+11.0$ ppm for γ_p and $+8.2$ ppm for V_e. These results are of necessity approximate because of the limited amount of data available for structures of this type, but the rough parameters should have some utility in predicting the carbon-13 chemical shifts of other structures having locked boat conformations.

(C) The Conformation Ground States of the Paraffin Polycyclics. In previous work[1] it was noted that close agreement between predicted and experimental cmr spectra was highly indicative that the conformational ground states of cis- and trans-decalin are the two-chair forms. The same conclusion must obtain in general for the tricyclic compounds as for the decalins. The proton spectrum of the perhydroanthracene containing a cis and a trans ring junction (CT) indicates some proton averaging, and the same seems to be true for TAC- and TSC-PHP (on the basis of the proton spectra of somewhat impure compounds). The predicted and experimental spectra for the latter three compounds compare as well as those of the other compounds studied, and thus any of the possible higher energy

(40) (a) D. M. Grant and B. V. Cheney, J. Amer. Chem. Soc., 89, 5315 (1967); (b) D. K. Dalling and D. M. Grant, ibid., 89, 6612 (1967).

forms cannot constitute significant amounts of the conformational population. The high energy all-chair ground state of CSC-PHP makes the possibility that boat forms contribute to the conformational population more probable, but again the agreement between calculated and experimental spectra indicates such contributions are probably not significant.

(D) Carbon-13 Magnetic Resonance as a Tool in Conformation Analysis and Compound Identification. It must be concluded from the results presented here that carbon-13 spectroscopy is a powerful and relatively simple tool for identification of uncharacterized paraffin hydrocarbon isomers and for analyzing the conformational properties of molecular systems. Although much remains to be done, an accumulating library of chemical shift and parametric values and relevant ex-

perience will provide an increasingly useful technique in the field of conformational and configurational analysis and characterization of complex molecules.[41]

(41) It has come to our attention that between the time at which this work was completed (D. K. Dalling, Ph.D. Thesis, University of Utah, 1969) and that at which it was accepted for publication, other workers (N. L. Allinger, B. J. Gorden, I. J. Tyminski, and M. T. Wuesthoff, *J. Org. Chem.*, **36**, 739 (1971)) have characterized the four PHP isomers treated in this work by synthetic organic methods. Their results are in agreement with those presented herein, and upon comparing the requisite labor involved the advantages of using cmr spectroscopic techniques as compared with traditional chemical methods are readily apparent.

¹³C Relaxation Studies on the Manganese(II)–Adenosine 5′-Triphosphate Complex in Solution

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Abstract: The nature of binding between manganese ions and adenosine 5′-triphosphate (ATP) was studied using natural abundance Fourier transform ¹³C nmr techniques. Relaxation times for the ¹³C nuclei in the presence of Mn(II) ions were determined together with their temperature dependence. The adenine base carbons show specific effects while the ribose carbons remain unaffected. The transverse relaxation time data indicate a consecutive binding mechanism, namely that the metal ion binds first to the phosphate groups of ATP and then, in the second step, the metal interacts with the N(7) nitrogen. The equations for this exchange process are derived. The rate constant for the interaction of the metal ion with the adenine base is $2.7 \times 10^7 \ \text{sec}^{-1}$ at 27°. The distances between the metal ion and the carbon and proton nuclei of the adenine base of ATP were evaluated on the basis of the longitudinal relaxation time studies. The results indicate that the metal binds directly to the N(7) nitrogen.

The interaction between metal ions with nucleotides has been studied extensively for several years.[2,3] The search has been for the elusive backbound phosphate–metal ion–ring interaction that was originally proposed by Szent-Györgyi in 1957.[4] This hypothesis was to explain why in many enzymatic reactions which require adenosine 5′-triphosphate (ATP) the actual enzyme substrate was the complex Mg–ATP.

Nmr has shown that the divalent metal ions Zn(II), Cu(II), Ni(II), Co(II), and Mn(II) all interact with the adenine ring of ATP[5–7] as well as with the phosphate groups. The nature of this ring interaction has only been established in the case of Ni(II) and Co(II). With these two metal ions it has been demonstrated[8,9] that

there is a bridging water molecule between the metal ion and the adenine ring and that this "trapped" water molecule probably forms a hydrogen bond with the N(7) nitrogen of the base. The metal ion Mn(II) substitutes for Mg(II) *in vitro* in most enzymatic reactions that require Mg–ATP as a substrate. The nature of the paramagnetic ion–Mn–ring interaction of ATP is therefore important as the study may shed light on the diamagnetic metal ion Mg–ATP complex.

Recently, natural abundance ¹³C nmr transverse relaxation times due to the presence of paramagnetic metal ions have been measured[10] and these measurements indicate the potential of using the ¹³C nmr probe for studying nucleotide–metal ion systems. In this paper we wish to report our studies on ¹³C longitudinal and transverse relaxation time measurements on the Mn–ATP system. The results yield information about the nature of the metal ion binding site on the adenine ring. In addition, the most consistent interpretation of our data indicates that the following consecutive binding mechanism (eq 1) occurs in solution, where L

$$M + L \rightleftharpoons ML_P \rightleftharpoons ML_{P+R} \qquad (1)$$
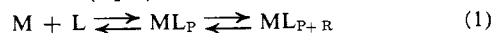
(1) Postdoctorate Fellow, 1973–1974.

(2) R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, **71**, 439 (1971), and references therein.

(3) C. M. Frey, J. L. Banyasz, and J. E. Stuehr, *J. Amer. Chem. Soc.*, **94**, 9198 (1972), and references therein.

(4) A. G. Szent-Györgyi, "Bioenergetics," Academic Press, New York, N. Y., 1957, p 64.

(5) M. Cohn and T. R. Hughes, Jr., *J. Biol. Chem.*, **237**, 176 (1962).

(6) H. Sternlicht, R. G. Shulman, and E. W. Anderson, *J. Chem. Phys.*, **43**, 3123 (1965).

(7) H. Sternlicht, R. G. Shulman, and E. W. Anderson, *J. Chem. Phys.*, **43**, 3133 (1965).

(8) T. A. Glassman, C. Cooper, L. W. Harrison, and T. J. Swift, *Biochemistry*, **10**, 843 (1971).

(9) G. P. P. Kuntz, T. A. Glassman, C. Cooper, and T. J. Swift, *Biochemistry*, **11**, 538 (1972).

(10) G. Kotowycz and K. Hayamizu, *Biochemistry*, **12**, 517 (1973).