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ANNUAL REPORT

CARBON-13 MAGNETIC RESONANCE OF HYDROCARBONS

by

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DISCLAIMER

I. Introduction

The first year's work on this project has been concentrated on three paths: 1) synthesis of hydroaromatic species that represent important models to be used in establishing correlative chemical shift paramaters in this class of compounds; 2) spectral interpretation of the resulting species in both the liquid and solid state coupled with force field calculations which provide information on conformational averaging and bond distortion; 3) relaxation measurements on a number of condensed polynuclear aromatic, alkyl- and hydroaromatic species at 25 and 75 MHz in order to establish the relative contributions of dipole-dipole spin rotation, and chemical shift anisotropy relaxation mechanisms. Results of work in these three areas are treated below.

II. Organic Synthesis

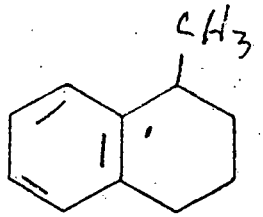
Our interests in studying hydroaromatic compounds such as tetralin, 1,2,3,4-tetrahydrophenanthrene, 9,10-dihydroanthracene, etc. and their methyl derivatives necessitates a considerable synthetic effort since most of the compounds of interest are not available commercially and few are available from non-commercial sources. Hence, the desired methyl derivatives were synthesized by Professor Horton in our laboratory. A sketch is given of the synthetic procedures employed, most of which exist in the literature but these procedures often necessitate modification in order to obtain sufficient purity and yield to be of value. While this portion of the effort has, in some cases, been repetitive of existing organic synthetic procedures, the products are indispensible to the program. Furthermore, it can be argued that the investment in resources required are quite modest (25% effort by Horton plus $1,500-2000 in supplies and chemicals).

A. Tetralins

The following tetralins have been prepared:

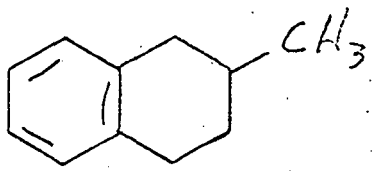
1-Methyltetralin

4-methyl-1-tetralone ⟶ (clemmensen reduction)



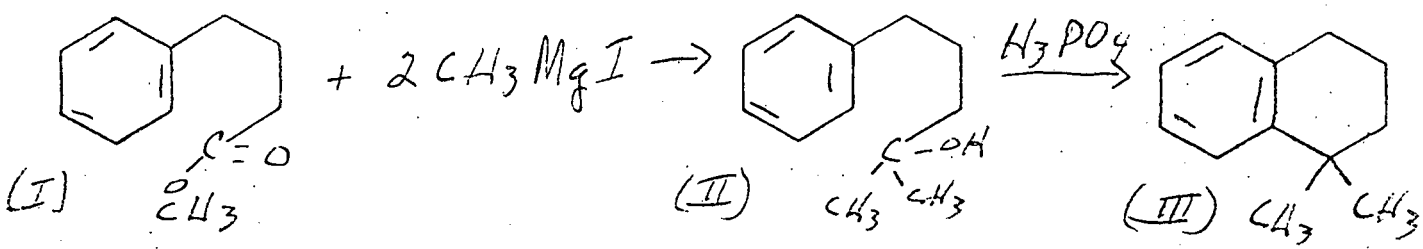
2-Methyltetralin

2-methyl-1-tetralone ⟶ (Clemmensen reduction)



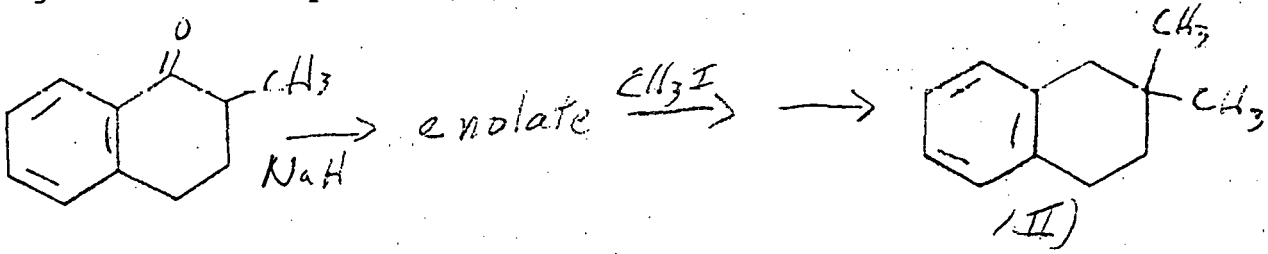
1,1-Dimethyltetralin

Commercial 4-phenylbutyric acid was converted to the methyl ester (I) and this, treated with excess methylmagnesium iodide, gave 2-methyl-5-phenyl-2-pentonal (II). Cyclization with phosphoric acid gave the product (III) in 87% yield.



2,2-Dimethyltetralin

2-methyl-1-tetralone (I) was converted to the enolate with sodium hydride and this was nmethylated with methyl iodide. Clemmensen reduction gave the deisred product (II)



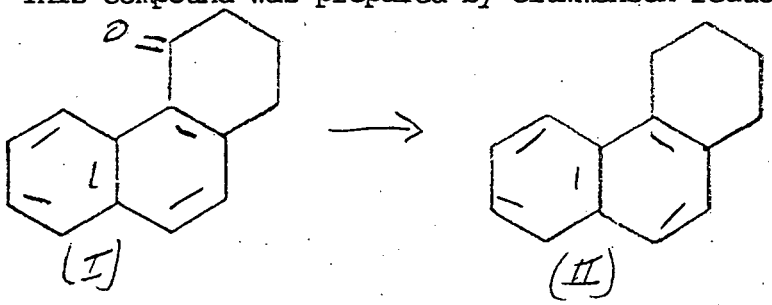
In addition work is in progress on the synthesis of the following dimethyltetralins: 1,2 (cis and trans), 1,3 (cis and trans), 1,4 (cis and trans) and 2,3 (cis and trans).

B. Tetrahydrophenanthrenes

To date two methyl derivatives of 1,2,3,4-tetrahydrophenanthrene have been prepared.

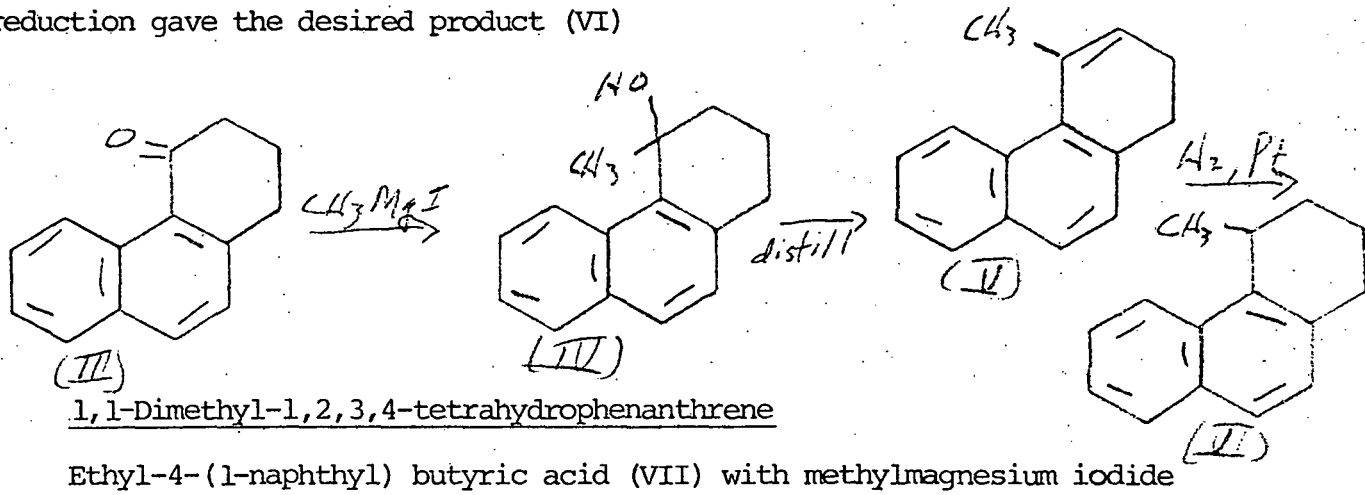
1,2,3,4-tetrahydrophenanthrene

This compound was prepared by Clummensen reduction of the ketone (I)



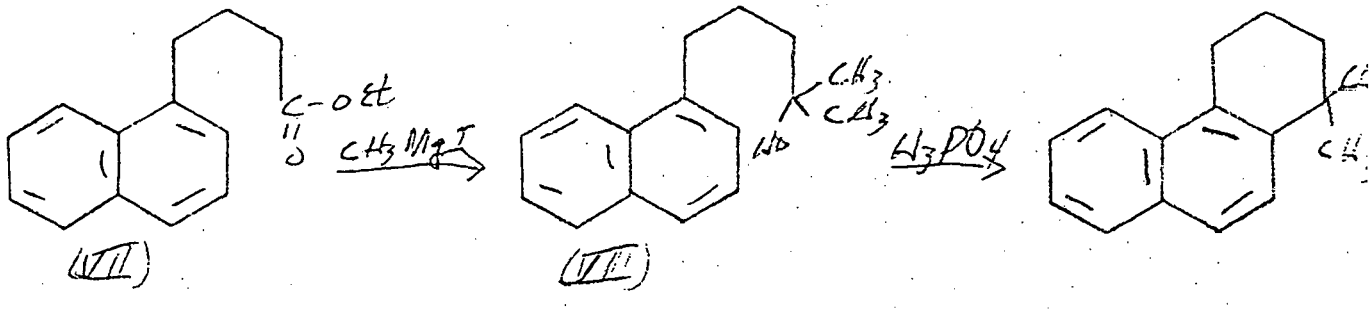
4-methyl-1,2,3,4-tetrahydrophenanthrene

The ketone, (III) prepared by Howorth's procedure gave (IV) with methylmagnesium iodide. Following distillation to obtain (V), catalytic reduction gave the desired product (VI)



1,1-Dimethyl-1,2,3,4-tetrahydrophenanthrene

Ethyl-4-(1-naphthyl) butyric acid (VII) with methylmagnesium iodide gave 2-methyl-5-(1-naphthyl)-2-pentonal (CIII). Ring closure with phosphoric acid gave the desired product (IX)



C. 9,10-Dihydroanthracenes

All six 9,10-methyl derivatives of 9,10-dihydroanthracene have been prepared as follows:

9-methyl-9,10-dihydroanthracene

The 9-methyl derivative of 9,10-dihydroanthracene was prepared from commercial 9-methylanthracene as described by H. Wieland, (Ber., 45, 492 (1912)), and was crystallized from methanol. Thin layer chromatograping using benzene gave a single spot.

9,9-Dimethyl-9,10-dihydroanthracene

9,9-dimethyl-9,10-dihydroanthracene was prepared as reported (J. Med. Chem., 7, 88 (1964)) except that the cyclization of 2-(2-benzylphenyl)-2-propanol (obtained as an oil) was carried out in polyphosphoric acid (PPA). The oil, from methyl 0-benzylbenzoate and methyl lithium, was combined with PPA and heated for two hours in a boiling water bath. After cooling and addition of ice, greenish oily crystals were obtained which, when crystallized from ice cold pentane gave pure product as determined by ^{13}C NMR.

cis-9,10-Dimethyl-9,10-dihydroanthracene

The cis- and trans- isomeric pairs are obtained by sodium-absolute ethanol reduction of 9,10-dimethylanthracene. The cis isomer was obtained by refluxing the isomeric mixture for 24 hours under nitrogen in 50/50 (vol/vol) of 45% KOH and methanol.

trans-9,10-Dimethyl-9,10-dihydroanthracene

The isomeric mixture of cis- and trans- 9,10-dimethyl-9,10-dihydro-anthracene, obtained from 9,10-dimethylanthracene as previously described, was separated into the cis- and trans- components on a Varian Aerograph GLC using 5/8" x 20' column packed with SP-2100.

9,9,10-Trimethyl-9,10-dihydroanthracene

10,10-Dimethylanthrone was reacted with methyl lithium to produce 9,10,10-trimethylanthranol (G. Hafelinger and A. Streitwieser, Jr., Chem. Ber., 101, 657 (1968)). The latter was catalytically reduced to 9,9,10-

trimethyl-9,10-dihydroanthracene as described by Hafelinger and Streitwieser.

9,9,10,10-Tetramethyl-9,10-dihydroanthracene

The tetramethyl compound was prepared as reported by Granoth (I. Granoth, Y. Segall, H. Leader, and R. Alkabets, J. Org. Chem., 41, 3682 (1976).). The sample was pure as shown by ^{1}H and ^{13}C NMR.

III. Relaxation Measurements

Several aromatic and hydroaromatic compounds (napthalene, phenanthrene, pyrene, acenaphthane, tetralen, 1,2,3,4,5,6,7,8-octahydrophenanthrene, sym-hexahydropyrene, phenyloctane, and xanthane) have been studied at 25.1 and 75.3 MHz, and 33° C. The ^{13}C spin-lattice relaxation measurements, T_1, were measured at the two frequencies along with determination of the nuclear Overhauser effect (NOE). Estimations of the various relaxation contributions have been made for the dipolar, chemical shift anisotropy, and the spin rotation mechanisms. T_1 and NOE values of representative compounds are given in Tables 1-3. For the carbon-13 nuclei with attached protons, the NOE measurements approached the maximum value of 3.0 (dipolar relaxation domination), and the values of T_1 are in the range of 1-10 seconds. These values were relatively unaffected by field variations. In contrast, the values of the NOE parameter for non-protonated carbons varied from 1.1 to 2.7. Generally, the value of NOE in such cases was about 2 at 25.1 MHz and 1.5 at 75.3 MHz. For these non-protonated carbons, the relative contributions of T_1^D, T_1^{CSA}, and T_1^{SR} are approximately equal and relatively large at 25.1 MHz (greater than 100 seconds and as large as 300-1000 seconds). At 75.3 MHz, the T_1^{CSA} contribution is dominant in these non-protonated carbons; the chemical shift anisotropy contribution to T_1 is in the range of 30-90 seconds at this field strength and the data on pyrene is particularly striking. Chemical shift anisotropies similar to those measured in simple aromatic compounds (200 to 250 ppm) are adequate to account for the observed values of T_1^{CSA}.

IV. ^{13}C Chemical Shift Studies

Work has been going forward on three series of compounds, as described below:

A) Methylated 1,2,3,4-Tetrahydronaphthalenes (tetralins). This set of compounds is not yet complete. ^{13}C data has been collected only for the parent, 1-methyl, 1,1-dimethyl, 2-methyl, and 2,2-dimethyl-tetralins. Preliminary analysis indicated that the CH_3 of the 1-methyl compound must spend a major portion of its time in the pseudoaxial conformation, while the 1,1-dimethyl averages between conformers of equal energy.

The spectra from the 2-methyl and 2,2-dimethyltetralins indicate somewhat reduced steric interactions, presumably as a result of the flattened nature of the aliphatic ring.

B) Methylated 1,2,3,4-Tetrahydrophenanthrenes. Some difficulty has been experienced in the synthesis of this series of compounds, so only the parent, 1-methyl, 4-methyl, and 1,1-dimethyl species have become available for study. Very few conclusions can be obtained from the data set to date. There is an indication that the 4-methyl CH_3 is strongly pseudo-axial compared to the 1-methyl species. Further conclusions must await the availability of additional compounds in the series.

C) Methylated 9,10-dihydroanthracenes. ^{13}C and ^{1}H NMR data have been acquired for the parent and the six possible 9,10-dihydroanthracenes having methyls at C-9 and C-10. These are the 9-methyl, 9,9-dimethyl, cis-9,10-dimethyl, trans-9,10-dimethyl, 9,9,10-trimethyl, and 9,9,10,10-tetra-methyl-9,10-dihydroanthracenes. Only the parent compound was available commercially; the other materials were synthesized in our laboratory by Dr. W. J. Horton as previously described.

By analysis of coupling patterns and through selective decoupling experiments all assignments of ^{13}C resonance lines to specific carbon positions have been made, with the exception of C-2,7 and C-3,6 of the 9-methyl species. Spectra for the 9-methyl, cis-9,10-dimethyl, and 9,9,10-trimethyl examples indicate that one conformation is predominant with the methyls preferring the pseudoaxial orientation. The other compounds are compelled by symmetry to equilibrate between two conformers of equal energy by inverting the center ring boat. Preliminary analysis of the data (in conjunction with spectra taken in the solid state) indicates that the three compounds which appear to exhibit a single dominant conformer in fact have significant contributions from the higher energy (equ torial) forms. The results of the analysis of the liquid and solid spectra for the methyl group in these compounds are given in Table 4. Representative spectra correlating the data in the solid and liquid are given in Figures 1-3. There are also implications from the chemical shift data that those compounds having geminal methyls undergo a considerable flattening through opening up of the angle between the planes defined by the two aromatic rings. Preliminary force field calculations substantiate these implications. The out of plane angle of C-9,10 in the parent species has been measured by X-ray diffraction as 31^{o} while force field calculations place the angle at 28^{o}. The calculations of the methyl derivatives indicate that flattening of the boat ring does occur with a predicted value of $12\text{-}13^{o}$ for the tetramethyl derivative for which calculations have not yet been completed. The equatorial methyl interacts with the proximate aromatic ring protons in such a way as to give a double minima of approximately 12^{o} on either side of the planar structure as the ring inverts. The full implications of these potential surfaces have not been fully explored as of yet.

The interpretation of the solid data for the dihydroanthracenes is not complete due to an apparent break in the symmetry of the solid as exhibited in the extra lines noted in the aromatic region (see Figure 4). One possible explanation of these data is bond distortion but crystal packing in the unit cell cannot be ruled out at this time. An important conclusion of the chemical shift data, however, is the fact that simple correlative relationship are non-existant in the liquid state because of the low barrier to conformational averaging in these compounds. Comparison of liquid and solid spectra enable one to better define the contributions from the various conformers and estimate the energy differences.

V. Publications

The results of work supported by this contract have been presented as follows:

1. The Effects of T_1 and NOE Considerations in Quantitative Applications of Carbon-13 NMR to the Analysis of Complex Hydrocarbon Mixtures, T. D. Alger, R. J. Pugmire, W. D. Hamill, Jr., and D. M. Grant, paper presented in the Fuel Chemistry Section of the American Chemical Society Meeting, April 1-6, 1979, Honolulu, Hawaii.
2. CP/MAS Studies of Methylated Species: Changes of Symmetry in the Solid State as Compared to the Liquid State, R. J. Pugmire, K. W. Zilm, D. K. Dalling, and D. M. Grant, paper to be presented at the 21st Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, July 30-August 1, 1979.
3. Carbon-13 Spin Lattice Relaxation in Condensed Aromatic Compounds, T. D. Alger, D. W. Hamill, Jr., R. J. Pugmire, D. M. Grant, G. D. Silcox and M. Solum, preprint attached.

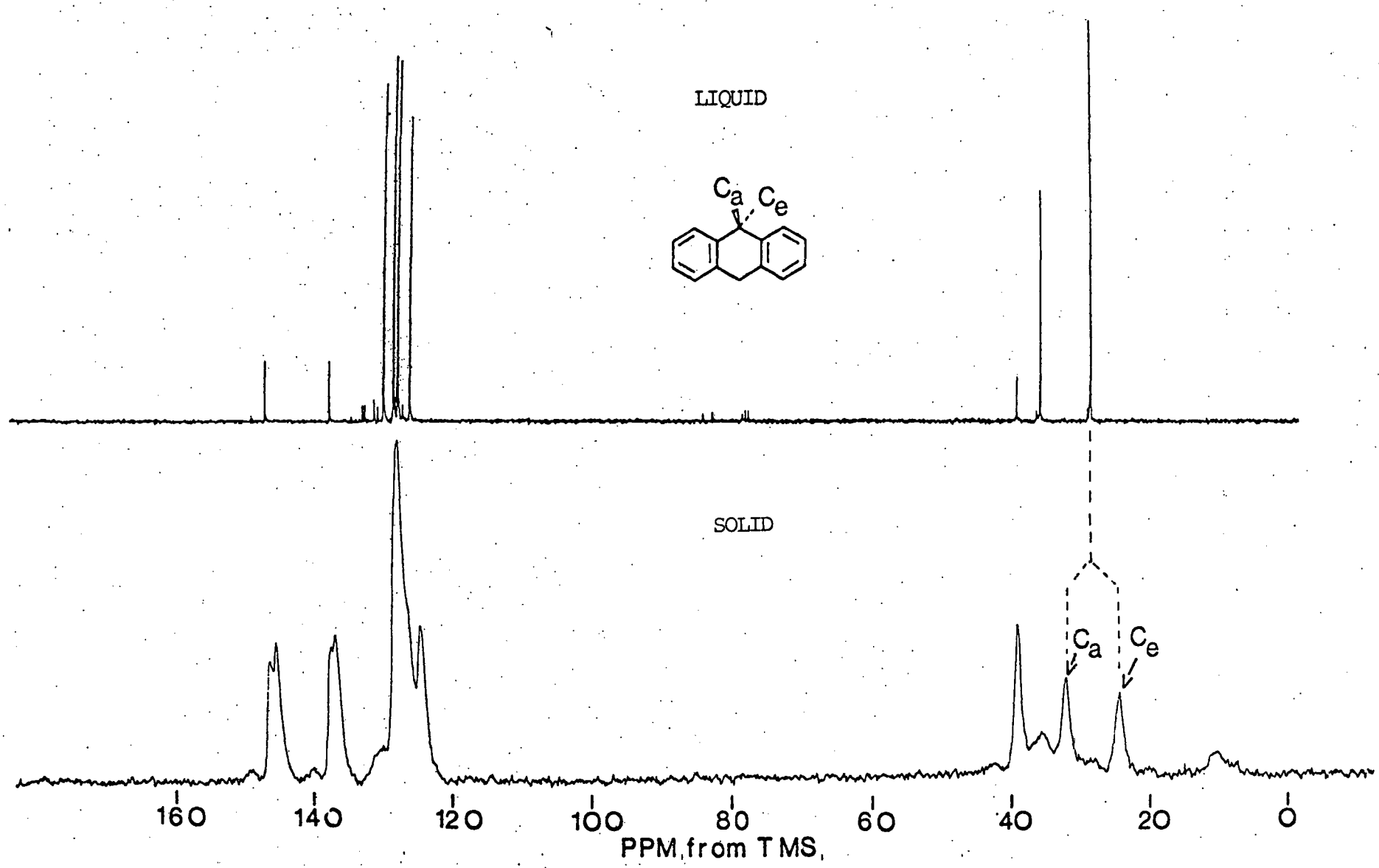


Figure 1. Comparison of liquid and solid spectra of 9,9-dimethyl9,10-dihydroanthracene exhibiting effects of conformational averaging in the liquid state

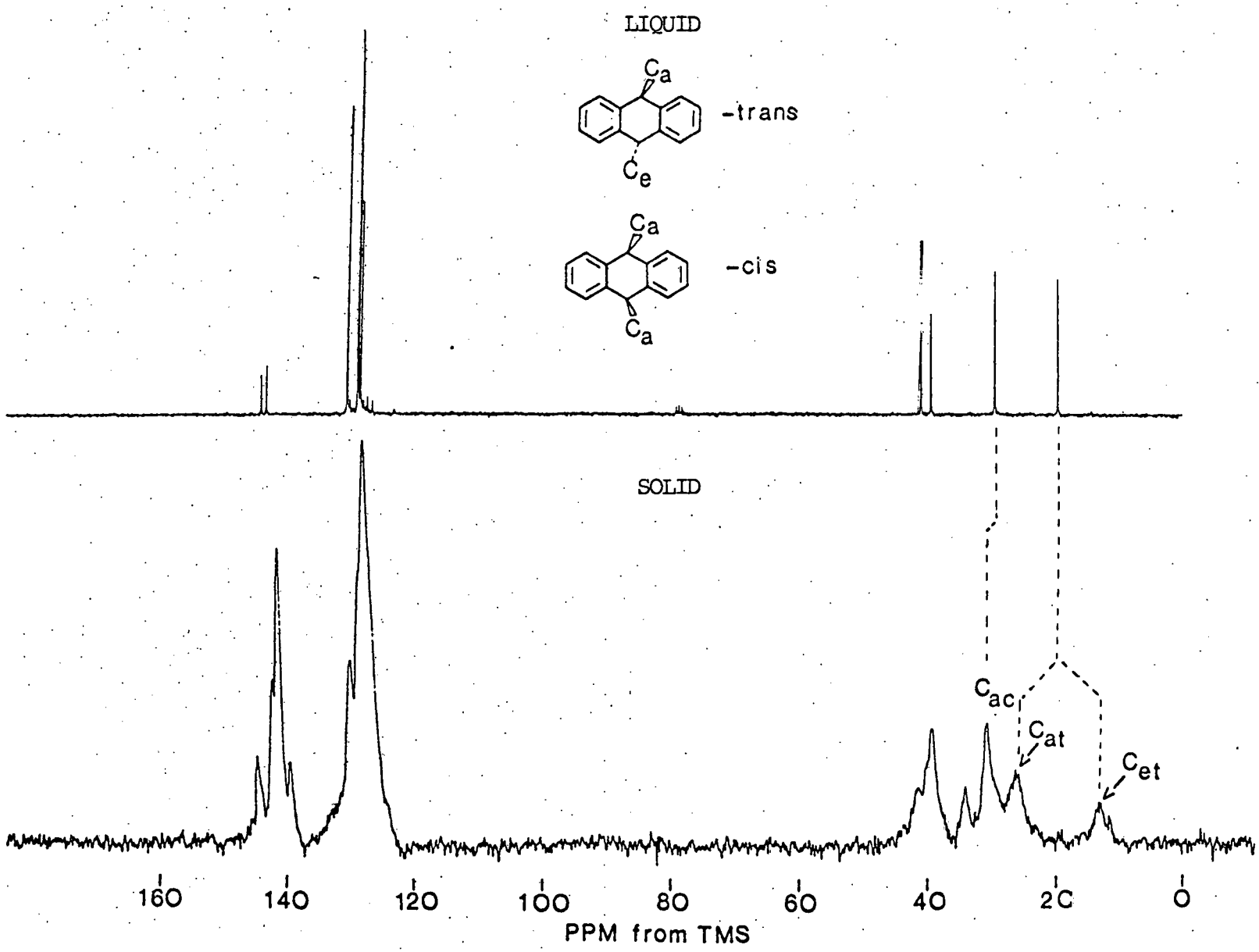


Figure 2. Liquid and solid spectra of a mixture of cis- and trans- 9,10-dimethyl-9,10-dihydroanthracene. Note that the equatorial and axial methyls of the trans- isomer are resolved as are the methyls in the cis- isomer

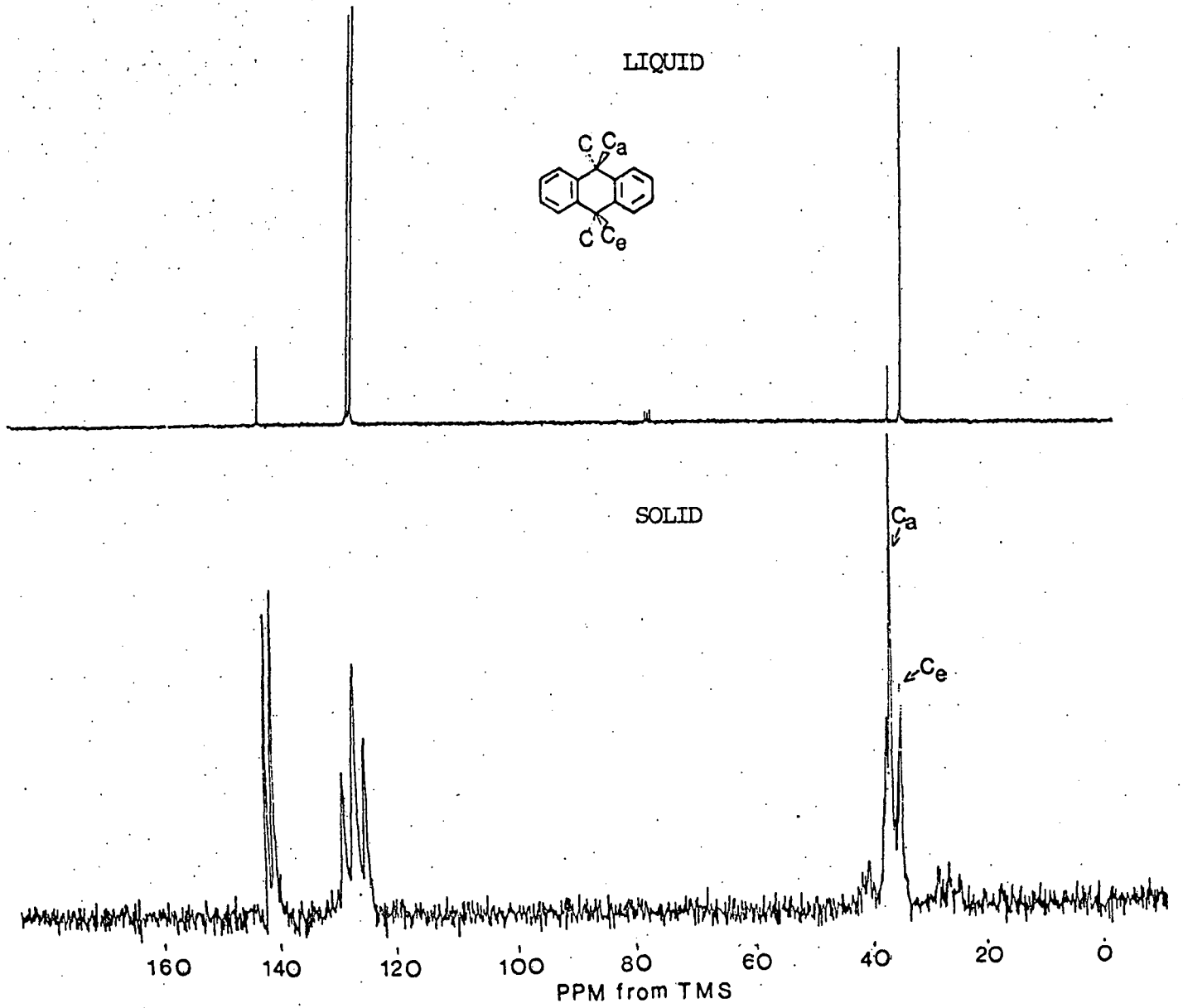
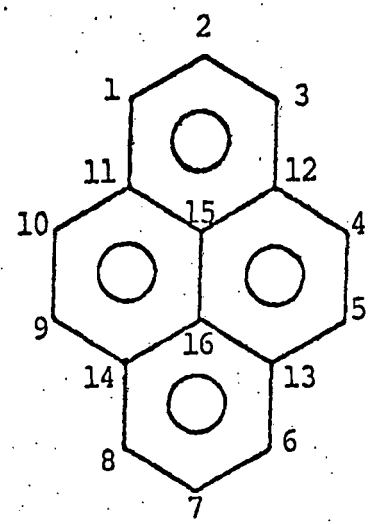


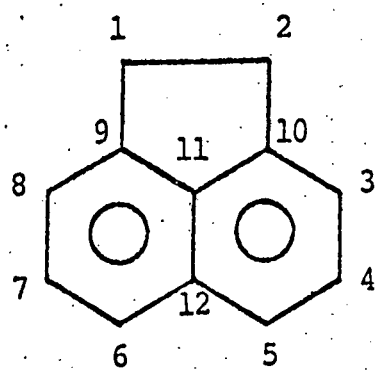
Figure 3. Liquid and solid spectra of 9,9,10,10-tetramethyl-9,10-dihydroanthracene. Note the separation of the equatorial and axial methyl groups as well as the additional lines observed in the aromatic region

TABLE 1



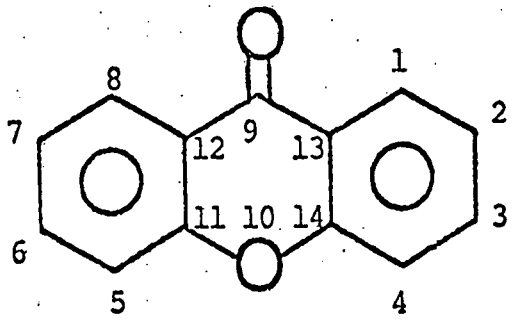
	25 MHz				75 MHz			
	T_1	T_1^D	T_1^O	T_1^{CSA}	T_1	T_1^D	T_1^O	T_1^{CSA}
,6,8	6.0	6.0	-	-	4.9	4.9	-	-
	5.2	5.2	-	-	4.5	4.5	-	-
,9,10	5.4	5.4	-	-	5.4	5.4	-	-
12,13,14	129	215	322	261	26	104	35	29
16	228	760	326	331	35	538	37	37

TABLE 2



	25 MHz				75 MHz			
	T_1	T_1^D	T_1^O	T_1^{CSA}	T_1	T_1^D	T_1^O	T_1^{CSA}
1,2	3.1	3.1	00	-	3.0	3.1	93	-
3,8	5.6	6.2	58	-	6.0	6.5	78	-
4,7	5.6	6.2	58	-	6.6	7.1	94	-
5,6	6.4	7.1	65	-	6.5	7.0	91	-
9,10	87	134	249	712	44	88	88	79
11	208	520	348	707	62	413	73	79
12	128	233	284	432	58	127	54	48

TABLE 3



	25 MHz				75 MHz			
	T_1	T_1^D	T_1^O	T_1^{CSA}	T_1	T_1^D	T_1^O	T_1^{CSA}
1,8	3.0	3.0	-	-	2.7	3.1	21	-
3,6	4.0	4.1	164	-	3.9	4.8	21	-
2,7	3.8	3.8	-	-	2.8	3.1	29	-
4,5	2.9	3.1	45	-	3.8	4.4	28	-
9	116	314	182	354	32	200	38	39
11,14	106	168	286	602	44	138	65	67
12,13	109	145	435	613	45	161	62	68

TABLE 4

CONFORMATIONAL AVERAGING IN METHYL 9,10-DIHYDROANTHRACENES

SOLID				LIQUID
C_A	C_E	δ	Ave	
26.5	13.4	13.1	19.9	18.8
32.8	25.1	7.7	28.9	28.8
36.9	35.3	1.6	36.1	35.1

LIQUID	SOLID
23.5	C_A 26.4
	C_A 26.5
	C_E 13.4

$$\% \text{ Axial} = \frac{23.5 - 13.4}{26.5 - 13.4} \times 100 = 77\ \%$$

LIQUID	SOLID
28.6	C_A 31.0
	C_A = 26.5
	C_E = 13.4

$$\% \text{ Diaxial} = \frac{28.6 - 13.4}{31.0 - 13.4} \times 100 = 86\%$$

TABLE 4

(Continued)

LIQUID	SOLID
28.6	C_A 31.0
36.3	C_{9A} = 37.5
29.0	C_{10A} = 30.5
30.4	C_{9E} = 30.5

$$\% \text{ Diaxial} = \frac{29.0 - 13.4}{30.5 - 13.4} \times 100 = 91\% \; C_{10A}$$

$$\% \text{ Diaxial} = \frac{36.3 - 30.5}{37.5 - 30.5} \times 100 = 83\% \; C_{9A}$$