

A Solution and Solid Carbon-13 Magnetic Resonance Study of the Conformation of 9,10-Dihydroanthracene and Its 9,10-Methylated Derivatives

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Abstract: The ^{13}C NMR chemical shifts of the 9,10-methylated 9,10-dihydroanthracenes have been obtained, both in the traditional manner in solution and in the solid state by use of cross polarization and magic angle spinning techniques. In addition, the temperature dependence of the solution chemical shifts was measured from about -70 to 40 $^{\circ}\text{C}$. Chemical shift effects resulting from methyl substitution are discussed. A nonlinear-least-squares regression analysis was performed on the variable-temperature methyl shifts for three of the compounds demonstrating unequally weighted conformational averaging, and the relevant thermodynamic and chemical shift parameters are presented. Both solid and solution spectra indicate ring flattening when geminal methyls are present. Furthermore, the methyls in the more sterically crowded molecules are in environments which differ substantially from those of the simpler molecules, indicating considerable variety in the conformational features.

Methylated derivatives of 9,10-dihydroanthracene have been of interest for many years.¹⁻³ X-ray analysis demonstrated that the parent compound is not planar but instead has a dihedral angle of 145° between the planes defined by the two aromatic rings.⁴ This forces the center ring to assume a boat conformation, which has been shown by proton NMR to undergo rapid boat-to-boat interconversion, even at low temperatures.⁵ For this boat structure, substituents at carbon 9 and 10 will assume either a pseudoaxial (a) or a pseudoequatorial (e) configuration, as shown in Figure 1. Due to erroneous proton assignments, there was initially some confusion as to which orientation was preferred by a single substituent.^{7,8} Later work indicated that larger substituents occupy exclusively the a conformation,⁹⁻¹¹ while smaller groups like phenyl or methyl may exist somewhat in the e form at equilibrium.¹⁰ Dialkyl substituents in a cis-9,10 orientation were presumed to occupy a pseudodiaxial conformation although some flattening of the central ring was indicated for bulky groups.¹¹

Hydroaromatic compounds have been the subject of renewed interest in recent years, since such compounds appear to serve as hydrogenation agents in coal gasification and liquefaction processes.^{12,13} Carbon-13 magnetic resonance appears to be a particularly relevant analytical tool for characterizing the compounds¹⁴ and the reactions involved in these conversion processes.¹⁵ Additional insights are to be gained by utilization of the rapidly developing technology of high-resolution, solid-state ^{13}C NMR, through use of techniques such as magic angle spinning (MAS) and proton-carbon cross polarization¹⁵ (CP). The complete set

of 9,10-methylated 9,10-dihydroanthracenes studied in this work is given in Figure 2, along with the symbols by which they will be designated. A ^{13}C NMR study of the various compounds in solution and in the solid state has been conducted in order both to clarify the conformational properties of the molecules and to demonstrate the relationships existing between the spectra in the two states of matter.

Experimental Section

The parent compound, P, was purchased from Fluka and was recrystallized from 95% ethanol before use; mp $103-110$ $^{\circ}\text{C}$ (lit.¹⁶ mp $108-109$ $^{\circ}\text{C}$).

Compound I was obtained by reduction of 9-methylanthracene (Pfaltz and Bauer) with sodium in ethanol, according to ref 17; mp $55-60$ $^{\circ}\text{C}$ (lit.¹⁷ mp $59-60$ $^{\circ}\text{C}$), while IIg was prepared as reported,¹⁸ except that cyclization of 2-(2-benzylphenyl)-2-propanol was accomplished in polyphosphoric acid; mp $44-50$ $^{\circ}\text{C}$ (lit.¹⁹ mp $51.5-52.0$ $^{\circ}\text{C}$).

Reduction of 9,10-dimethylanthracene (Aldrich) in 95% ethanol produced a mixture of both IIc and IIl, but the product was predominantly cis. Two recrystallizations from 95% ethanol produced pure cis, melting at $123-127$ $^{\circ}\text{C}$ (lit.¹⁷ mp $130-131$ $^{\circ}\text{C}$). Reduction of 9,10-dimethylanthracene with sodium in absolute ethanol resulted in a 50:50 mixture of IIc and IIl. Pure IIl, as determined by NMR, was obtained by separation on a Varian Aerograph GLC using a $5/8$ in. \times 20 ft column packed with SP-2100.

III was prepared by addition of methyl lithium to 10,10-dimethylanthrone, followed by reduction of the resulting alcohol according to published procedures.^{18,19} The resulting product melted at $73-76$ $^{\circ}\text{C}$ (lit.¹⁹ mp $78-79$ $^{\circ}\text{C}$). IV was also prepared as reported;²⁰ mp $163-172$ $^{\circ}\text{C}$ (lit.²⁰ mp $166-167$ $^{\circ}\text{C}$).

All solution data were collected on a Varian SC-300 spectrometer operating at 75.5 MHz in the Fourier transform mode with simultaneous proton decoupling. Data tables of 16K words or larger were employed with a 12-KHz spectral window. Deuteriochloroform was utilized as solvent for all compounds, with tetramethylsilane (Me_4Si) as internal reference. On the variable-temperature studies all chemical shifts were referenced to Me_4Si at 0 $^{\circ}\text{C}$ by adjusting for the temperature dependence of Me_4Si according to the equation $\delta_{\text{corr}} = \delta_{\text{obsd}} - 0.009751T - 0.000021597T^2$, T being temperature in degrees Celsius.²¹ The probe temperature was calibrated by using a ^{13}C chemical shift thermometer²¹ similar to the one proposed by Schneider et al.²²

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Table I. Solution Carbon-13 Chemical Shifts^a for the Methylated 9,10-Dihydroanthracenes

compd	1	2 and 3	4	4a	8a	9	10	Me
P ^b	127.6	126.3		136.9		36.2		
I	127.1	126.6, 126.2 ^c	127.9	136.0	142.0	41.1	35.1	23.6
IIg ^b	124.4	126.7, 126.0 ^c	128.0	135.8	145.2	39.1	35.8	28.8
IIc	128.0	126.4		140.6		40.0		28.6
IIt ^b	126.0	126.4		141.5		38.5		18.8
III	126.2	126.6, 126.4 ^c	128.1	139.5	143.7	38.3	38.9	36.3 (9a) 30.4 (9e) 29.0 (10)
IV ^b	127.0	126.4		142.1		37.2		35.1

^a In parts per million from internal Me₄Si at 28 °C with deuteriochloroform as solvent. Values representing more than one position because of symmetry are only listed for the lowest numbered carbon. Thus it is never necessary to list positions 5–8, 9a, or 10a. ^b These compounds are averaging between conformers of equal energy. ^c While these two carbons are structurally different, the two chemical shift values are so close together that they can not be assigned unequivocally at the present time.



Figure 1. The possible substituent conformations for boat-to-boat interconversion of substituted 9,10-dihydroanthracenes.

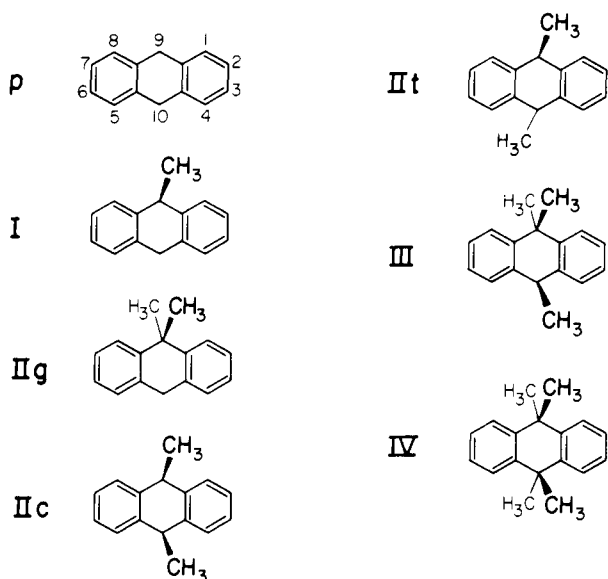


Figure 2. The methylated 9,10-dihydroanthracenes studied in this work: P, parent; I, 9-methyl-; IIg, 9,9-dimethyl-; IIc, *cis*-9,10-dimethyl-; IIt, *trans*-9,10-dimethyl-; III, 9,9,10-trimethyl-; IV, 9,9,10,10-tetramethyl-.

Solid ¹³C spectra were taken by using magic angle spinning and carbon-proton cross polarization techniques (MAS/CP). A Bruker CXP-200 SC spectrometer²³ was employed for examining several of the compounds, but the bulk of the data was acquired on a slightly modified Varian XL-100 spectrometer.^{24,25} The probe for the latter instrument, including external D₂O lock, and the rotor and stator assembly were constructed in this laboratory.²⁵ Samples were prepared by firmly packing from 80 to 100 mg of finely powdered material in a conical Kel-F rotor. When "internal" referencing was desired,²⁶ a small amount of adamantane was packed on top of the sample. A drop of fast-curing cyanomethacrylate resin was added to prevent loss of sample from the

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(26) Use of external adamantane as a reference source (i.e., in a different rotor) produced chemical shift values which varied from those referenced "internally" by less than 0.2 ppm in general.

rotor during data acquisition. Spinner rotation rates were approximately 5000 rps. The spectra were acquired by using a single contact time of 3.0 ms and a cycle time of 5.0 s. Normally, accumulation of a few hundred to a few thousand transients provided peaks of reasonable signal to noise.

Computer calculations and nonlinear-least-squares regression analyses were performed on a DEC PDP 11/70 computer using the program developed by Mayne.²⁷

Results

Solution ¹³C chemical shifts for the six possible methylated 9,10-dihydroanthracenes, plus those of the parent molecule, are given in Table I. It was possible to make most assignments of resonance lines to specific carbon positions by use of off-resonance and selective decoupling techniques. Some of the aromatic carbons were assigned by the characteristic features of the patterns in their coupled spectra.²⁸ It was not possible to distinguish between C-2 and C-3 in several cases, because the proton chemical shifts of H-2 and H-3 are generally degenerate, even at 300 MHz. However, the difference in carbon chemical shifts is small in such cases and of no serious consequence. The two methyls at position 9 in the trimethyl derivative are designated as 9-*trans* (9t) and 9-*cis* (9c) on the basis of their orientation relative to the methyl at position 10. In the low-energy conformer it is presumed that methyl-10 is pseudoaxial; therefore 9c should be pseudoaxial and 9t pseudo-equatorial. The 9t methyl in the trimethyl compound was assigned on the basis of the upfield shift expected for an *e* orientation.

In solution the P, IIg, IIc, and IV compounds of Table I are rapidly interconverting between conformers of equal energy. A rather low energy barrier to conformational inversion in these compounds is indicated by the observation that the resonance lines do not broaden at low temperatures. For example, the lines in IIc were not noticeably broadened at –60 °C when compared with their widths at 35 °C.

The three remaining compounds, I, IIc, and III, have conformations which are of unequal energy. A previous investigation¹⁰ of long-range proton-proton coupling constants, however, indicated that the higher energy *e* conformer of I contributes substantially to the population distribution, and it is reasonable to suppose that IIc and III will also exist to an appreciable extent in their higher energy conformations. Hence, the chemical shifts of all seven of the molecules were acquired over the range of ~–70 to ~40 °C for the purpose of investigating their conformational and thermodynamic properties. Since the methyl carbons display a range of chemical shifts more than double that of any other position in the molecules, the CH₃ chemical shifts are the most sensitive indicators of variation in conformational populations. The temperature dependence of the methyl resonances are displayed in Figure 3. These data were taken relative to Me₄Si and have been corrected by removing the temperature variation which Me₄Si displays (cf. the Experimental Section of this paper). It may be

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Table II. Thermodynamic^a and Conformational Parameters^b Derived from Nonlinear-Least-Squares Regression Analysis of Variable-Temperature Carbon Chemical Shifts

compd	resonance	δ_a	δ_e	ΔH	ΔS	$\Delta G(300\text{ K})^c$	fraction of low-energy conformer at 300 K
I	CH ₃	25.2 ^d	12.6 ^d	1507 ± 54	1.2 ± 0.1	1147	0.87
IIc	CH ₃	30.8 ± 0.1	(12.6) ^e	1249 ± 62	0.2 ± 0.1	1186	0.88
III	CH ₃ -10	31.4 ± 0.1	(12.6) ^e	1347 ± 54	0.7 ± 0.1	1137	0.87
	CH ₃ -9c	38.1 ± 0.1	24.9 ± 0.2				
	CH ₃ -9t	31.3 ± 0.0 ₃ ^f	24.7 ± 0.1 ^f				

^a ΔH and ΔG in calories, ΔS in entropy units. Errors given are the marginal standard deviations produced by the least-squares analysis. ^b In parts per million from Me₄Si at 27 °C. To convert to 27 °C, 0.3 ppm has been added to value at 0 °C. ^c ΔG calculated from ΔH and ΔS . ^d These values were originally derived for $T = 0$ °C from $18.56 \pm x$ (x being the fitting parameter) where $x = 6.30 \pm 0.04$ ppm. ^e Not used as a fitting parameter. See text. ^f These parameters are, of course, associated with the appropriate conformer, opposite to the values above them in the same column.

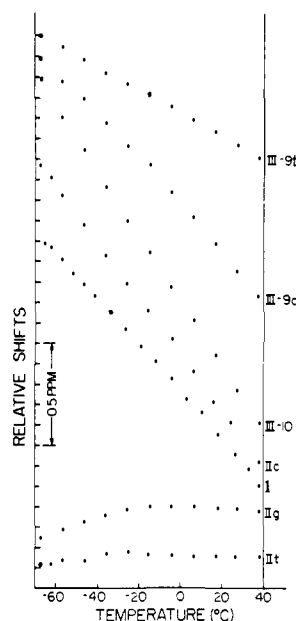


Figure 3. Temperature dependence of the ¹³C chemical shifts for the methyl carbons of several of the dihydroanthracenes studied in this work.

noted that the methyl resonances of IIg and IIt (i.e., those converting between conformations of equal energy) are almost temperature independent, showing only the small variation characteristic of most hydrocarbons,²⁹ whereas the methyl resonances of I, IIc, and III all move strongly upfield with increasing temperature. As these latter three compounds have conformations of unequal energy, the populations of the two forms can be expected to vary with changing temperature.

The chemical shift, δ , of a methyl which is exchanging rapidly (on an NMR time scale) between a and e environments is given by

$$\delta = \chi_a \delta_a + \chi_e \delta_e \quad (1)$$

where χ_a and χ_e are the mole fractions and δ_a and δ_e are the corresponding chemical shifts pertaining to the pure a and e conformations, respectively. The Boltzman expression then relates the populations of the two states, p_a and p_e , according to

$$p_e = p_a e^{-\Delta G/RT} \quad (2)$$

where the free energy is $\Delta G = G_e - G_a$. If the total population is p , the mole fractions are given by p_i/p . Substitution of the latter into eq 1, and use of eq 2 gives

$$\delta = (p_a/p)(\delta_a + \delta_e e^{-\Delta G/RT}) \quad (3)$$

Since $p_a/p = (1 + e^{-\Delta G/RT})^{-1}$ and $\Delta G = \Delta H - T\Delta S$, ΔH and ΔS

being the enthalpy and entropy changes, respectively, the temperature dependence of the chemical shift is given by

$$\delta = \frac{\delta_a + \delta_e e^{-\Delta H/RT} e^{\Delta S/R}}{1 + e^{-\Delta H/RT} e^{\Delta S/R}} \quad (4)$$

A nonlinear-least-squares regression analysis²⁷ was first performed according to eq 4 on the temperature-dependent methyl data of I, as depicted in Figure 3; δ_e , δ_a , ΔH , and ΔS were employed as parameters of the fit. Because of mathematical ill conditioning due to lack of sufficient curvature in the data, it proved impossible to achieve a satisfactory fit of the data with four independent parameters. The number of fitting parameters was reduced to three by noting that the chemical shift (18.5₆ ppm at 0 °C) of the methyl carbon in III should represent the average of δ_a and δ_e . Assuming that these two parameters are relevant for I, δ_a in eq 4 may be replaced by $(18.56 + x)$ and δ_e by $(18.56 - x)$. With use of x , ΔH , and ΔS as the fitting parameters, the mathematical difficulties were overcome, and convergence was obtained. The results for δ_e , δ_a , ΔH , and ΔS in I are given in Table II, using the value of 6.30 obtained for x .

For IIc, it was not possible to use the same scheme for fitting both δ_a and δ_e as used above for I because of a diaxial structural moiety being present in one of the conformations. Instead, the three fitting parameters were taken to be δ_a , ΔH , and ΔS . The fourth parameter, δ_e , was fixed at 12.3 ppm, as determined by the fit of I, because the e environment for the methyls in question is assumed to be very similar to that encountered above. The results from the nonlinear regression analysis are also contained in Table II.

In III all three sets of methyl shifts were fit simultaneously, using ΔH , ΔS , $\delta_{10,a}$, $\delta_{9c,a}$, $\delta_{9c,e}$, $\delta_{9t,a}$, and $\delta_{9t,e}$ as fitting parameters. Because of the relative isolation of the 10-methyl in the equatorial position, the shift parameter $\delta_{10,e}$ was set again at 12.3 ppm. As the data base was 3 times larger, no difficulty was encountered in achieving a good convergence with this seven-parameter fit. The results are given in Table II. For determination of the sensitivity of the fitted parameters to the selection of 12.3 ppm for the $\delta_{10,e}$ parameter, values of 10 and 14 ppm were also introduced into the fitting program for $\delta_{10,e}$. This had essentially no effect (<0.1 ppm) upon the parameters ($\delta_{10,a}$, $\delta_{9c,a}$, $\delta_{9t,e}$) for the low-energy conformer and only modest effects upon ΔH and ΔS . On the other hand $\delta_{9c,e}$ and $\delta_{9t,a}$ for the high-energy conformer do vary significantly (~ 1 ppm) with the selection of $\delta_{10,e}$. This is quite reasonable as $\delta_{10,e}$ is also a parameter of the high-energy conformer. These results are understandable when it is remembered that the experimental data for the conformational mixture will be much closer to the low-energy conformational shift values, thereby fixing that end of the shift range with relatively greater accuracy. In all three molecules contained in Table II, the values for δ_e and δ_a differ significantly from the corresponding isotropic solution values contained in Table I, confirming that these molecules are not conformationally pure in the liquid state at room temperature.

The chemical shifts determined for the various methylated 9,10-dihydroanthracenes in the solid state are presented in Table

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Table III. Carbon-13 Chemical Shifts^a for the Methylated 9,10-Dihydroanthracenes in the Solid State

compd	position					
	1-4 ^c	4a	8a	9	10	Me
P	126.7	136.7		<i>b</i>		
I	126.7, 128.4, 128.8	137.0 ^d	143.7 ^d	41.3	35.6	26.4
IIg ^e	123.9, 125.7, 126.9	133.9	141.6			
IIc	123.9, 125.7, 126.9	137.0 ^d	145.6 ^d	39.7	36.2	33.1 (a)
IIc	125.3, 126.5, 127.2, 128.7 ^d	136.1	144.7			25.6 (e)
IIc		140.7 ^d		39.7		31.0
IIc		139.7				
II ^t	124.1, 126.6, 128.4	144.0 ^d	140.8 ^d	41.9 ^f	34.4	26.6 (a)
II ^t		142.1	139.1			13.4 (e)
III ^e	126.6, 127.8, 129.9	140.0 ^d	143.7 ^d	37.7	38.6	33.7 (9c) ^g
III ^e		138.9	143.2			32.8 (10)
III ^e		138.0	142.3			29.4 (9t)
IV	124.9, 126.7, 128.6 ^d	141.4 ^d		36.6		37.2
IV		140.3				35.0

^a In parts per million from Me₄Si. Shifts converted from external or "internal" adamantane reference (37.7 and 28.6 ppm). ^b This line is very broad and somewhat unsymmetrical, so that its exact position is in question. ^c Assignment of these multiplets and bands to specific carbon positions is not presently possible because of close proximity of lines. All independent resonances are listed in ascending order pending a more complete assignment. ^d These positions unexpectedly yield double or triple lines in the solid. Assignment is tentative. See text. ^e These data were also acquired on a CXP-200 spectrometer, for which we thank Bruker-Physik AG. ^f This compound is numbered so that Me-9 is a. ^g Methyls are tentatively assigned here on the basis of the temperature results.

III. Accuracy in the recorded values is estimated to be about 1 ppm, although the interpeak spacings are accurate to better than 0.4 ppm. Assignments, in general, have been made on the basis of line widths and by comparison with the solution data. Examples of the solid spectra are presented in Figure 4 for the compounds in this study. It is to be observed that both peak intensities and line widths vary quite widely for different peaks within the same spectrum. Line widths were typically about 20 Hz at half-height, but this varied depending upon the number of protons attached to the carbon of interest. Integrated intensities often did not conform to the expected relative numbers of carbons, but this is typical for MAS/CP spectra where variations in peak widths and areas depend significantly upon cross polarization efficiencies for different carbons.

Many of the solid shifts correlate rather favorably with those found in solution and were so assigned except in the instances where two or more solid peaks appear within 2 ppm of the liquid position. In such cases the assignments must be considered to be tentative. Whenever discrete lines were observed for these molecules, the single chemical shift values are reported. In some compounds, however, the aromatic lines overlap extensively and only a banded structure exists. Thus, we have chosen to report the aromatic carbons as sets of peaks for positions C-1 through C-4.

There is strong circumstantial evidence that line shapes and peak intensities can also be used in making some provisional assignments. This approach appears to be especially useful in the aliphatic region. Whenever methylene carbons (CH₂) existed at position 9 or 10, peaks were found in the spectrum which were invariably broader and lower in peak intensity than the remaining aliphatic carbons (quaternaries, methynes, and methyls). These broad peaks found in P, I, and IIg have been assigned to the methylenes. In each case the solid methylene peak was very close to the corresponding methylene peak in the liquid spectrum. Conversely a very sharp and intense peak was found in every spectrum having a quaternary carbon (i.e., IIg, III, and IV). Liquid results for IIg corroborate the solid assignment based upon these criteria, but both liquid and solid quaternary shifts in the tri- and tetramethyl compounds are not sufficiently dispersed from other aliphatic peaks to use the liquid data as corroborative evidence for these proposed assignments.

The intensities of methyl and methyne carbons are rather similar and are intermediate between the broadened methylenes and the very sharp quaternary carbons. The assignments for these carbons in Table III largely follows the corresponding liquid shifts, as augmented by systematic substituent effects. This approach is very reasonable where the methyne and methyl carbons are separated by large shifts, such as compounds I, IIc, and II^t. For

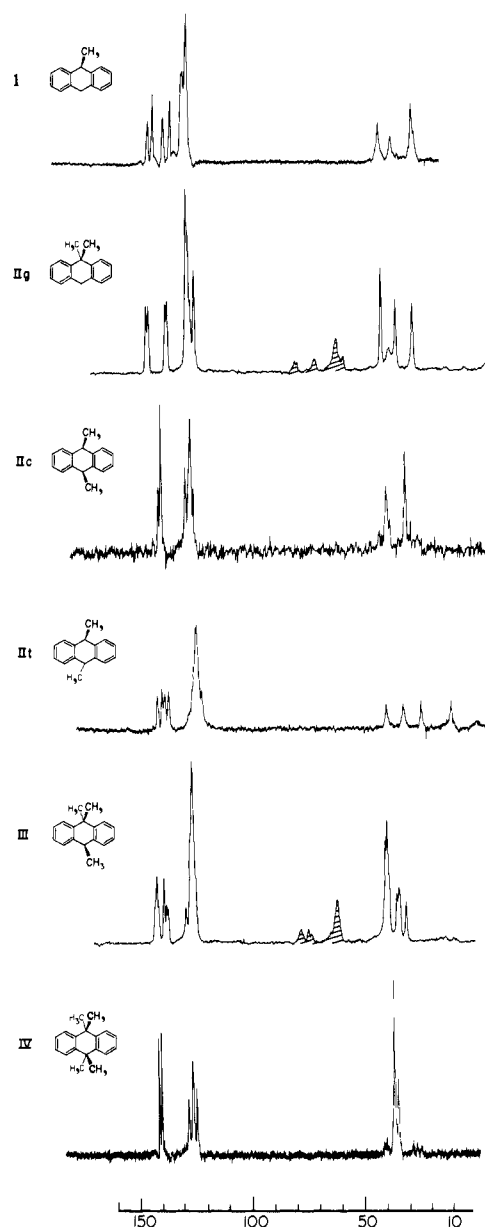


Figure 4. Solid ¹³C NMR spectra for the 9,10-methylated 9,10-dihydroanthracenes. Crosshatched areas indicate spinning sidebands.

these cases, the line separations greatly exceed the experimental error of about 1 ppm as well as anticipated intermolecular shifts. Discrimination between the two methyl peaks in both III and IIg is based upon the prominent upfield γ steric effect³⁰ expected for the interaction of an e methyl with the adjacent α -aromatic carbons (either C-1,8 or C-4,5). Assignment of the methyne peaks in solid III is made by analogy with related resonances in I and IIc. The axial methyl is arbitrarily designated as attached to C-9.

Assignment of the solid peaks in III is confronted by several problems. Well-resolved individual peaks are not found for each different type of carbon, and at the same time, inflections and partial splittings of some of these bands actually suggest that the spectrum may contain more resonances than there are unique carbons in the molecule. This is especially pronounced in the aromatic bridgehead region where there appears to be six spectral components in the band, representing only four aromatic bridgehead carbons. The same result was obtained on two different instruments. The liquid spectrum of this compound dissolved in deuteriochloroform exhibits no impurity peaks or similar anomalies.

In III the assignment of aromatic carbons into two subsets, protonated ring carbons and bridgehead carbons, is made with reasonable confidence. The unprotonated bridgeheads, similar to the aliphatic quaternary carbons, exhibit relatively sharp resonances. For both types of aromatic carbons, the liquid and solid data fall within characteristic spectral ranges. For the time being, no attempt is made to assign the various aromatic resonances to specific positions in the molecule as the lines are too close together to make these detailed assignments with confidence.

The aliphatic region in III contains five distinct peaks. The two peaks at lowest field (37.7 and 38.6 ppm) correspond very closely with the C-9 and C-10 liquid peaks, which appear respectively at 38.3 and 38.9 ppm. Furthermore, the peak assigned to C-9 exhibits the sharpness of a quaternary carbon. The remaining three peaks (29.4, 32.8, and 33.7 ppm), all appearing upfield from the bridge carbons, vary quite significantly in integrated intensity from each other and from the C-9 and C-10 carbons. Of more interest, some of these peaks deviate significantly in their position from the shifts recorded for the three methyl peaks in the liquid (29.0, 30.4, and 36.3 ppm from Table I). Furthermore, when these solid shifts are compared with the temperature-dependent data extrapolated to the low-temperature limit (31.3, 31.4, and 38.1 ppm from Table II), the agreement does not improve. One may only conclude that the molecular conformational features in the solid deviate greatly from those important in the liquid state. The assignment in Table III of the methyl peaks in the solid have been made on the basis of the shift ordering found in the liquid but must be considered to be tentative.

Discussion

1. Comparison of Liquid and Solid Chemical Shifts. When a comparison is made between the chemical shifts found for liquids (Tables I and II) and for solids (Table III), it may be noted for many carbon positions that the shift values are the same within the ± 1.0 -ppm experimental error estimated for referencing the peak positions in the solid spectra. This similarity between the solid and liquid spectral features provided a basis for making many peak assignments in the solid spectra, but perhaps of greater importance, this result also confirms that the chemical shielding parameter is primarily a property of the molecule itself and does not depend greatly upon the environment created by neighboring molecules. Relatively small shifts (less than 2–3 ppm in this study) are attributed to intermolecular shielding terms, as clearly indicated by the existence of some multiple resonances in the solid where only one peak is found in the corresponding liquid spectrum. Such small splittings of a few parts per million indicate that the crystalline environment³¹ is lifting the nominal spatial equivalence

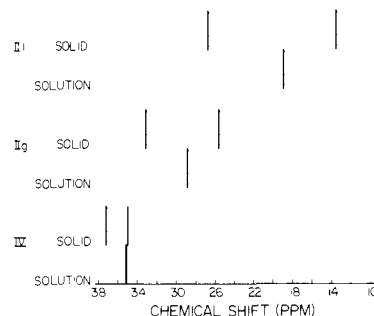


Figure 5. Comparison of the solid and solution chemical shifts for the methyl carbons of some methylated dihydroanthracenes. Symbols are defined in Figure 2 caption. See text for discussion.

found for those carbons related to each other by unimolecular symmetry elements.

2. Methyl Carbon Shifts. The greatest differences between corresponding solid and liquid shifts are found for methyl carbons. In the liquid these resonances are being rapidly averaged due to conformational interconversions, while in the solid these compounds are locked into a single conformation. This difference is especially pronounced in the methyl resonances of IIg and IIi where both a and e methyls have been locked into the solid structure and can be observed as separate resonances. Figure 5 compares the liquid and solid methyl data for these two compounds along with that of IV, where the methyl peak also splits into two resonances in the solid. In IIi the two methyl groups are separated by five carbon-carbon bonds and also are isolated sterically from each other. The values observed in the solid state, therefore, characterize an isolated a (26.6 ppm) and e (13.4 ppm) methyl in these systems. The corresponding values for I obtained from the temperature-dependent liquid data and given in Table II are respectively 25.2 and 12.6 ppm. Each of these values is about 1 ppm below the corresponding solid values in IIi. As the average liquid (18.8 ppm) and average solid (20.0 ppm) values also differ by about 1 ppm, the agreement between the solid and liquid values for δ_a and δ_e is felt to be good. The differences in I between δ_a and δ_e ($\Delta\delta = 13.2$ ppm in solid and $\Delta\delta = 12.6$ ppm in the liquid) is easily rationalized on the basis of two upfield γ shifts which the e methyl will experience with the two protons on the adjacent aromatic ring carbons (C-1,8 for a 9e methyl). Thus a γ parameter of -6.6 (solid) or -6.4 ppm (liquid) would be calculated for each interaction. This value is slightly larger but still comparable with γ values encountered in previous work.^{30b}

In Figure 5, it is noted that the average of the two solid and liquid methyl shifts for IIg are respectively 9.3 and 10.0 ppm downfield from that found for an a and e average in IIi. This 10-ppm shift may be rationalized by noting that each methyl in IIg experiences a geminal β -carbon shift. The 10-ppm value is comparable to β shifts found in previous studies^{30b} on quite different compounds. While the variation in δ_{av} from IIi to IIg may be easily rationalized on the basis of a β -geminal parameter, the corresponding decrease of ($\Delta\delta = \delta_e - \delta_a$) from 13.2 to 7.5 ppm for the same two compounds is rather surprising. The γ parameter, which is one-half of $\Delta\delta$, drops to 3.75 ppm in IIg, suggesting considerable structural deformation about the C-9 position. Variable γ parameters have been noted previously^{30b} in molecules which deform to relax the strain energy. The reduction of $\Delta\delta$ in IIg is probably best interpreted in terms of flattening of the central ring which would relax the interaction between the protons on C-1,8 and a methyl in the e position while increasing the steric shift for the a-methyl. The $\Delta\delta$ of 7.5 ppm is still large enough that it should exceed any differential intermolecular shielding values, and, therefore, significant pucker in the central ring must be present to guarantee the nonequivalence of the two methyl carbons.

The separation between the two methyls in IV is reduced to only 2.2 ppm, a value which is now small enough to be explained solely with intermolecular effects, and one need not invoke ring puckering requirements. This suggested that IV be submitted for

(30) (a) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315–5318; (b) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 5318–5324.

(31) Neustadt, R.; Zilm, K. W.; Carter, C.; Cagle, F. W.; Grant, D. M., manuscript to be published.

Table IV. Structural Dependence of the Chemical Shifts^a of Aliphatic Bridge Carbons in the Methylated 9,10-Dihydroanthracenes

compd	structure type							
	liquid	solid	liquid	solid	liquid	solid	liquid	solid
P	36.2							
I	35.1	35.6	41.1	41.3				
Ilg	35.8	36.2						
Iic			40.0	39.7			39.1	39.7
Iit			<i>b</i>	41.9	<i>b</i>	34.4		
III			38.9	38.6			38.3	37.7
IV							37.2	36.6

^a In parts per million from Me₄Si. ^b The average liquid value of 38.5 ppm compares favorably with the average solid value of 38.2 ppm. Because both conformations in Iit are of equal energy, there is no means whereby the two liquid conformational parameters may be obtained.

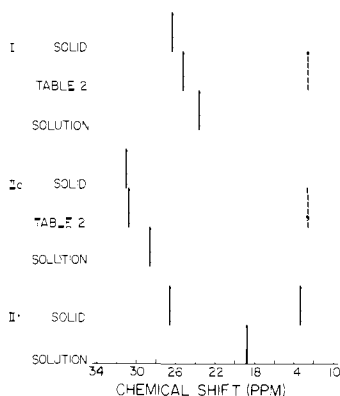


Figure 6. A comparison of the methyl chemical shifts extracted from solid, solution, and temperature data of some methylated 9,10-dihydroanthracenes. Symbols are defined in Figure 2 caption.

an X-ray analysis; a preliminary crystal structure indicated that the two aromatic rings do lie in the same plane, but the mirror plane symmetry found in the liquid no longer obtains. Only an element of inversion symmetry is present. Thus, adjacent molecules are located in such a manner that they split the peak for the four methyls and for four aromatic bridgehead carbons into two peaks each as observed. As the liquid methyl shift in IV is reasonably close to the δ_{av} in the solid, there is also no need to propose significant molecular structural differences between the solid and the liquid states, and it is likely that IV is planar in both conditions.

In Figure 6 we compare the methyl chemical shifts for I, Iic, and Iit. This figure not only gives the thermal equilibrium shifts contained in Table I but also has the extrapolated values for Table II for the low-energy (solid line) and high-energy (dashed lines) conformations of I and Iic. The agreement between solid and extrapolated δ_a values in I and Iit provides support for the validity of the analysis of the temperature data on I where the liquid methyl shift for Iit was used to set the midpoint of δ_a and δ_e in I. No attempt is made to explain the small discrepancies (up to about 1 ppm) between liquid and solid shifts for methyl carbons as these are comparable with experimental errors in referencing solid shifts, and any attempt to improve agreement for methyl carbons by shifting the whole solid scale would in many cases lead to worse agreement at the other carbons.

The diaxial methyl shielding in Iic is found to be 30.8 ppm for the extrapolated liquid data (Table II) in excellent agreement with the 31.0 in solid Iic (see Table III). By comparison of these shifts with the corresponding methyl shift in I, the effect of an ϵ diaxial shift parameter can be determined to be 5.6 ppm from the liquid data and 4.6 ppm from the solid data. Although such downfield shifts have been previously noted for sterically interacting carbons separated by four bonds,³² this is the first example of which we

are aware where a large ϵ steric effect (about 5 ppm) is observed between carbons separated by five bonds. Force-field calculations on Iic indicated that the methyls preferred the staggered configurations relative to the other bonds at the C-9 and C-10 carbons. This requires one of the hydrogens on each axial methyl to orient toward the other axial methyl. The force-field calculations indicated, however, that both the diaxial methyls and the center ring structurally distort to relax this unfavorable steric interaction. These types of angular deformations are known to correlate with other steric shifts^{30b} and as such may account for this anomalously large ϵ -shift parameter.



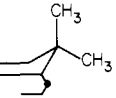
The chemical shifts in I, Iig, Iic, and Iit have thus been rationalized in terms of reasonable shift parameters of about 10 ppm for geminal methyls (β shift), of about 5 ppm for diaxial methyls (ϵ -steric shift), and of a variable γ shift of -3--6 ppm for the interaction of pseudoequatorial methyls with the α protons in the aromatic rings. These parameters, along with the 12.6-ppm pseudoequatorial methyl shift, were applied to the shifts in the more sterically hindered III and IV compounds. This attempt encountered only mixed success, as the predicted methyl shifts vary by several parts per million from the corresponding experimental values. Better fits can be achieved by selecting either smaller negative γ shifts or larger ϵ shifts. Deformations can be expected to reduce the magnitude of the negative γ parameters, but one would expect the large positive ϵ parameter also to be greatly reduced by such deformations. Hence, no totally systematic explanation of the methyl shifts in III and IV has therefore been found. The failure to find a completely systematic parameterization of the shifts establishes a strong case for conformational variability of the basic 9,10-dihydroanthracene fused ring system.

3. Aliphatic Bridge Carbons. Table IV summarizes the liquid and solid shifts for the 9- and 10-carbons for the four different structural types: simple methylene, axial methyl, equatorial methyl, and geminal dimethyl. In all cases where both solid and liquid values are available, the agreement between the corresponding values is within the experimental error in the solid measurement. This agreement argues rather forcibly for the position that the geometry of each of these compounds does not vary greatly between the liquid and solid states. Furthermore, a reasonably consistent and characteristic shift for each of the four different structural types is found, if III and IV are excluded from consideration.

Only a single entry is found in Table IV for the equatorial methyl structural type and it actually appears slightly upfield from the shift found for the simple methylene structure. This is somewhat anomalous, as a methyl substitution on a methylene carbon generally is accompanied by a downfield shift, as found when the methylene carbon is substituted in the α conformation. Substitution in the 9e position is accompanied by significant "gauche-like" interactions at positions 1 and 8, which are known to produce upfield shifts.^{30b} We can therefore only presume that in this case the effects of such steric distortions are so strong that they are cancelling the normal downfield effects of an α -methyl substituent. The geminal dimethyl structural type in Iig exhibits

(32) Casper, C. L.; Stothers, J. B.; Wilson, N. K. *Can. J. Chem.* **1975**, *53*, 1958-1959.

Table V. Substituent Effects on the Liquid Chemical Shifts^a of the 1-, 4-, 5-, and 8-Carbons of the Methylated 9,10-Dihydroanthracenes

compd	structural type		
			
P	127.6		
I	127.9	127.1	
IIg	128.0		124.4
IIc		128.0	
III		128.1	126.2
IV			127.0

^a In parts per million from Me₄Si.

a shift value which could be obtained from the 35.7-ppm unsubstituted bridge carbon plus a 5-ppm axial α shift and a -1-ppm equatorial α shift. However, the geminal dimethyl shifts at C-9 in III and C-9,10 in IV change significantly from that observed in IIg. As the C-9 and C-10 carbons will experience geminal angular deformations with central ring flattening, it is not surprising that systematic trends are found in Table IV. In every case where ring flattening can be expected to relieve steric strain, an upfield shift is noted at C-9 or C-10 or at both positions.




4. Aromatic Carbons. It was not possible to make unambiguous assignments for carbons 2, 3, 6, and 7. Since the observed chemical shift range for these carbons is relatively small (0.7 ppm), the ambiguity is of little consequence. Conversely, the negligible variations in chemical shifts do not provide diagnostic information about the nature of substitution or the conformational features.

Aromatic carbons 1, 4, 5, and 8, on the other hand, are affected by the methyl substitution whenever an e methyl is present in the molecule. Table V illustrates that these carbons are found in the range of 127.1–128.1 ppm whenever the adjacent C-9 and C-10 position is either a methylene or an axially oriented methyl. Whenever a geminal dimethyl moiety is present, one of the methyls will be obliged to occupy the e position unless, of course, the central ring has been flattened. We note from Table V that in IIg this produces a γ methyl substituent effect of about -3.6 ppm at C-1,8 relative to the C-4,5 shift. Such γ shifts are relatively common. We have no liquid-state molecule which has a single methyl group in the e position, and therefore this is a combined geminal dimethyl effect. Table V documents, however, that the a methyl in singly substituted compounds does not perturb the C-1, -4, -5 or -8 shifts. These data also indicate that there are no significant cross ring shift parameters (i.e., a methyl at C-9 has no effect at C-4,5). The variety of shifts found for the geminal dimethyl substituent as one compares IIg, III, and IV again suggests a conformational variation among these three molecules. The trend 124.4, 126.2, and 127.0 ppm, respectively, indicates an almost total relaxation of the steric strain. This may be taken as further evidence for ring flattening which moves a 9e methyl away from the C-1,8 positions.

Because of ambiguity in assigning solid aromatic ring shifts, a discussion of these solid data must be somewhat restricted. It should be indicated that there is in every case one or more solid peaks in the appropriate shift range to correspond to a liquid peak. Thus the solid data are compatible with those obtained on liquids. Because of its importance we note that there is one isolated aromatic peak at 124.1 ppm in IIc. As this molecule has a single methyl locked into the e position, this supports the position that only the e methyl in IIg determines the substituent effect.

The effect of methyl substitution on the bridgehead aromatic carbons is summarized in Table VI. Unlike the C-1, -4, -5, -8 data, an a 9-methyl shifts the C-8a,9a positions downfield by about 6.0 ppm (see I in Table VI). A geminal dimethyl effect as determined from the IIg data in Table VI is 9.4 ppm. While these values are on the low side of typical β -substituent parameters, they are not unreasonable for highly crowded substituent groups. The upfield shifts noted at the aromatic bridgeheads in both III and

Table VI. Chemical Shifts^a of the Bridgehead Carbons of the Methylated 9,10-Dihydroanthracenes as a Function of Structure

compd	structural type					
						
	liquid	solid	liquid	solid	liquid	solid
P	136.9	136.7				
I	136.0	137.0	142.0	143.7		
IIg	135.8	137.0			145.2	145.6
		136.1				144.7
IIc			140.6	140.7		
				139.7		
				140.0		143.7
III			139.5	138.9	143.7	143.2
				138.0		142.3
IV					142.1	141.4
						140.3

^a In parts per million from Me₄Si.

IV again suggests a flattened central ring.

5. Thermodynamic Considerations. Even though the structural variations between I, IIc, and III are appreciable, the difference in ΔG at 300 K between the two conformations for each molecule is almost the same in all three cases. This leads to the equilibrium ratios being the same within experimental error. This similarity is largely a coincidence as the ΔH and ΔS values do exhibit some variation. To a first approximation one might argue that the ΔH for IIc should be twice that for I if the ΔH were to be due solely to the steric interactions of an e methyl with the adjacent aromatic ring protons. In fact, the ΔH for IIc is about 250 cal less than for I. This result is attributed to the destabilization energy associated with the relatively strong interaction between the two pseudoaxial methyls in IIc. A similar result is found for III which also includes the diaxial structure. One therefore must conclude that the diaxial interaction is comparable or slightly stronger than each equatorial methyl steric interaction. The relatively large, positive entropy for the axial methyl conformation in I probably results from differences in mobility in the internal rotational characteristics of the methyl group since other entropy-producing features of the molecules would appear to be similar. A single methyl in an a position is governed by a relatively stiff threefold barrier to rotation. Conversely, an e methyl is in an environment very similar to that of 9-methylanthracene, which has been shown³³ to encounter a softer, sixfold barrier to rotation and is more aptly described as a "free rotor". Admittedly, the threefold contribution of an e methyl in the dihydroanthracenes must be greater than for the corresponding methylanthracene, but the steric interactions of an H-1,8 with a 9e methyl will enhance the sixfold contribution and increase the torsional mobility of e methyl groups. A similar argument holds for IIc and III, except that in the low enthalpy form, the diaxial interaction also contributes a sixfold term into the torsional barriers of these methyl groups and could increase the torsional mobility and therefore the entropy of these conformations.

As ring flattening in III and IV may largely be the consequence of the combined diaxial and e methyl steric interactions, the matter of ring flattening is not independent of these other steric discussions. Increased planarity in the central ring can only be accomplished with the deformation of the CCC angles in this ring, and this angular change will contribute a destabilization energy. Force-field calculations of the boat-plane-boat conformational interconversion process indicates the barrier to interconversion is relatively low. Calculation of these relatively small difference values for molecules of this size unfortunately provides only qualitative, or at best semiquantitative, characterization of the

(33) Ladner, K. H.; Dalling, D. K.; Grant, D. M. *J. Phys. Chem.* **1976**, *80*, 1783-1786.

thermodynamics associated with the ring-flattening feature, and possibly some of the variations in ΔH and ΔS in Table II are associated with changes in the extent of pucker in the central ring.

Conclusion

This study has demonstrated the manner in which both liquid and solid high-resolution NMR methods can be used as complementary techniques in conformational and structural analysis. Freezing of a pure conformational structure in the solid state provides specific structural shift parameters for characterizing molecules with highly mobile conformations in the liquid state. The thermodynamic quantities obtained from the temperature-dependent liquid chemical shifts were thus corroborated by this dual approach.

It was found that the chemical shifts for the parent and mono- and dimethyl-substituted 9,10-dihydroanthracenes could all be rationalized with standard methyl substituent parameters. Chemical shift deviations for the tri- and tetramethyl derivatives could be explained in terms of ring flattening of the central ring. Failure to find clearly distinguishable axial and equatorial methyls for the tetramethyl compound in the solid state indicated the

general structural similarity of all methyls in this compound and suggested a planar or near planar structure for this highly methylated species. The close similarity of liquid and solid parametric shifts argues strongly for the similarity of the structural features in both the solid and liquid states. Should the crystal packing forces have resulted in major conformational changes between the solid and liquid, these would have led to greater discrepancies between the liquid and solid parametric shifts. Even though the solid and liquid conformations for a given compound are very similar when proper consideration is given to the dynamic averaging taking place in the liquid, the data clearly indicate that the degree of puckering for the central ring does vary considerably between members of this series. This conformational flexibility undoubtedly is one of the unique features of the 9,10-dihydroanthracenes and the other related hydroaromatic molecules.

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Decomposition and Isomerization of Bridgehead Cis 1,2-Diazenes (Azoalkanes)¹

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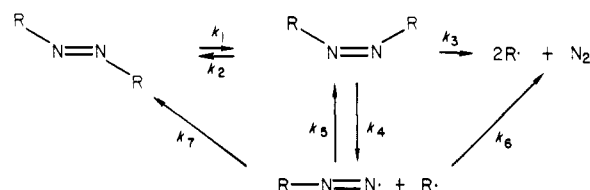
Abstract: Four acyclic cis 1,2-diazenes, azo-1-adamantane (*cis*-ada), azo-1-bicyclo[2.2.2]octane (*cis*-[2.2.2]), azo-1-bicyclo[2.2.1]heptane (*cis*-[2.2.1]), and azo-1-bicyclo[2.1.1]hexane (*cis*-[2.1.1]) have been generated by UV irradiation of the corresponding trans isomers. These compounds differ greatly in stability, *cis*-[2.1.1] easily surviving at 100 °C and *cis*-ada not being isolable. Whereas *cis*-[2.1.1] and *cis*-[2.2.1] only isomerize back to trans on heating, the other two compounds undergo competing loss of nitrogen. The observation that the energy of the transition state for isomerization remains at 42 ± 1 kcal mol⁻¹ regardless of the *cis* ground state energy is used to argue that thermal isomerization proceeds via semilinearization rather than rotation. A remarkable correlation of *cis* ground state energy with *cis* n, π^* excitation energy has emerged from this study.

It has been known for over 40 years that irradiation of *trans*-diaryldiazenes (azobenzenes, *trans*-Ar-N=N-Ar) produces the *cis* isomers, which revert to *trans* on mild heating.² Since thermal *cis* \rightarrow *trans* isomerization is exothermic by about 12 kcal mol⁻¹, the cycle *trans* $\xrightarrow{h\nu}$ *cis* $\xrightarrow{\Delta}$ *trans* has been considered for solar energy storage.^{3,4} Diaryldiazenes have also been incorporated as photosensitive groups to control the properties of crown ethers, membranes, and related species.⁵

Aliphatic⁶⁻¹⁰ and alkylaryl^{11,12} *cis* diazenes are of more recent vintage and their chemistry is more varied than that of the diaryldiazenes. Thus, *cis*-dialkyldiazenes can isomerize directly to *trans* or they can decompose by stepwise or simultaneous C-N bond cleavage. Most of these compounds are thermally labile but *cis*-dimethyldiazene and *cis*-diisopropyldiazene have been isolated.^{7,8}

The goals of the present research were to prepare stable *cis*-dialkyldiazenes and to study the effect of structure on their thermal behavior. As will be seen below, some of these new diazenes are not only more stable than *cis*-azobenzene but they liberate more heat during the isomerization process. Whereas two of them only

Scheme I. Reaction Pathways of Cis Diazenes



revert to *trans* on heating, two others undergo simultaneous *cis* \rightarrow *trans* isomerization and decomposition to radicals. The

(1) For a preliminary report of this work, see Engel, P. S.; Melaugh, R. A.; Page, M. A.; Szilagyí, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 1971.

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