tion of 0.41 G for the pair of satellite line positions under consideration for the $M_H = \pm 1$ lines.

It may be pointed out that detailed investigations in our laboratory on the durosemiquinone (DSQ)–K and DSQ–Na systems in both DME and tetrahydrofuran also point to the fact that the alkali metal migration is responsible for the alternation in the widths of the hyperfine components in the esr spectra in agreement with observations made by other investigators.[3,6,7]

VII. *g* Shifts and Ion Pairing

One of the interesting features in the present results is the difference in the *g* values observed for the A and B species. At −75° the *g* value for the A species is 2.00551 ± 0.00002 and for the B species is 2.00543 ± 0.00002. It is not possible to obtain accurate *g* values from our spectra for the A and B species at higher temperatures. Consequently, any temperature dependence in the *g* values of these species could not be determined at the present stage.

Zandstra[39] has reported *g* value variations in PBSQ resulting from solvent interactions, and it has been observed that the *g* value is higher in dimethyl sulfoxide as compared to ethanol–water solutions where the solvent interaction is greater. Similar effects have been reported for benzophenone anions[40] in which there is a decrease in the *g* value resulting from an increase in cationic perturbation. The decrease has been attributed to a shift in the spin density from the carbonyl group into the ring[40] which results in a reduction in the orbital contribution to the *g* value. In the present case also the intimate ion pair has a smaller *g* value and the lowering of the *g* value can be attributed to increased cationic perturbation. There is also evidence for a shift in the spin density from the oxygen atoms to the ring that results from ion pairing. Further work on the *g* value variations with difference in cations and also from variations resulting from a change in temperature is under progress.

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Magnetic Resonance Study of Conformational Inversion In Some Substituted 10,10-Dimethyl-9,10-dihydroanthracenes[1,2]

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Abstract: The ring inversion in 10,10-dimethyl-9-methylene-1,8-dichloro-9,10-dihydroanthracene (I), 9-(dichloromethylene)-10,10-dimethyl-9,10-dihydroanthracene (II), and 9-(dibromomethylene)-10,10-dimethyl-9,10-dihydroanthracene (III) in 1,1,2,2-tetrachloroethane solution has been studied using nmr complete line-shape analysis methods. Exchange rates were calculated from the nmr spectrum of methyl group protons by treating them as uncoupled exchanging AB systems with equal population. The low-field methyl peak in the spectra of compounds studied was assigned to the equatorial methyl and the high-field peak to the axial methyl. The $\Delta F^{\ddagger}$ for ring inversion was found to be 15.9, 17.4, and 19.0 kcal/mol in compounds I, II, and III and qualitative interpretation was proposed in terms of nonbonded interactions between the exocyclic methylene substituents and the *o*-aryl substituents in the assumed planar transition state. The changes in the activation parameters obtained by using different $1/T_2$ values for line-shape calculations were also studied.

Considerable attention has recently been devoted to the question of conformational stability in 9,10-dihydroanthracene systems.[5] From these studies it appears that the preferred conformation of the center ring in substituted 9,10-dihydroanthracenes is influenced to largest degree by the nature and bulk of the substituent in either the *o*-aryl or *meso* positions. Curtin and coworkers[6] have synthetized a series of substituted 10,10-dimethyl-9-methylene-9,10-dihydroanthracenes and measured their nmr spectra. The nmr spectra of the methyl resonance region in these compounds showed varying degrees of equivalence depending upon the substituents on the methylene carbon. These observations were consistent with a hindered boat–boat

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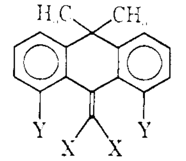
interconversion of the center ring in which the methyl groups occupy nonequivalent axial and equatorial positions. The source of this hindrance was postulated to arise from the steric interaction between the methylene substituent and the *o*-aryl hydrogens. Curtin and coworkers[6] have investigated ring inversion in 9-carbomethoxybromomethylene-10,10-dimethyl-9,10-dihydroanthracene, 9-dibromomethylene-10,10-dimethyl-9,10-dihydroanthracene, and 9-phenylbromomethylene-10,10-dimethyl-9,10-dihydroanthracene using a line coalescence technique.[7] It was concluded that the general order of inhibition to inversion was the same as that observed in the hindered rotation of *ortho*-substituted biphenyls.[8] In this connection, it seemed to be of interest to determine if a different steric orientation of halogen substituents does influence the barrier to interconversion in a significant way. Pertinent models for such a study are the isomeric methyleneanthracenes—10,10-dimethyl-9-methylene-1,8-dichloro-9,10-dihydroanthracene (I) and 9-(dichloromethylene)-10,10-dimethyl-9,10-dihydroanthracene (II). An nmr study using a complete line-shape analysis method[9] was undertaken to examine the magnitude of the apparent difference in the barrier to interconversion in I and II. Since a quantitative comparison between the barrier to interconversion resulting from a dichloromethylene substituent and the larger dibromomethylene substituent would be desirable, it was decided to reexamine[6] the kinetics of ring inversion for 9-(dibromomethylene)-10,10-dimethyl-9,10-dihydroanthracene (III) by the more rigorous complete line-shape analysis technique.[9] The ring inversion process in I, II, and III has been discussed in terms of $\Delta F^{\ddagger}$ which is the most reliable activation parameter obtainable from nmr exchange studies. Special attention has been devoted to the question of the effect of $1/T_2$ on calculated rates and activation parameters.



I, X = H; Y = Cl
II, X = Cl; Y = H
III, X = Br; Y = H

Experimental Section

Nmr Measurements. The synthesis of compounds I, II, and III is given in ref 10 and 11. Samples of olefins I, II, and III were prepared for the variable-temperature study by dissolving 100 mg of the dried pure sample in 0.45 ml of 1,1,2,2-tetrachloroethane containing about 1.5% tetramethylsilane as internal standard. The solvent was purified prior to its use by the usual procedure.[12] The dissolved sample was then filtered into an A-60 nmr tube through a plug of glass wool. The samples were degassed by several of the usual freeze–thaw cycles and then sealed under vacuum. In the case of compound III, however, the tube was filled with argon and sealed at atmospheric pressure.

The spectra were measured on Varian Associates Models A56-60 and A-60A analytical high-resolution nmr spectrometers equipped with the V-6040 variable-temperature probes. The probe temperature was measured by means of a copper–constantan thermocouple. The sweep time was kept constant at 250 sec. The sweep width was 100 Hz below coalescence and 50 Hz above coalescence. Calibration of the spectra was carried out by audio-side-band technique using a Hewlett-Packard Model 200CD audiooscillator and Hewlett-Packard Model 5245L frequency counter. Usually, only two spectra were measured at each temperature. Chemical shift differences generally agreed to ±0.3 Hz while line widths at half-maximum intensity agreed to ±0.05 Hz for narrow bands and to ±0.1 Hz for broad bands. Additional spectra were measured only if one of the two was significantly different.

Line-Shape Analysis. The digitization of experimental spectra was carried out on a Benson-Lehner Model F curve reader equipped with an Oscar Model F decimal converter and an IBM 26 printing card punch.

A Fortran program CURVE 2 was used to perform the line-shape analyses on an IBM 7094 computer. The program is very similar to those described in detail in our previous papers dealing with coupled AB systems[9] and uncoupled AB systems with different relative populations.[13] The input to CURVE 2 includes the chemical shift, $\delta\nu$, total line width, $\Delta\nu_{1/2}$, in the absence of exchange, the observed spectrum as a set of about 100 digitized absorption intensities at stated intervals in frequency, and a "guessed value" for the exchange rate k. In the CURVE 2 program we used dichotomous search routines[14] to obtain best fit between the experimental and calculated spectrum. A graphical output using a Calcomp plotter provided a convenient visual check of the agreement between calculated and experimental line shapes.

Results and Discussion

Proton High-Resolution Spectra. In the slow exchange region the nonequivalent axial and equatorial methyl groups in I, II, and III give rise to a pair of lines centered at approximately τ 8.4. The chemical shifts in the absence of exchange are found to be 28.3 Hz (14.9°) for I, 27.4 Hz (36.5°) for II, and 25.6 Hz (57.4°) for III. The solvent used was 1,1,2,2-tetrachloroethane which produced, however, broadening of the peaks observed due to its high viscosity at temperatures below *ca.* 40°. It was found that the low-temperature line width of the high-field peaks in both compounds I and II reached a minimum value of 2.4 and 1.9 Hz, respectively, and then began to broaden again. As the temperature is lowered progressively to −12.6°, the high-field peak in I and II continues to broaden to *ca.* 3.6 Hz while the downfield peaks broaden at a slightly faster rate. For compound I at 3.1°, for example, the downfield peak has a band width of 3.4 Hz while at −12.6° it reaches 6.0 Hz. Similar behavior was found for compound II. These data are summarized in Table I. In chloroform, on the other hand, the line widths of the methyl signals for both compounds at similar temperatures are considerably narrower, the limiting minimum values being about 1.5 Hz for the high-field peak and 1.8 Hz for the low-field peak. From the data for compound III in Table I it appears that the line width of the high-field peak is 1.5 Hz. It is therefore concluded that no excessive viscosity broadening is observed at ~45° and that any broadening above this temperature will be predominantly due to exchange.

The difference in line width observed in 1,1,2,2-tetrachloroethane and in chloroform can be ascribed mainly to viscosity effects. However, even in a con-

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Table I. The Effect of Solvent on the Line Width at Half-Maximum Intensity for Compounds I, II, and III Measured at Low Temperature

Chloroform			1,1,2,2-Tetrachloroethane		
	$\Delta\nu_{1/2}$, Hz			$\Delta\nu_{1/2}$, Hz	
t, °C	Downfield	Upfield	t, °C	Downfield	Upfield
		Compound I			
−12.6	1.9	1.5	−12.6	6.0	3.6
−4.8	1.8	1.6	−2.0	4.4	2.6
4.8	2.0	1.8	3.1	3.4	2.4
8.0	3.6	2.6	8.8	3.6	2.7
		Compound II			
−4.8	1.8	1.5	−12.6	7.1	3.6
4.8	1.7	1.4	−2.0	5.1	2.4
10.3	1.6	1.4	8.0	3.8	2.2
16.3	1.8	1.4	14.5	2.9	1.9
23.5	1.9	1.7	20.3	2.9	2.1
		Compound III[a]			
40.0	2.3	1.5	62.5	3.6	3.0
45.6	2.2	1.5	67.8	4.4	4.0
51.4	2.3	2.0	73.5	6.4	6.0
57.2	2.7	2.5	78.7	9.8	9.7

[a] Only 1,1,2,2-tetrachloroethane was used as solvent.

siderably less viscous solvent such as chloroform, the line width is much broader than the line width of 0.6–0.8 Hz observed in the fast exchange limit. One also observes a difference in line width between the high-field and low-field peaks. Furthermore, the line width of tetramethylsilane in both solvents is 0.5–0.6 Hz at low temperatures. From the line width of TMS one can estimate the inhomogeneity broadening at these temperatures. We propose that the major contribution to the line width, at these temperatures, is the long-range coupling between the nonequivalent methyl groups. A strong evidence for this explanation is the experimental finding that the line width is only 0.6–0.8 Hz in the fast exchange limit. One expects a decrease of this broadening due long range CH_3–CH_3 coupling with increasing inversion rate and this coupling should disappear altogether in the fast exchange limit. From the larger line width of the low-field peak (see Table I), however, it is apparent that this explanation is not sufficient since the same line width for both peaks would be expected if only long-range CH_3–CH_3 coupling was present.

Before suggesting an explanation for this additional differential broadening, it would be instructive to examine the geometry of the molecules in question and to assign resonance frequencies to the respective methyl groups. In the ground state the center ring of 9,10-dihydroanthracene has been shown[6] to have a boat conformation. The 10,10-dimethyl groups would therefore be magnetically nonequivalent since one would occupy a nearly axial position and almost perpendicular to the plane of the aromatic rings and the other a nearly equatorial position and parallel to the plane of the rings. Based on ring currents alone the predicted separation is 35 Hz.[6] One would expect that the equatorial methyl group would be deshielded by ring currents and appear at lower field. The axial methyl, on the other hand, lies in the positive shielding region over the aryl rings[15] and one would expect this group to lie farther upfield relative to the equatorial methyl group.

There are some examples in the literature that lend support to this predicted relationship. Barclay and Chapman[16] have reported the nmr spectrum of 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene. In this molecule the methyl groups must be in the equatorial position and were shown to absorb at τ 8.04 while the axial methylene protons appeared at 8.34. The fact that the methylene protons lie further upfield than the methyl protons illustrates the deshielding effect of the equatorial position. In compounds I, II, and III the low-field methyl signals appear at τ 8.15–8.25. Another example is provided by Lansbury, Bieron, and Lacher[17] in the 7,12-dihydropleiadene series. They found that the axial methoxy methyl group appears at τ 6.65 whereas its equatorial counterpart appears at 6.38. These assignments were verified recently by the application of the nuclear Overhauser effect.[18] Thus, it is reasonable to assign the low-field peak in the spectra of I, II, and III to the equatorial methyl and the high-field peak to the axial methyl group.

The apparent additional broadening observed for the low-field peak can be ascribed to stereospecific long-range coupling to aryl protons, or to more efficient relaxation of equatorial methyl protons due to the close proximity of the *o*-aryl protons. Stereospecific broadening due to long-range coupling was rationalized on the basis of Sternhell's[19] suggestion that benzylic protons which are nearly perpendicular to the plane of the aryl ring undergo long-range coupling with *ortho* and *para* protons. If analogy can be drawn from these examples,[20] it appears from models that the equatorial methyl protons in 10,10-dimethylanthracenes are more nearly perpendicular to the planes of the aryl rings and, therefore, would be more likely to experience a greater degree of long-range coupling with the aryl protons. There might also be a contribution to broadening due to efficient spin–lattice and spin–spin relaxation by direct dipole–dipole interaction with the *o*-aryl protons. Owing to the presence of differential broadening it was decided to carry out the line-shape analysis only of the high-field peak in the slow exchange region.

Rate Measurements. The rates of inversion were obtained from the nmr spectra of the methyl group protons by treating them as an uncoupled exchanging AB system with equal population. The input parameters for such line-shape analysis are the chemical shift $\delta\nu$ and T_2, the spin–spin relaxation time. There has been a growing tendency in recent literature to assess the over-all accuracy of nmr rate determinations (for detailed discussion, see ref 21). One of the possible sources of error can be the incorrect choice of $1/T_2$, the effective relaxation time which includes usually also the inhomogeneity broadening. The $1/T_2$ is estimated from the line width of the peak in the absence of chemical exchange ($1/\pi T_2 = \Delta\nu_{1/2}$) and a number of different procedures have recently been used by various

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(20) We are aware of the serious limitation of this explanation; see, *e.g.*, discussion of long-range coupling in toluene derivatives by Sternhell.[19]

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authors.[22] Fortunately, it has been repeatedly noted[22] that the choice of $1/T_2$ does not affect significantly the calculated rate if one carries out the analysis for intermediate exchange rates and excludes slow and fast exchange rates. The specific situation concerning line widths of compounds I, II, and III, namely, viscosity effects and broadening due to long-range coupling, requires a brief discussion of the value $1/T_2$ used in the line-shape analysis. For compounds investigated one can write for the slow exchange limit

$$1/T_2 = 1/T_2^0 + 1/T_2' + 1/T_2'' \qquad (1)$$

where $1/T_2$ is obtained from the observed line width in hertz at half-maximum intensity, T_2^0 is the "true" spin-spin relaxation time, $1/T_2'$ represents the inhomogeneity and other instrumental contributions to the observed line width, and $1/T_2''$ corresponds to broadening due to coupling. We assume that the main contribution to $1/T_2''$ is the long-range coupling between nonequivalent methyl groups. At temperatures below 0° $1/T_2^0 > 1/T_2''$, $1/T_2'$ due to viscosity broadening; at approximately 30-40° $1/T_2'' > 1/T_2'$, $1/T_2^0$. At high temperatures in the fast exchange limit we can neglect $1/T_2''$ in the first approximation as there is no coupling between equivalent methyl groups and the main contribution to observed line width is due to magnetic inhomogeneity broadening, $1/T_2' > 1/T_2^0$, $1/T_2''$. The line width of TMS (0.5-0.6 Hz) does not change within the whole temperature region studied and thus indicates that the term $1/T_2'$ is constant. We assume that the best choice for $1/T_2$ in the line-shape analysis is to calculate $1/T_2$ by interpolation at each temperature from an assumed linear dependence between $1/T_2$ and temperature. The linear relationship was calculated from the low temperature value (at temperatures where no appreciable viscosity broadening is evident) and fast exchange high temperature value. The same procedure was used by Binsch and Roberts[22c] in their study of *trans*-cyclodecene-1,2,4,4,9,9-d_6. The error introduced by the incorrect value of $1/T_2$ is not large; one could practically eliminate its effect by restricting the rate study to the temperature region of intermediate exchange rates. However, this narrows the temperature range of measurements and could result in serious errors in activation parameters as has previously been noted.[21,23]

The rates of ring inversion for I, II, and III are given in Table II (see Figure 1). The calculated activation parameters are summarized in Table III. Table IV was included to illustrate the effect of $1/T_2$ ($1/\pi T_2 = \Delta\nu_{1/2}$) on the calculated activation parameters for ring inversion in compound II. From the results in Table IV it is apparent that E_a, log A, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are significantly changed by using different values of $1/T_2$ as input parameter for the line-shape analysis. $\Delta F^\ddagger$ is not very sensitive to changes in $1/T_2$, which is in agreement with expectation.[24] In spite of the fact that the largest error in rates and activation parameters is introduced by uncertainty in temperature, the results given indicate that the effect of $1/T_2$ should not be disregarded in many specific cases of chemical exchange studies.

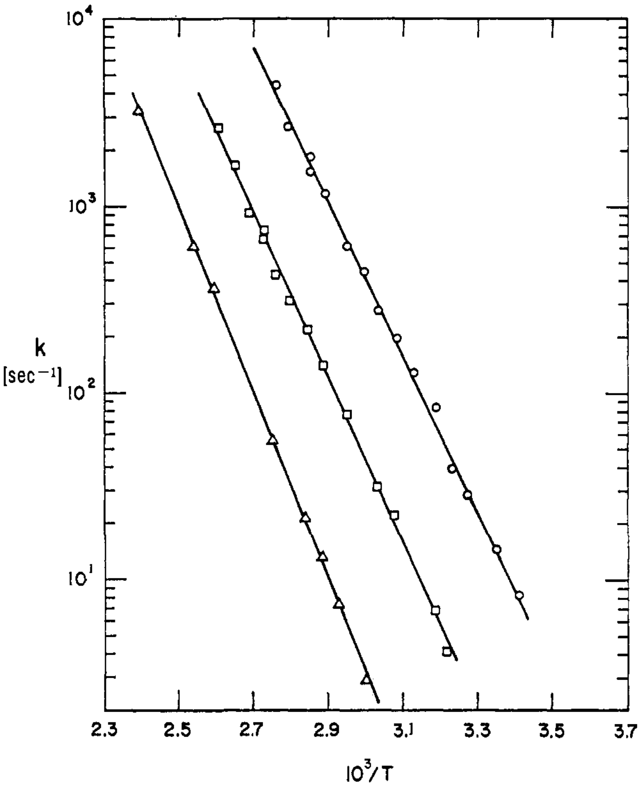

Figure 1. Arrhenius plots of the ring inversion rate for compounds I (○), II (□), and III (△).

Table II. Rates for Ring Inversion in Compounds I, II, and III

t, °C	k, sec^{-1}	t, °C	k, sec^{-1}
	Compound I		
20.1	8.1	61.1	447
25.9	14.5	65.8	608
33.0	28.4	73.3	1180
36.5	39.2	77.2	1520
41.0	83.3	77.5	1872
46.9	129.6	84.7	2700
51.5	199.2	89.1	4440
56.5	277		
	Compound II		
37.8	4.2	89.1	430
41.0	6.9	93.4	670
51.6	20.2	93.7	750
56.5	32	99.1	960
65.8	76	99.3	900
73.3	140	104.8	1680
78.7	220	111.0	2600
84.7	312	114.0	2700
	Compound III		
57.4	2.9	90.1	55.0
67.8	7.4	112.5	364.5
73.5	13.2	120.5	610.0
78.7	21.5	144.8	3360

Ring Inversion. The data given in Table III suggest that E_a, log A, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are within experimental error which is nearly the same for all three compounds,

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Table III. Thermodynamic Parameters for Ring Inversion in Compounds I, II, and III

	Compound^a		
	I	II	III^b
Temperature	20.1–89.1	37.8–111.4	57.4–144.8
E_a, kcal/mol^c	19.2 ± 1.7	20.3 ± 1.8	22.3 ± 2.0
Log A	15.1 ± 0.6	14.9 ± 0.6	15.2 ± 0.6
$\Delta H^{\ddagger}$, kcal/mol^{c,d}	18.6 ± 1.7	19.7 ± 1.8	21.7 ± 2.0
$\Delta F^{\ddagger}$, kcal/mol^{c,d}	15.9 ± 0.3	17.4 ± 0.3	19.0 ± 0.3
$\Delta S^{\ddagger}$, eu^{c,d}	+8.9 ± 7.0	+7.6 ± 6.0	+8.9 ± 9.0

[a] $1/T_2$ used in line-shape calculations estimated by interpolation (see text). [b] Activation parameters obtained by line-coalescence technique:[6] $E_a = 15.1 - 16.5$ kcal/mol; log $A = 10.8 - 11.6$; $\Delta H^{\ddagger} = 14.5 - 15.9$ kcal/mol; $\Delta F^{\ddagger} = 17.9 - 18.1$ kcal/mol; $\Delta S^{\ddagger} = -7.2 - (-11.2)$ eu; $\Delta H^{\ddagger}$, $\Delta F^{\ddagger}$, $S^{\ddagger}$ evaluated at 305.2°K. [c] The error limits are sums of the following contributions: probable error from least-square treatment (Arrhenius plot), error due to temperature uncertainty ±1°, systematic error due to assumed ±0.2 Hz uncertainty in line width; in the case of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ also the error due to estimated ±10% error in rate. The largest contribution for E_a and $\Delta H^{\ddagger}$ is due to temperature error. [d] Evaluated at 298.1°K.

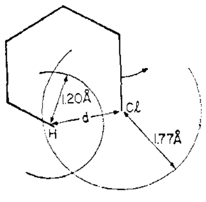
Table IV. Activation Parameters of Compound II Calculated by Using Different Values of Line Width for Line-Shape Calculations

$\Delta\nu_{1/2}$, Hz	E_a^{a}	Log A	$\Delta H^{\ddagger}_{298.1°}$^{a}	$\Delta F^{\ddagger}_{298.1°}$^{a}	$\Delta S^{\ddagger}_{298.1°}$^{b}
0.4	16.9	12.8	16.3	17.0	−2.1
0.6	17.8	13.4	17.2	17.0	+0.6
0.8	18.8	14.0	18.2	17.2	+3.5
1.0	18.6	13.9	18.0	17.1	+2.5
1.2	19.6	14.5	19.0	17.2	+5.9
1.4	20.2	14.8	19.7	17.5	+7.3
1.9	21.6	15.8	21.0	17.5	+11.8
Variable^c	20.3	14.9	19.7	17.4	+7.6

[a] In kilocalories per mole. [b] In entropy units. [c] See text.

I, II, and III, although a higher value in E_a and $\Delta H^{\ddagger}$ for compound III is indicated. In view of the rather large experimental error, however, little in the way of conclusions can be drawn from this indication. The free energy of activation, $\Delta F^{\ddagger}$, has been shown to be the most reliable activation parameter obtained by the nmr technique.[24] The data in Table IV show its relative insensitivity even at the extremes of $1/T_2$ used to calculate the rate constants and activation parameters. Furthermore, although the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for compound III obtained in this study are different from the values obtained (see Table III) by the coalescence technique,[6] the $\Delta F^{\ddagger}$ agrees to within experimental error at the coalescence temperature. The differences in rate constants for inversion in compounds studied are well outside the experimental error. Any discussion of the energetics of these ring inversions should be limited to consideration of the free energies of activation only.

As is apparent from Table III, the rate of inversion varies in the order I > II > III. Most striking is the difference in the rate constants for inversion of compounds I and II. At first glance, it would appear that the transition states should be identical in that the same atoms are involved. Before possible sources for the difference observed will be evaluated, some assumptions must be made. First of all, it is assumed that the contribution to the barrier from the 10,10-dimethyl groups will be identical in both compounds. Secondly, it is assumed that the presence of chlorine atoms on the exocyclic double bond will not alter the bond length of the olefinic linkage. It has been observed that in 1,1-difluoroethylene[25] and 1,1-difluoropropene[26] the olefinic bond is shorter than it is in ethylene and propene. From the literature electron diffraction data[27] it appears that this is not so important in chloroolefins. It is reasonable to assume that the olefinic bond length will be very nearly the same in I and II. One has also to realize that the difference in barrier can originate from a difference in energy in the transition states, *i.e.*, the transition state for II is of higher energy than that for I, or, alternatively, that the ground state for II is of lower energy than that for I. From inspection of Dreiding models of both compounds one can assume that the difference in barrier between I and II arises from the energy difference in highly strained transition states as the ground-state boat conformation seems to be relatively free from strong repulsion interactions between exocyclic CH_2, or CCl_2 groups, and adjacent *o*-aryl groups. We also assume that the nonbonded interactions between the exocyclic methylene substituents and *o*-aryl substituents are the dominant interactions giving rise to the potential barrier for ring inversion in I, II, and III. On the basis of analogy with racemization of substituted diphenyl[6,8] we propose a planar model for the transition state. Using equilibrium values of bond angles and bond lengths one calculates the interatomic distance of 1.6 Å between hydrogen and chlorine in the planar transition state of compounds I and II. If one compares the sum (3.97 Å) of the van der Waals radii[28] of hydrogen (r_w = 1.2 Å) and chlorine (r_w = 1.77 Å) with this calculated distance of 1.6 Å one arrives at an unambiguous conclusion that in the transition state the bond angles will be distorted and bonds stretched in order to increase the hydrogen–chlorine distance and to reduce their strong repulsion. For the distance of 1.6 Å the use of the potential function for H–Cl interactions introduced by Howlett[29] yields the value E > 100 kcal/mol for the repulsive energy. In direct analogy with I is the situation in the planar transition state of 2,2′-dibromo-4,4′-dicarboxydiphenyl for which Westheimer[30] calculated that the various bonds are stretched and bond angles changed so as to increase the distance between bromine and hydrogen atoms by 0.7 Å. The in-plane deflection of the two carbon to bromine bonds by about 12° is the major factor in relieving the strain (H–Br repulsion) in the planar activated complex. From schematic drawing[31] A it follows that also in I the deflection of the



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(31) Only the bonds assumed important in determining the energy barrier in I are depicted. For symmetry reasons only half of the molecule is shown.

C–Cl bonds[32] is expected to be the main distortion to increase distance *d*. The energy corresponding to an in-plane deformation of the C–Cl bond by $\theta°$ is $U = {}^1/_2 k \cdot d_{\mathrm{C-Cl}}{}^2\theta^2$, where k is the in-plane bending force constant,[33] $k = 0.96 \times 10^5$ dyn cm^{-1}, $d_{\mathrm{C-Cl}}$ is the C–Cl bond distance, 1.71 Å, and θ is the deformation angle. For $\theta = 5$ and 10° one obtains $U = 3.1$ and 12.3 kcal/mol, respectively. This increases the distance *d* by 0.2 and 0.33 Å. The geometry of the interactions in compound II is not so favorable as that in I. First, the decrease in CCCl angle which will result in an increase in *d* requires energy to overcome both the repulsion due to the second chlorine on the exocyclic methylene and to deform the C–Cl bond angles. The two chlorines at the exocyclic methylene group have a "butressing effect" on each other.

An interesting experiment which could contribute to our understanding of the origin of the energy barrier would involve measuring the ring inversion in derivatives of compounds I and II substituted with chlorines in positions 2 and 7. These chlorines would be expected particularly in compound I to inhibit bending of C–Cl bonds through a "butressing effect." Similar effects have been observed in the biphenyl series.[34]

The explanation of the larger barrier to inversion in II when compared to I is relatively simple; the difference undoubtedly arises from the larger size of the bromine atoms in comparison to chlorine atoms. Since the analogy between the gross structure of the transition states in the racemization of optically active biphenyls and the inversion in compounds of the kind exemplified by I, II, and III has been drawn, it is of interest to compare the data for the racemization of 2,2′-dibromo-4,4′-dicarboxybiphenyl (IV) and the inversion data for III. Harris[35] measured the rate constants for the racemization of IV in ethanol and found that the Arrhenius activation energy was 18.9 kcal mol^{-1} while $\Delta S^{\ddagger}$ was -4.9 eu. Using the experimental data $\Delta F^{\ddagger}$ was found to be 20.0 kcal mol^{-1} at 25°. These data compare quite favorably with the $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ for III.

In view of the difficulty with line widths it appears that the errors might have been somewhat alleviated if compounds I, II, and III with one methyl-d_3 had been used. An approach similar to that used for cyclohexane-d_{11}[22d] may have given more reliable values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. It appears that long-range CH_3–CH_3 coupling would be eliminated; however, in view of the fact that methyl-d_3 has different steric requirements, the populations at sites A and B would not be equal.

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Nuclear Magnetic Resonance Studies of Phenoxy Radicals. Spin Delocalization in Cyclic Aliphatic Substituents

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Abstract: We have taken the nmr spectra of a series of phenoxy radicals with cyclic aliphatic substituents in the free radical solvent di-*t*-butyl nitroxide Rapid spin exchange between solvent and solute molecules allows one to observe relatively sharp lines from the solute radicals in dilute solutions. Spectra from two different geometric isomers were observed in each case. The coupling constants for the various groups of protons in the radicals were found to depend on the relative geometries of the molecules. Long-range couplings through the aliphatic rings were observed in most cases. Electron spin resonance spectra of each of the radicals were taken and were found to be in good agreement with the results predicted from the nmr experiments.

There have been numerous theoretical and experimental studies of π-electron spin densities in aromatic radicals reported in the past few years. In contrast to this there is a relatively meager amount of information available about spin delocalization through aliphatic chains.[1] The resolution of esr spectra is generally too poor to allow one to resolve splittings from protons on carbons removed more than two positions from an aromatic ring, and no information is obtained about the signs of the coupling constants. Most of the information available about long-range coupling through aliphatic chains has been obtained from nmr strudies of transition metal chelates.[2,3] In this article we report nmr studies of a series of phenoxy radicals with cyclic aliphatic substituents. This study has produced information about coupling to protons in

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