Steric Effects in Fast Thermal Z, E Isomerization of Overcrowded Ethylenes. Conformational Behavior of N,N'-Dimethylbiacridans[1]

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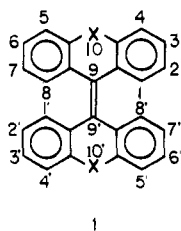
Abstract: The ground-state conformation of 2,2'-disubstituted N,N'-dimethylbiacridans (5) in solution was studied by various ^{1}H NMR spectroscopic techniques. A folded A-type structure with N-Me groups occupying predominantly the axial positions fits the experimental findings. The existence of geometrical isomers in this series is established, the Z:E ratio in solution being dependent on the bulkiness of the 2 and 2' substituents. In the 2,2'-di-i-Pr derivative (5d) only the E form was detected in the crystalline state. A DNMR study of 5 revealed low values of free energy of activation for thermal Z, E isomerization: $\Delta G_c^{\ddagger}$ ~ 21 kcal/mol. These unusual low energy barriers are ascribed predominantly to the high energy contents of the folded ground-state conformations of 5. The increase of $\Delta G_c^{\ddagger}$ with the bulkiness of the 2,2' substituents found is interpreted in terms of [R(2)-H(7')] type secondary steric interactions in the transition state for the process. An isomerization pathway in which the transition state is not the orthogonal biradical $\pi/2$ twisted ethylene is suggested.

Introduction

It is well known that restricted rotation about the $p_\pi-p_\pi$ double bond leads to geometrical isomers (Z, E isomerism). The activation energies for Z, E isomerization are usually high: in (E)-1,2-dideuterioethylene, E_a = 65 kcal/mol with a "normal" log A value of 13. These high energy barriers may, in principle, be reduced by a stabilization of the transition state or a destabilization of the ground state for isomerization.[2-6]

The transition state for thermal Z, E isomerization in simple ethylenes is considered to be the orthogonal (biradical or dipolar) $\pi/2$ twisted ethylene.[2-7] Steric accelerations of the rate of rotation about the $p_\pi-p_\pi$ carbon–carbon double bond have been attributed to ground-state destabilization: the steric interactions are relieved in the orthogonal transition state.[2-10] The studies of the mechanisms of thermal Z, E isomerizations around carbon–carbon double bonds have been focused mainly on polarized systems, e.g., push–pull ethylenes, and on electronic effects. Very little attention has been drawn to Z, E isomerizations in symmetrical overcrowded ethylenes, in which steric effects may become the most significant.[1-3,5,6] Liebman and Greenberg[6] have recently surveyed strained organic molecules and it is evident that the data on the conformational behavior of overcrowded ethylenes is scarce.[6,11]

The bistricyclic ethylenes (1) are attractive substrates for

1

2, X = C=O, Bianthrone

3, X = O, Dixanthylene

4, X = CH₂, 10,10,10',10'-Tetrahydrobianthrylidene

the study of the ground-state conformation and the dynamic behavior of symmetrical overcrowded ethylenes. An idealized coplanar bistricyclic ethylene would maintain very short nonbonded carbon–carbon and hydrogen–hydrogen distances (e.g., C(1)-C(1'), H(1)-H(1')), leading to a considerable overlap of the van der Waals radii in the region of the central double bond ("pinch"). The associated repulsive interactions could, in principle, be relieved by deviations from coplanarity

and by various distortions, e.g., folding in opposite directions at the olefinic termini, torsion around the pinch, stretching of the pinch (and a combination of these effects).[6,12,13] Indeed, an early x-ray crystallographic determination of the crystal and molecular structure of bianthrone (2) indicated that the molecule adopts (in the ground state) a folded centrosymmetric geometry (A form): the central rings are boat shaped and the
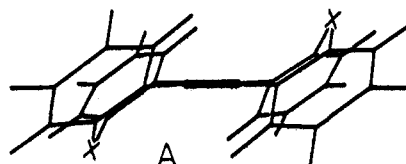
tricyclic halves are folded in opposite directions.[14] On the other hand, the colored B form of bianthrone is assumed to exist in a twisted conformation with a calculated torsional angle of 57°.[13,15] It is usually accepted that the ground-state structure of 5 resembles the A form of bianthrone.[16]

In the past, the existence of Z, E isomers and thermal isomerization in the overcrowded bistricyclic systems (1) has hardly been noticed.[1] The "void" of geometrical isomerism served as a basis for explaining the thermochromic properties of the bianthrones.[12] The extensive studies of the origin of the thermochromism, photochromism, and piezochromism exhibited by these systems generally overlooked the possibilities of Z, E isomerism and isomerization.

Fast diastereomerizations were observed in 1,1'-disubstituted $\Delta^{9,9'}$-bisfluorenylidenes carrying bulky groups,[17] but it was not clear whether these exchange processes represented Z, E isomerizations or the interconversion between twisted and folded ethylenes of a chiral conformation.[2] In any event, these phenomena are not an intrinsic feature of the unsubstituted bisfluorenylidene system.[18]

The objective of our investigation was to reveal the ground-state conformations and the dynamic stereochemistry in the bistricyclic ethylenes series (1), in solution. Representatives of 1 are bianthrone (2), dixanthylene (3), 10,10,-10',10'-tetrahydrobianthrylidene (4), and N,N'-dimethylbiacridan (5). Special emphasis was drawn to the role of steric effects in Z, E isomerizations of these symmetrical overcrowded ethylenes. The present article is devoted to the 5 series.

The Ground-State Conformation and Spatial Arrangement of N,N'-Dimethylbiacridans in Solution. The substrates of the present investigation were 2,2'-disubstituted N,N'-dimethyl-
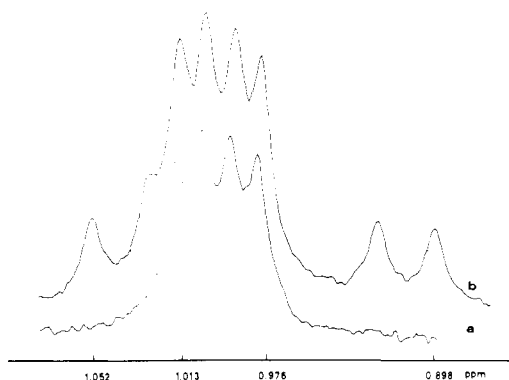
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Figure 1. 270-MHz ¹H NMR spectra of the *i*-Pr groups (methyl protons) of **5d** in CDCl₃ (δ, Me₄Si), at −42 °C: (a) pure *E* isomer; (b) *E* and *Z* isomers after equilibration at room temperature. See text for details.

Figure 2. 100-MHz ¹H NMR spectra of the aromatic protons of **5b** in CDCl₃ (δ, Me₄Si).

biacridans (**5**). The introduction of tag substituents at the 2 and 2′ positions permits an NMR study of *Z*, *E* isomerism and thermal isomerization, without substantially changing the ground-state steric overcrowding around the pinch relative to the parent compound (**5a**). Tag substituents at the 3 and 3′

5a, R = H

5b, R = Me

5c, R = Et

5d, R = i-Pr

5e, R = t-Bu

5f, R = OCH₃, 6,6'-di-Cl
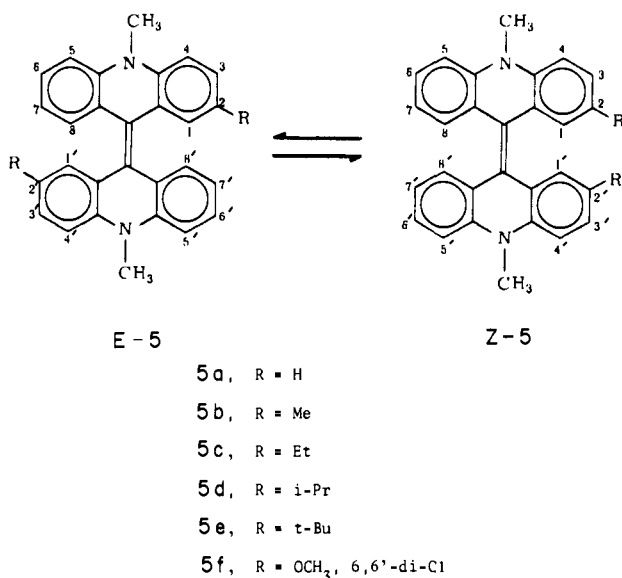
positions would be too far away from the other half of the molecule and therefore inconvenient probes for detection of inequivalent magnetic environment in the two geometrical isomers by conventional NMR techniques. On the other hand, the introduction of substituents at the 1 and 1′ positions would lead (in most cases) to the exclusive formation of *E* isomers because of enhanced steric repulsions in the corresponding *Z* isomers.[19]

The ¹H NMR spectra of all the *N,N'*-dimethylbiacridan derivatives (**5b–f**) studied show the presence of two geometrical forms, *Z* and *E* (see Experimental Section).[20] The *E* isomer has a center of inversion (i) while the *Z* isomer has a *C₂* symmetry axis; hence,˙ symmetry causes both substituents at each geometrical isomer to be isochronous. A folded ground-state conformation of **5** would tend to prevent additional steric interactions between the 2,2′, 7, and 7′ positions, as long as the substituents are small. Indeed, the *Z:E* isomeric ratio in **5b** and **5f** is 1 while in the cases of the bulkier substituted derivatives **5c**, **5d**, and **5e**, it differs from 1, in accordance with the corresponding steric radii.[21] In order to examine whether the *N,N'*-dimethylbiacridan system adopts a folded A type form in solution, the isopropyl prochiral substituent was employed. If the geometry is in fact a folded one, the two methyl groups of the *i*-Pr become diastereotopic and may show chemical shift
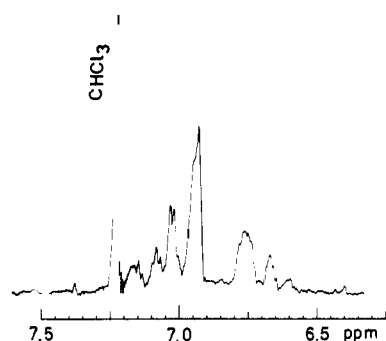
nonequivalence.[22,23] The methyl region of a 270-MHz ¹H NMR spectrum of **5d** is shown in Figure 1. It indicates the presence of both the *Z* and the *E* isomer in the ratio of 1:2.4. The *i*-Pr groups of each isomer appear as a double doublet (two lines at the left of the spectrum overlap incidentally). This spectrum is consistent with a structure lacking a plane of symmetry, e.g., the folded A form. Additional support for the folded geometry in solution may be obtained by examining the region of the aromatic protons in the ¹H NMR spectrum (Figure 2). In all derivatives of **5** examined, more than half of the aromatic protons appear at a high field (6.50–6.95 ppm). These are identified as the protons ortho to the nitrogen bridge [H(4), H(4′), H(5), H(5′)] and the protons ortho to the pinch [H(1), H(1′), H(8), H(8′)]. The latter ones are shifted to a high field by the ring current of the opposing benzene rings. Such a shift indicates the proximity of these protons to the sixfold axes of the opposite benzene rings, in accordance with the folded A form.

In a recent investigation of the photochromic properties of *N,N'*-dimethylbiacridan (**5a**), it has been assumed that the *N*-methyl groups adopt an equatorial position in the A form.[16] This assumption seems oversimplified, in view of the controversy concerning the question of axial vs. equatorial preference of the lone pair in piperidine systems,[24] and in view of the low barriers to nitrogen inversion found in N-Me piperidine derivatives carrying exocyclic double bonds.[25] An insight into this problem may be gained by examining the large ASIS effect[26] on the ¹H NMR N-Me signals of **5a** and its derivatives. Table I summarizes the experimental results of **5b** and the model compound 2,2′-dimethyl-10,10,10′,10′-tetrahydrobianthryl-idene (**4a**).[27] It is reasonable to assume that the model system (**4a**) adopts a folded conformation in the ground state (analogous to the A form of bianthrone)[16,28] in which the two hydrogens of each methylene bridge would occupy an axial and an equatorial position, respectively. Such a folded conformation of **4a**, in which the central ring adopts a boat-shaped conformation, has a substantial barrier to inversion. This is revealed by the ¹H NMR spectrum of the methylene protons of **4a** at room temperature. It shows the presence of an AB quartet (Table I) in which the low-field part contains broadened peaks due to additional coupling and the high-field part contains sharp, uncoupled peaks. The high-field sharp absorptions represent the axial protons shielded by the ring current of the benzene rings underneath. These axial protons form a ca. 90° angle with the neighboring ring protons ortho to the methylene bridge [H(4), H(5), H(4′), H(5′)], thus avoiding any mutual coupling. On the other hand, the equatorial protons are shifted to low field by the ring current and are allylically coupled with H(4), H(5), H(4′), and H(5′), the corresponding angles being ca. 0°. By changing the solvents from deuteriochloroform to 1-bromonaphthalene, only the axial methylene protons in **4a** are substantially shifted to a high field, while the equatorial protons retain their chemical shift.
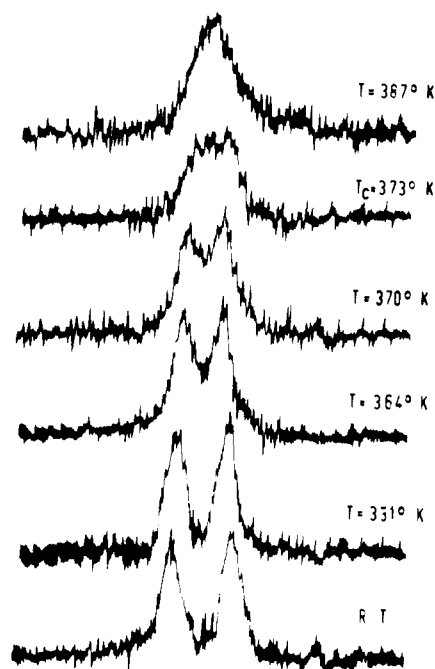
Figure 3. ^{1}H DNMR spectra of **5f** in 1-bromonaphthalene.

Table I. The ASIS Effect in **5b** and **4a**[a]

A. 2,2′,N,N′-Tetramethylbiacridan (**5b**)

| | N-CH$_3$ resonance, ppm | |
solvent	δ_{Me_4Si}	$\Delta = \delta_{CDCl_3} - \delta_{Ar}$
CDCl$_3$	3.49	0
pyridine	3.42	0.07
bromobenzene	3.21	0.28
benzene	3.02	0.47
1-bromonaphthalene	2.95	0.54

B. 2,2′-Dimethyl-10,10,10′,10′-tetrahydrobianthrylidene (**4a**)

| | 10,10′-CH$_2$ resonances, ppm | | | |
| | H$_A$ | | H$_B$ | |
solvent	δ_{Me_4Si}	$\Delta = \delta_{CDCl_3} - \delta_{Ar}$	δ_{Me_4Si}	$\Delta = \delta_{CDCl_3} - \delta_{Ar}$
CDCl$_3$	3.72		4.12	
	3.88		4.29	
1-bromonaphthalene	3.51	0.21	4.12	0.00
	3.67	0.21	4.29	0.00

[a] Measured at 100 MHz, concentration 6 mg/0.4 mL. The resonances indicated show major dependence on the solvent and only minor dependence on concentration. Other resonances were only slightly changed with the solvent. Accuracy of the data is ±0.01 ppm.

Thus, it may be concluded that only the axial position is strongly affected by the interaction with the aromatic solvent. By comparison, the substantial high ASIS shielding effect shown by the N-Me groups in the *N,N′*-dimethylbiacridan series (**5**) (as illustrated for **5b**) is interpreted in terms of a significant occupation of the axial positions by the N-Me groups. The low barriers to nitrogen pyramidal inversion in related compounds assure a rapid interchange (at room temperature) between the axial and the equatorial position, with a significant population of the former.

A preliminary x-ray study[29] of a single crystal of **5d** revealed the presence of two molecules in the unit cell, and the *P*2$_1$/*c* space group. On the basis of the molecular center of symmetry indicated by this finding, it is concluded that the single crystal of **5d** is composed exclusively of the *E* isomer. This conclusion is supported by the ^{1}H NMR spectrum of **5d** dissolved at low temperature (−42 °C) in CDCl$_3$ (Figure 1). The *i*-Pr region in this spectrum contains only signals due to the more populated isomer at room temperature. After gradually warming the solution to room temperature an appearance of additional signals due to the less populated isomer (at room temperature) is observed. Such a "diastereomeric transformation"[30] in passing from a mixture of two isomers in solution to one isomer in the crystalline state has previously been observed in several systems of dynamic isomers. These phenomena are a direct consequence of the phase rule.[31] On the basis of the x-ray study and the low-temperature ^{1}H NMR investigations, it is concluded that the more populated isomer in solution at room temperature is the *E* isomer. An analogous experiment employing random crystals obtained by a conventional recrystallization showed a major preference of the *E* isomer in the solid state, as compared with the relative population in solution (at room temperature).

Dynamic Behavior of *N,N′*-Dimethylbiacridans (5). The thermal behavior of **5** in solution was studied by the DNMR[3,32,33] method. Table II summarizes the ^{1}H DNMR results. The data were calculated by the usual coalescence approximation[3,32,33] or the graphic method approximation.[34] It is now generally accepted[33,35-37] that these methods give good approximations of the free energy of activation at the coalescence temperature, $\Delta G_c^{\ddagger}$. Usually $\Delta G_c^{\ddagger}$ values are the only reliable parameters obtained from the DNMR method,

while substantial errors may be involved in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters obtained by this method.[33,35-37] The $\Delta S^{\ddagger}$ values for monomolecular isomerizations such as $Z(5) \rightleftharpoons E(5)$ are expected to be similar and essentially zero.[2,4,25,37,38] Thus, valid conclusions may be drawn from $\Delta G_c^{\ddagger}$ values, in view of the narrow temperature range of their evaluation. The dependence of $\Delta \nu$ on the temperature in the low exchange limit was taken into account by a linear plot of $\Delta \nu$ vs. *T*, and extrapolating to T_c.[3] The ^{1}H DNMR spectra of **5f** are shown in Figure 3.

The most fascinating result indicated in Table II is the low values of free energy of activation at the coalescence temperature for the thermal *Z*, *E* isomerizations of **5b-f**: $\Delta G_c^{\ddagger} \sim 21$ kcal/mol. These unusual low energy barriers are ascribed *predominantly* to the high-energy contents of the folded ground-state conformations.

The introduction of substituents at the 2 and 2′ positions of the biacridan system permits an evaluation of the dependence of $\Delta G_c^{\ddagger}$ on the "size" of the substituents. Vögtle has recently emphasized the role of the "size" ("spatial requirement") of the substituents in evaluating conformational processes.[21] The picture that emerges in the case of **5** (Table II) is a significant *increase* in $\Delta G_c^{\ddagger}$ (for the process major conformer → minor conformer) on going to a bulkier substituent. This is contrary to the traditional[2,3,5,6,8-10] significant *decrease* in $\Delta G_c^{\ddagger}$ in substituted twisted ethylenes when the "size" of the substituent increases.

In order to rationalize this unconventional trend, the steric interactions in the vicinity of the pinch in the transition state as well as in the ground state should be considered. In an idealized planar model of **5**, the substantial overlaps of the van der Waals radii in the 1, 1′, 8, and 8′ positions (see Introduction) result in strong primary steric interactions. Consequently, the molecule deviates from coplanarity and adopts the folded A geometry in the ground state. The fast rates of *Z*, *E* isomerization of **5** indicate that the folded conformations are of relatively high energy owing to the transmission of primary steric interactions into π and σ electronic strain. As stated previously the folded A ground-state structure tends to prevent additional steric interactions between the 2, 2′, 7, and 7′ positions. However, these secondary steric interactions may be fully realized in the transition state. It would involve only one secondary steric interaction between a hydrogen and a substituent [R(2)–H(7′) or R(7)–H(2′)]. On the other hand, any secon-

Table II. ^{1}H NMR and Activation Data for the Process *E*-5 → *Z*-5 (Major → Minor Conformer)

compd	R in **5**	solvent	$\Delta\nu_c$, Hz (at 100 MHz)	T_c, K[a]	$\Delta G_c^{\ddagger}$, kcal/mol[b]	$\Delta G°$, kcal/mol
5f	OCH_3	1-bromonaphthalene	4.2 ± 0.1	373	20.3	0
5b	CH_3	1-bromonaphthalene	2.4 ± 0.2	375	20.8	0
5c	CH_2CH_3[c]	bromobenzene	3.3 ± 0.3	385	21.4	0.13 ± 0.05
5e	$C(CH_3)_3$	1-bromonaphthalene	5.5 ± 0.3	383	21.8	1.1 ± 0.1

[a] ±(3-4) K. [b] ±(0.2-0.3) kcal/mol. [c] The data of **5c** refer to the methyl triplets.
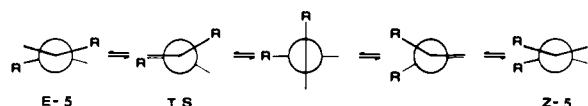
Figure 4. A proposed *Z, E* isomerization scheme of **5**.

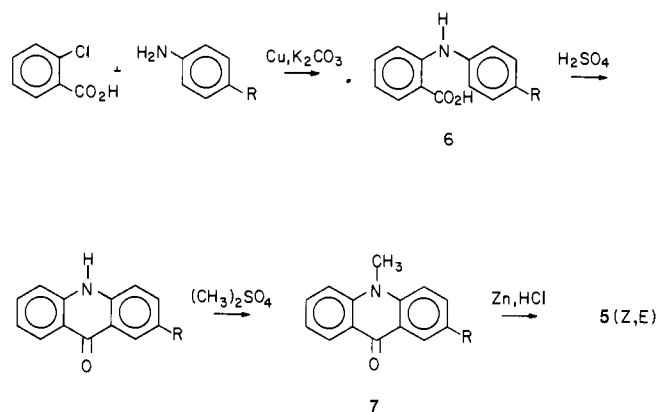**Figure 5.** Synthesis of *N,N'*-dimethylbiacridans (**5**).

dary steric interaction between two nonhydrogen substituents [R(2)-R(2')] would be avoided. The secondary steric interactions in the transition state are responsible for the observed trend in the $\Delta G_c^{\ddagger}$ values. A possible isomerization pathway involving only one-way rotations and avoiding R(2)-R(2') interactions is presented in Figure 4. Note that the suggested transition state is not the orthogonal biradical $\pi/2$ twisted ethylene. Thus, the DNMR evidence points toward a more complex isomerization pattern than that encountered in ground-state twisted ethylenes with the traditional orthogonal transition state for *Z, E* isomerization. This conclusion and the suggested transition state (Figure 4) are consistent with the calculated dependence of the strain energy on torsion around the pinch in bianthrones.[15] The calculations showed that the structure of highest energy is not the orthogonal ethylene but a ~40° twisted form. In this hypothetical transition state, only one primary [e.g., H(1)-H(8')] steric interaction is fully realized and an additional secondary [e.g., H(2)-R(7')] interaction may be displayed as well. The observed trend in the $\Delta G_c^{\ddagger}$ values is the result of these 2-7' interactions. Other ethylenes with steric barrier greater than π electronic barrier are known.[8] In the 2,2'-disubstituted *N,N'*-dimethylbiacridans under study, the full steric radius[21] of the bulkier groups (cf. ν_x parameters[39]) is not realized in the $\Delta G_c^{\ddagger}$ values. These values reflect the difference in energies between the ground state and the transition state; both energy states may be influenced by the "spatial requirements" of the substituents. In the process major → minor conformer, the secondary steric interactions are more pronounced in the transition state than in the ground state of the *E* isomer, as expressed in the trend of the $\Delta G_c^{\ddagger}$ values.

In conclusion, the steric strain in the overcrowded ethylenes studied may operate in two different directions. It may raise the ground-state energy through primary (1-8' and 1'-8) steric interactions leading to fast *Z, E* isomerization, but it may also raise the barriers to isomerization, if secondary steric effects [e.g., H(2)-R(7') interactions] are decisive in the transition state.

Synthetic Scheme. The synthesis of the model compounds, outlined in Figure 5, was based on known reactions. However, the application to new derivatives required several modifications (see Experimental Section). A good entry to the synthesis in this series is found in Albert's book.[40]

Experimental Section

General. The ^{1}H DNMR spectra were obtained using a Varian HA-100 NMR spectrometer equipped with a variable-temperature unit. The NMR changes proved to be reversible and characteristic of a dynamic exchange (apart from minor decomposition at high temperatures). Temperatures were measured with ethylene glycol using the substitution technique and the Varian correlation chart, and

are considered accurate within ±2 °C. ^{1}H NMR spectra were obtained on a Varian HA-100, CFT-20, and Bruker WH-270 NMR spectrometers using internal locking. ^{1}H NMR data reported were obtained on the HA-100 spectrometer unless otherwise stated, and are reported in parts per million downfield from Me_4Si as internal reference (δ units). IR spectra were recorded on a Perkin-Elmer 457 spectrometer. Electronic spectra were recorded on a Unicam SP-800 spectrometer. Mass spectra were recorded on a Varian MAT 311 spectrometer. Melting points were measured on a Fischer-Jones capillary melting point apparatus and are uncorrected. Samples were dried over P_2O_5 under vacuum (ca. 1 mm), usually at 100 °C, before analysis. No attempts were made to optimize yields.

4'-Methyldiphenylamine-2-carboxylic Acid (6a). To dry cyclohexanol (300 mL) previously boiled for some minutes to remove the azeotrope with water, anhydrous K_2CO_3 (83.0 g, 0.6 mol), dried over an open flame, *o*-chlorobenzoic acid (31.4 g, 0.2 mol), *p*-toluidine (23.6 g, 0.22 mol), and 0.3 g of copper bronze were added. The reaction mixture was then refluxed for 2 h (185-190 °C, oil bath). The solvent was removed by steam distillation, and the reaction mixture was filtered off. The solution was acidified (HCl) while still hot, and the precipitating acid was filtered off and washed with hot water to remove unreacted *o*-chlorobenzoic acid. Recrystallization from benzene-petroleum ether (bp 40-60 °C) gave the acid (**6a**) as colorless crystals: mp 197 °C (lit.[41-42] mp 197 °C); yield 62%; IR (Nujol) 1650 cm^{-1} (C=O); ^{1}H NMR (CDCl₃) δ 2.34 (s, 3 H), 6.45-7.40 (m, 7 H), 8.04 (dd, J_1 = 2, J_2 = 8 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 223 (4.23), 286 (4.17), and 352 (3.86); *m/e* 227 (M[+], 88%), 209 ([M − H₂O][+], 100%). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.84; H, 5.70; N, 6.32.

4'-Ethyldiphenylamine-2-carboxylic acid (6b) was prepared from *p*-ethylaniline by the procedure described above for **6a**, in 68% yield. It was obtained as colorless crystals: mp 171-172 °C (from benzene) (lit.[43] mp 174-175 °C); IR (Nujol) 1655 cm^{-1} (C=O); ^{1}H NMR (CDCl₃) δ 1.25 (t, *J* = 8 Hz, 3 H), 2.65 (q, *J* = 8 Hz, 2 H), 6.60-7.40 (m, 7 H), 8.02 (dd, J_1 = 8, J_2 = 2 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 287 (4.19) and 352 (3.88); *m/e* 241 (M[+], 100%).

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.45; H, 6.34; N, 5.87.

4'-Isopropyldiphenylamine-2-carboxylic acid (6c) was prepared from *p*-aminocumene by the procedure described above for **6a** in 39% yield. It was obtained as colorless crystals: mp 172-174 °C (from methanol-water); IR (Nujol) 1662 cm^{-1} (C=O); ^{1}H NMR (CDCl₃) δ 1.30 (d, *J* = 7 Hz, 6 H), 2.95 (m, *J* = 7 Hz, 1 H), 6.50-7.50 (m, 7 H), 8.03 (dd, J_1 = 8, J_2 = 2 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 286 (4.20) and 354 (3.90); *m/e* 255 (M[+], 98%), 222 (100%).

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.24; H, 6.77; N, 5.46.

4'-*tert*-Butyldiphenylamine-2-carboxylic acid (6d) was prepared from 4-*tert*-butylaniline by the procedure described above for **6a** in 50% yield. It was obtained as colorless crystals: mp 201–202 °C (lit.[44] mp 205–206 °C) (from benzene–hexane); IR (Nujol) 1653 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 9 H), 6.80–7.40 (m, 7 H), 8.04 (dd, $J_1 = 2, J_2 = 8$ Hz, 1 H); UV λ$_{max}$ (EtOH), nm (log ε), 287 (4.19) and 352 (3.87); *m/e* 269 (M$^+$, 50%), 254 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 76.06; H, 7.37; N, 5.09.

2,*N*-Dimethylacridone (7a). The acid **6a** (10 g) was added to concentrated H$_2$SO$_4$ (15 mL) and the mixture heated with magnetic stirring for 3–4 h, keeping the temperature within the reaction flask at ca. 85 °C. The reaction was terminated by pouring the mixture into hot water with efficient stirring. The greenish-yellow 2-methylacridone was collected and washed with water and 5% sodium bicarbonate. After drying, the crude product (6 g) was treated with KOH (6 g) and absolute ethanol (80 mL) and the mixture refluxed for a few minutes. The solvent was distilled off, and dry benzene was added and again distilled off to incomplete dryness. Dry benzene (130 mL) was added, and the stirred mixture was treated dropwise with dimethyl sulfate (7.5 mL) at room temperature. The reaction mixture was then warmed to 60 °C for another 1 h and poured on ammonia with water and the benzene was steam distilled. The precipitate was filtered off and washed with water. Recrystallization from ethanol–water gave **7a** in 91% yield as yellow crystals: mp 148–149 °C (lit.[42] mp 150–151 °C); IR (Nujol) 1630 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 2.41 (s, 3 H), 3.75 (s, 3 H), 7.05–7.65 (m, 5 H), 8.30 (bs, 1 H), 8.53 (dd, $J_1 = 2, J_2 = 8$ Hz, 1 H); UV λ$_{max}$ (EtOH), nm (log ε), 254 (4.29), 297 (3.03), 390 (3.54), and 408 (3.60); *m/e* 233 (M$^+$, 100%).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.60; H, 5.76; N, 6.53.

2-Ethyl-*N*-methylacridone (7b) was prepared from **6a** by the procedure described above for **7a** in 92% yield. It was obtained as yellow crystals: mp 138–139 °C (from benzene–petroleum ether, bp 40–60 °C); IR (Nujol) 1630 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 1.30 (t, $J = 8$ Hz, 3 H), 2.77 (q, $J = 8$ Hz, 2 H), 3.85 (s, 3 H), 7.00–7.80 (m, 5 H), 8.36 (d, $J = 2$ Hz, 1 H), 8.54 (dd, $J_1 = 2, J_2 = 8$ Hz, 1 H); UV λ$_{max}$ (EtOH), nm (log ε), 257 (4.71), 297 (3.45), 307 s (3.04), 389 (3.89), and 408 (3.95); *m/e* 237 (M$^+$, 83.3%), 222 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.78; H, 6.31; N, 6.23.

2-Isopropyl-*N*-methylacridone (7c) was prepared from **6c** by the procedure described above for **7a** in 93% yield. It was obtained as yellow crystals: mp 136–137 °C (from methanol–water); IR (Nujol) 1632 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 1.33 (d, $J = 7$ Hz, 6 H), 3.07 (m, $J = 7$ Hz, 1 H), 3.84 (s, 3 H), 7.00–8.00 (m, 5 H), 8.35–8.65 (m, 2 H); UV λ$_{max}$ (EtOH), nm (log ε), 257 (4.70), 297 (3.45), 308 s (3.08), 389 (3.88), and 407 (3/95(: *M/e* 251 (M$^+$, 33%), 236 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.08; H, 6.83; N, 5.95.

2-*tert*-Butyl-*N*-methylacridone (7d) was prepared from **6d** by the procedure described above for **7a** in 90% yield. It was obtained as yellow crystals: mp 169–170 °C (from ethyl acetate); IR (Nujol) 1631 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 1.39 (s, 9 H), 3.76 (s, 3 H), 7.00–7.80 (m, 5 H), 8.35–8.50 (m, 2 H); UV λ$_{max}$ (EtOH), nm (log ε), 256 (4.73), 296 (3.45), 307 s (3.11), 388 (3.89), and 406 (3.96); *m/e* 265 (M$^+$, 36%), 250 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.45, H, 7.34; N, 5.55.

2-Methoxy-6-chloro-*N*-methylacridone (7e). Commercial 2-methoxy-6,9-dichloroacridine (20 g) was hydrolyzed to 2-methoxy-6-chloroacridone by heating it at 120–130 °C for 2 h with 1 N HCl (100 mL). The product (6-chloro-2-methoxyacridone) was methylated by the procedure described above for **7a** in 89% yield. **7e** was obtained as yellow crystals: mp 244–245 °C (lit.[45] mp 245–246 °C) (from 1-butanol); IR (Nujol) 1634 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 3.81 (s, 3 H), 3.91 (s, 3 H), 7.00–7.45 (m, 4 H), 7.86 (d, $J = 2$ Hz, 1 H), 8.45 (d, $J = 9$ Hz, 1 H); UV λ$_{max}$ (EtOH), nm (log ε), 260 (4.62), 279 (4.72), 405 (3.86), and 424 (3.90); *m/e* 275 (M$_1$$^+$, 32%), 273 (M$_2$$^+$, 100%).

Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; Cl, 12.95. Found: C, 65.28; H, 4.74; Cl, 13.36.

2,2',*N*,*N*'-Tetramethylbiacridan (5b). To a magnetically stirred suspension of **7a** (2.0 g), zinc powder (5.2 g), and absolute ethanol (80 mL), a saturated solution of HCl in ethanol (80 mL) was added dropwise, while cooling with ice. The cooling bath was then removed and the reaction continued until most of the zinc was consumed (about 20 min). The reaction was terminated by pouring the mixture on water. The crude greenish product was filtered off and rinsed well with water. Recrystallization from toluene gave **5b** in quantitative yield, as a greenish powder: mp >300 °C (lit.[46] mp 330 °C); IR (Nujol) 1610, 1590, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.028, 2.045 (2 s, 1:1 ratio, 6 H), 3.49 (s, 6 H), 6.45–7.25 (m, 14 H); ^{1}H NMR (1-bromonaphthalene) δ 2.01, 2.04 (2 s, 1:1 ratio, 6 H), 2.95 (s, 6 H), ν$_Z$ – ν$_E$ (Me signals) = 3.5 Hz; UV λ$_{max}$ (CH$_2$Cl$_2$), nm (log ε), 273 (4.72), 293 (4.21), and 429 (4.17); *m/e* 414 (M$^+$, 65%), 399 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.23; H, 6.31; N, 6.87.

2,2'-Diethyl-*N*,*N*'-dimethylbiacridan (5c) was prepared from **7b** by the procedure described above for **5b** in quantitative yield. It was obtained as a greenish powder: mp 252 °C dec (from benzene-petroleum ether, bp 40–60 °C); IR (Nujol) 1610, 1593, 1581 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.96, 0.98 (2 t, 1:1.3 ratio, $J = 7$ Hz, 6 H), 2.35 (q, $J = 7$ Hz, 4 H), 3.48 (s, 6 H), 6.50–7.20 (m, 14 H); ^{1}H NMR (bromobenzene) δ 0.94, 0.98 (2 t, 1:1.18 ratio, $J = 7$ Hz, 6 H), 2.30 (q, $J = 7$ Hz, 4 H), ν$_Z$ – ν$_E$ (Me signals) = 4.1 Hz; UV λ$_{max}$ (CH$_2$Cl$_2$), nm (log ε), 238 (4.73), 296 (4.26), and 428 (4.14); *m/e* 443 (M$^+$, 100%).

Anal. Calcd for $C_{32}H_{30}N_2$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.80; H, 6.65; N, 6.64.

2,2'-Diisopropyl-*N*,*N*'-dimethylbiacridan (5d) was prepared from **7c** by the procedure described above for **5b** in 96% yield. It was obtained as a greenish powder: mp 265–268 °C dec (from benzene-hexane); IR (Nujol) 1607, 1590, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$, Bruker WH-270 MHz) δ 0.91–1.05 (m, 12 H), 2.60 (h, $J = 7.05$ Hz, 2 H), 3.53 (s, 6 H), 6.60–7.30 (m, 14 H); δ *E* (Me) 0.999, 1.009 (2 d, $J = 7.05$ Hz, 70%), δ *Z* (Me) 0.926, 1.036 (2 d, $J = 7.05$ Hz, 30%); UV λ$_{max}$ (EtOH), nm (log ε) 235 (4.74), 264 s (4.41), 285 s (4.26), and 422 (4.15); *m/e* 470 (M$^+$, 76%), 455 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{34}H_{34}N_2$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.77; H, 7.23; N, 6.26.

2,2'-Di-*tert*-Butyl-*N*,*N*'-dimethylbiacridan (5e), was prepared from **7d** by the procedure described above for **5b** in quantitative yield. It was obtained as a greenish powder: mp >300 °C (from toluene); IR (Nujol) 1608, 1590, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.05 (s, 18 H), 3.52 (s, 6 H), 6.60–7.25 (m, 14 H); ^{1}H NMR (1-bromonaphthalene) δ 0.91, 0.97 (2 s, 1:4 ratio, 18 H), 2.87 (s, 6 H), ν$_Z$ – ν$_E$ (Me signals) = 6.4 Hz; UV λ$_{max}$ (CH$_2$Cl$_2$), nm (log ε), 238 (4.68), 292 (4.24), and 426 (4.15); *m/e* 499 (M$^+$, 58%), 484 ([M – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{36}H_{38}N_2$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.91; H, 7.63; N, 5.82.

2,2'-Dimethoxy-6,6'-dichloro-*N*,*N*'-dimethylbiacridan (5f) was prepared from **7e** by the procedure described above for **5b** in 98% yield. It was obtained as an orange powder: mp >300 °C (from bromobenzene); IR (Nujol) 1610, 1590, 1560 cm^{-1}; ^{1}H NMR (CDCl$_3$, Varian CFT-20) δ 3.43 (s, 6 H), 3.45, 3.46 (2 s, 1:1 ratio, 6 H), 6.40–7.30 (m, 12 H); ^{1}H NMR (1-bromonaphthalene) δ 2.58 (s, 6 H), 3.12, 3.16 (2 s, 1:1 ratio, 6 H), ν$_Z$ – ν$_E$ (OMe signals) = 4.2 Hz; UV λ$_{max}$ (CH$_2$Cl$_2$), nm (log ε), 241 (4.71), 302 (4.24), and 446 (4.20); *m/e* 518 (M$^+$, 10%), 516 (M$_2$$^+$, 45%), 514 (M$_3$$^+$, 66%), 499 ([M$_3$ – CH$_3$]$^+$, 100%).

Anal. Calcd for $C_{30}H_{24}Cl_2N_2O_2$: C, 69.91; H, 4.69; Cl, 13.76; N, 5.44. Found: C, 70.10; H, 4.92; Cl, 14.43; N, 5.32.

References and Notes

(1) Preliminary reports of this study have appeared: I. Agranat and Y. Tapuhi, *J. Am. Chem. Soc.*, **98**, 615 (1976); *Nouveau J. Chim.*, **1**, 361 (1977); Abstracts, Third International Symposium on the Chemistry of Novel Aromatic Compounds (ISNA 3), San Francisco, Calif., Aug 21–25, 1977, Paper 14.
(2) H. O. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1973).
(3) I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, **4**, 71 (1971).
(4) R. B. Cundall, *Prog. React. Kinet.*, **2**, 165 (1964).
(5) L. M. Jackman in "Dynamic Nuclear Magnetic Resonance Spectroscopy",

L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, p 203.
(6) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976).
(7) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
(8) J. Sanström, U. Sjöstrand, and I. Wennerbeck, *J. Am. Chem. Soc.*, **99**, 4526 (1977).
(9) Y. Shvo, *Tetrahedron Lett.*, 5923 (1968).
(10) A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. B*, 111 (1969).
(11) There is recent renewed activity in the field of overcrowded ethylenes: G. A. Olah and G. K. Surya Prakash, *J. Org. Chem.*, **42**, 580 (1977); B. Feringa and H. Wynberg, *J. Am. Chem. Soc.*, **99**, 602 (1977).
(12) Reviews on the structure and the thermochromic, photochromic, and piezochromic properties in this series: G. Kortüm, *Ber. Bunsenges. Phys. Chem.*, **78**, 391 (1974); T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, **24**, 531 (1970); J. H. Day, *Chem. Rev.*, **63**, 65 (1963); E. D. Bergmann, *Prog. Org. Chem.*, **3**, 81 (1955).
(13) H. L. Ammon and G. L. Wheeler, *J. Am. Chem. Soc.*, **97**, 2326 (1975).
(14) E. Harnic and G. M. J. Schmidt, *J. Chem. Soc.*, 3295 (1954); E. Harnic, F. H. Herbstein, G. M. Schmidt, and F. L. Hirshfeld, *ibid.*, 3288 (1954).
(15) R. Korenstein, K. A. Muszkat, and S. Sharafy-Ozeri, *J. Am. Chem. Soc.*, **95**, 6177 (1973).
(16) R. Korenstein, K. A. Muszkat, and G. Seger, *J. Chem. Soc., Perkin Trans. 2*, 1536 (1976).
(17) I. R. Gault, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 269 (1970).
(18) I. Agranat, M. Rabinovitz, A. Weitzen-Dagan, and I. Gosnay, *J. Chem. Soc., Chem. Commun.*, 732 (1972).
(19) I. Agranat and Y. Tapuhi, to be published.
(20) In most cases, the resolution of the ¹H NMR signals of the substituents in both isomers was significantly improved by using aromatic solvents (ASIS effect). In conventional NMR solvents these signals were in many cases accidentally isochronous.
(21) H. Förster and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **16**, 429 (1977).
(22) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).
(23) W. B. Jennings, *Chem. Rev.*, **75**, 307 (1975).
(24) E. L. Eliel and F. W. Vierhapper, *J. Am. Chem. Soc.*, **96**, 2257 (1974); P. J. Growley, M. J. T. Robinson, and M. G. Ward, *J. Chem. Soc., Chem. Commun.*, 825 (1974); I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *J. Am. Chem. Soc.*, **96**, 682 (1974); F. A. L. Anet and I. Yavari, *ibid.*, **99**, 2794 (1977).
(25) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).

(26) P. Laszlo, *Prog. Nucl. Magn. Reson. Spectrosc.*, **3**, 231 (1967); J. Ronayne and D. H. Williams, *Annu. Rev. NMR Spectrosc.*, **2**, 83 (1969); M. I. Foreman in "Nuclear Magnetic Resonance, Specialist Periodical Reports", R. K. Harris, Ed., The Chemical Soc., London, Vol. 1, Chapter 9, 1971; Vol. 2, Chapter 10, 1972; Vol. 3, Chapter 10, 1973; Vol. 4, Chapter 9, 1974; Vol. 5, Chapter 11, 1975.
(27) The synthesis and conformational dynamic behavior of this series will be described in a forthcoming publication.
(28) M. C. Grossel and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 2*, 1544 (1975); J. L. Marshall, L. G. Faehl, C. R. McDaniel, Jr., and N. D. Ledford, *J. Am. Chem. Soc.*, **99**, 321 (1977).
(29) D. Rabinovitch, personal communication.
(30) M. Raban and E. Carlson, *J. Am. Chem. Soc.*, **93**, 658 (1971).
(31) I. Agranat, B. Perlmutter-Hayman, and Y. Tapuhi, *Nouveau J. Chim.*, **2**, 183 (1978).
(32) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).
(33) L. M. Jackman and F. A. Cotton, Ed., "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1975.
(34) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970). A convenient numerical solution is available from K. Mislow (Dissertation by W. Egan), Princeton University.
(35) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).
(36) D. Kost and A. Zeichner, *Tetrahedron Lett.*, 4533 (1974); W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6205 (1971); M. Bernard, L. Canuel, and M. St-Jacques, *ibid.*, **96**, 2929 (1974); R. C. Neuman and V. Jonas, *J. Org. Chem.*, **39**, 925 (1974); K. I. Dahlquist, S. Forsen, and T. Alm, *Acta Chem. Scand.*, **24**, 651 (1970); S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **97**, 3660 (1975).
(37) F. A. L. Anet and R. Anet in "Determination of Organic Structures by Physical Methods", Vol. 3, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N.Y., 1971, Chapter 7.
(38) F. A. L. Anet and R. Anet in ref 32, Chapter 14.
(39) M. Charton and B. Charton, *J. Am. Chem. Soc.*, **97**, 6472 (1975).
(40) A. Albert, "The Acridines", 2nd ed, Edward Arnold, London, 1966.
(41) F. Ullmann, *Justus Liebigs Ann. Chem.*, **355**, 325 (1907).
(42) K. Gleu and S. Nitzsche, *J. Prakt. Chem.*, **153**, 200 (1939).
(43) L. J. Sargent, *J. Org. Chem.*, **19**, 599 (1954).
(44) R. M. Acheson and C. W. C. Harvey, *J. Chem. Soc., Perkin Trans. 1*, 465 (1976).
(45) N. S. Drozdov, *J. Gen. Chem. USSR (Engl. Transl.)*, **9**, 1456 (1939); *Chem. Abstr.*, **34**, 2847⁴ (1940).
(46) K. Gleu and S. Nitzsche, *J. Prakt. Chem.*, **153**, 233 (1939).

Intersystem Crossing Observed by Ultrasonic Relaxation of the $^2T \rightleftharpoons {}^6A$ Spin Equilibrium of Hexadentate Iron(III) Complexes in Solution

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Abstract: Ultrasonic relaxation techniques have been employed to investigate the dynamics of the spin equilibria of several hexadentate iron(III) complexes in solution. For aqueous solutions of bis(salicylaldiminato)triethylenetetramineiron(III) nitrate-1.5 hydrate, $[Fe^{III}(Sal_2trien)]NO_3 \cdot 1.5H_2O$, the relaxation time at 25 °C is 5.33 ± 0.05 ns. From the relaxation amplitude the high-spin state is calculated to be 10.8 ± 0.5 cm³ mol⁻¹ larger than the low-spin state. From the relaxation time at 25 °C and the equilibrium constant measured by the Evans' ¹H NMR method, the forward (k_{26}) and reverse (k_{62}) rate constants have been calculated to be 8.72×10^7 and 1.01×10^8 s⁻¹, respectively. The temperature dependence of the rate constants implies activation enthalpies for the doublet-sextet interconversion of $\Delta H^{\ddagger}_{26} = 6.38 \pm 0.28$ kcal mol⁻¹ and $\Delta H^{\ddagger}_{62} = 1.92 \pm 0.28$ kcal mol⁻¹. Using absolute rate theory the transmission coefficient, κ, is calculated to be $\geq 10^{-3.4}$ for this formally spin forbidden, $\Delta S = 2$, intersystem crossing process. The value of κ is estimated to lie in the range 10^{-2}–10^{-3}, indicating that both thermodynamic and electronic factors determine the rate of intersystem crossing. This process can be described as nonadiabatic electron transfer between two electronic isomers possessing distinct, different nuclear geometries. Preliminary observations of ultrasonic relaxations for solutions of $[Fe^{III}(acac_2trien)]NO_3$ in water and $[Fe^{III}(benzac_2trien)]NO_3$ in methanol are also described.

Introduction

The relaxation of the thermal spin equilibrium of metal complexes provides a convenient means of determining the dynamics of intersystem crossing processes which are otherwise only accessible in excited states.[2] Their kinetics are important

for understanding those electron transfer reactions which are accompanied by changes in spin multiplicity and also provide new insights to the intersystem crossing barriers between excited states, especially those of metal complexes. Solution kinetic techniques have been pursued to ensure that the dynamics observed are those of the independent molecules.[3]