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Crowded Hydrocarbons. 2.[1] Conformational Study of 9,9′-Bifluorenyls by Dynamic Nuclear Magnetic Resonance Spectroscopy

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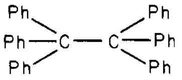
Several 9,9′-bifluorenyls were studied by dynamic NMR spectroscopy. In each compound there is hindered motion about the central C–C bond, and at low temperature the molecules freeze in the gauche conformation. The energy barriers for the interconversion of the equivalent gauche conformers were determined by complete line-shape analysis of the NMR spectra at various temperatures. In the case of 9-*tert*-butyl-9,9′-bifluorenyl, restricted rotation about the axial bond of the *tert*-butyl group was also observed.

Since 1968 when Lankamp et al.[2] proved that Gomberg's hydrocarbon was not hexaphenylethane (1) but rather a methylenecyclohexadiene derivative (2) there has been considerable interest in the structures and properties of polyarylethanes.



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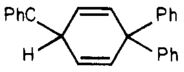

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Although the parent compound 1 has yet to be synthesized, it has been the subject of several theoretical investigations, and Mislow et al.[3-5] have recently calculated the geometries of 1 and other highly substituted ethanes by an empirical force field approach. The calculated ground-state conformation of 1 is almost eclipsed, although the completely staggered geometry is only marginally less stable. Significant steric repulsion between the two trityl fragments results in considerable deformation of the molecule, notably the lengthening of the central C–C bond (1.64 Å).

Table I. Molecular Conformation and Central C–C Bond Distances in Polyarylethanes by X-ray Crystallography

compd	central C–C (sp^3–sp^3) bond length, Å	molec conformn	ref
bibenzyl	1.53	anti	6
1,1,1-triphenylethane	1.553	staggered	7
1,1,1,2-tetraphenylethane	1.567	staggered	8
1,1,2,2-tetraphenylethane	1.540	anti	9
1,1,2,2-tetramesitylethane		anti	10
1,1,2,2-tetrakis(2-methoxyphenyl)ethane	1.555	anti	11
pentaphenylethane	1.606	staggered	12
hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane	1.47?	staggered	13
9,9′-bifluorenyl	1.542	gauche	4
9-*tert*-butyl-9,9′-bifluorenyl	1.585	gauche	14
10,10′-bianthronyl	1.60	gauche	15

In highly crowded ethanes, steric interactions must play a dominant role in determining the molecular geometry. The structures of several polyarylethanes have been determined by X-ray crystallography, and the more highly substituted compounds are significantly distorted, principally by the lengthening of the central C–C (sp^3–sp^3) bond (Table I). In contrast, a preliminary crystal structure of hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane[13] exhibits

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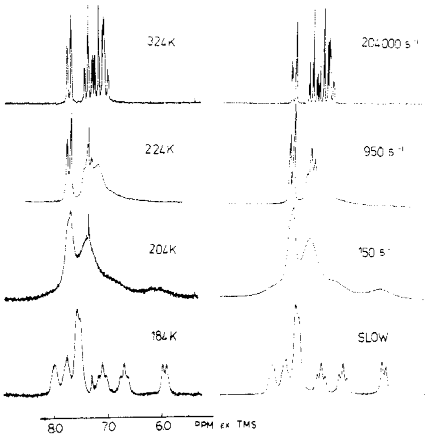


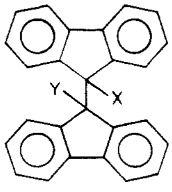
Figure 1. Observed and simulated proton NMR spectra (100 MHz) of 9,9′-bifluorenyl (solvent $CS_2/CDCl_3$, 4:1; aromatic region only).

a remarkably short central C–C bond (1.47 Å), but this results needs substantiation since it appears contrary to the trend observed in all other related compounds.

Some crowded ethanes have been studied in solution, and in those molecules where the comparison is possible, the conformation in the crystalline state is the same as that in solution. Mislow et al.[16,17] have reported that various 1,1,2,2-tetraarylethanes adopt the anti conformation in solution, which contrasts with 1,1,2,2-tetra-*tert*-butylethane and 1,1,2,2-tetrakis(trimethylsilyl)ethane which prefer the gauche conformation.[18a]

Bifluorenyls are members of the class of "clamped" polyarylethanes, i.e., molecules where the aryl rings are constrained away from the central sp^3–sp^3 bond (therefore reducing steric interactions between the ends of the molecule). The clamped systems which have been studied[18b] in solution (bianthranyl, bixanthyl, bitetralone, etc.) adopt a gauche conformation. Bifluorenyl has a gauche geometry in the solid state, and the same conformation is implied in solution from the magnitude of the H_9–$H_{9'}$ vicinal coupling constant in its proton NMR spectrum.[4]

In continuation of our study of crowded ethanes, we report the dynamic NMR spectroscopic study of 9,9′-bifluorenyl (**3a**) and several of its derivatives, **3b–f**.



3a, X = H; Y = H
b, X = Me; Y = Me
c, X = Cl; Y = Cl
d, X = Br; Y = Br
e, X = *t*-Bu; Y = H
f, X = Ph; Y = H

Results and Discussion

At room temperature, the aromatic region of the proton NMR spectrum of **3a** or **3b** is typical of first-order four-spin systems. In both cases, as the temperature is lowered, the spectrum broadens and on further cooling sharpens again to a well-resolved spectrum spanning about 3 ppm (Figure 1).

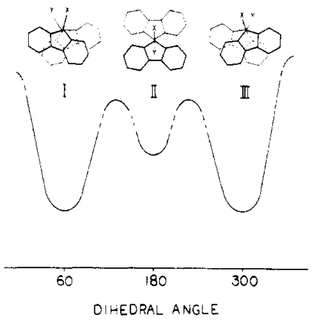
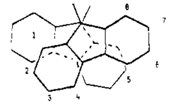


Figure 2. Schematic rotational energy profile for 9,9′-disubstituted 9,9′-bifluorenyls.

Table II. Slow-Exchange Chemical Shift Values for 9,9′-Disubstituted 9,9′-Bifluorenyls



compd	chemical shift[a] ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
3a (X = H)	5.90	6.65	7.05	7.48	7.74	7.50	7.50	7.96
3b (X = Me)	5.65	6.59	6.93	7.22	7.55	7.48	7.48	7.90
3c (X = Cl)	5.89	6.64	7.01	7.17	7.46	7.48	7.51	8.41
3d (X = Br)	5.88	6.60	6.96	7.13	7.43	7.42	7.48	8.55

[a] δ values in parts per million from internal Me_4Si. Solvent $CS_2/CDCl_3$ (4:1).

The low-temperature spectra can be analyzed as *two* distinct but overlapping four-spin subspectra. Computer-simulated spectra for an exchange process which interconverts the two subspectra reproduces the high-temperature spectrum as well as the broad spectra obtained at intermediate temperatures. The spectra of **3c** and **3d** show an analogous dynamic behavior. For **3a** and **3b**, the protons of the substituents at C-9 (and C-9′) do not broaden even at the low temperature extreme of the study.

In the rotational potential energy profile for symmetric 9,9′-disubstituted 9,9′-bifluorenyls, the probable minima are the three staggered conformations. Purely on symmetry grounds, the occurrence of *two* independent subspectra in the low-temperature spectra of **3a–d** is only consistent with the gauche rotamer (I or III) of the bifluorenyl skeleton (Figure 2). The observed dynamic behavior of the NMR spectra thus represents an exchange between the two equivalent gauche rotamers, I $\rightleftarrows$ III, which occurs with internal rotation about the C-9,C-9′ bond.

The slow-exchange chemical shifts for the protons in each of the compounds studied are listed in Table II. In each of the bifluorenyls studied, one of the two subspectra is significantly more shielded than the other; this is consistent with the gauche ground-state conformation where one of the phenyl rings in each fluorene fragment is positioned within the shielding zone of its companion fluorene moiety. The slow-exchange NMR spectra of **3e** and **3f** are exactly analogous to those of the bifluorenyls so far described, although the lower symmetry of these molecules (and the presence of overlapping resonances from the 9-phenyl substituent in **3f**) makes the spectra too complex for a DNMR analysis. The similarity of the low-temperature spectra of **3a** and **3f** to those of the other bifluorenyls indicates that these molecules also adopt a gauche

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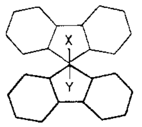
Table III. Activation Parameters for the Inversion of Bifluorenyls

compd	temp, K	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{240}$, kcal mol^{-1}
3a	190–324	7.5 ± 0.5	−10.8 ± 1	9.9
3b	195–324	6.3 ± 0.7	−15.3 ± 2	10.0
3c	257–348	12.2 ± 0.5	−4.8 ± 2	13.2
3d	257–348	12.2 ± 1	−5.0 ± 2	13.2
3e	206–268	9.4 ± 0.5	−7.7 ± 0.5	11.2

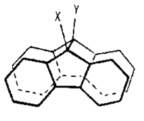
ground-state conformation in solution.

Rotational Barriers. The large chemical shift differences between the exchanging environments in the bifluorenyls and the complexity of the spin system make the line shape particularly sensitive to the rate constant for exchange. Kinetic data for the exchange process could be obtained over a large temperature range (typically >100 °C). Dynamic NMR spectroscopy has been criticized as a method for obtaining accurate activation parameters (ΔH^{*} and ΔS^{*}) for exchange processes. However, when a large temperature range is accessible, errors in any individual measurement have a less significant effect on the activation parameters, and consequently ΔS^{*} and ΔH^{*} are more reliable. Table III lists the activation parameters obtained for compounds **3a–f**.

Interconversion of the gauche rotamers can be accomplished by either of two distinct pathways, i.e., via the anti conformation, II, or the fully eclipsed form, IV.



II



IV

An examination of molecular models suggests that steric interactions in IV are more severe than those in II, but irrespective of the pathway, the observed dynamic behavior can be viewed as a "rocking" motion from one gauche conformer to the other.

The bromo and chloro derivatives (**3c** and **3d**) have substantially larger barriers than **3a** or **3b**. Superficially the exceptionally low barrier for **3b** is unexpected since steric interactions are obviously responsible for the observed barriers, and a methyl group is usually considered approximately isosteric to a chlorine or bromine atom.[19,20] The observed barrier heights reflect the *difference* in energy between a ground state and a transition state, and, in such crowded systems, interactions in *both* states may be substantial and may obscure the true origin of the barrier. Alternatively, the methyl group may appear anomalously small because of its unique ability to "cogwheel" in crowded situations.[20]

9-*tert*-Butyl-9,9′-bifluorenyl (3c). Dynamic effects in the NMR spectrum of **3e** have been previously noted by Bartle et al.[21] Again, the similarity of the low-temperature spectrum of this compound to those of the other

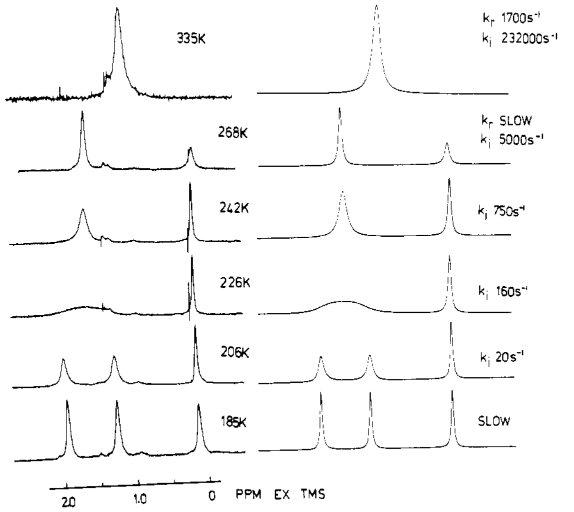


Figure 3. Observed and simulated proton NMR spectra (100 MHz) of the *tert*-butyl group of 9-*tert*-butyl-9,9′-bifluorenyl (solvent $CS_2/CDCl_3$, 4:1). k_r is the rate constant for rotation of the *tert*-butyl group; k_i is the rate constant for inversion of the bifluorenyl skeleton.

bifluorenyls indicates a gauche ground-state conformation. Additionally, rotation of the *tert*-butyl group about its axis is sufficiently slow on the NMR time scale to be clearly observable at low temperature. At high temperature the resonance of the *tert*-butyl group is a sharp singlet. At lower temperatures the resonance broadens and divides into two singlets with intensities in the ratio 1:2. At still lower temperatures the larger resonance collapses further to two signals of equal intensity (Figure 3). Such behavior must arise from two independent dynamic processes, and these can be ascribed to restricted rotation of the *tert*-butyl group about its axis and to the gauche–gauche equilibrium of the bifluorenyl skeleton. The process with the higher activation energy distinguishes one methyl from the other two in the *tert*-butyl group, and this corresponds to the slowing of rotation of the *tert*-butyl group. At temperatures where the gauche–gauche interconversion is fast on the NMR time scale, the molecule possesses dynamic C_2 symmetry which gives rise to the observed 2:1 ratio of signal intensities. At lower temperatures rotation about the C9–C9′ bond is also frozen, and this makes all three methyls of the *tert*-butyl group nonequivalent. ΔG^{*}_{240} for the *tert*-butyl rotation and bifluorenyl inversion are 14.4 kcal mol^{-1} and 11.2 kcal mol^{-1}, respectively.

Conclusions. The low-temperature ^1H NMR spectra of 9,9′-bifluorenyl and several of its derivatives are consistent with a gauche ground-state conformation for these molecules. This is in agreement with reported calculations[3] where the gauche conformation of **3a** was predicted to be more stable than the corresponding anti structure by about 6 kcal mol^{-1}.

In a gauche conformation, the bifluorenyls are chiral, and rotation about the C9–C9′ bond interconverts the enantiomers. The inversion process can be followed by dynamic NMR spectroscopy to give the activation parameters for the process.

Experimental Section

NMR Spectra. All NMR spectra were recorded on a Varian XL-100 spectrometer operated in the FT mode. The temperature of the spectrometer probe was measured immediately after each spectrum was acquired by using the peak separation between the methyl and hydroxyl resonances in a methanol sample.[22] Dy-

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namic NMR spectra were analyzed by using a modified version of the computer program DNMR3.[23] Chemical shifts of the nuclei participating in the exchange were obtained initially from slow-exchange spectra. The shifts of some nuclei varied slightly (and monotonically) with temperature, and over the region where peaks coalesced the shifts were extrapolated from slow- and fast-exchange spectra. For the purpose of analysis, proton–proton coupling constants for all compounds were taken to be the same as those in fluorene,[24] and these values provided good matches between simulated and experimental spectra.

Bifluorenyls. 9,9′-Bifluorenyl (3a) was available commercially (Aldrich) and was used without further purifications.

9,9′-Dimethyl-9,9′-bifluorenyl (3b) was prepared according to the procedure of Murahashi and Moritani[25] from bifluorenylidene (4).[26]

9,9′-Dichloro-9,9′-bifluorenyl (3c). Chlorine was bubbled through a solution of 4 (0.5 g) in carbon tetrachloride (50 mL) at 10 °C until the orange/red color of 4 disappeared. The solvent was removed, and a sample of the crude product was recrystallized from heptane/toluene to yield **3c** as a colorless crystalline solid, mp 245.1 °C (lit.[27] mp 237–240 °C).

9,9′-Dibromo-9,9′-bifluorenyl (3d). Bromine (0.3 g, 1.9 mmol) was added dropwise to a stirred solution of 4 (0.5 g, 1.5 mmol) in carbon tetrachloride (50 mL) at 0 °C. The solution was allowed to warm to ambient temperature, and stirring was continued for 1 h. The solvent was removed under reduced pressure and a sample of the crude product was recrystallized from carbon tetrachloride to yield **3d** as a colorless, crystalline solid, mp 245.4 °C (lit.[25] mp 237–238 °C).

9-*tert*-Butyl-9,9′-bifluorenyl (3e) was prepared from 4 according to the procedure of Fuson and Porter.[26]

9-Phenyl-9,9′-bifluorenyl (3f) was prepared according to the the procedure of Ziegler and Schafer.[28]

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Registry No. 3a, 1530-12-7; **3b**, 15300-82-0; **3c**, 37167-64-9; **3d**, 15300-79-5; **3e**, 26456-16-6; **3f**, 76756-37-1; **4**, 746-47-4.

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Substituent Effects on the Activation Parameters for the Methoxymercuration of *p*-Substituted Styrenes

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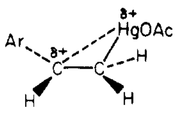
The activation parameters for the methoxymercuration of a series of *p*-substituted styrenes in anhydrous methanol have been determined. The values of ΔH^* and ΔS^* are consistent with the formation of bridged activated complexes in the rate-determining step of these reactions. Analysis of the substituent effects on the values of $\delta\Delta G^*$ for these reactions using the Yukawa–Tsuno equation required the use of small values for the *r* parameter. This finding is also consistent with the formation of bridged activated complexes in the rate-determining step. Variations of the substituents have small effects on ΔH^* but large effects on ΔS^*. $\delta\Delta H^*$ is not linearly related to either $\delta\Delta S^*$ or $\delta\Delta G^*$. However, $\delta\Delta G^*$—as expected for a reaction series in which the values of $\delta\Delta H^*$ are small and/or constant—is a linear function of $\delta\Delta S^*$. Product studies on styrene and its *p*-MeO and *p*-NO_2 derivatives show that these reactions are clean and that they occur regiospecifically, giving the expected Markovnikov addition product in each case.

Introduction

In our initial study of the methoxymercuration of a series of *p*-substituted styrenes, based on the values of ρ and ρ^+ obtained from excellent linear Hammett plots, we[1] proposed that these reactions involve the formation of an unsymmetric bridged intermediate (1) in their rate-determining step. As a part of our continuing investigations into the nature of this intermediate, we have extended our initial study to include several additional styrenes (the *p*-MeO, *p*-Ac, and *p*-COOMe derivatives) and we have examined the substituent effects on both the activation parameters and the products of these reactions. It was our aim, therefore, to obtain additional supporting information on this proposed structure and to evaluate the substituent effects on the activation parameters for this reaction in order to determine which, if any, relationships exist among ΔG^*, ΔH^*, and ΔS^*.



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Electrophilic addition reactions involving styrenes usually exhibit small positive values of ΔH^* and large negative values of ΔS^*.[2] In most cases the values of these parameters, in particular ΔS^*, have been used to argue for the formation of bridged or cyclic activated complexes, hence intermediates in the rate-determining steps of these reactions. In the case of the bromination of substituted styrenes, however, it has been suggested by some investigators[2c,3] that the values of ΔS^* merely reflect greater

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