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STERIC EFFECTS IN THE PROTON MAGNETIC RESONANCE SPECTRA OF FLUORENES AND BIFLUORENYLS*

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Abstract—High-resolution PMR spectra, measured at 60 MHz over temperatures between −80° and +160° in CS_2, $CDCl_3$ and $(CD_3)_2SO$ solution, are described for bifluorenyl (IIa), 9-methyl-9,9'-bifluorenyl (IIc), 9-t-butyl-9,9'-bifluorenyl (IIb), five 9-substituted fluorenes, and two 9,9-disubstituted fluorenes. Both 9-(α-naphthyl)-fluorene (Ib) and IIb show coexistence of topographical variants at low temperatures, and comparison of 9-methyl-9-t-butyl- (Ig) and 9-ethyl-9-t-butylfluorene (Ih) spectra with that of 9-t-butylfluorene (If) indicates a reduction in primary proximity deshielding as the size of the second substituent increases. In IIb, the t-butyl resonance is broad at low temperatures, narrows with increasing temperature, and then passes through a remarkable maximum in width of 30 Hz at room temperature before sharpening at high temperatures, when rotation appears to be free about both the 9,9' and 9-t-butyl bonds.

INTRODUCTION

PMR spectra commonly display sensitivity to stereochemical exchange processes so that, for example, spectra observed at room temperature or above may represent time averages over conformational rotamers. Among polynuclear aromatics, the widely occurring 6,5,6-fused ring system of fluorene (Ia) is of special interest in that it provides a rigid structure wherein substituents may be located at an sp^3 carbon. Diffraction measurements[2] show that Ia is at least very nearly planer in the crystalline state. In solution, the lack of coupling between H-4 and H-5 and the similarity of J values with those in biphenyl imply surprisingly little interaction[1] between the two 6-rings. Further, steric effects may be detectable by PMR as a result of hindrance to free rotation about the 9,9' bond in 9,9'-bifluorenyl (IIa).

Unlike the 9,9'-bisfluorenylidenes, which display thermochromism, derivatives of II have not previously received detailed PMR examination, although brief reference to the spectrum of IIa has been made in connection with a PMR study of biphenyleneëthene.[3] In the course of our PMR investigation of hindered rotation in Ib and IIb, evidence accumulated that molecular overcrowding may also influence chemical shifts in fluorenes. In order to investigate the possibility of extracting further information about their molecular structure, spectra were also recorded for the series Id–Ih of 9- and 9,9-substituted fluorenes.

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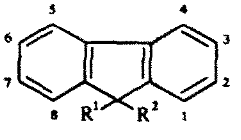
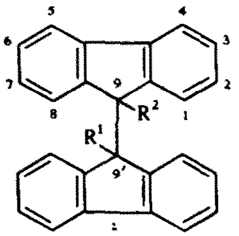
* High-resolution proton magnetic resonance spectra of fluorene and its derivatives. Part 2[1].



I

Ia : $R^1 = R^2 = H$
Ib : $R^1 = H; R^2 =$ naphthyl
Ic : $R^1 = H; R^2 =$ phenyl
Id : $R^1 = H; R^2 = CH_3$
Ie : $R^1 = H; R^2 = C_2H_5$
If : $R^1 = H; R^2 = C(CH_3)_3$
Ig : $R^1 = CH_3; R^2 = C(CH_3)_3$
Ih : $R^1 = C_2H_5; R^2 = C(CH_3)_3$



II

IIa : $R^1 = R^2 = H$
IIb : $R^1 = H; R^2 = C(CH_3)_3$
IIc : $R^1 = H; R^2 = CH_3$

RESULTS AND DISCUSSION

Restricted rotation in 9-fluorenes

Early suggestions that hindered rotations to be expected[4] in certain 9-substituted fluorenes should be detectable[5] by PMR have led only recently to estimates of the high energy barriers.[6, 7] 9-Mesitylfluorene and several 9-methylaryl-9-hydroxyfluorenes all give Me resonances corresponding to more than one environment,[6] while Siddall and Stewart[7] report PMR evidence for restricted rotation in five other 9-arylfluorenes. In contrast to 9-mesitylfluorene-9-ol, which according to Chandross and Sheley[6] consistently exhibits three separate Me signals up to at least[6] 200°, 9-(α-naphthyl)-fluorene (Ib) has, like 9-chloro-9-mesitylfluorene,[7] a strongly temperature-dependent spectrum (Table 1).

Table 1. Temperature dependence of PMR spectral data for 9-(α-naphthyl)-fluorene

Solvent	T°C	H(9) Resonances: chemical shifts (δ ppm)	H(9) Resonances: Δ(Hz)	Aromatic protons (δ ppm)	log k	log($\pi\Delta T_2 - 1$)
$CDCl_3$	−35	5·30 6·00	3·0 3·0	6·38–8·13		
	0	5·28 6·00	2·8 3·0	6·42–8·08		
	+30	5·25 5·97	2·8 3·0	6·42–8·08		
	+60	5·25 5·98	3·5 3·5	6·35–8·00		
$(CH_3)_2SO$	+70	5·45 6·13	5·0 5·0	6·75–8·08		
	+90	5·87	15	6·75–8·08	2·32	0·644
	+100	5·87	13	6·75–8·08	2·39	0·562
	+107	5·86	10	6·75–8·08	2·54	0·420
	+115	5·85	7	6·75–8·08	2·79	0·176
	+130	5·83	5	6·75–8·08	3·06	−0·08
	+140	5·80	3·8	6·75–8·08	3·41	−0·44
	+160	5·80	2·8	6·77–8·08	—	—

The observation for 9-(α-naphthyl)fluorene (Ib) in chloroform-*d* solution, at ambient probe temperature, and below, of two H(9) signals in intensity ratio approximately 2:1 (but equal to one proton in total) implies the presence of two isomers, of which the lower-field (more-deshielded) one, labelled A in Fig. 1 predominates. Both low-temperature H(9) lines have a breadth appropriate to unresolved benzylic coupling.[1,8,9] At higher temperatures, in dimethylsulphoxide-d_6 solution, the H(9) signals of Ib broaden, and coalesce at 90° to a broad singlet; by 160° this has narrowed to a width at half-height (Δ) of 2·8 Hz, rather wider than in most 9-substituted fluorenes.[10] Changes with temperature in the aromatic region, other than the shift above 90° down to the main aromatic region of the highest-field lines (corresponding to protons shielded by the other aromatic nucleus), are so slight as to be attributable to solvent effects.

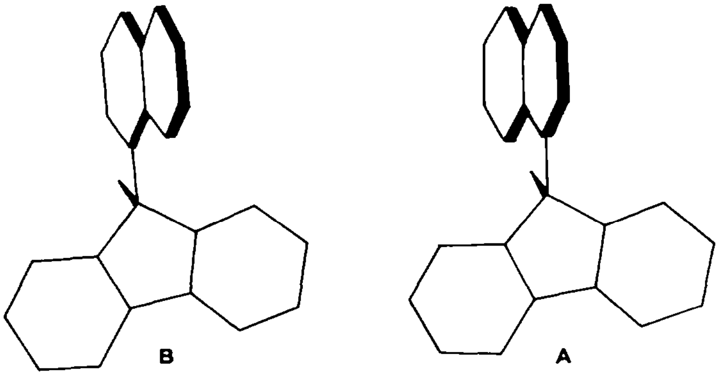


Fig. 1 Approximate forms of conformational variants proposed for 9-(α-naphthyl) fluorene (Ib).

If the fractional populations of rapidly exchanging conformations are no longer equal[11] but given by p_a and p_b, and the sites are uncoupled, the rate constant is given[12] by

$$k = 2\pi\, p_a p_b\, \delta\nu^2\, (\Delta - \Delta_0)^{-1} \qquad (1)$$

where Δ_0 is the line-width in the absence of exchange and $\delta\nu$ the chemical-shift separation. Arrhenius and thermodynamic parameters for Ib in dimethylsulphoxide-d_6 have been derived from (i) the least-squares plot of log k vs $1/T$ (Fig. 2) given in Table 2; (ii) a graph (Fig. 3) of log $(\lambda\Delta T_2 - 1)$ vs $1/T$, where[13] $T_2 = (\lambda\Delta_0)^{-1}$; and (iii) complete line-shape analysis.[11] Closely similar kinetic parameters (Table 2) have been extracted[7] by line-shape analysis and by line-width analysis from PMR measurements on Ib in $CCl_2{=}CCl_2$ as solvent. This similarity is pertinent to a decision between the most likely mechanisms for interchange between the forms A and B of Ib illustrated in Fig. 1:

(i) inversion at C-9 of fluorene *via* an ionic (or free-radical or charge-transfer) transition state in which the sp^3—sp^2 bond is in the fluorene plane; and

(ii) rotation about the sp^3—sp^2 bond.

The choice between these affects the applicability of the parameters in Table 2.

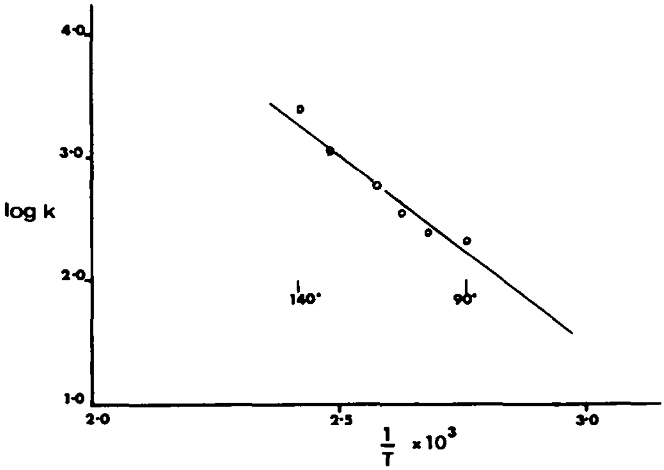


FIG. 2 Arrhenius graph for interconversion of 9-(α-naphthyl) fluorene conformers (Ib).

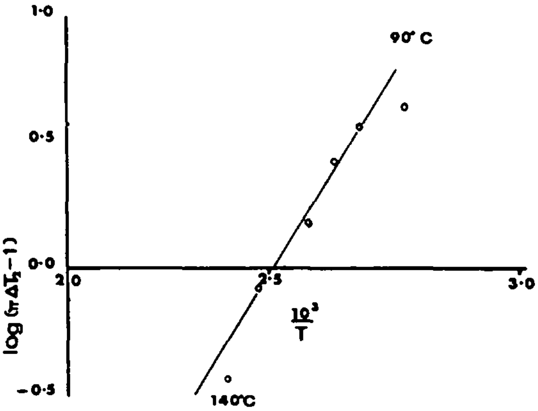


FIG. 3 Graph of log (πΔT/2 − 1) vs I/T for 9-(α-naphthyl) fluorene (Ib).

TABLE 2. ARRHENIUS AND THERMODYNAMIC PARAMETERS FOR THE ACTIVATION OF THE INTERCONVERSION OF THE TWO ISOMERS OF 9-(α-NAPHTHYL) FLUORENE

Parameter/Solvent	$(CD_3)_2SO$	$CCl_2 = CCl_2$ (ref. 7)
E_a (kcal/mole)	15·6 (line-shape analysis) 14·6 (line-width only; mean of two methods)	14·8
log A	11·4 (line-shape analysis) 10·8 (line-width only)	10·8
$\Delta G^‡$ (kcal/mole)	17·8 at 60° (line-width)	18·0 at 60°C 18·7 at 116°C
$\Delta H^‡$ (kcal/mole)	14·8 at (60°C) (line-shape) 13·9 (60°) (line-width)	
$\Delta S^‡$ e.u	−8·4 (line-width)	

Since, in process (i), the intermediate would have a finite probability of reverting to the original isomer,[14] k would not be the observed value; E_a would be unaffected, however. In both 9-phenyl- and 9-naphthyl-fluorenes, NMR lines are narrower than would be expected if free radicals were present; moreover, we were unable to detect any ESR signal in the X-band spectrum of a sample recorded in a cylindrical cavity on a Varian-V-4500 spectrometer.

In 9-o-tolylfluorene, independence of the isomeric exchange rate of solvent (and hence of dielectric constant of medium) is plausibly interpreted[7] as favouring a mechanism of type (ii). In 9-chloro-9-mesitylfluorene, on the other hand, despite consistent temperature behaviour of NMR spectra (showing the emergence of an additional conformer below 10°) in solvents covering a range of polarities, ionisation and heterolytic cleavage of the C—Cl bond seems to have been established;[6] Chandross and Sheley assume tight ion pairs, not separated much by solvent molecules.

However, a rotation interpretation in 9-chloro-9-mesitylfluorene is not excluded by Rieker and Kessler,[15] who also observed that, in 1,2,4-trichlorobenzene solution, the methyls of 9-mesitylfluorene-9-ol broaden at 100° and coalesce at 145°. This difference from the behaviour in *m*-dibromobenzene as solvent (separate Me peaks up to at least 150°), reported by Chandross and Sheley,[6] implies an appreciable solvent dependence.

In order to distinguish between (i) and (ii), deuteration of 5% Ib in dimethylsuphoxide-d_6 was attempted. Constancy of the H(9) intensity in the presence of 5% D_2O at 100°, showed that no deuterium had been incorporated and appeared to confirm (ii). Under similar treatment, however, 9-phenyfluorene (Ic) had its H(9) intensity reduced tenfold, relative to dimethylsulphoxide-d_6 alone as a solvent, and a strong HOD signal emerged at $\delta = 3$ ppm. It is difficult to see why the mechanisms in Ib and Ic should differ. No recent estimates are available for the relative acidities of Ib and Ic; early measurements gave pK_a values[16] of about 19 for both. Admittedly, it may be that, by what might be regarded as an effect analogous either to macroscopic friction, or to macroscopic rotational inertia, the binding of different solvents to the solute could alter appreciably the freedom of rotation in both 9-fluorenes and 9,9′-bifluorenyls.

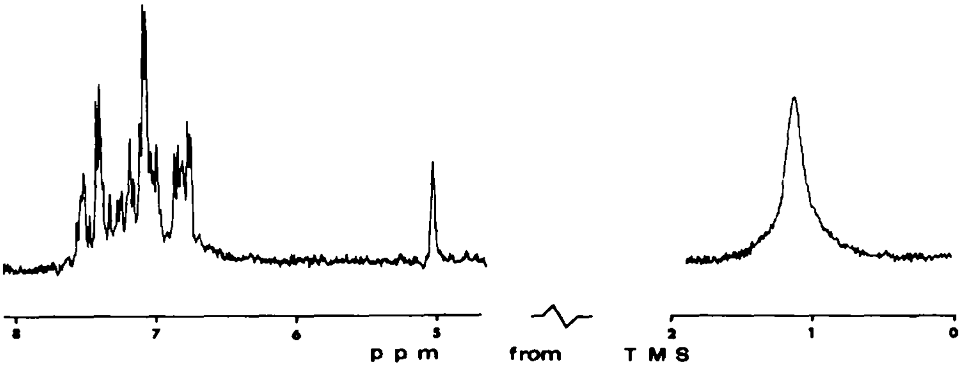


Fig. 4 Spectrum of 9-t-butyl-9,9′-bifluorenyl (IIb) in $CDCl_3$ at 50°.

Restricted rotation in 9,9'-bifluorenyls

The spectrum (Fig. 4) of 9-t-butyl-9,9'-bifluorenyl (IIb) displays an interesting dependence on temperature. The 30 Hz breadth of the t-butyl signal at normal probe temperature (Fig. 5) may be presumed to reflect hindered and slow rotation about the t-butyl-C-9 bond. Although the lines of the complex aromatic multiplet gradually narrow further with increasing temperature, their narrowness even at room temperature (Fig. 6) implies that rotation about C-9-C-9' is fairly free at room temperature. Below room temperature, there is a slight shift in the overall range of aromatic protons from 450–390 Hz at +30° to 475–360 Hz at −80° in CS_2 solution and about 10 Hz

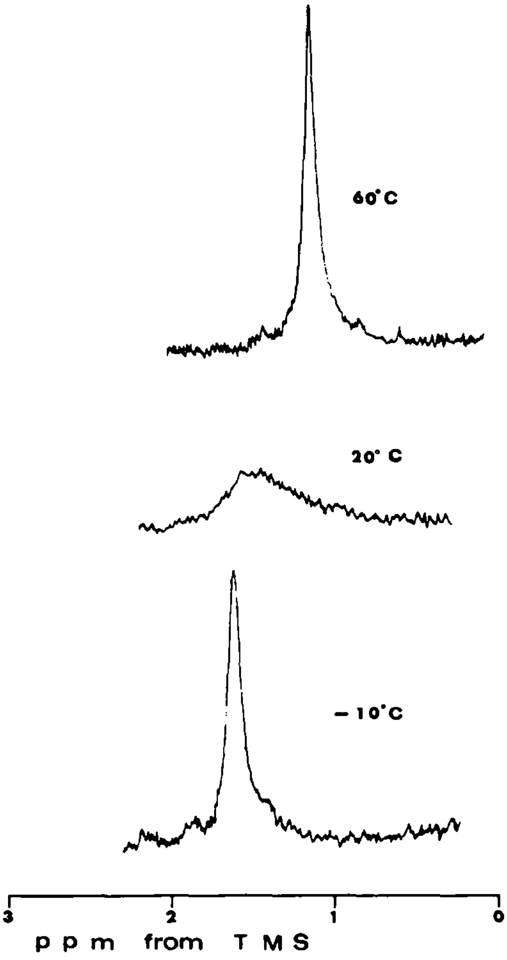


FIG. 5 High-temperature variation of methyl resonance of 9-t-butyl-9,9'-bifluorenyl (IIb) in $CDCl_3$.

further downfield in $CDCl_3$ solution (Fig. 6). More particularly, marked intensity changes indicate that individual aromatic chemical shifts are changing. Thus, in CS_2 solution, for example, whereas at −10° the aromatic protons may be regarded as multiplets of intensity ratio 2:4:2 centred approximately on 435, 417 and 400 Hz, the centre of gravity of the intensity distribution has shifted appreciably downfield by −40°, and by −80° threequarters of the aromatic intensity is within the range 470–430 Hz (Fig. 6). No such change is evident in the aromatic resonances (Fig. 7) of 9-methyl-9,9′-bifluorenyl (IIc). The H-9 resonance is almost constant in width (from 1·8 to 2·5 Hz) and chemical shift (near 4·9 ppm in CS_2, rather higher in $CDCl_3$ and $(CD_3)_2SO$) throughout the temperature range −50° to +120°; moreover, splitting has not been detected.

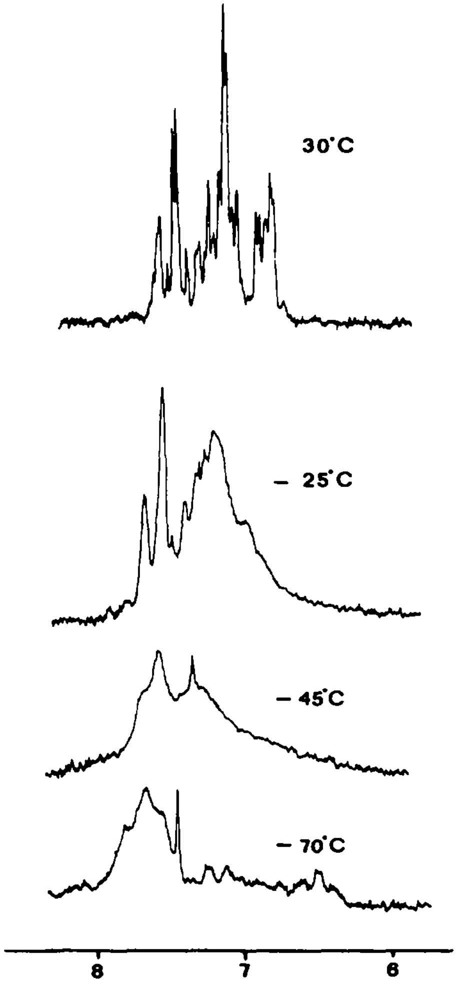


Fig. 6 Variation with temperature of aromatic spectrum of 9-t-butyl-9,9′-bifluorenyl (IIb) in $CDCl_3$.

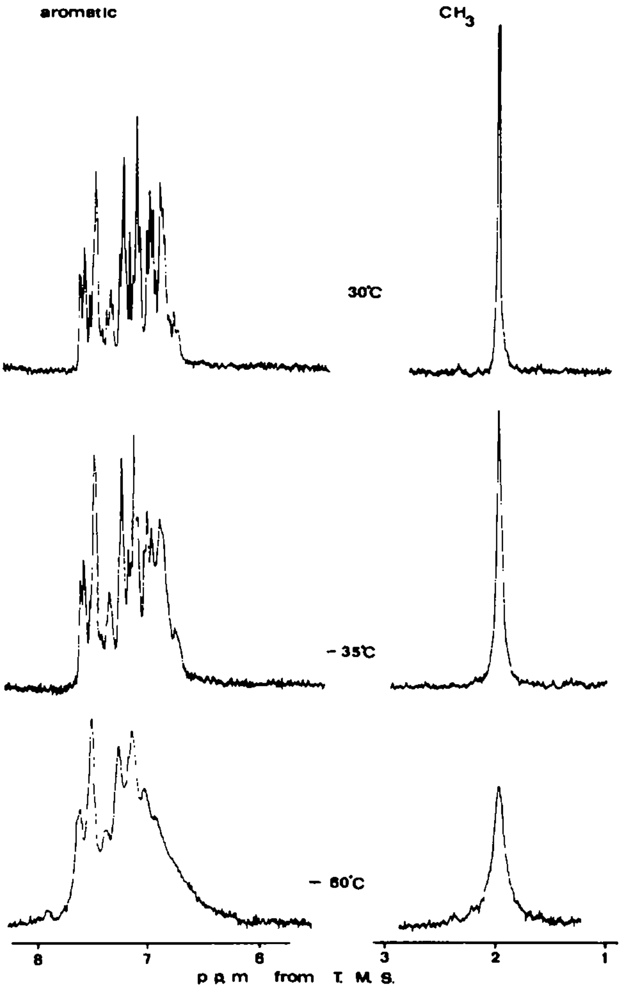


FIG. 7 Variation with temperature of aromatic and methyl resonances of 9-methyl-9,9'-bifluorenyl (IIc).

Above 30°, in dimethylsulphoxide-d_6 solution, the t-butyl resonance of IIb narrows (Fig. 5) from 30 Hz to a minimum of 1·2 Hz at 120°. When the temperature is reduced, the resonance narrows to 4·8 Hz (in chloroform-d) at $-20°$, before broadening again at lower temperature (Fig. 8); below $-55°$, two t-butyl peaks emerge of approximately equal intensity (Fig. 9). At all higher temperatures investigated, only one chemical shift is observed for t-butyl but this changes from 65–70 Hz at 30° and above to 95 Hz between 0° and $-40°$.

In IIc, the Me resonance (Fig. 7) gradually broadens with decreasing temperature from 1·0 Hz at 50° to 2·0 Hz at $-20°$ and then, rather more rapidly, to 3 Hz at $-35°$ and 6 Hz at $-60°$; evidently, rotation of the Me group is restricted at low temperature.

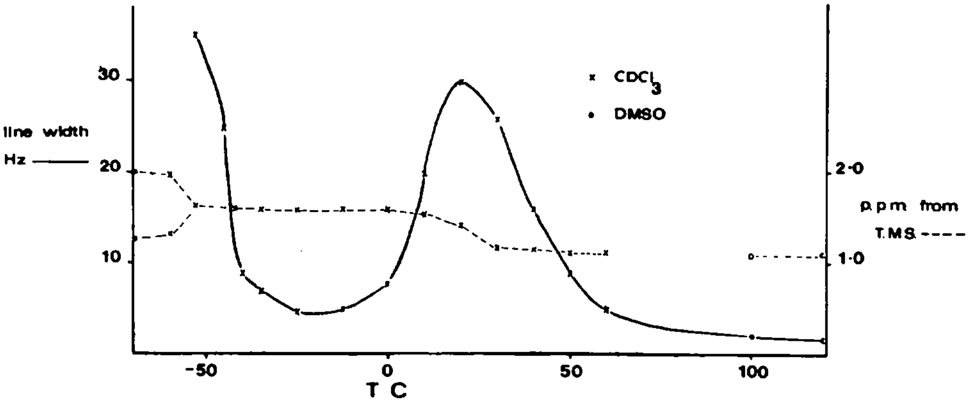


FIG. 8 Temperature variation of line width (Δ) (full line) and chemical shift(s) (broken line) of methyl resonance of t-butyl-9,9′-bifluorenyl (IIb).

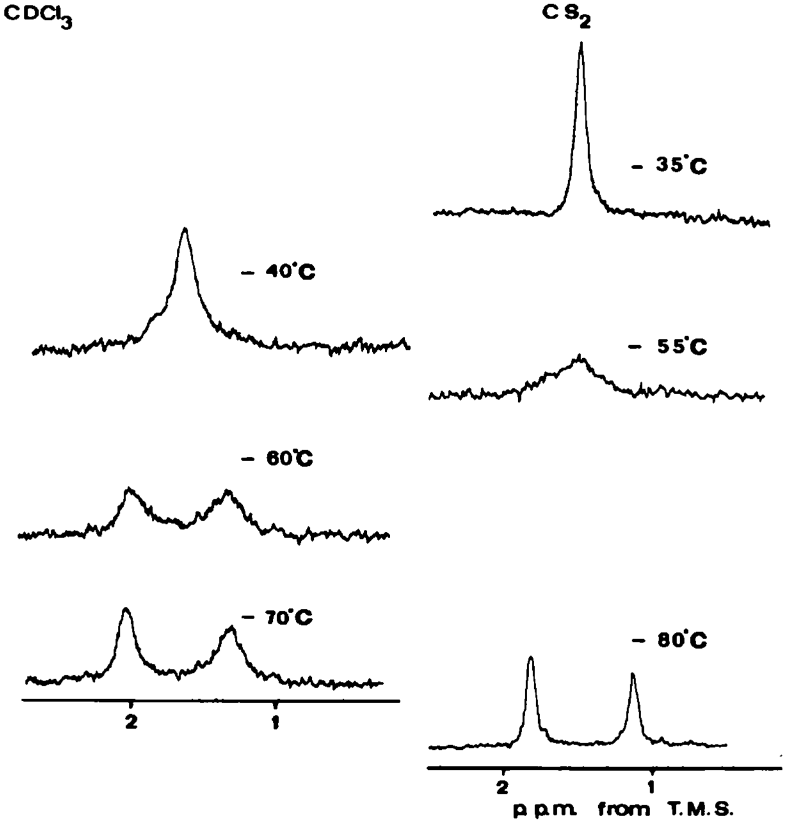


FIG. 9 Methyl resonances of 9-t-butyl-9,9′-bifluorenyl (IIb) in $CDCl_3$ and CS_2 solutions at temperatures from −35° to −80°.

There is also a small chemical shift change from 115 Hz above 0° to 118 Hz below −20°. Since much the same broadening of the aromatic signals occurs at low temperature with IIc (in chloroform-*d* solution) as with IIb, the averaging process in IIb is likely to be associated with the t-butyl group. At least two processes are involved in IIb; rotations about the C-9-C-9′ and C-9-t-butyl bonds; restricted rotations about several bonds usually present interpretive problems. From graphs of $\log(\lambda\Delta T_2 - 1)$ vs $1/T$ (Fig. 10), the least squares value for the apparent activation energy, E_a^* is about

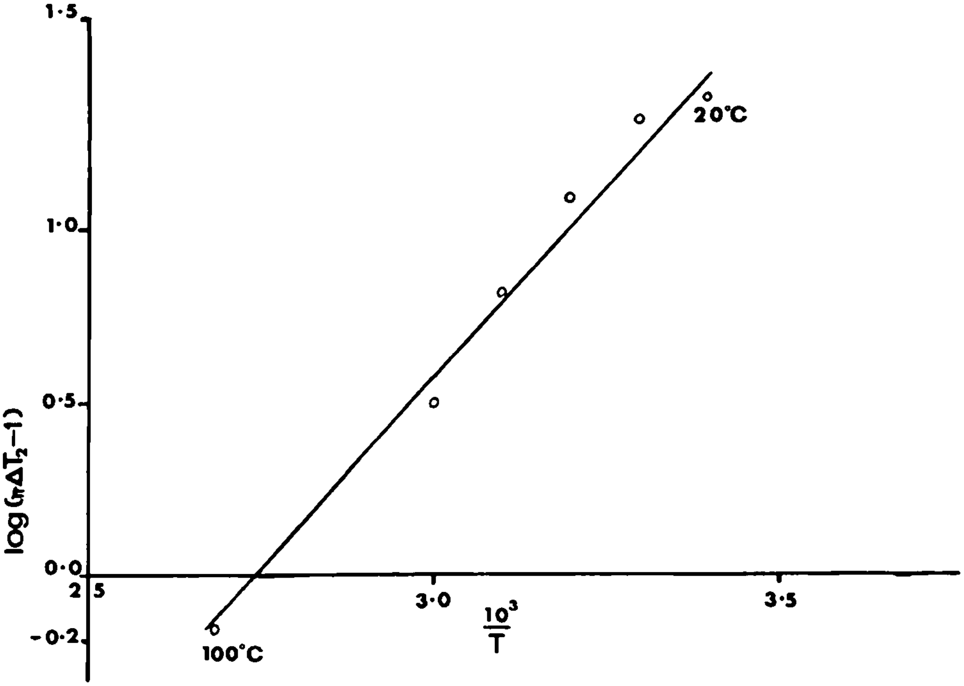


FIG. 10 Graph of $\log(\pi\Delta T_2 - 1)$ vs I/T for methyl resonance of t-butyl-9,9′-bifluorenyl (IIb).

10·4 kcal mole^{-1} for the high-temperature process. Magnetic non-equivalence of t-butyl protons is not unknown[15, 17, 19–22] although, apart from 9-hydroxy-9-t-butylfluorene,[15] examples among polycyclics are rare. In *peri* di-t-butylnapthalenes,[23] the remarkably sharp singlet signals indicate, no doubt as a result of bending, an absence of both locking and rotation. Free energies of activation, $\Delta G^\ddagger$, which are probably the least unreliable thermodynamic quantities that can be extracted from PMR data, have been reported to be in the range 6 to 9·5 kcal mole^{-1} for rotation for t-butyl groups in t-butyl-cycloalkanes,[19] cyclohexadien-2,5-ones,[20] and 9-hydroxy-9-t-butyfluorene,[15] mostly at temperatures of −80° to −100°.

Magnitudes of activation energies do not appear to provide quantitative support for the expectation that the high-temperature rotation is about the 9-9′ bond and that the t-Bu rotation occurs, as is usual, at low temperatures. At the lowest temperatures studied, it will be recalled (Fig. 9), the t-Bu group, gives two chemical shifts, equal in intensity (rather than in 1:1:1 or 1:2 ratio as individual Me shifts in a static t-Bu group might require[19, 20]) with chemical shifts above and below the 0° to −45°

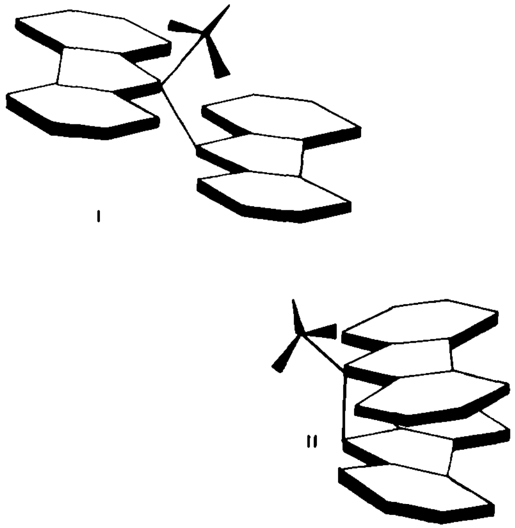


FIG. 11 Approximate forms of conformational variants proposed for t-butyl-9,9'-bifluorenyl.

single value. This implies the existence of two conformers (Fig. 11), between which interconversion with a low activation energy is slow at this temperature; the restriction on t-Bu rotation that is responsible is not necessarily the fluorene nuclei. Above −20°, when this interconversion is rapid, it is not certain which of the bond rotations loses its hindrance first. One possibility is that, as the high temperature rotation about the 9-9' bond becomes less free in the region 0 to 10°, it is less of an impediment to the rotation of the t-Bu group, which is occurring only with difficulty at lower temperature; the low-field t-Bu shift would be a consequence of the fluorene nuclei locking in a more deshielding arrangement. A concerted rotation of t-Bu and fluorenyl, analogous to a stroboscopic effect, is a possibility, but this might be expected to involve a series of critical frequencies. Tentatively, however, it is suggested that a more probable interpretation of the spectra is that between −20° and 30° rotation about C-9-C-9' becomes fast enough increasingly to impede t-Bu rotation; the rate of the latter increases only (above 30°) after C-9-C-9' rotation has already become rapid.

In the spectrum of IIa, measured in chloroform-*d* solution, we find that at normal probe temperature the H(9) resonance occurs at 289·5 Hz for 2·8 % w/w and 291·3 Hz at infinite dilution at 60 MHz (and at the equivalent of 288·6 Hz at 60 MHz from 100 MHz spectra for 3 % in $CDCl_3$), i.e. about 7 Hz to lower field than has been reported[3] previously.

Chemical shifts in 9-t-butylfluorenes

In fluorene[1] (Ia) and its derivatives,[10] the ABCD spectrum of the aromatic protons can be approximated as ABMX [$H - 1 = M$, $H - 2,3 = AB$, $H - 4 = X$] so that chemical shifts may readily be measured from multiplet centres. Inspection of Table 3

Table 3. Chemical shifts (δ ppm) in spectra of 9-t-butyl fluorenes

	Compound	Solvent and Concentration	H(1)	H(2,3)	H(4)	CH_3	$C\underline{H}_2CH_3$	$CH_2C\underline{H}_3$	$C(CH_3)_3$
Ia	Fluorene	Infinite	7·43	7·21	7·71				
Id	9-Methylfluorene	dilution	7·44	7·23	7·69	1·53			
Ie	9-Ethylfluorene	in	7·45	7·23	7·69		2·08	0·65	
If	9-t-Butylfluorene	CCl_4	7·52	7·18	7·63				0·98
If	9-t-Butylfluorene	10% w/w	7·49	7·18	7·59				0·96
Ig	9-Methyl-9-t-butylfluorene	in CS_2	7·42	7·18	7·58	1·47			0·86
Ih	9-Ethyl-9-t-butylfluorene		7·30	7·13	7·54		2·18	0·13	0·83

shows that, while Me (Id) and Et (Ie) have little effect on the aromatic shifts, t-Bu (If) deshields $H-1$ but shields $H-4$ with respect to the shifts in Ia; $\delta_{2,3}$ is almost constant.

Progressively increasing the size of the second group at the 9-position from H (If) to Et (Ih) might similarly be expected to deshield $H-1$, just as overcrowded protons in many other polynuclear hydrocarbons suffer the low-field shifts recently rationalised by Cheney.[18] In fact, in 9-methyl-9-t-butylfluorene (Ig), the Me group does not shift $H-4$ much further but shields $H-1$ to give it a shift similar to that in fluorene itself. This effect is enhanced in Ih, in which the methyl is constrained to a position above the plane of the rings so that ring-current shielding causes δ to be very small (0·13 ppm).

Two kinds of proximity effects on shielding must be distinguished.[24] The (a) primary, or "van der Waals" shift is related to the component of the repulsive[18] force acting on the hydrogen directed along the CH bond; in (b) the secondary effect, steric interaction, may cause a proton to take up a new position where it experiences different anisotropy or primary van der Waals shifts. Introduction of Me or Et into 9-t-butylfluorene appears to force the t-Bu group further away from the ring plane and $H-1$ with consequent reduction in the primary proximity or anisotropy deshielding of $H-1$ (Fig. 12). This explanation is borne out by the increased ring-current shielding of the t-Bu proton in the series If, Ig, Ih.

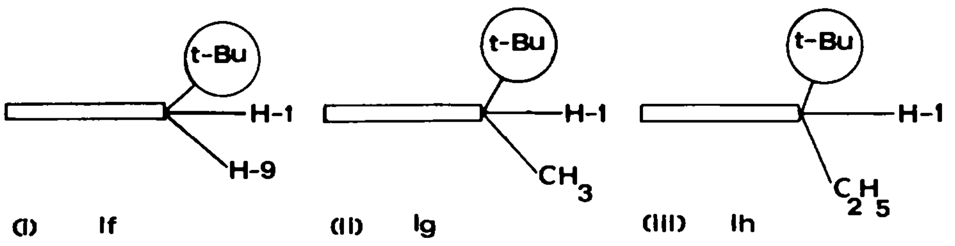


Fig. 12 Relative positions of H-1, t-butyl group and fluorene ring in (i) 9-t-butyl (If); (ii) 9-methyl-9-t-butyl (Ig); and (iii) 9-ethyl-9-t-butyl (Ih) fluorenes.

EXPERIMENTAL

PMR spectra were recorded on a Varian A-60 spectrometer equipped with a V-6057 variable-temperature probe. Sweep widths were calibrated versus the separation between 2% benzene, 2% TMS in CS_2, checked against an Advance TC2 timer/counter. Probe temp below normal were measured by recording spectra of MeOH and higher temp with ethylene glycol; "PMR thermometer" graphs, reported recently by van Geet,[25] were used to relate resonance separation precisely to temp.

PMR solvents were CS_2 [B.D.H. laboratory reagent "for IR spectroscopy"], CCl_4 [B.D.H. "Analar" grade], DMSO-d_6 and $CDCl_3$ [both Ciba, isotopic purity >99% atom %D]; all contained a little TMS as internal reference.

Preparations of most of the compounds involve Grignard reactions. Ib[26] and Ic[27] were derived by hydrolysis of the corresponding carbinol obtained from magnesium α-bromonaphthalene and ethereal fluorene by the methods of Ullman and Wurstemberger. For Id and Ie, the method of Wislicenus and Mocker[28] was followed except that the carboxylic acid was decomposed in boiling ethylene glycol containing KOH. Preparative details for Ig, Ih and IIb will be published elsewhere.[29]

IIa was prepared[30] by addition of ethereal MeMgI to 9-bromofluorene and MeI with decomposition of the complex by NH_4Cl. IIc was obtained[30] by warming difluorenylidene with ethereal MeLi which had been freed from MeI.

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