Conformational Behaviour of Bisfluorenylidenes

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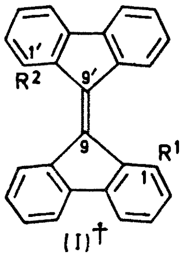
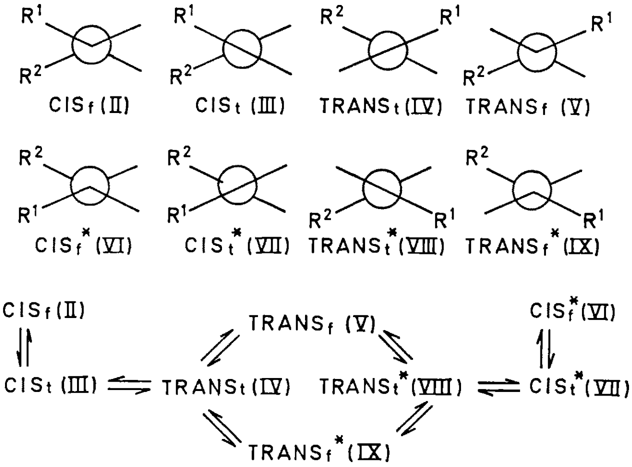
Summary The interconversion between various folded and twisted conformations of bisfluorenylidenes (I) have been examined by temperature-dependent n.m.r. spectroscopy.

IT has been known for some time that bisfluorenylidenes are non-planar in the crystalline state[1] and in solution,[2] but no detailed information regarding their conformational behaviour has been available hitherto, although the lack of success in obtaining optically active bisfluorenylidenes[3] has been interpreted as probably indicating fairly easy conformational isomerisation. 1,1′-Disubstituted bisfluorenylidenes (I)† can, in principle, exist in *cis*- and *trans*-diastereomeric forms,[4] and in order to relieve steric strain each of these diastereomers could adopt a number of non-planar chiral conformations. These conformations are conveniently represented by Newman projections (looking along the 9–9′ bond direction) and are called the *cis*-folded (CIS$_f$; II), *cis*-twisted (CIS$_t$; III), *trans*-twisted (TRANS$_t$; IV) and *trans*-folded (TRANS$_f$; V) conformations. In the four conformational projections (II—V), the inclination of the plane of each aromatic ring to the mean molecular plane is illustrated and the association of the fluorenylidene residues with the substituents R^1 and R^2 is indicated. Each of the four chiral conformations, CIS$_f$ (II), CIS$_t$ (III), TRANS$_t$ (IV), and TRANS$_f$ (V) are partnered by four enantiomeric conformations, CIS$_f$* (VI), CIS$_t$ *(VII), TRANS$_t$* (VIII), and TRANS$_f$* (IX).



(I)†

(a) $R^1 = R^2 = CO_2Me$
(b) $R^1 = R^2 = CO_2CHMe_2$
(c) $R^1 = CO_2Me; R^2 = CO_2CHMe_2$



SCHEME 1. *The conformational changes of bisfluorenylidenes associated with conformational inversion and with rotation about the 9,9′-double bond. For the bisfluorenylidenes* (I; $R^1 = R^2$) *then* TRANS$_f$ (V) *and* TRANS$_f$* (IX) *are identical and Scheme* 1 *is appropriately modified.*

If it is assumed that for steric reasons the interconversion between enantiomeric folded conformations involves twisted

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† The formula (I) is not intended to have any stereochemical significance and it refers to both the *cis*- and *trans*-diastereomers.

conformations as intermediates, then it is possible to devise a reasonable scheme for the conformational changes of the 1,1′-disubstituted bisfluorenylidenes (I) in solution (Scheme 1). Steric reasons also exclude direct interconversion of the conformations CIS$_t$ (III) $\leftrightharpoons$ CIS$_f$* (VI) and CIS$_f$ (II) $\leftrightharpoons$ CIS$_t$* (VII). We have now investigated the conformational behaviour of a number of bisfluorenylidenes by temperature-dependent n.m.r. spectroscopy,[5] and the results for the three cases (Ia, b, and c) are now reported.

N.m.r. parameters and energy barriers to conformational inversion (process A) and cis–trans-*isomerisation (process B) of bisfluorenyliden*

	Temperature-dependent signals[a]									
	CO_2Me[b]		$CO_2CH(Me)_2$[c]							
Compound	ν_A	ν_B	ν_A	ν_B	ν_C	ν_D	$\Delta G^{\ddagger}_{363°}$	E_a	$\log_{10}A$	Process
(Ia)	188·5	175·5					20·1 ± 0·2	28·7 ± 1·4	18·1 ± 0·8[d]	B[b]
(Ib)			57·5	36·5			21·0 ± 0·2	22·7 ± 0·9	13·9 ± 0·5	A
(Ic)	193·0	175·5					20·9 ± 0·3	26·7 ± 2·0	16·4 ± 1·2[d]	B[b]
			54·5	35·5	54·5	44·0	20·8 ± 0·3	23·2 ± 1·9	14·4 ± 1·2	A and B[b]

[a] In Hz. to low-field of Me_4Si at 60 MHz. for pentachlorethane solutions at 50°.

[b] Activation parameters refer to the change, major conformer → minor conformer.

[c] ν_A and ν_B refer to the high-intensity doublets, in all cases the chemical shift refers to the centre of the doublet signals [J (CH–CH_3) 6·0 Hz].

[d] These high values of $\log_{10}A$ suggest that some systematic error may be involved in the n.m.r. line-shape analysis for cases involving exchange between two sites having very different populations. The value of $\Delta G^{\ddagger}_{363°}$ is therefore a more reliable parameter for comparison.

The results are summarised in the Table. The activation parameters for conformational and configurational change were determined by line-shape analysis in the usual way.[5,6] The n.m.r. spectra of the 1,1′-di(alkoxycarbonyl)bisfluorenylidenes (Ia, b, and c) showed temperature-dependence which could be associated both with conformational inversion (process A) and with interconversion between diastereomeric conformations (process B). Processes of the type A could be recognised by the temperature-dependence of the n.m.r. signals assignable to the diastereotopic[7] methyl groups of the isopropyl groups of the compounds (Ib and c). These signals were observable as two doublets for each isopropyl group at low temperatures which broadened and eventually coalesced to a single doublet at higher temperatures. Processes of type B were identified by the temperature-dependence of the geometrically non-equivalent methoxycarbonyl group signals observable at low temperatures in the n.m.r. spectra of compounds (Ia and c). These signals at low temperatures were observable in each case as two singlets of unequal intensity which coalesced to a single singlet signal at higher temperatures.

Conformational change	Rate constant	Site exchange	Rate constant
TRANS$_f$ $\rightarrow$ TRANS$_f$* TRANS$_f$* $\rightarrow$ TRANS$_f$	k_1	A $\rightarrow$ B, B $\rightarrow$ A	k_1
TRANS$_f$ $\rightarrow$ CIS$_f$ TRANS$_f$* $\rightarrow$ CIS$_f$ TRANS$_f$ $\rightarrow$ CIS$_f$* TRANS$_f$* $\rightarrow$ CIS$_f$*	k_1	A $\rightarrow$ C, B $\rightarrow$ D, A $\rightarrow$ D, B $\rightarrow$ C	k_1
CIS$_f$ $\rightarrow$ TRANS$_f$ CIS$_f$ $\rightarrow$ TRANS$_f$* CIS$_f$* $\rightarrow$ TRANS$_f$ CIS$_f$* $\rightarrow$ TRANS$_f$*	k_2	C $\rightarrow$ A, D $\rightarrow$ B, D $\rightarrow$ A, C $\rightarrow$ B	k_2

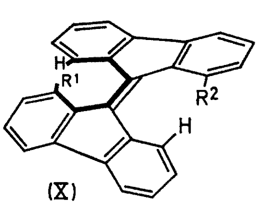
SCHEME 2. *Rate constants for the conformational change of the bisfluorenylidene* (Ic) *and the associated exchange between the sites indicated by* $CHMe_AMe_B$ *and* $CHMe_CMe_D$. *The assignment of sites to particular conformations is arbitrary but the Scheme is not altered in its essentials if other assignments are used.*

The results obtained with the methyl isopropyl diester (Ic) are of particular interest in that the isopropoxycarbonyl group provides information about processes A and B, whereas the methoxycarbonyl group provides complementary information only about process B. The isopropyl methyl signals (Table) of the diester (Ic) were analysed by comparison with line shapes computed[6] for exchange between the four n.m.r. sites (A, B, C, and D) associated with two geometrically non-equivalent isopropyl groups: $CHMe_AMe_B$ and $CHMe_CMe_D$. These two geometrically non-equivalent isopropyl groups were necessarily associated with diastereomerically related conformations and each of the geometrically non-equivalent methyl groups Me_A, Me_B, Me_C, and Me_D, as a result of Me–H vicinal coupling, gave doublet signals. These features were included in the line-shape analysis of the temperature-dependent n.m.r. spectrum of the compound (Ic). The diastereomer populations and the exchange rates (k_1 and k_2) which were obtained for this compound (Ic) by analysis of the temperature-dependence of the methoxycarbonyl signals gave satisfyingly good agreement with the exchange rates (k_1 and k_2) deduced for site exchange involving the isopropoxycarbonyl groups. The assignments for site exchange are listed in Scheme 2. The results, although not yet definitive in all respects, are nevertheless consistent with rapid rate processes involving *observably* populated conformations which are assumed to be TRANS$_f$, TRANS$_f$*, CIS$_f$, and CIS$_f$* (Scheme 1). For the compound (Ia) the population of the major conformer is 0·70 (mole fraction) at 363°K and the corresponding figure is 0·84 for the compound

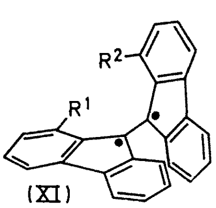
(Ic). These facts can be interpreted on the basis of the assumption that the TRANS$_f$ and TRANS$_f^*$ conformations are of lower free energy, and are therefore more highly populated, than the CIS$_f$ and CIS$_f^*$ conformations. This assumption is not yet directly validated by our present results, but it appears to be reasonably based from a consideration of non-bonded interactions for these diastereomerically related conformations.

Adopting the methods used to examine the solid-state conformation of tri-*o*-thymotide,[6b,c] the determination of the n.m.r. spectra of the compounds (Ia, b, and c) immediately after solution at low temperature shows that the compound (Ia) has the conformation in the solid state corresponding to its ***minor*** conformation, after equilibration in solution, whereas the compounds (Ib and c) have conformations in the solid state corresponding to their ***major*** conformations in solution. This situation, as well as the possibility that these compounds may undergo spontaneous resolution [6b,c] during crystallisation, is under examination.

The energy barriers associated with conformational inversion (process A) and *cis–trans*-isomerisation (process B) are both remarkably low ($\Delta G^{\ddagger}_{363^\circ} = 20$—$21$ kcal.mole^{-1}). The low energy barrier for process A is surprising as this process would involve the highly strained transition state (X) in which the thickened bonds are coplanar. Presumably the low energy barrier for process A is a reflection of ground state strain. The low energy barrier for process B is even more remarkable in that in this case rotation about a formal carbon–carbon double bond is involved. However, this unusually rapid *cis–trans*-isomerisation of an ethylene derivative may well be encouraged by ground-state strain as well as the involvement of an excellently stabilised transition state (XI). This transition state (XI) is probably a diradical (*cf.* ref. 8) in which effective delocalisation of the unpaired electrons is possible and ground state strain is effectively relieved because the two fluorenylidene residues are accommodated in orthogonal planes.



(X)



(XI)

(*Received, December 29th, 1969; Com. 1952.*)

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