Anomalous Behaviour in the Helical Twist Sense and Spontaneous Polarization of Ferroelectric Liquid Crystals

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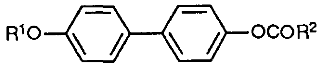
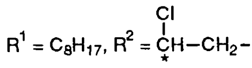
The inductive effect of substituents at the chiral centres in a series of biphenyls does not affect the helical twist sense and the sign of spontaneous polarization.

Much interest has been focused on ferroelectric liquid crystals, because of their practical application to electrooptical devices in view of their quick response and bistability[1] which are intimately related to the helical twist sense and the sign of spontaneous polarization (P_s). Goodby[2] reported that the helical twist sense and the sign of P_s are inverted if the sign of the inductive effect ($\pm I$) of a substituent at a chiral centre is inverted, *e.g.* from a methyl system to a chloro system. We now report anomalous cases demonstrating that the helical twist sense and P_s are not inverted even though the sign of the inductive effect is changed.

The helical twist sense of ferroelectric liquid crystals is usually determined by the contact method with a standard material of known twist sense, but there are some exceptions whereby the helical pitch of the mixture is unwound irrespective of their helical twist sense.[3] Thus, we determined the helical twist sense of the ferroelectric liquid crystals directly by observing the direction of rotation in circularly polarized light transmitted through the samples under homeotropic orientation.

Gray and McDonnell's rules[4] can be applied to the biphenyl series **1a–c** and **2a–d** (Tables 1 and 2): (*i*) as the chiral centre is moved incrementally away from the central core or (*ii*) as the absolute configuration is inverted, the helical twist sense and the sign of P_s changes from dextro (+) to laevo (−). However, the helical twist sense does not change if the flow distribution of electrons about the chiral centre is inverted (for example, a methyl branch at a chiral centre is replaced by chlorine or a methoxy branch). Moreoever, the sign of P_s does not change if the flow distribution of electrons at a chiral centre is inverted (**1a–c**). As shown in Table 2, the helical twist sense and the sign of P_s are determined primarily by the position of the chiral



1a; 
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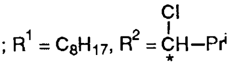
1b; 
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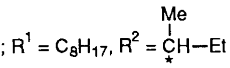
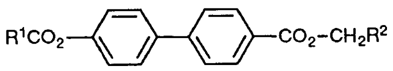
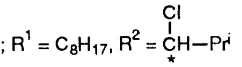
1c; 
$R^1 = C_8H_{17}$, $R^2 = \overset{Me}{\underset{*}{C}}H{-}Et$



2a; 
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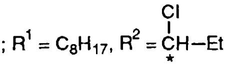
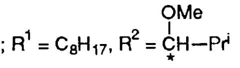
2b; 
$R^1 = C_8H_{17}$, $R^2 = \overset{Cl}{\underset{*}{C}}H{-}Et$

2c; 
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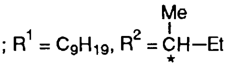
2d; 
$R^1 = C_9H_{19}$, $R^2 = \overset{Me}{\underset{*}{C}}H{-}Et$

Table 1 Transition temperatures of biphenyls[5]

	Absolute configuration	Transition temperatures/°C[a]			
		I-S_A	S_A-S_C*	S_C*-S_X*	M.p.
1a	*S*	68	64	—	75
1b	*S*	80	69	—	76
1c	*S*	—	75	—	75
2a	*S*	54	40	10	37
2b	*S*	56	22	—	25
2c	*R*	39	19	10	25
2d	*S*	61	47	—	38

[a] We determined the transition temperatures of compounds and mixtures by microscopic observations, the temperature dependence of dielectric constant and differential scanning calorimetry (DSC).

Table 2 Helical twist sense and spontaneous polarization of biphenyls

	Abs. config.	Chiral position	Optical rotation	Twist sense[a]	Induced effect	Sign of P_s[b]
1a	*S*	o	(−)	RH	−*I*	(−)
	R	o	(+)	LH	−*I*	(+)
1b	*S*	o	(−)	RH	−*I*	(−)
	R	o	(+)	LH	−*I*	(+)
1c	*S*	o	(−)	RH	+*I*	(−)
2a	*S*	e	(+)	LH	−*I*	(+)
	R	e	(−)	RH	−*I*	(−)
2b	*S*	e	(+)	LH	−*I*	(+)
2c	*S*	e	(+)	LH	−*I*	(+)
	R	e	(−)	RH	−*I*	(−)
2d	*S*	e	(+)	LH	+*I*	[c]

[a] See the text. [b] The sign of P_s was determined by observing the changes of the polarity with applying DC voltage. [c] The sign of P_s of **2d** is inverted by temperature.[6] However, the helical twist sense does not become inverted through the S_C* phase.

centre with respect to the core and the absolute configuration. It could be said that the helical twist sense and the sign of P_s of biphenyls are probably steric-driven rather than dipolar-driven. For the series **1a–c** and **2a–d**, the carbonyl groups which have the largest dipole and the chiral centres are relatively close to the central core, and these molecular features may be responsible for the anomalous behaviour demonstrated.

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