Helical Twist Sense and Spontaneous Polarization of Ferroelectric Liquid Crystals with Vicinal Chiral Centres

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The helical twist sense and spontaneous polarization of ferroelectric liquid crystals with vicinal chiral centres are shown to be dominated by the absolute configuration of the chiral centre closer to the central core.

Many studies have been devoted to ferroelectric liquid crystals, because of their potential applications to electro-optical devices of quick response and bistability.[1] A series of ferroelectric liquid crystals, in which the chiral centres are substituted by chlorine,[2] have been reported to have an extremely large spontaneous polarization (P_S) which is important for the quick response of electrooptical devices. Among these series of chlorinated ferroelectric liquid crystals, the biphenyls with vicinal chiral centres (abbreviated as **BP-vc**) exhibit a lower melting point and wider S_C* temperature range, closer to room temperature, than those of biphenyls with a single chiral centre.[3] In this communication, we report the helical twist sense and the sign of the P_S of **BP-vc**.† Table 1 shows the transition temperatures.

† The helical twist sense and the sign of P_S are intimately related to the bistability and the fast-switching of electrooptical devices, and Gray and McDonnell's rules[5] for cholesterics can be applied to the helical twist sense and the sign of P_S of ferroelectric liquid crystals with a single chiral centre.[6]

Table 1 Transition temperatures of biphenyls with vicinal chiral centres[3]

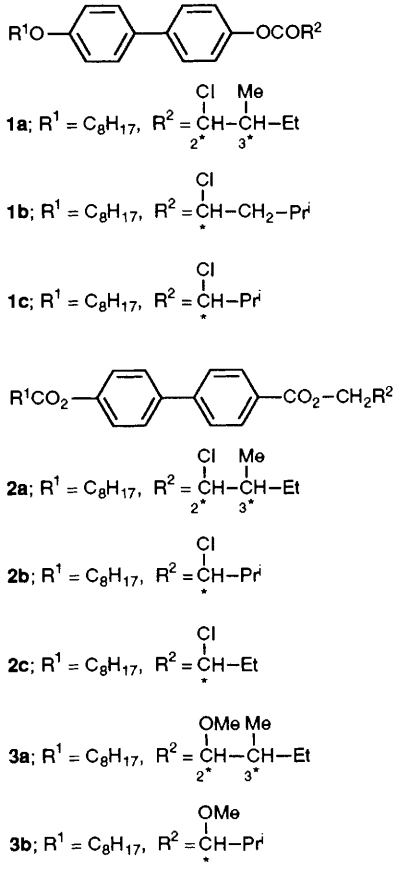
	Absolute configuration	Transition temperature/°C[a]			
		I–S_A	S_A–S_C*	S_C*–S_X*	M.p.
1a	2*S*,3*S*	64	53	36	48
	2*R*,3*S*	60	59	—	—
1b	*S* or *R*	68	64	—	75
1c	*S* or *R*	80	69	—	76
2a	2*S*,3*S*	50	35	—	15
	2*R*,3*S*	47	37	—	6
2b	*S* or *R*	54	40	10	37
2c	*S* or *R*	56	22	—	25
3a	2*S*,3*S*	37	18	—	38
3b	*S* or *R*	39	19	10	25

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

Table 2 Helical twist sense and the sign of P_S of biphenyls with vicinal chiral centres[4]

	Abs. config.	Chiral position[a]	Optical rotation	Twist sense[b]	Induced effect	Sign of P_S[c]	Magnitude of P_S[d,4] (T_{SA-SC})	Pitch length[e]/μm
1a	2*S*,3*S*	o	l(−)	RH	−*I*, +*I*	(−)	−210 (19)	0.8
	2*R*,3*S*	o	d(+)	LH	−*I*, +*I*	(+)	—	—
1b	*S*	o	l(−)	RH	−*I*	(−)	—	—
	R	o	d(+)	LH	−*I*	(+)	—	—
1c	*S*	o	l(−)	RH	−*I*	(−)	−98 (5)	0.6
	R	o	d(+)	LH	−*I*	(+)	—	—
2a	2*S*,3*S*	e	d(+)	LH	−*I*, +*I*	(+)	+80 (22)	0.5
	2*R*,3*S*	e	l(−)	RH	−*I*, +*I*	(−)	+95 (22)	0.5
2b	*S*	e	d(+)	LH	−*I*	(+)	+104 (23)	0.6
	R	e	l(−)	RH	−*I*	(−)	+103 (24)	0.6
2c	*S*	e	d(+)	LH	−*I*	(+)	+53 (16)	—
3a	2*S*,3*S*	e	d(+)	LH	−*I*, +*I*	(+)	+17 (5)	0.3–0.7
3b	*R*	e	l(−)	RH	−*I*	(−)	+11 (6)	0.25
	S	e	d(+)	LH	−*I*	(+)	+15 (11)	0.25

[a] o = Odd no. of atoms from core, e = even. [b] We determined the helical twist sense of ferroelectric liquid crystals directly for all compounds by observing the direction of rotation in circularly polarized light transmitted through the samples under homeotropic orientation. [c] The sign of P_S was determined easily by observing changes of polarity with applied d.c. voltage. [d] The magnitude of P_S was evaluated utilizing the Sawer–Tower method. [e] The pitch length was measured at a reduced temperature (T_{A-C}) of −10 °C.



As shown in Table 2, the helical twist sense and sign of P_S of **BP-vc** are dominated by the absolute configuration of the chiral centre closer to the central core. The helical twist sense and sign of P_S of the biphenyl monoesters, (2*S*,3*S*)-**1a**, are opposite to those of the (2*R*,3*S*)-epimer and are the same as those of **1b** and **1c** which have a single chiral centre of the same absolute configuration without the other chiral centre farther from the central core. Similar behaviour is also found for the biphenyldiesters **2a–c**. Furthermore, a similar trend is found even if the chiral centre closer to the central core is substituted by a methoxy branch; the helical twist sense of (2*S*,3*S*)-**3a** is the same as that of **3b** without the chiral centre at the 3* position. Although in these series of biphenyls, the chiral centre closer to the central core is substituted by a chlorine or methoxy branch which has a negative inductive effect (−*I*), we have already reported[4] that the sign of P_S and the helical twist sense of these biphenyls are steric-driven rather than dipolar-driven.‡ Thus the helical twist sense and the sign of P_S of **BP-vc** are dominated by the chiral centre closer to the central core. It could be said that in these series of **BP-vc**, the helical sense and sign of P_S are more likely to be affected by the rigid part of the molecular structures.

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‡ The helical twist sense and the sign of P_S of this series of biphenyls are not changed by the direction of the inductive effect or the flow distribution of electrons about the chiral centre.