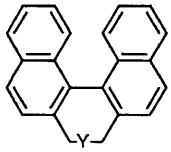
A Study of the Conformation of some Chiral Binaphthyl and Bithienyl Derivatives in the Solid State and in Solution. An Approach by X-Ray Diffraction, Circular Dichroism Spectroscopy and Induced Cholesteric Mesophase Analysis

Bernadette Suchod,[a,*] Anne Renault,[a] Janine Lajzerowicz[a] and Gian Piero Spada[b]
[a] *Laboratoire de Spectrométrie Physique, Université Joseph Fourier (Grenoble I), Boite postale 87, 38402 Saint-Martin-d'Hères Cedex, France*
[b] *Dipartimento di Chimica Organica 'A. Mangini', Universita di Bologna, Via San Donato 15, 40127 Bologna, Italy*

The crystal structures of enantiomeric 4,5,6,7-tetrahydrodinaphtho[2,1-*b*:1′,2′-*d*][1,6]dioxecine, **1a**, and of enantiomeric dimethyl 2,2′-dinitro-3,3′-bithienyl-4,4′,dicarboxylate, **3**, are reported. The solid state conformations of these compounds and of related derivatives with bridged and non-bridged 1,1′-binaphthyl structures are analysed. The conformation in the crystal structure is compared with the conformation in solution obtained from the twisting powers of these compounds in nematic liquid crystal solvents and from circular dichroism measurements. For *quasi*-rigid bridged binaphthyls the different sets of data agree. For mobile biaryls they may differ.

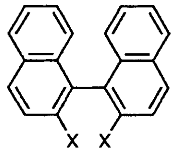
Recently a simple technique for investigating the conformation of biaryls in solution has been proposed. The addition of chiral compounds to nematic liquid crystals induces cholesteric mesophases.[1] The cholesteric helix is characterised by its handedness and pitch. The different ability of a chiral dopant to twist the nematic phase is expressed by its twisting power $\beta = (pcr)^{-1}$ where p is the pitch, c the concentration of the dopant and r its optical purity. When both the solute and the nematic solvent have a biaryl structure, it is possible to correlate the helicity of the aryl groups to the handedness of the induced cholesteric phase;[2–4] therefore if the absolute configuration is known, the cisoid conformation (θ, angle between the two aryl planes, less than 90°) or transoid conformation ($\theta > 90°$) of the biaryl system can be deduced from the sign of the twisting power (positive for a right-handed cholesteric and negative for a left-handed one). Precisely, for *S* absolute configuration a positive β value indicates a cisoid conformation and a negative β value a transoid one. Furthermore, from the absolute value of β, it is possible to gain an indication of the dihedral angle between the two aryl units in the dopant. In the case of biphenyl derivatives, when the two aromatic groups are at $\theta = 90°$ (or $\theta = 0°$) the value of β is expected to be around zero. On the other hand, the maximum value of β is expected when $\theta = 45°$.

This technique was applied, in this and in previous work, to many biaryls compounds ranging from bridged (**1**) and open-chain (**2**) 1,1′-binaphthyl derivatives to 3,3′ bithienyl derivatives (**3**).[1–4]



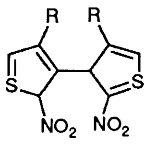
1

a Y = O(CH$_2$)$_4$O
b Y = S$_2$

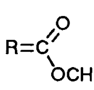


2

a X = OCH$_3$
b X = CH$_2$Br
c X = OH
d X = NH$_2$
e X = H



3



$R{=}C(=O)OCH_3$

In this article we compare, for some biaryl derivatives, the molecular conformations in solution, deduced by this method, with the conformations found in the solid state. To increase the number of structural data already published, we solved the structures of 4,5,6,7-tetrahydrodinaphtho [2,1-*b*:1′,2′-*d*][1,6]-dioxecine (**1a**), 2,2′-dimethoxy-1,1′-binaphthyl (**2a**) and dimethyl 2,2′-dinitro-3,3′-bithienyl-4,4′-dicarboxylate (**3**). However, the structure of **2a** has already been published.[5]

Further information about the conformation of binaphthyls in solution can be obtained from the analysis of the exciton CD couplet originating from the ${}^1B_b$ electronic transition of the naphthalene chromophore at *ca.* 230 nm.[6–8] For *S* absolute configuration, a cisoid conformation exhibits a couplet with the positive branch at low energy and the negative one at high energy (positive couplet); a transoid conformation shows instead the inverted order of the two components of the couplet (negative couplet). However, the critical angle at which the couplet signals vanish (and then invert) is not exactly 90°, but is calculated to be around 100–110°.

Results and Discussion

Table 1 collects the X-ray diffraction results and the data from the induced cholesteric analysis for compounds **1**–**3** and also the sign of the CD couplet at *ca.* 230 nm for binaphthyl derivatives. β values are measured in a nematic solvent of the biaryl type which is structurally similar to the dopant.

Bridged Binaphthyls (**1**).—The two compounds **1a** and **1b** have a high twisting power. The conformations of the biaryl moiety obtained from the liquid crystal technique and from crystallographic results are in agreement. For **1a**, the solvent dependence of β is reported in Table 2: β is maximum in K15, the nematic which has the structure most similar to that of the inducing molecule. In any case, a right-handed cholesteric is induced by (*S*)-**1a** in all the solvents tested indicating a cisoid conformation.

Open-chain Binaphthyls (**2**).—The measured β values are much smaller than for the preceding compounds (except for **2c**, see below). This finding could be associated either with a preferred conformation having a dihedral angle near 90° or with the existence of nearly equally populated cisoid and transoid conformations. The former agrees with the dihedral angle calculated from crystallographic analysis for **2a**–**d**. Furthermore one must not forget that the conformation obtained from the solid state can be influenced by packing effects, particularly in

Table 1 Comparison between crystallographic results, induced cholesteric results and CD data (for the details of solvents see Table 2 caption)

	Crystallographic results			Twisting power				CD exciton couplet	
Compound	Dihedral angle $\theta/°$	Cisoid or transoid	Ref.	Configuration (S or R)	$\beta/°$ Solvent	Cisoid or transoid	Ref.	Sign	Ref.
Bridged binaphthyls **1**									
1a	75–70	C	this work	S	+79 PCB	C	2		
1b	56	C	6	R	−65 E7	C	2	−	6
Open chain binaphthyls **2**									
2a	111–111	T	5	S	+1.5 K15	C	3	+	this work
2b	92	T	10	S	−4.6 K15	T	3	−	3
2c	89	C	11	S	+32 K15	C	3		
2d	85	C	11	S	+2 E7	C	3	+	7
2e	68 (rac) 103 (en.)	C T	9	S	+10 E7		this work	+	8
Bithienyls **3**									
3	88–90	~	this work	R	−5.5 E7	C	5		

Table 2 The twisting powers[a] of (S)-**1a**, (S)-**2a** and (S)-**2e** in different nematic solvents[b]

	$\beta/°$		
Solvent	(S)-**1a**	(S)-**2a**	(S)-**2e**
E7	+55		+9.9
K15	+79 (from ref. 2)	+1.5 (from ref. 3)	
Phase 1052	+42 (from ref. 2)	+1.2	+11
Phase 1083	+47		+13
Phase IV	+53	−6.3	+9
MBBA	+65 (from ref. 2)	−3.8	+ 9
ZLI 1167	+33		

[a] β values are in μm^{-1}, concentration being expressed in molar fraction. The determinations were carried out at room temperature (22–23 °C) for all solvents except ZLI 1167 (T = 35 °C). [b] E7: a commercial mixture (from BDH) of 4-cyano-4′-aryl and 4′-alkylbiphenyl; K15: 4-cyano-4-pentylbiphenyl; Phase 1052: a mixture (from Merck) of phenylcyclohexane derivatives; Phase 1083: a mixture (from Merck) of aromatic esters; Phase IV: 4-methoxy-4′-butylazoxybenzene (from Merck); MBBA: N-(4-methoxybenzylidene)-4-butylaniline (from Reidel-de Haan); ZLI 1167: a mixture of 4-cyano-4′-alkylbicyclohexane (from Merck).

Table 3 Spectroscopic characteristics of the ^1B_b transition of (S)-**2a** in different solvents

Solvent	Absorption $\varepsilon_{max}/10^4$ dm^3 mol^{-1} cm^{-1} (λ_{max}/nm)	Circular dichroism $\Delta\varepsilon_{max}$/dm^3 mol^{-1} cm^{-1} (λ_{max}/nm)
Ethanol	7.93 (228)	+165 (235); −110 (220)
Acetonitrile	8.44 (228)	+145 (235); −104 (220)
Dioxane	7.96 (230)	+166 (237); −109 (222)
Cyclohexane	8.79 (228)	+184 (235); −132 (220)

the case of mobile conformations such as these open-chain compounds. For example, for 1,1′-binaphthyl, **2e**, in enantiomeric crystals, the θ value is 103° while in racemic crystals it is 68°;[9] for this derivative, CD signals due to the ^1B_b couplet indicate a conformation in solution with θ lower than the critical angle and β values measured in different liquid crystals (Table 2) clearly indicate a cisoid conformation with θ markedly less than 90° (as one may expect because of the lack of the two bulky *ortho*-substituents).

In the case of **2a**, which we studied more thoroughly (we solved the structure) the liquid crystal results obtained in different solvents (see Table 2) seem to be contradictory: right-handed helicity in some solvents and left-handed in others. On the other hand this behaviour supports the hypothesis that the preferred conformation in solution has a dihedral angle not far from 90°; in such a case, a small variation in the structural characteristics of the solvent can invert the helicity of the diaryl unit and hence of the cholesteric. Furthermore, the assumption of a relation between solute biaryl helicity and cholesteric handedness is based on a model of induction that requires a strict similarity between solute and solvent: this is true only for K15 and E7 solvents.

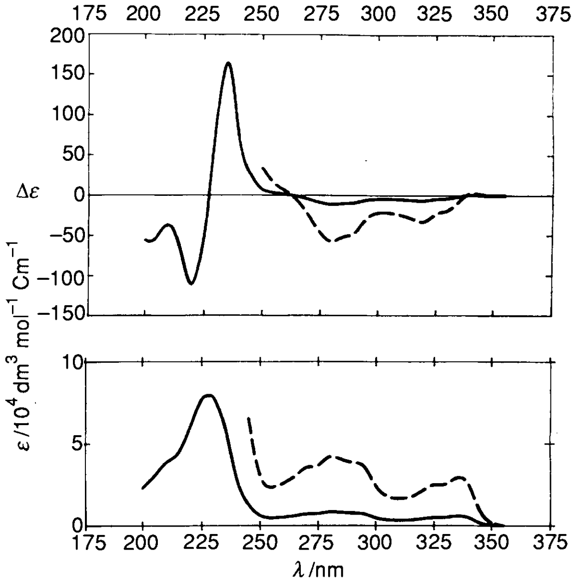


Fig. 1 Circular dichroism (upper part) and absorption (lower part) spectra of compound **2a** in ethanol. Dashed lines represent spectra magnified five times.

It is interesting to note the fact (which was not mentioned in the structure determination paper) that the structure of enantiomer **2a** is isomorphous to that of enantiomer **2e** and the molecular conformations are similar (transoid with θ = 103° for **2e** and transoid with θ = 111° for both independent molecules of the cell for dimethoxy compound **2a**).

We have recorded the CD spectrum of **2a** in several solvents. Fig. 1 shows the circular dichroism and absorption spectra in ethanol, while the characteristics of the exciton splitting in the

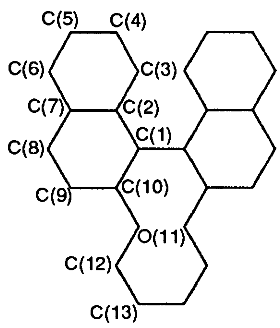


Fig. 2 Labelling scheme for compound **1a**

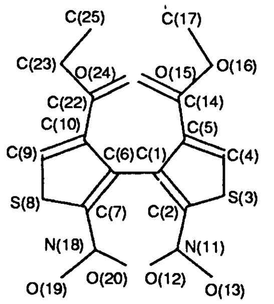


Fig. 4 Labelling scheme for compound **3**

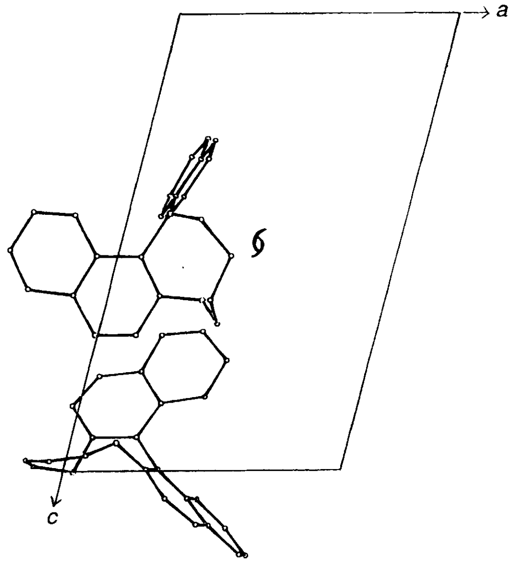


Fig. 3 Compound **1a**: orientation of the two independent molecules in the cell. There are four molecules in the cell: the other two are defined by space group $P2_1$.

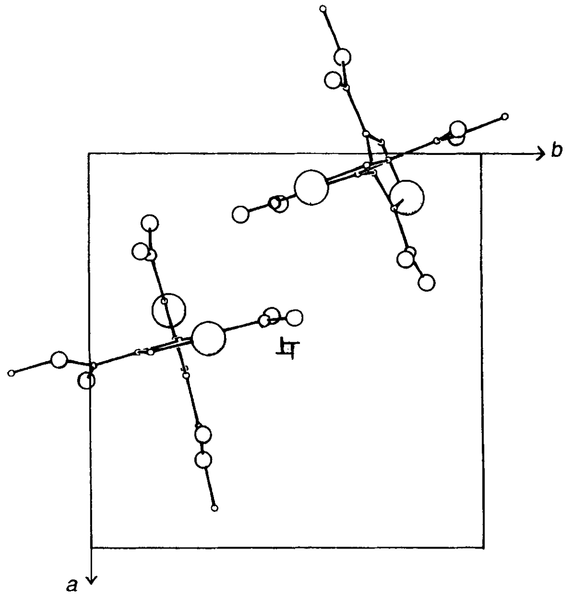


Fig. 5 Compound **3** orientation of the two independent molecules A and B in the cell (big circles represent S atoms, medium circles O). There are eight molecules in the cell: the other six are defined by space group $P4_1$.

Table 4 Atomic coordinates for non-hydrogen atoms of compund **1a**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(1a)	0.145(2)	0.316(2)	0.440(1)	C(1c)	0.234(2)	0.194(3)	0.924(1)
C(2a)	0.154(2)	0.227(3)	0.398(1)	C(2c)	0.292(3)	0.154(3)	0.850(1)
C(3a)	0.118(2)	0.143(3)	0.440(2)	C(3c)	0.443(2)	0.176(2)	0.835(1)
C(4a)	0.131(2)	0.059(3)	0.399(2)	C(4c)	0.487(3)	0.138(3)	0.757(2)
C(5a)	0.175(3)	0.056(3)	0.313(2)	C(5c)	0.376(3)	0.082(3)	0.694(2)
C(6a)	0.215(2)	0.131(3)	0.273(1)	C(6c)	0.233(3)	0.062(3)	0.699(2)
C(7a)	0.210(2)	0.220(3)	0.318(1)	C(7c)	0.192(2)	0.098(3)	0.781(2)
C(8a)	0.242(2)	0.304(3)	0.276(1)	C(8c)	0.046(3)	0.084(3)	0.791(2)
C(9a)	0.237(3)	0.388(2)	0.317(1)	C(9c)	−0.021(3)	0.116(3)	0.856(2)
C(10a)	0.182(2)	0.391(2)	0.400(1)	C(10c)	0.078(2)	0.174(3)	0.926(2)
O(11a)	0.151(2)	0.476(2)	0.4350(9)	O(11c)	0.039(2)	0.213(3)	1.002(1)
C(12a)	0.266(2)	0.548(2)	0.447(1)	C(12c)	−0.113(5)	0.244(4)	0.988(2)
C(13a)	0.408(3)	0.527(3)	0.526(2)	C(13c)	−0.144(3)	0.344(5)	0.985(4)
C(1b)	0.083(2)	0.318(2)	0.527(1)	C(1d)	0.341(3)	0.254(3)	0.997(2)
C(2b)	−0.075(2)	0.304(2)	0.526(1)	C(2d)	0.475(3)	0.218(3)	1.063(1)
C(3b)	−0.190(2)	0.291(3)	0.438(1)	C(3d)	0.509(3)	0.125(3)	1.065(2)
C(4b)	−0.344(2)	0.280(3)	0.429(2)	C(4d)	0.641(4)	0.094(3)	1.129(2)
C(5b)	−0.392(2)	0.277(3)	0.511(2)	C(5d)	0.736(2)	0.158(4)	1.189(2)
C(6b)	−0.293(3)	0.290(2)	0.598(2)	C(6d)	0.712(5)	0.250(3)	1.186(2)
C(7b)	−0.124(2)	0.303(2)	0.611(1)	C(7d)	0.572(3)	0.288(4)	1.123(1)
C(8b)	−0.009(3)	0.319(3)	0.699(1)	C(8d)	0.529(4)	0.377(3)	1.121(2)
C(9b)	0.137(2)	0.335(3)	0.698(2)	C(9d)	0.392(4)	0.408(3)	1.061(2)
C(10b)	0.186(2)	0.336(2)	0.613(2)	C(10d)	0.295(3)	0.351(3)	0.996(2)
O(11b)	0.342(2)	0.350(2)	0.6233(9)	O(11d)	0.164(2)	0.380(2)	0.936(1)
C(12b)	0.420(3)	0.428(3)	0.675(1)	C(12d)	0.066(5)	0.447(3)	0.966(3)
C(13b)	0.371(2)	0.519(3)	0.623(2)	C(13d1)	−0.090(7)	0.438(5)	0.953(4)
				C(13d2)	−0.03(1)	0.397(6)	1.008(6)

Table 5 Bond lengths/Å and bond angles/° for the two independent molecules of compound **1a** (first molecule: atoms a and b, second molecule: atoms c and d)

Bond distances/Å				Bond angles/°			
C(1a)–C(2a)	1.42(5)	C(1c)–C(2c)	1.44(3)	C(2a)–C(1a)–C(10a)	120(2)	C(2c)–C(1c)–C(10c)	119(2)
C(1a)–C(10a)	1.31(4)	C(1c)–C(10c)	1.42(3)	C(2a)–C(1a)–C(1b)	116(3)	C(2c)–C(1c)–C(1d)	118(2)
C(1a)–C(1b)	1.52(3)	C(1c)–C(1d)	1.50(4)	C(10a)–C(1a)–C(1b)	124(3)	C(10c)–C(1c)–C(1d)	122(2)
C(2a)–C(3a)	1.42(5)	C(2c)–C(3c)	1.44(3)	C(1a)–C(2a)–C(3a)	122(2)	C(1c)–C(2c)–C(3c)	124(2)
C(2a)–C(7a)	1.40(3)	C(2c)–C(7c)	1.41(4)	C(1a)–C(2a)–C(7a)	120(3)	C(1c)–C(2c)–C(7c)	119(2)
C(3a)–C(4a)	1.37(5)	C(3c)–C(4c)	1.42(4)	C(3a)–C(2a)–C(7a)	118(3)	C(3c)–C(2c)–C(7c)	117(2)
C(4a)–C(5a)	1.41(4)	C(4c)–C(5c)	1.41(4)	C(2a)–C(3a)–C(4a)	120(2)	C(2c)–C(3c)–C(4c)	120(2)
C(5a)–C(6a)	1.31(5)	C(5c)–C(6c)	1.32(4)	C(3a)–C(4a)–C(5a)	120(3)	C(3c)–C(4c)–C(5c)	117(2)
C(6a)–C(7a)	1.45(5)	C(6c)–C(7c)	1.44(4)	C(4a)–C(5a)–C(6a)	123(3)	C(4c)–C(5c)–C(6c)	127(3)
C(7a)–C(8a)	1.40(5)	C(7c)–C(8c)	1.35(4)	C(5a)–C(6a)–C(7a)	118(2)	C(5c)–C(6c)–C(7c)	116(3)
C(8a)–C(9a)	1.36(5)	C(8c)–C(9c)	1.34(5)	C(2a)–C(7a)–C(6a)	121(3)	C(2c)–C(7c)–C(6c)	124(2)
C(9a)–C(10a)	1.42(3)	C(9c)–C(10c)	1.42(4)	C(2a)–C(7a)–C(8a)	117(3)	C(2c)–C(7c)–C(8c)	116(3)
C(10a)–O(11a)	1.37(4)	C(10c)–O(11c)	1.37(4)	C(6a)–C(7a)–C(8a)	121(2)	C(6c)–C(7c)–C(8c)	120(2)
O(11a)–C(12a)	1.44(4)	O(11c)–C(12c)	1.37(5)	C(7a)–C(8a)–C(9a)	122(2)	C(7c)–C(8c)–C(9c)	129(3)
C(12a)–C(13a)	1.50(3)	C(12c)–C(13c)	1.47(8)	C(8a)–C(9a)–C(10a)	117(3)	C(8c)–C(9c)–C(10c)	115(3)
C(13a)–C(13b)	1.54(4)	C(13c)–C(13d1)	1.59(9)	C(1a)–C(10a)–C(9a)	123(3)	C(1c)–C(10c)–C(9c)	121(3)
		C(13c)–C(13d2)	1.1(1)	C(1a)–C(10a)–O(11a)	117(2)	C(1c)–C(10c)–O(11c)	114(2)
C(1b)–C(2b)	1.40(3)	C(1d)–C(2d)	1.41(3)	C(9a)–C(10a)–O(11a)	120(3)	C(9c)–C(10c)–O(11c)	126(2)
C(1b)–C(10b)	1.37(3)	C(1d)–C(10d)	1.44(6)	C(10a)–O(11a)–C(12a)	119(2)	C(10c)–O(11c)–C(12c)	117(2)
C(2b)–C(3b)	1.44(3)	C(2d)–C(3d)	1.37(6)	O(11a)–C(12a)–C(13a)	112(3)	O(11c)–C(12c)–C(13c)	119(4)
C(2b)–C(7b)	1.42(3)	C(2d)–C(7d)	1.46(5)	C(21a)–C(13a)–C(13b)	113(2)	C(12c)–C(13c)–C(13d1)	141(4)
C(3b)–C(4b)	1.34(3)	C(3d)–C(4d)	1.36(4)			C(12c)–C(13c)–C(13d2)	120(6)
C(4b)–C(5b)	1.37(4)	C(4d)–C(5d)	1.40(5)	C(1a)–C(1b)–C(2b)	125(2)	C(1c)–C(1d)–C(2d)	122(3)
C(5b)–C(6b)	1.34(3)	C(5d)–C(6d)	1.34(8)	C(1a)–C(1b)–C(10b)	118(2)	C(1c)–C(1d)–C(10d)	114(2)
C(6b)–C(7b)	1.47(3)	C(6d)–C(7d)	1.42(5)	C(2b)–C(1b)–C(10b)	117(2)	C(2d)–C(1d)–C(10d)	123(3)
C(7b)–C(8b)	1.44(3)	C(7d)–C(8d)	1.33(6)	C(1b)–C(2b)–C(3b)	119(2)	C(1d)-C(2d)–C(3d)	121(3)
C(8b)–C(9b)	1.31(3)	C(8d)–C(9d)	1.37(5)	C(1b)–C(2b)–C(7b)	122(2)	C(1d)–C(2d)–C(7d)	114(4)
C(9b)–C(10b)	1.42(3)	C(9d)–C(10d)	1.37(5)	C(3b)–C(2b)–C(7b)	119(2)	C(3d)–C(2d)–C(7d)	125(2)
C(10b)–O(11b)	1.37(3)	C(10d)–O(11d)	1.32(3)	C(2b)–C(3b)–C(4b)	123(2)	C(2d)–C(3d)–C(4d)	118(3)
O(11b)–C(12b)	1.42(4)	O(11d)–C(12d)	1.42(6)	C(3b)–C(4b)–C(5b)	118(2)	C(3d)–C(4d)–C(5d)	119(4)
C(12b)–C(13b)	1.50(5)	C(12d)–C(13d1)	1.35(8)	C(4b)–C(5b)–C(6b)	123(2)	C(4d)–C(5d)–C(6d)	123(3)
		C(12d)–C(13d2)	1.4(1)	C(5b)–C(6b)–C(7b)	122(2)	C(5d)–C(6d)–C(7d)	121(4)
		C(13d1)–C(13d2)	1.0(1)	C(2b)–C(7b)–C(6b)	115(2)	C(2d)–C(7d)–C(6d)	113(4)
				C(2b)–C(7b)–C(8b)	118(2)	C(2d)–C(7d)–C(8d)	122(3)
				C(6b)–C(7b)–C(8b)	127(2)	C(6d)–C(7d)–C(8d)	125(3)
				C(7b)–C(8b)–C(9b)	119(2)	C(7d)–C(8d)–C(9d)	122(3)
				C(8b)–C(9b)–C(10b)	122(2)	C(8d)–C(9d)–C(10d)	122(4)
				C(1b)–C(10b)–C(9b)	122(2)	C(1d)–C(10d)–C(9d)	116(3)
				C(1b)–C(10b)–O(11b)	123(2)	C(1d)–C(10d)–O(11d)	121(3)
				C(9b)–C(10b)–O(11b)	115(2)	C(9d)–C(10d)–O(11d)	123(4)
				C(10b)–O(11b)–C(12b)	121(2)	C(10d)–O(11d)–C(12d)	120(3)
				O(11b)–C(12b)–C(13b)	112(2)	O(11d)–C(12d)–C(13d1)	126(5)
				C(13a)–C(13b)–C(12b)	116(3)	O(11d)–C(12d)–C(13d2)	109(5)
						C(13c)–C(13d1)–C(12d)	112(5)
						C(13c)–C(13ds)–C(12d)	143(9)

^1B_b transition in different solvents are summarized in Table 3. The spectra are practically insensitive to solvent variations; the sign of the couplet centred at *ca.* 230 nm (equal to those of *cis*-bridged analogues of the same absolute configuration) indicates that the dihedral angle between the two aryl moieties is less than the critical angle; however, this does not tell us whether the preferred conformation is cisoid or transoid with a dihedral angle smaller than 100–110°.

In summary, the LC and CD techniques indicate that in solution these unbridged derivatives adopt conformations with θ around 90° that undergo small changes in different solvents.

One apparently anomalous value appears for **2c** ($\beta = 32$) especially when comparing **2c** and **2d** which are pseudoisomorphs in the crystalline state and have very similar conformations. In the case of **2c**, intramolecular hydrogen bonding may play an important role in determining the actual conformation in solution.

Bithienyl (**3**).—Again a small value of β was found, and θ was close to 90° (in the crystal there are two independent molecules in the cell for which we find $\theta = 88°$ and 90°). Studies of the dipolar momentum have been done:[4] the experimental dipole moments are rather high and compatible with a non-planar conformation and a dihedral angle near 90° (the calculation gives 86°).

Conclusions

The helicity of optically active biaryls is likely to be the main factor in determining the twisting power in biphenyl nematic liquid crystals.

In the case of bridged binaphthyls, **1a**–**b**, whose rotation about the interaromatic bond is highly restricted, the conformation determined in the crystal state is the same as the conformation determined in nematic solution, that is, a cisoid one.

In non-bridged derivatives, **2a**, **2b**, **2d** and **3**, both the techniques again agree and indicate preferred conformations with a dihedral angle not far from 90°. However in these compounds the actual conformation, *i.e.* cisoid or transoid, is determined by crystal packing in the solid state while solvent effects and intramolecular hydrogen bonding play a role in solution. So the conformations observed in the crystal are not necessarily those in solution.

Table 6 Atomic coordinates for non-hydrogen atoms of compound **3**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(1A)	0.769 67	0.475 72	0.741 43	C(1B)	1.048 20	0.725 80	0.451 62
C(2A)	0.671 26	0.454 20	0.770 69	C(2B)	1.138 73	0.778 06	0.424 59
S(3A)	0.696 58	0.469 39	0.839 06	S(3B)	1.109 25	0.806 80	0.360 17
C(4A)	0.844 28	0.506 83	0.827 76	C(4B)	0.971 44	0.745 28	0.366 06
C(5A)	0.875 99	0.506 82	0.773 93	C(5B)	0.949 41	0.706 31	0.416 84
C(6A)	0.780 19	0.472 91	0.682 65	C(6B)	1.051 40	0.686 03	0.508 57
C(7A)	0.808 69	0.375 10	0.652 26	C(7B)	1.086 16	0.582 64	0.527 45
S(8A)	0.797 52	0.398 00	0.586 00	S(8B)	1.083 74	0.564 78	0.595 39
C(9A)	0.757 31	0.549 24	0.594 72	C(9B)	1.028 70	0.708 13	0.600 77
C(10A)	0.753 09	0.567 02	0.650 32	C(10B)	1.016 60	0.762 71	0.553 24
N(11A)	0.554 60	0.424 78	0.753 33	N(11B)	1.250 36	0.816 33	0.446 28
O(12A)	0.537 03	0.411 14	0.706 44	O(12B)	1.264 89	0.807 83	0.494 02
O(13A)	0.477 19	0.416 38	0.787 12	O(13B)	1.326 02	0.858 78	0.415 87
C(14A)	0.991 10	0.543 03	0.754 34	C(14B)	0.831 65	0.657 05	0.432 99
O(15A)	1.008 39	0.579 42	0.710 37	O(15B)	0.811 89	0.622 72	0.476 88
O(16A)	1.078 55	0.524 56	0.790 21	O(16B)	0.753 19	0.646 27	0.394 48
C(17A)	1.200 47	0.561 44	0.772 50	C(17B)	0.634 08	0.597 68	0.405 21
N(18A)	0.842 80	0.256 27	0.674 32	N(18B)	1.124 36	0.474 25	0.497 29
O(19A)	0.846 39	0.175 60	0.640 93	O(19B)	1.126 16	0.485 65	0.449 65
O(20A)	0.868 06	0.247 31	0.719 75	O(20B)	1.153 37	0.386 08	0.521 42
C(22A)	0.722 16	0.694 93	0.669 32	C(22B)	0.965 89	0.886 50	0.548 40
O(23A)	0.710 48	0.777 71	0.635 34	O(23B)	0.954 10	0.937 00	0.501 10
O(24A)	0.712 67	0.289 01	0.466 77	O(24B)	0.935 70	0.940 40	0.587 30
C(25A)	0.682 50	0.899 95	0.652 75	C(25B)	0.904 19	1.059 80	0.494 20

Experimental

Synthesis.—Racemic and optically active 2,2′-dimethoxy-1,1′-binaphthyl, **2a**, was synthesized from the commercial 1,1′-bi-2-naphthol by reaction with dimethyl sulfate.[12] Optically active dimethyl 2,2-dinitro-3,3′-bithienyl-4,4′-dicarboxylate, **3**, was synthesized as reported in ref. 13. Optically active 4,5,6,7-tetrahydrodinaphtho[2,1-*b*:1′,2′-*d*][1,6]dioxecine, **1a**, was synthesized from the commercial 1,1′-bi-2-naphthol following ref. 14.

Induced Cholesteric Experiments.—A detailed description of the experiments is reported in ref. 15*a*.

Pitch values were measured with the lens-version of the Grandjean–Cano method[15b,c] using a Zeiss Standard 16 Microscope. This method is based on the observation of the discontinuity lines appearing when a cholesteric liquid crystal is inserted into a cell of variable thickness. A drop of cholesteric solution was placed between a plano-convex lens and a glass plate, both rubbed previously with tissue paper, the rubbing direction of the lens and plate being parallel. From the radii of the circular disinclinations observed under this linear boundary condition, the pitch values were obtained.

The same samples observed with plane-polarized light show coloured rings connected with the variation of the rotatory power with sample thickness. Helical handedness was determined from the sign of the rotatory power.

A cross-check of the helical handedness was obtained by the Heppke–Oestreicher method[15d] in which the plano-convex lens is circularly rubbed. Under this circular boundary condition a double spiral disinclination line appears whose handedness is connected to cholesteric handedness.

Circular Dichroism.—CD spectra of 10^{-4} mol dm^{-3} solutions of (*S*)-**2a** were recorded in a 1 cm path length cell with a Jasco J-500A spectropolarimeter. Solvents used were of spectroscopic grade.

Crystallography.—Crystals of (*S*)-4,5,6,7-tetrahydrodinaphtho[2,1-*b*:1′,2′-*d*][1,6]dioxecine (**1a**) $C_{24}O_2H_{20}$ (M_r = 340) are white and almost transparent. X-Ray intensities were measured, at room temperature, on a Nicolet diffractometer with graphite monochromator, ω scan mode, λ Mo-Kα = 0.710 73 Å, $2\theta_{max} = 45°$ ($h_{max} = 8$, $k_{max} = 14$, $-14 < l < +14$): 2180 reflections were measured of which 1284 with $F_o > 2\sigma(F_o)$; no absorption corrections. Lattice parameters were determined from least-squares refinement of 25 reflections: monoclinic $P2_1$ (n° 14) a = 8.847(9) Å, b = 14.33(1) Å, c = 14.65(1) Å, β = 105.43(7)°. Z = 4 (two independent molecules per cell, noted ab and cd); D_x = 1.263; R_w = 0.08, R = 0.07 for 1284 reflections and 468 variables. We had difficulties in finding the structure by direct methods and we were helped by the knowledge of a molecular model obtained from a program of conformational energy minimisation.[16] Having a good approximate model we were able to solve the structure by means of a program from the XTAL chain of crystallographic programs,[17] PATSEE which combines Patterson methods and direct methods. The final molecular model is close to the result given by the energy program (θ angle of 70° and 75° for the two different molecules instead of 60° for the theoretical model). The structure was refined with the XTAL system of crystallographic programs:[17] hydrogen atoms were found on a Fourier difference or calculated, unit weights, atomic scattering factors from International Tables of Crystallography, anisotropic temperature factors for non-hydrogen atoms. The angles between bicycle planes are, respectively, 105° (0.6) and 110° (0.6) for the two molecules. In the second molecule there is probably a disorder in the bridge: according to Fourier peaks we tried to put two possible positions for atom C(13d), but the result remains unsatisfactory for distances and angles. Fig. 2 shows the labelling scheme. Atomic coordinates for non-hydrogen atoms are given in Table 4 for both molecules. Table 5 gives the angles and distances of the models obtained. The orientation of the two molecules in the cell is shown in Fig. 3.

Crystals of *R*-(+)-dimethyl 2,2′-dinitro-3,3′- bithienyl-4,4′-dicarboxylate (**3**), $C_{12}O_8H_8S_2N_2$, (M_r = 372) are pale yellow. X-Ray intensity data were registered on a Philips diffractometer with graphite monochromator, ω scan mode, λ Mo-Kα = 0.710 73 Å, $2\theta_{max} = 60°$ ($h_{max} = 16$, $k_{max} = 16$, $l_{max} = 36$). 5000 reflections were measured, 1190 with $F_o > 2\sigma(F_o)$; no absorption correction. Lattice parameters were determined from least-squares refinement of 25 reflections: tetragonal $P4_1$ (n° 76) $a = b$ = 11.173(5) Å, c = 25.30(1) Å, V = 3158(3) Å^3, Z = 8 (2 independent molecules per cell, A and B), D_x = 1.52 g cm^{-3}, R_w = 0.06, R = 0.05 for 1289 reflections and 432 para-

Table 7 Bond lengths/Å and bond angles/° for the two independent molecules (A and B) of compound **3**

Bond distances/Å				Bond angles/°			
C(1N)–C(2A)	1.35(3)	C(1B)–C(2B)	1.35(3)	C(2A)–C(1A)–C(5A)	113(2)	C(2B)–C(1B)–C(5B)	109(2)
C(1A)–C(5A)	1.49(3)	C(1B)–C(5B)	1.43(3)	C(2A)–C(1A)–C(6A)	127(2)	C(2B)–C(1B)–C(6B)	126(2)
C(1A)–C(6A)	1.49(3)	C(1B)–C(6b)	1.51(3)	C(5A)–C(1A)–C(6A)	120(2)	C(5B)–C(1B)–C(6B)	124(2)
C(2A)–S(3A)	1.76(2)	C(2B)–S(3B)	1.69(2)	C(1A)–C(2A)–S(3A)	113(2)	C(1B)–C(2B)–S(3B)	115(2)
C(2A)–N(11A)	1.41(3)	C(2B)–N(11B)	1.43(3)	C(1A)–C(2A)–N(11A)	129(2)	C(1B)–C(2B)–N(11B)	126(2)
S(3A)–C(4A)	1.73(2)	S(3B)–C(4B)	1.69(2)	S(3A)–C(2A)–N(11A)	118(2)	S(3B)–C(2B)–N(11B)	119(2)
C(4A)–C(5A)	1.41(3)	C(4B)–C(5B)	1.38(3)	C(2A)–S(3A)–C(4A)	91(1)	C(2B)–S(3B)–C(4B)	91(1)
C(5A)–C(14A)	1.44(3)	C(5B)–C(14B)	1.48(3)	S(3A)–C(4A)–C(5A)	114(2)	S(3B)–C(4B)–C(5B)	112(2)
C(6A)–C(7A)	1.37(3)	C(6B)–C(7B)	1.31(3)	C(1A)–C(5A)–C(4A)	110(2)	C(1B)–C(5B)–C(4B)	113(2)
C(6A)–C(10A)	1.37(3)	C(6B)–C(10B)	1.47(3)	C(1A)–C(5A)–C(14A)	126(2)	C(1B)–C(5B)–C(14B)	125(2)
C(7A)–S(8A)	1.70(2)	C(7B)–S(8B)	1.73(2)	C(4A)–C(5A)–C(14A)	124(2)	C(4B)–C(5B)–C(14B)	122(2)
C(7A)–N(18A)	1.49(3)	C(7B)–N(18B)	1.49(3)	C(1A)–C(6A)–C(7A)	126(2)	C(1B)–C(6B)–C(7B)	128(2)
S(8A)–C(9A)	1.76(3)	S(8B)–C(9B)	1.72(2)	C(1A)–C(6A)–C(10A)	124(2)	C(1B)–C(6B)–C(10B)	124(2)
C(9A)–C(10A)	1.42(3)	C(9B)–C(10B)	1.35(3)	C(7A)–C(8A)–C(10A)	109(2)	C(7B)–C(6B)–C(10B)	108(2)
C(10A)–C(22A)	1.55(3)	C(10B)–C(22B)	1.50(3)	C(6A)–C(7A)–S(8A)	115(2)	C(6B)–C(7B)–S(8B)	117(2)
N(11A)–O(12A)	1.21(3)	N(11B)–O(12B)	1.22(3)	C(6A)–C(7A)–N(18A)	124(2)	C(6B)–C(7B)–N(18B)	128(2)
N(11A)–O(13A)	1.22(3)	N(11B)–O(13B)	1.24(3)	S(8A)–C(7A)–N(18A)	121(2)	S(8B)–C(7B)–N(18B)	115(1)
C(14A)–O(15A)	1.20(3)	C(14B)–O(15B)	1.20(3)	C(7A)–S(8A)–C(9A)	92(1)	C(7B)–S(8B)–C(9B)	89(1)
C(14A)–O(16A)	1.35(3)	C(14B)–O(16B)	1.32(3)	S(8A)–C(9A)–C(10A)	105(2)	S(8B)–C(9B)–C(10b)	113(2)
O(16A)–C(17A)	1.49(3)	O(16B)–C(17B)	1.46(3)	C(6A)–C(10A)–C(9A)	119(2)	C(6B)–C(10B)–C(9B)	113(2)
N(18A)–O(19A)	1.24(4)	N(18B)–O(19B)	1.21(3)	C(6A)–C(10A)–C(22A)	125(2)	C(6B)–C(10B)–C(22B)	125(3)
N(18A)–O(20A)	1.19(4)	N(18B)–O(20B)	1.20(3)	C(9A)–C(10A)–C(22A)	116(2)	C(9B)–C(10B)–C(22B)	122(3)
C(22A)–O(23A)	1.27(3)	C(22B)–O(23B)	1.36(3)	C(2A)–N(11A)–O(12A)	119(2)	C(2B)–N(11B)–O(12B)	118(2)
C(22A)–O(24A)	1.22(3)	C(22B)–O(24B)	1.21(3)	C(2A)–N(11A)–O(13A)	117(2)	C(2B)–N(11b)–O(13B)	118(2)
O(23A)–C(25A)	1.47(3)	O(23B)–C(25B)	1.49(4)	O(12A)–N(11A)–O(13A)	124(2)	O(12B)–N(11B)–O(13B)	124(2)
				C(5A)–C(14A)–O(15A)	124(2)	C(5B)–C(14B)–O(15B)	123(2)
				C(5A)–C(14A)–O(16A)	112(2)	C(5B)–C(14B)–O(16B)	115(2)
				O(15A)–C(14A)–O(16A)	124(2)	O(15B)–C(14B)–O(16B)	122(2)
				C(14A)–O(16A)–C(17A)	115(2)	C(14B)–O(16B)–C(17B)	120(2)
				C(7A)–N(18A)–O(19A)	114(3)	C(7B)–N(18B)–O(19B)	115(2)
				C(7A)–N(18A)–O(20A)	120(2)	C(7B)–N(18B)–O(20B)	119(2)
				O(19A)–N(18A)–O(20A)	126(3)	O(19B)–N(18B)–O(20B)	126(2)
				C(10A)–C(22A)–O(23A)	119(2)	C(10B)–C(22B)–O(23B)	120(3)
				C(10A)–C(22A)–O(24A)	119(2)	C(10B)–C(22B)–O(24B)	120(3)
				O(23A)–C(22A)–O(24A)	122(2)	O(23B)–C(22B)–O(24B)	120(3)
				C(22A)–O(23A)–C(25A)	120(2)	C(22B)–O(23B)–C(25B)	122(3)

meters. The structure was solved and refined with XTAL.[17] Hydrogen atoms were found on a Fourier difference or calculated, unit weights, atomic scattering factors from International Tables of Crystallography, anisotropic temperature factors for non-hydrogen atoms. Atomic coordinates for non-hydrogen atoms are given in Table 6 for both molecules A and B. Bond lengths and angles are given in Table 7. Lists of thermal parameters and hydrogen atom coordinates for **1a** and **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC).* Fig. 4 shows the labelling scheme. We did not solve the absolute configuration; the model described for the molecules happens to have a *R* configuration. The orientation of the two molecules in the cell is shown on Fig. 5.

The angle between the planes of the cycles inside a molecule is 90(1)° for molecule A, 88(1)° for B. The comparison between the two molecules shows a few differences of conformation. The angles between cycle and ester group are respectively 24° and 6° for A, 4° and 178° for B (σ *ca.* 1°).

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* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

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