NOTES *Bull. Chem. Soc. Jpn.*, *59*, *1607—1608 (1986)*

Induced Cholesteric Mesophases as a Probe for the Stereochemistry of Chiral Biphenyls

Giovanni Gottarelli,* Gian Piero Spada, Kaoru Seno,† Sanji Hagishita,†
and Kaoru Kuriyama†
Istituto di Scienze Chimiche, Universita' di Bologna,
Via S. Donato 15, 40127 Bologna, Italy
†Shionogi Research Laboratories, Shionogi Co., Ltd., Fukushima-ku, Osaka 553
(Received July 6, 1985)

Synopsis. In the studies of the induced cholesteric mesophases, the twisting powers of cisoid- and transoid-bridged 2,2′-diaminobiphenyl derivatives having *R*-configuration were found to be negative and positive respectively. In the cases where CD spectroscopy is inadequate, the liquid crystal method is sensitive to the helicity of the biphenyl moiety. The conformation of 2,2′-diamino-6,6′-dimethylbiphenyl is discussed.

The stereochemistry of chiral biaryl derivatives is a subject of continuous interest.[1)]

In particular, chiroptical techniques have been extensively employed for the configurational and conformational analysis of the system.[2,3)]

In several cases the chiroptical techniques are unable to characterize the skew sense (i.e. the cisoid or transoid conformation) of the biaryl moiety. In the exciton approximation,[3,4)] this indetermination is connected to the fact that the dipole–dipole interaction potential is not zero for a dihedral angle θ=90°; the value of θ at which the potential goes to zero depends in fact on the locations and directions of the electric dipole transition moments of the chromophores and therefore also on the substituents present. This point was emphasized in the recent work of Hagishita et al.[1)] where cisoid- and transoid-bridged biphenyls having the same absolute configuration and therefore opposite helicity of the biphenyl skeleton, were shown to display very similar circular dichroism spectra in several cases.

In a recent work[5)] we have shown that the configurations of a number of chiral cisoid-bridged biaryls, having various chemical structures, can be correlated by comparing the handedness of the cholesteric mesophases induced by traces of these derivatives dissolved in nematic liquid crystals of the biphenyl type.

Bridged biaryls having M-helicity induce M-cholesterics, while those of P-helicity induce P-cholesterics. The method, which allows the determination of configurations for cisoid-bridged systems, could be useful for the conformational analysis of non-bridged compounds of known absolute configuration; however, we needed experimental proof that rigid transoid derivatives also follow the helicity rule summarized above.

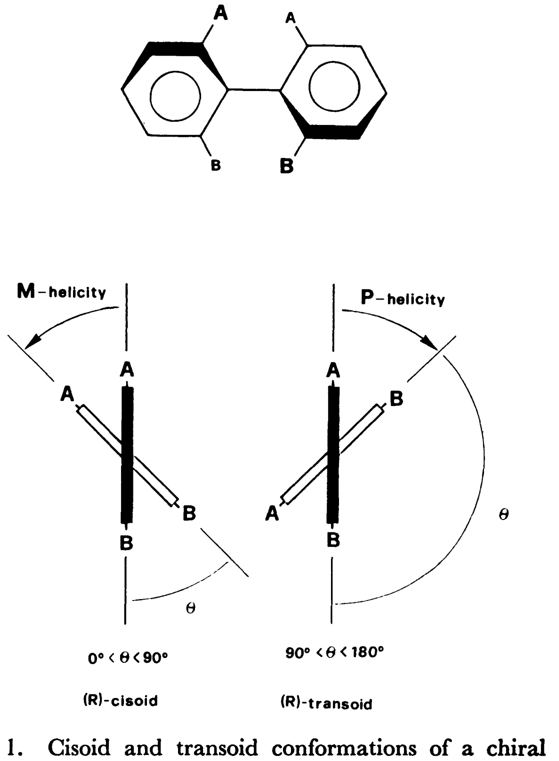
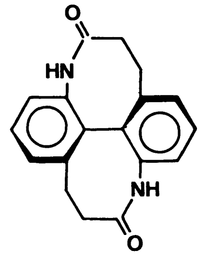
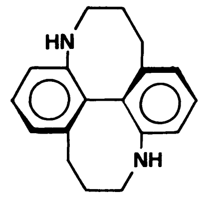


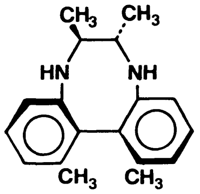
Fig. 1. Cisoid and transoid conformations of a chiral biphenyl derivative having *R*-configuration and the relative helicities of the biphenyl skeleton.



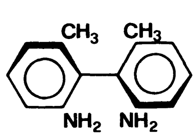
(1)



(2)



(3)



(4)

We report here the twisting powers β[6)] of four diaminobiphenyls (Table 1), whose structure is known in detail from X-ray diffraction.[1)] In particular, derivatives **1** and **2** constitute two examples of the rare trans-skew derivative (dihedral angle of 118° for **2**).[1)]

Table 1. Characteristics of Derivatives **1**—**4** and Their Twisting Powers in a Biphenyl-Type Liquid Crystal

Compound	Absolute configur.	Dihedral angle[a)]/°	Biphenyl helicity	β/μm^{-1} in E7[b)]	Cholesteric handedness
1	*R*		P	+58	P
2	*R*	118	P	+19.8	P
3	*R*	66	M	−21[c)]	M
4	*R*	93	P	+2.0	P

a) From crystallographic data; Ref. 1. b) E7: A mixture of 4-cyano-4′-aryl and 4′-(normal alkyl)biphenyl from BDH Chemicals. c) The enantiomer was measured.

Indeed derivatives **1** and **2** also follow the rule proposed for cisoid compounds and show values of β of the order of magnitude expected:[7)] their twisting powers have signs opposite to those of cisoid derivative **3** and other cisoid-bridged biaryls reported in Ref. 5. The liquid crystal method is therefore able to characterize the helicity of the biphenyl skeleton in the cases where CD spectroscopy fails.

Furthermore, derivatives **2** and **3**, which contain similar chemical groups, have quantitative values of β which are identical within the experimental error; this fact is a prerequisite for attempting the conformational analysis of non-bridged derivatives.

Derivative **4** has a small positive value of β indicating a P-helicity of the biphenyl system, which for the *R*-configuration is connected to a transoid conformation. The small value of β could be due either to the fact that the dihedral angle is very near to 90°,[7)] or to the presence of cisoid and transoid conformers giving opposite contributions to the observed value with a slight prevalence of the transoid structure. X-Ray diffraction gives a dihedral angle of 93° (transoid), furthermore a comparison between the CD spectra measured in solution and in a KBr disc indicates a dihedral angle larger than 90°.[1)]

The liquid crystal method therefore seems useful for the determination of the preferred conformation of chiral biphenyls in solution and could be a valid complement to circular dichroism studies. There are of course limitations due to the nature of substituents, which should not interfere with the alignment of the solute in the liquid crystal[7)] or with the close contact between molecules of solvent and solute.[7)]

Experimental

Measurements of the pitches were carried out with the "lens method"[8)] with a standard Zeiss microscope.

The handedness of the cholesterics was deduced from the sign of the rotatory power[9)] and cross-checked with the double spiral method.[10)]

The synthesis and the characteristics of derivatives **1**—**4** are described in Ref. 1.

The liquid crystal mixture E7 is a commercial product from BDH Chemicals.

G. Gottarelli and G. P. Spada thank CNR and MPI (Rome) for financial support.

References

1) K. Seno, S. Hagishita, J. Sato, and K. Kuriyama *J. Chem. Soc., Perkin Trans. 1*, **1984**, 2013.

2) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl Jr., *J. Am. Chem. Soc.*, **86**, 1710 (1964) and references therein.

3) S. F. Mason, "Molecular Optical Activity and the Chiral Discrimination," Cambridge University Press, Cambridge (1982), Chp. 6.

4) N. Harada and K. Nakanishi, "Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry," Oxford University Press, Oxford (1983).

5) G. Gottarelli, M. Hibert, B. Samori', G. Solladie', G. P. Spada, and R. Zimmermann, *J. Am. Chem. Soc.*, **105**, 7318 (1983).

6) The twisting power of a chiral solute in a nematic liquid crystal is defined as $\beta=(p.c.r)^{-1}$ where p the pitch (μm), c is the concentration (mol of solute/mol of solution) and r the enantiomeric excess of the dopant.

7) G. Gottarelli and G. P. Spada, *Mol. Cryst. Liq. Cryst.*, **123**, 377 (1985).

8) G. Heppke and F. Oestreicher, *Z. Naturforch.*, **A32**, 899 (1977).

9) J. P. Berthault, J. Billard, and J. Jacques, *C. R. Acad, Sci. Paris,* **C155**, 284 (1977).

10) G. Heppke and F. Oestreicher, *Mol. Cryst. Liq. Cryst.*, **41**, (letters), 245 (1978).