Conformational Study of 2,2′-Homosubstituted 1,1′-Binaphthyls by Means of UV and CD Spectroscopy

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Abstract: The dihedral angle θ of 1,1′-binaphthyl derivatives is quantitatively related to the wavelength splitting $\Delta\lambda_{max}$ of the 220 nm couplet of the CD spectra. This relation is almost independent of measurement conditions (solvent, concentration). Its reliability has been quite successfully tested on about 10 compounds derived from 2,2′-dimethyl-1,1′-binaphthyl. A simple and versatile method for the conformational assessment of this class of compounds is reported.

Introduction

1,1′-Binaphthyl derivatives constitute a class of compounds largely employed in any sort of chiral recognition processes and especially as auxiliaries in asymmetric organic synthesis.[1] In particular, metal complexes of 1,1′-bi(2-naphthol) (BINOL) and 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP) have been used in the last years as homogeneous catalysts in an impressive number of asymmetric reactions.[2,3]

Among these derivatives, 2,2′-homosubstituted ones preserve C_2 symmetry which makes them ideal chiral auxiliaries;[4] in addition to this, proper functionalities and the characteristic structural pliancy are essential in ensuring a high level of diastereo- and enantioselection.[5] The largely unrestricted rotation about the dihedral angle θ defined by the two naphthyl planes, which is the most important structural variable for these compounds, makes it possible to accommodate every 2 or 2′ substituent, irrespective of its steric requirements. That is the reason 1,1′-bi(2-naphthol) and BINAP can chelate so large a number of metal centers without appreciable strain as to represent two of the most versatile ligands for transition metals.

The crucial role played by the dihedral angle θ in determining the discrimination ability of 1,1′-binaphthyl-derived auxiliaries in enantioselective reactions and chiral recognition processes has been recently demonstrated.[6] Unfortunately, direct experimental access to θ is somewhat hampered by the C_2 symmetry of the systems, which prevents the use of most common NMR experiments for conformational investigations. As a consequence, studies such as in ref 6 rely upon molecular mechanics or semiempirical structure calculations; it is then of the utmost interest to have a reliable method of assessment of the value that θ takes in solution.

Mason and co-workers[7] first used the exciton model of optical activity[8] to derive a relation between the amplitude of CD spectra of 1,1′-binaphthyl derivatives and θ; the correlation they obtained found numerous qualitative applications as discussed below. We shall demonstrate how the very same model provides a fully *quantitative* relation between θ and a second spectral parameter, namely the wavelength splitting of CD spectra.

We also report the application of our model to about ten 2,2′-dimethyl-1,1′-binaphthyl derivatives, which represent ideal model compounds because of an electronic structure similar to that of naphthalene; some of these compounds were synthesized and newly characterized, while the remaining spectra were found in the literature.

A. Conformational Studies of 1,1′-Binaphthyl Derivatives. 1,1′-Binaphthyl crystallizes in two distinct forms.[9] The optically active and high melting A form crystallizes rapidly in acetone by spontaneus resolution; the lower melting B form consists of racemic crystals. X-ray studies have revealed that the A form is transoid with $\theta = 103.1°$,[10] while the B form is cisoid and has $\theta = 68.6°$.[11] Anyhow, various experimental[12,13] and theoretical methods[14] agree upon a quasiorthogonal conformation in solution, i.e., with $\theta \approx 90°$. Moreover, molecular mechanics and semiempirical methods calculate for the torsional mode of 1,1′-binaphthyl a potential curve, as a function of θ, with a flat-bottomed well located around $\theta \approx 90°$ and delimited

(1) (a) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405.

(2) (a) Narasaka, K. *Synthesis* **1991**, 1. (b) Bao, J.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3814 and references therein. (c) Bao, J.; Wulff, W. D.; Dominy, J. B.; Fumo, M. J.; Grant, E. B.; Rob, A. C.; Whitcomb, M. C.; Yeung, S.-M.; Ostrander, R. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 3392 and references therein.

(3) (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Ohta, T.; Miyake, T.; Seido, N.; Kumobayashi, H.; Takaya, H. *J. Org. Chem.* **1995**, *60*, 357 and references therein.

(4) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

(5) Noyori, R.; Takaya, H. *Chem. Scr.* **1985**, *25*, 83.

(6) (a) Mikami, K.; Motoyama, Y.; Terada, M. *Inorg. Chim. Acta* **1994**, *222*, 71. (b) Harada, T.; Takeuchi, M.; Hatsuda, M.; Ueda, S.; Oku, A. *Tetrahedron: Asymm.* **1996**, *7*, 2479. (c) Lustenberger, P.; Martinborough, E.; Mordasini Denti, T.; Diederich, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 747.

(7) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671.

(8) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy − Exciton Coupling in Organic Stereochemistry*; Oxford University Press: Oxford, 1983.

(9) Badar, Y.; Cheung King Ling, C.; Cooke, A. S.; Harris, M. M. *J. Chem. Soc.* **1965**, 1543.

(10) (a) Kress, R. B.; Duesler, E. N.; Etter, M. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1980**, *102*, 7709. (b) Kuroda, R.; Mason, S. F. *J. Chem. Soc., Perkin Trans. 2* **1981**, 167.

(11) Kerr, K. A.; Robertson, J. M. *J. Chem. Soc. B* **1969**, 1146.

(12) Lacey, A. R.; Craven, F. J. *Chem. Phys. Lett.* **1986**, *126*, 588.

(13) Wormell, P.; Ritchie, G. L. D. *J. Mol. Struct.* **1990**, *240*, 331.

at $\theta \approx 60-65°$ and $115-130°$ by steep walls due to the strong steric interactions proper of the structure approaching planarity.[14]

This discrepancy between crystalline and solution structure, typical of highly flexible molecules, makes necessary a conformational analysis in solution. This has been accomplished, up to the present, with a few methods valid for the entire class of 1,1'-binaphthyl compounds. UV and chiroptical properties can lead to a first sharp distinction between unbridged (**A**) and chain-bridged (**B**) derivatives, on account of the markedly
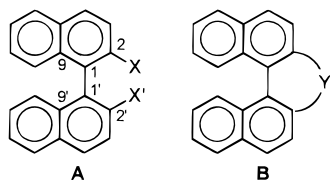
different values that θ takes in these two classes of compounds.[15] A second method, consisting of the comparison between calculated and experimental dipole moments, has been applied only to unbridged heterosubstituted derivatives.[16] Very recently, a promising relation between θ and nonlinear optical properties has been highlighted for 1,1'-bi(2-naphthol) derivatives, but it is restricted to substrates substituted at 6 and 6' with electron-withdrawing groups.[17]

Two less empirical and widely employed approaches make use of the results of CD spectroscopy (the already mentioned Mason model)[7] and of analysis of cholesteric phases induced in biphenyl-like nematic liquid crystals. Since 1983, Gottarelli et al. have developed a quite simple and versatile technique for the investigation of biaryls in solution,[18] based on the measurement of the twisting power of these compounds in nematic liquid crystal solvents. In recent years, this technique has been applied to a large number of 1,1'-binaphthyl derivatives,[19] in order to provide semiquantitative information about their stereochemical arrangement; it must, however, be emphasized that it refers to a very peculiar molecular environment, in analogy to diffractometric studies. Consequently, at least for quasidegenerate

conformational manifolds, the structural inference in liquid crystals has to be very cautiously transferred to ordinary organic solvents.[20]

These considerations reveal the need for a quantitative method of investigation of the solution conformation of 1,1'-binaphthyl derivatives, approaching as closely as possible the real situation of application of these componds as chiral auxiliaries in asymmetric synthesis.

B. The Optical Activity of 1,1'-Binaphthyl Derivatives. Within the independent systems approach (ISA)[21] to the theory of optical activity, the coupled dipoles or exciton mechanism[8] can be usefully employed when the molecular system under examination consists of two or more well separated chromophoric groups undergoing only electrically allowed transitions. This mechanism has also been treated in a classical physics frame (DeVoe's theory).[22]

B.1. Theory. It is well-known[8] that two equivalent electronic transitions localized on equal chromophores constituting a dissymmetric dimer interaction giving rise to two coupling modes at energies $E_{A,B} = E_a \pm V_{12}$, where E_a is the individual transition energy and V_{12} the coupling potential expressed by

$$V_{12} = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{R_{12}^3} - 3 \frac{(\vec{\mu}_1 \cdot \vec{R}_{12})(\vec{\mu}_2 \cdot \vec{R}_{12})}{R_{12}^5} \qquad (1)$$

where $\vec{\mu}_i \equiv \vec{\mu}_{i0a}$ is the transition dipole moment of monomer i and $\vec{R}_{12} = \vec{R}_2 - \vec{R}_1$ the interchromophoric distance vector. The electronic spectrum of the dimer will result from the summation of two bands split by the quantity $2V_{12}$ (called Davydov splitting) with intensities proportional to[23]

$$D_{A,B} = \frac{1}{2}|\vec{\mu}_1 \pm \vec{\mu}_2|^2 \qquad (2)$$

while the CD spectrum will consist of two bands of opposite sign and equal intensities (the bisignate exciton couplet), symmetrically located around $\nu_a = E_a/h$ and whose rotational strengths are given by

$$R_{A,B} = \mp \frac{\pi}{2} \nu_a \vec{R}_{12} \cdot (\vec{\mu}_1 \times \vec{\mu}_2) \qquad (3)$$

A very similar result is obtained with a classical physics approach by the DeVoe method.[22]

The results of these two theories have been widely applied in the past to make qualitative to quantitative predictions about the optical activity of dimeric and polymeric systems. DeVoe's approach makes it possible to calculate complete CD spectra to be compared with experimental ones to draw structural conclusions.[24] The exciton coupling mechanism, by means of semiempirical rules derived from it, has proved to be essential for immediate configurational assessment of various com-

(14) (a) Gamba, A.; Rusconi, E.; Simonetta, M. *Tetrahedron* **1970**, *26*, 871. (b) Carter, R. E.; Liljefors, T. *Tetrahedron* **1976**, *32*, 2915. (c) Busing, W. R. *J. Am. Chem. Soc.* **1922**, *104*, 4829. (d) Baraldi, I.; Ponterini, G.; Momicchioli, F. *J. Chem. Soc., Perkin Trans. 2* **1987**, *83*, 2139. (e) Leister, D.; Kao, J. *J. Mol. Struct. (THEOCHEM)* **1988**, *168*, 105. (f) Tsuzuki, S.; Tanabe, K.; Nagawa, Y.; Nakanishi, H. *J. Mol. Struct.* **1990**, *216*, 279. (g) Kranz, M.; Clark, T.; Schleyer, P. v. R. *J. Org. Chem.* **1993**, *58*, 3317.

(15) (a) Mislow, K.; Glass, M. A. W.; O'Brien, R. E.; Rutkin, P.; Steinberg, D. H.; Weiss, J.; Djerassi, C. *J. Am. Chem. Soc.* **1962**, *84*, 1455. (b) Mislow, K.; Bunnenberg, E.; Records, R.; Wellman, K.; Djerassi, C. *J. Am. Chem. Soc.* **1963**, *85*, 1342.

(16) Gagulin, V. V.; Gur'yanova, E. N.; Chayanov, B. A. *Zh. Obshch. Khim.* **1980**, *50*, 2768.

(17) (a) Deussen, H.-J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841. (b) Hendrickx, E.; Boutton, C.; Clays, K.; Persoons, A.; van Es, S.; Biemans, T.; Meijer, B. *Chem. Phys. Lett.* **1997**, *270*, 241. (c) Deussen, H.-J.; Boutton, C.; Thorup, N.; Geisler, T.; Hendrickx, E.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *Chem. Eur. J.* **1998**, *4*, 240.

(18) (a) Gottarelli, G.; Hilbert, M.; Samori, B.; Solladié, G.; Spada, G. P.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318. (b) Gottarelli. G.; Spada, G. P.; Bartsch, R.; Solladié, G.; Zimmermann, R. *J. Org. Chem.* **1986**, *51*, 589. (c) Solladié, G.; Gottarelli, G. *Tetrahedron* **1987**, *43*, 1425. (d) Spada, G. P.; Proni, G. *Enantiomer* **1998**, *3*, 301.

(19) (a) Suchod, B.; Renault, A.; Lajzerowicz, J.; Spada, G. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1839. (b) Rosini, C.; Franzini, L.; Salvadori, P.; Spada, G. P. *J. Org. Chem.* **1992**, *57*, 6820. (c) Rosini, C.; Rosati, I.; Spada, G. P. *Chirality* **1995**, *7*, 353. (d) Bhatt, J. C.; Keast, S. S.; Neubert, M. E.; Petschek, R. C. *Liq. Cryst.* **1995**, *18*, 367. (e) Deussen H.-J.; Shibaev, P. V.; Vinokur, R.; Bjørnholm, T.; Schaumburg, K.; Bechgaard, K.; Shibaev, V. P. *Liq. Cryst.* **1996**, *21*, 327. (f) Ferrarini, A.; Nordio, P. L.; Shibaev, P. V.; Shibaev, V. P. *Liq. Cryst.* **1998**, *24*, 219.

(20) (a) Diehl, P. In *Nuclear Magnetic Resonance of Liquid Crystals*; Emstey, J. W., Ed.; Dordrecht: Boston, 1983; pp 147−180. (b) Naciri, J.; Spada, G. P.; Gottarelli, G.; Weiss, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4352. (c) Di Bari, L.; Persico, M.; Veracini, C. A. *J. Chem. Phys.* **1992**, *96*, 4782.

(21) Tinoco, I., Jr. *Adv. Chem. Phys.* **1962**, *4*, 113.

(22) (a) DeVoe, H. *J. Chem. Phys.* **1964**, *41*, 393. (b) DeVoe, H. *J. Chem. Phys.* **1965**, *43*, 3199.

(23) Harada, N.; Uda, H. *J. Chem. Soc., Chem. Commun.* **1982**, 230.

(24) For a few examples concerning diaryl systems see: (a) Zandomeneghi, M.; Rosini, C.; Salvadori, P. *Chem. Phys. Lett.* **1976**, *44*, 533. (b) Rosini, C.; Salvadori, P.; Zandomeneghi, M. *J. Chem. Soc., Dalton Trans.* **1978**, 822. (c) Rosini, C.; Zandomeneghi, M.; Salvadori, P. *Tetrahedron: Asymm.* **1993**, *4*, 545.

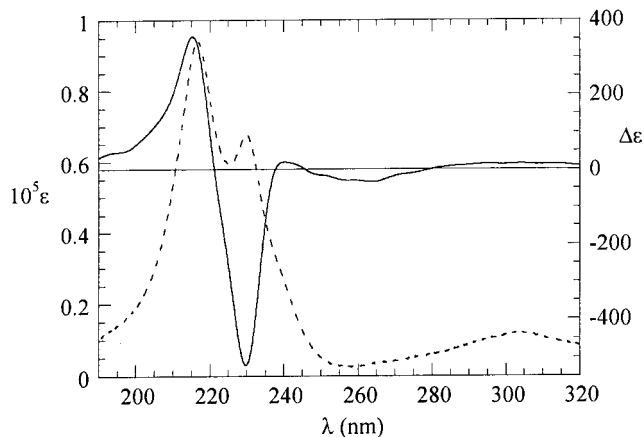**Scheme 1.** Polarization Directions of the Main Electronic Transition Moments of Naphthalene

^1L_a (285 nm)

^1B_b (220 nm)
^1L_b (310 nm)
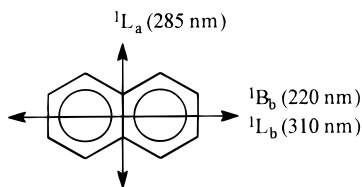
pounds;[8] in particular it has been quantitatively applied to diaryls by Mason.[7,25,26]

B.2. The Results of Exciton Theory: 1,1′-Binaphthyl as a Naphthalene Dimer. The electronic spectrum of naphthalene has been extensively studied in the past.[27] It consists of two main bands at 220 ($\epsilon_{max} \approx 10^5$ M^{-1} cm^{-1}) and 286 nm (0→0 transition, $\epsilon_{max} = 4000$);[28] a third smaller band appears at 310 nm. These three bands, named ^1B_b, ^1L_a, and ^1L_b by Platt,[29] have been assigned $^1B_{3u}{}^+$, $^1B_{2u}$, and $^1B_{3u}{}^-$ symmetry, respectively;[30] the polarization directions (Scheme 1) have been confirmed by single-crystal spectra.[31]

The UV and CD spectra of 1,1′-binaphthyl[32] can be almost completely explained on the basis of the above detailed electronic structure of the naphthalene chromophore restricted to the ^1B_b and ^1L_a transitions.[7,26] In particular, the strongest UV band ($\lambda_{max} = 220$ nm, $\epsilon_{max} = 108000$ in ethanol) and the couplet at 200−240 nm ($\lambda_{ext} = 214$ and 225 nm, $A = 430$) are due to the coupling of the two ^1B_b transitions located on distinct naphthalene rings. The sign of the couplet, positive for (S)-(+)-1,1′-binaphthyl, confirms the prediction made by means of eq 3.

Figure 1 reports the UV and CD spectra of (R)-(−)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]oxepine (**5**) as an example of a chain-bridged derivative. Here the two components of the 220 nm band are evident, since V_{12} is sufficiently large, and as expected, the shorter wavelength band is the strongest one; at the same time, the amplitude A of the 220 nm couplet is greatly enhanced.

If one wants to obtain an empirical rule that relates the absolute configuration of 1,1′-binaphthyl derivatives and the sign of the 220 nm exciton couplet, the analytical function of V_{12} vs the dihedral angle θ must be known. It has been first calculated by Mason[7] as in Figure 2 (full line); its derivation will be shown below. It can be seen how V_{12} decreases monotonally and vanishes at $\theta \approx 110°$. Accordingly (see also eq 3), a (S)-1,1′-binaphthyl derivative shows a positive 220 nm couplet if $\theta < 110°$. Since all 2,2′-homosubstituted (S)-1,1′-binaphthyl derivatives that will be taken into consideration show a positive couplet and all (R) derivatives a negative one, it may be concluded with no exceptions that all these compounds have $\theta < 110°$ in

(25) (a) Mason, S. F.; Vane G. W. *J. Chem. Soc. B* **1966**, 370. (b) Mason, S. F.; Vane, G. W.; Schofield, K.; Wells, R. J.; Whitehurst, J. S. *J. Chem. Soc. B* **1967**, 553. (c) Mason, S. F.; Vane, G. W.; Whitehurst, J. S. *Tetrahedron* **1967**, *23*, 553. (d) Gottarelli, G.; Mason, S. F.; Torre, G. *J. Chem. Soc. B* **1970**, 1349. (e) Mason, S. F. *J. Chem. Soc., Chem. Commun.* **1973**, 239.

(26) Mason, S. F. *Molecular Optical Activity and the Chiral Discrimination*; Cambridge University Press: Cambridge, 1982.

(27) Rubio, M.; Merchán, M.; Ortí, E.; Roos, B. O. *Chem. Phys.* **1994**, *179*, 395.

(28) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962.

(29) (a) Klevens, H. B.; Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 470. (b) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.

(30) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: New York, 1966.

(31) Bree, A.; Thirunamachandran, T. *Mol. Phys.* **1962**, *5*, 397.

(32) Browne, P. A.; Harris, M. M.; Mazengo, R. Z.; Singh, S. *J. Chem. Soc. C* **1971**, 3990.

Figure 1. UV (dashed line) and CD (solid line) spectra of (R)-(−)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]oxepine (**5**) (0.148 mM in CH$_3$-CN).
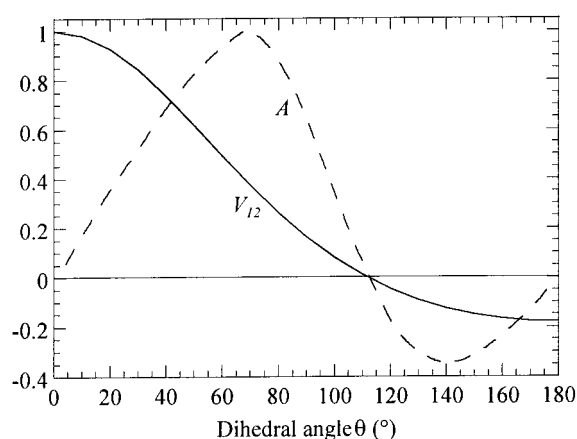
Figure 2. Theoretical dependence on θ of the CD couplet amplitude A (dashed line) and the coupling potential V_{12} (solid line) for a 1,1′-binaphthyl derivative according to the Mason model (ref 7).

solution, the absolute configuration of them all being in fact well established.[33]

To derive a quantitative relation between spectral CD parameters and θ, Mason[7] exploited the 220 nm couplet amplitude A, namely the difference $\Delta\Delta\epsilon_{max} = \Delta\epsilon_{1st} - \Delta\epsilon_{2nd}$ of the two Cotton effects intensities. This quantity can be calculated from eq 3 on assuming a definite band shape. For Gaussian absorption peaks, one obtains the curve shown in Figure 2 (dashed line). Even if it has been applied to assess θ values for some 1,1′-binaphthyl derivatives, this method could hardly be employed for a quantitative correlation, owing to two main facts:

(1) The strong solvent dependence of ϵ_{max} for the ^1B_b band of naphthalene chromophore and, as a consequence, of $\Delta\epsilon_{max}$ and A of 1,1′-binaphthyl derivatives: for example, ϵ_{max} (221 nm) for naphthalene may vary from 9.6×10^4 M^{-1}cm^{-1} in 95% EtOH to 1.3×10^5 in hexane (30% variation); moreover, the values of ϵ_{max} (225 nm) for 2-naphthol are 1.0×10^5 and 6.3×10^4, respectively (45% variation).

(2) The theoretical A values (calculated, for instance, with the DeVoe method, see below) are in general considerably larger than the experimental ones (two times and more); furthermore, this difference may greatly vary with the substrate, so no correction factor may be reliably introduced. As a consequence, the A vs θ relation cannot be satisfactorily employed to directly assess the value assumed by θ in solution, since in the best

(33) Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999.

Scheme 2. Geometrical Model Used in the Calculations
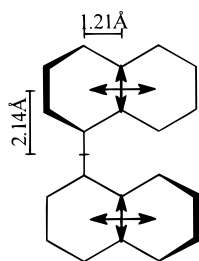
cases it takes a semiquantitative nature only leading to relative considerations based upon A ratios for different substrates.[7]

Results

1. Theory: The Quantitative Relation between θ and the Davydov Splitting. The theoretical (Davydov) splitting $\Delta\lambda_{Dav}$ between the two components of the 220 nm couplet of a 1,1′-binaphthyl derivative can be calculated as follows. Provided $V_{12} \ll E_a$ (which is the common case, since $V_{12} \leq 2.5$ kK and $E_a \approx 45$ kK, 1 kK $= 10^3$ cm^{-1}):

$$\Delta\lambda_{Dav} = \lambda_B - \lambda_A = hc\left(\frac{1}{E_a - V_{12}} - \frac{1}{E_a + V_{12}}\right) \approx \frac{2hcV_{12}}{E_a{}^2} = \frac{2}{hc}\lambda_a{}^2 V_{12} \quad (4)$$

The interaction potential V_{12} is obtained from eq 1. It has been calculated for a model geometry of 1,1′-binaphthyl with the following choices (see Scheme 2): (1) benzene rings have been approximated to regular hexagons with bond lengths of 1.40 Å and a C1−C1′ bond of 1.48 Å; (2) ^1B_b transition dipole moments have been reduced to point dipoles, each centered on one naphthalene ring; and (3) the polarization directions have been assimilated to the naphthalene one, so that the two ^1B_b dipoles have been considered perpendicular to the C1−C1′ bond. As for the remaining parameters, the dipolar strength $D_a = \vec{\mu}_1 \cdot \vec{\mu}_2 = |\vec{\mu}_a|^2$ of the two degenerate monomer transitions has been estimated to be 50.0 D^2 from the UV spectrum of naphthalene in acetonitrile, while it has been imposed that $\lambda_a = 225$ nm since this is a sort of best-fit value at which the couplets of 2,2′-substituted 1,1′-binaphthyl derivatives taken into consideration are centered on the average, i.e., CD vanishes.

The $V_{12}(\theta)$ function (Figure 3, line) is obviously coincident to that calculated by Mason.[7] As can be seen, in the common range of values assumed by θ for 2,2′-substituted 1,1′-binaphthyl derivatives (40 ÷ 100°), the Davydov splitting $\Delta\lambda_{Dav}$ decreases almost linearly with a slope of about 3.5 nm every 10°, which is sufficiently large with respect to the resolution of common CD instruments.

Owing to the mutual cancellation typical of the two oppositely signed bands of the couplet, however, the observed experimental splitting $\Delta\lambda_{max}^{obs}$ (the wavelength difference between the maximum and the minimum of the couplet) does not coincide with the true splitting $\Delta\lambda_{max}$ (the wavelength difference between the extrema of the two components), which is the quantity to be compared with theoretical splitting $\Delta\lambda_{Dav}$; generally $\Delta\lambda_{max}^{obs} \geq \Delta\lambda_{max}$ (see Figure 4). Consequently, the determination of $\Delta\lambda_{max}$ starting from experimental CD spectra requires a deconvolution procedure, whose details are reported in note 34.

To check the reliability of the $V_{12}(\theta)$ function and to test the real necessity of the deconvolution procedure, we calculated
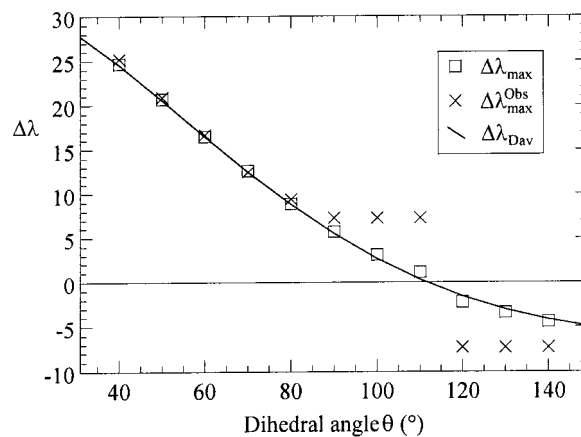
Figure 3. Dependence on θ of the theoretical Davydov splitting $\Delta\lambda_{Dav}$ (solid line) calculated with use of eq 4 and of the observed splitting of the CD spectra of 1,1′-binaphthyl calculated with DeVoe's method before ($\Delta\lambda_{max}^{obs}$, ×) and after ($\Delta\lambda_{max}$, □) the deconvolution.
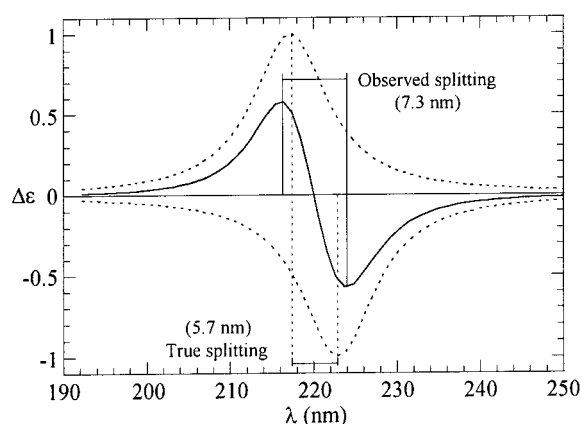
Figure 4. Definition of the observed $\Delta\lambda_{max}^{obs}$ and the true splitting $\Delta\lambda_{max}$ for a generic CD couplet.

theoretical CD couplets with DeVoe's method. This was accomplished by means of a program originally developed by Hug et al.[35] capable of an all-order calculation. We took into consideration only the two stronger bands, whose parameter values were again taken from the UV spectrum of naphthalene in acetonitrile and are summed up in Table 1. The model geometry for the DeVoe calculation is the same as above

(34) Each Cotton effect is assigned a Lorentzian band shape, which in the restricted range of a common 220 nm couplet can be expressed as:

$$\Delta\epsilon_i(\lambda) = \xi_i/[1 + \gamma(\lambda - \lambda_i)^2]$$

where $\Delta\epsilon_i(\lambda_i) = (\Delta\epsilon_{max})_i = \xi_i$ and γ is related to the half-height width $\Delta\lambda_{1/2}$ through $\Delta\lambda_{1/2} = 2/\sqrt{\gamma}$; since in the model naphthalene spectrum $\Delta\lambda_{1/2} \approx 10.5$ nm, it follows $\gamma = 0.035$. A generic couplet can be written:

$$\Delta\epsilon(\lambda) = \xi_2/[1 + \gamma(\lambda - \lambda_2)^2] - \xi_1/[1 + \gamma(\lambda - \lambda_1)^2]$$

The deconvolution consists of the least mean squares fitting of the experimental couplet according to the last expression in order to find the four parameters; from these, the required splitting then results, $\Delta\lambda_{max} = \lambda_2 - \lambda_1$. In a typical procedure percentage errors on λ values are lower than 0.1% and $R > 0.995$. The couplet can also be easily resolved into the two components through its second derivative; in general, the values of $\Delta\lambda_{max}$ found by the two methods agree within ±0.1 nm. Third, in a more immediate and rough way $\Delta\lambda_{max}$ can be approximated as:

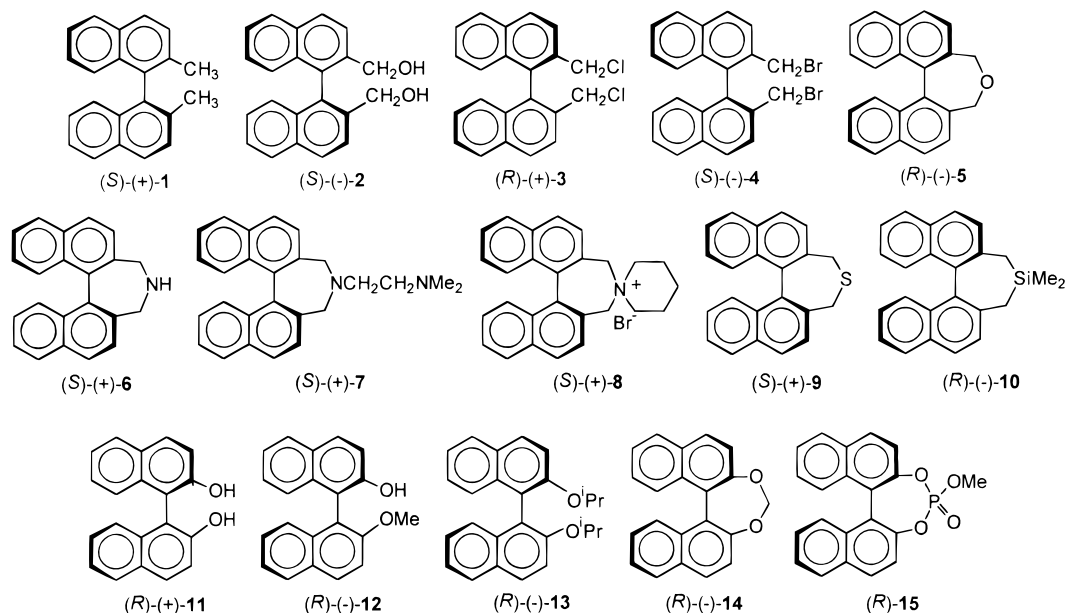$$\Delta\lambda_{max} \approx \sqrt{(\Delta\lambda_{max}^{obs})^2 - \Delta\lambda_{1/2}^2/2}$$

which can be easily found through derivation of $\Delta\epsilon(\lambda)$.

(35) (a) Cech, C. L.; Hug, W.; Tinoco, I., Jr. *Biopolymers* **1976**, *15*, 131. (b) Hug, W.; Ciardelli, F.; Tinoco, I., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3407.
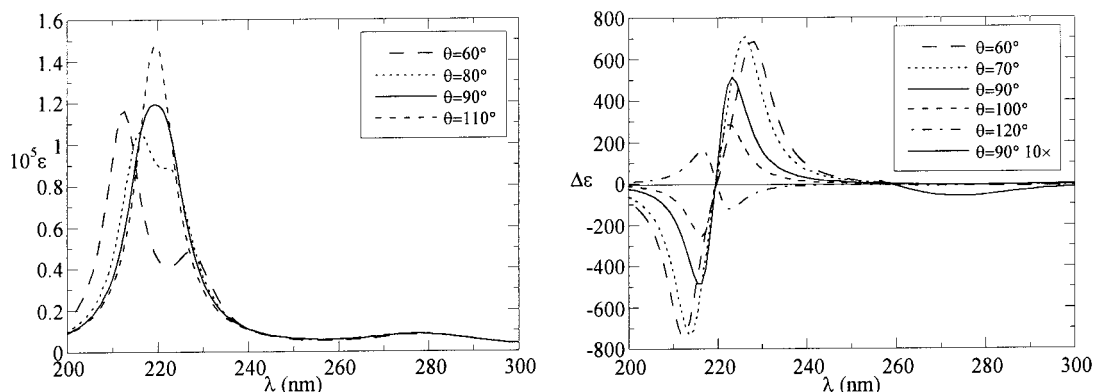
Figure 5. UV and CD spectra calculated by means of DeVoe's approach for 1,1′-binaphthyl as a function of θ.

Chart 1

(Scheme 2) with the addition of ^1L_a transition dipoles, chosen perpendicular to the ^1B_b dipoles. The UV and CD spectra obtained in this way for various values of θ are showed in Figure 5. DeVoe's model can satisfactorily reproduce the well-known characteristics of UV and CD spectra of 1,1′-binaphthyl derivatives; the calculated CD spectra emphasize how both the amplitude A and the splitting $\Delta\lambda_{max}^{obs}$ of the 220 nm couplet strongly depend on θ. From a quantitative point of view, however, and as previously noted, calculated A values are considerably larger than experimental ones. As an example, $A_{\theta=90°} = 900$, while in open chain 1,1′-binaphthyls (with a quasiorthogonal arrangement in solution) the largest observed A value is about 450.

The values of $\Delta\lambda_{max}^{obs}$ (before deconvolution) and $\Delta\lambda_{max}$ (after deconvolution) of calculated spectra are reported in Figure 3 as a function of θ along with the theoretical $\Delta\lambda_{Dav}$ function (eq 4). It clearly emerges that the deconvolution procedure is necessary for $\theta \geq 80°$. For smaller angles, in fact, V_{12} is sufficiently large so that $\Delta\lambda_{max} > \Delta\lambda_{1/2}$ (the wavelength bandwidth); with increasing θ, however, $\Delta\lambda_{max} < \Delta\lambda_{1/2}$ and the observed splitting is largely dominated by the bandwidth, which is a constant not depending on θ. Second, the agreement between classical physics (DeVoe) $\Delta\lambda_{max}$ values and the quantum-mechanical $\Delta\lambda_{Dav}$ function is almost complete. This is far from surprising, owing to common hypotheses and inparticular the Coulombic approximation of

Table 1. Spectral Parameters in Acetonitrile of the Main Electronic Transitions of Naphthalene (ν, Frequency Maximum; λ, Wavelength Maximum; D, Transition Dipole Moment; Γ, Half-height Width; 1 kK = 10^3 cm^{-1})

transition	ν (kK)	λ (nm)	D (D^2)	Γ (kK)	polarization[a]
^1B_b	45.5	220	50.0	2.1	long axis
^1L_a	36.4	275	6.0	4.4	short axis

[a] Bree, A.; Thirunamachandran, T. *Mol. Phys.* **1962**, *5*, 397.

the interaction potential; nevertheless, the observed agreement is indeed a strong confirmation of the reliability of our model.

2. Discussion. The theoretical function $\Delta\lambda_{Dav}(\theta)$ previously obtained can be directly compared to experimental $\Delta\lambda_{max}$ values obtained from CD spectra of 1,1′-binaphthyl derivatives. We first chose to study only 2,2′-methylhomo-substituted derivatives **1−10**; these compounds are in fact devoid of auxochromic substituting groups whose effects on the result are hardly predictable.

The comparison of theoretical $\Delta\lambda_{max}$ values with experimental ones unavoidably relies on an independent method of calculation of θ values for compounds **1−10**. We employed a geometry optimization with the semiempirical MNDO-PM3 method,[36]

(36) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

Table 2. Experimental CD Splitting before ($\Delta\lambda_{max}^{obs}$) and after ($\Delta\lambda_{max}$) Deconvolution and Dihedral Angles Calculated with PM3 for Compounds **1−10**

	compound									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
$\Delta\lambda_{max}^{obs}$(nm)	11.8^a	7.8	10.0	14.0^b	17.8	13.8^c	13.2^d	13.3^e	20.8	13.2^f
solvent	EtOH	EtOH	CH$_3$CN	EtOH	CH$_3$CN	EtOH	EtOH	H$_2$O	hexane/^{i}PrOH	dioxane
$\Delta\lambda_{max}$ (nm)	5.8	6.5	8.6	12.7	14.0	13.8	13.0	13.1	12.9^g	12.7
θ(2−1−1′−2′) (deg)	90	90	92	94	53	53	54	54	63	68
θ(9−1−1′−9′) (deg)			94	96	59	59	60	60	67	71

^{a} Harris, H. E.; Harris, M. H.; Mazengo, R. Z.; Singh S. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1059. ^{b} Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladié, G.; Zimmermann, R. *J. Org. Chem.* **1986**, *51*, 589. ^{c} Meyers, A. I.; Nguyen, T.; Stoianova, D.; Sreerama, N.; Woody, R. W.; Koslowski, A.; Fleischhauer, J. *Chirality* **1997**, *9*, 431. ^{d} Rosini, C.; Tanturli, R.; Pertici, P.; Salvadori, P. *Tetrahedron: Asymm.* **1996**, *7*, 2971. ^{e} Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671. ^{f} Noyori, R.; Sano, N.; Murata, S.; Okamoto, Y.; Yuki, H.; Ito, T. *Tetrahedron Lett.* **1982**, *23*, 2969. ^{g} The only reasonable value found with the second derivative method within a complex CD pattern between 210 and 250 nm, consisting of almost four bands.
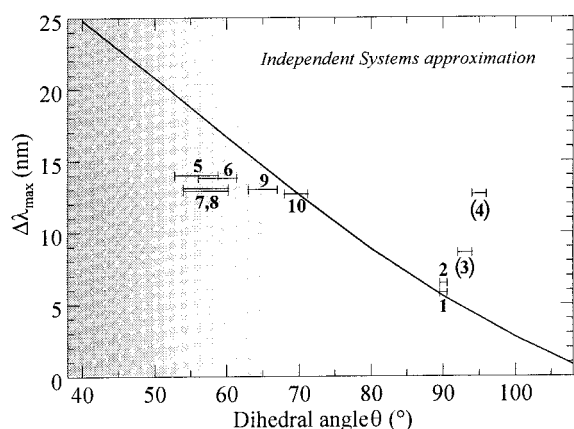
Figure 6. Relation between the experimental splitting $\Delta\lambda_{max}$ for compounds **1−10** after deconvolution and the dihedral angle θ calculated with PM3, compared with the theoretical function $\Delta\lambda_{max}(\theta)$; see text for the explanation of abscissa uncertainties. The shaded area represents the range where the ISA approximation becomes questionable. Compounds **3** and **4** (bracketed) have spectra unsuitable for the analysis, as discussed in the text.

since it provides acceptable results for ground-state structure calculations for 1,1′-binaphthyl derivatives;[14g] for instance, for 1,1′-binaphthyl itself PM3 calculates θ =92° and a configurational inversion barrier of 23.1 kcal/mol, very close to the experimental value (22.5 kcal/mol on average in common solvents).[37]

Table 2 reports $\Delta\lambda_{max}^{obs}$ and $\Delta\lambda_{max}$ values (before and after deconvolution) of the 220 nm couplet of CD spectra of compounds **1−10** along with PM3 θ values for the same substrates;[38] $\Delta\lambda_{max}$ and θ are finally correlated in Figure 6.

PM3 structures of chain-bridged derivatives reveal a substantial deviation from planarity of each naphthalene moiety; the calculated deviations from the least-mean-squares planes are on the average at least 10 times greater than those calculated for open derivatives. As a consequence, 2−1−1′−2′ and 9−1−1′−9′ angles for the former substrates are not always coincident and are both reported in Table 2 as a measure of the spread of the possible θ values; since the really significant parameter, namely the angle between ^1B_b dipole moments, is inaccessible, more rigorous calculations of θ are equally questionable and so unnecessary. Unbridged derivatives, on the contrary, should

have almost planar aromatic rings but a rather large molecular flexibility: the dihedral angle for these compounds is then better described as oscillating around an average value. Anyhow, if one assumes for the torsional mode a symmetrical potential curve, as for 1,1′-binaphthyl[14] and as confirmed by PM3 calculations for most of the open compounds studied, the almost linear $\Delta\lambda_{max}$ vs θ relationship ensures a good agreement between the observed $\Delta\lambda_{max}$, arising from the superimposition of various contributions of the overall conformational population, and that relative to the minimum energy structure (calculated with PM3).

From Figure 6 it emerges how, despite the numerous and considerable simplifications introduced, the theoretical $\Delta\lambda_{max}(\theta)$ function fits the experimental values quite well for $\theta \geq 70°$; for smaller angles the ISA approximations become poorer as a consequence of the increasing conjugation between the two naphthalene rings. An internaphthalenic charge-transfer transition has been claimed to give rise to the positive band at 240 nm in the CD spectrum of the oxepine **5**, and a similar band, though partially submerged by the tail of the oppositely signed couplet, is discernible for all bridged compounds **6−9**.[39] This charge transfer band not only witnesses that below $\theta = 70°$ the independent systems hypotheses may not completely hold, but it also alters the couplet structure, making extraction of $\Delta\lambda_{max}$ more prone to errors; for a chain-bridged derivative with a considerably smaller θ (two carbons chain), where the internaphthalenic conjugation becomes stronger, a CD spectrum completely different from the classical couplet feature is indeed reported.[7] As can be seen, however, the extent of this effect for compounds **5−9** is such that the sensitivity of $\Delta\lambda_{max}$ to changes in θ remains sufficiently high, and the usefulness of such an approach is not diminished: the main result is that *the value θ assumes in solution for 1,1′-binaphthyl derivatives can be simply assessed starting from their CD spectra*. A strong proof of the reliability of this method is that compounds **5−8**, for which PM3 calculates mean angles of 56 ± 1°, all have $\Delta\lambda_{max}$ = 13.5 ± 0.5 nm, irrespective of the solvent.

Two compounds, **3** (see Figure 7) and especially **4**,[18b] show unusually distorted CD spectra: the existence of bands of uncertain origin is apparent. The amplitude of the CD couplet is particularly reduced, which possibly allows contributions to emerge that would normally be overwhelmed by more prominent features. Given such spectra, a very poor agreement to the expected splitting for the two dihalo derivatives is not surprising; anyway, they were included in Figure 6 just to

(37) (a) Colter, A. K.; Clemens, L. M. *J. Phys. Chem.* **1964**, *68*, 651. (b) Cooke, A. S.; Harris M. M. *J. Chem. Soc.* **1963**, 2365.
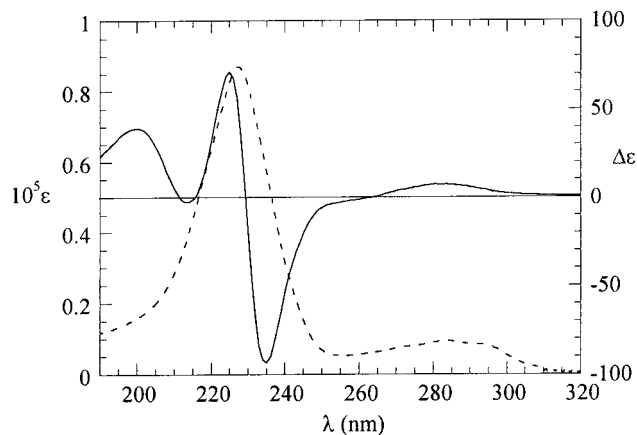
(38) PM3 calculations were executed with GAUSSIAN 94 (Gaussian Inc., Pittsburgh, PA); the initial geometry had been previously optimized through the MM2 force field in PCMODEL (Serena Software, Bloomington, IN).

(39) Hanazaki, I.; Akimoto, H. *J. Am. Chem. Soc.* **1972**, *94*, 4102.

Figure 7. UV (dashed line) and CD (solid line) spectra of (*R*)-(+)-2,2′-bis(chloromethyl)-1,1′-binaphthalene (**3**) (1.02mM in CH$_3$CN).

stress the strong spectral difference with respect to other compounds.[40]

We tried to release the restriction to nonauxochromic substituents. Unfortunately, 1,1′-bi(2-naphthol) derivatives **11**−**15** all have $\Delta\lambda_{max}^{obs}$ =12 ± 2 nm,[19c] irrespective of their PM3 dihedral angle, thus discouraging all efforts to include them in a treatment similar to the previous one. The only possible conformational assessment of these compounds in solution then relies on the degree of the splitting of the UV strongest band and on the relative intensity of its components.[19c]

The advantages of our method on those previously reported are clear. In particular, the $\Delta\lambda_{max}(\theta)$ relation is somewhat superior to the $A(\theta)$ one for various reasons:

(a) A simpler and almost linear analytical function.

(b) The complete indipendence of concentration (in a large range), simplifying the analysis of compounds difficult to handle and weigh.

(c) An almost complete independence of the solvent, too. λ_{max} values show in fact less variation with solvent, compared to ϵ_{max}; moreover, the difference $\Delta\lambda$ is expected to nullify even this small solvent effect. This observation allowed us to take into account all CD data for 2,2′-homosubstituted 1,1′-binaphthyls reported in the literature, irrespective of the solvent used (see Table 2).

(d) $\Delta\lambda_{max}$ seems to be less dependent than A on the overall conditions of measurement. CD spectra of **5** recorded at

increased speed showed an apparent simultaneous hypsochromic shift of the two extrema of the couplet, so that $\Delta\lambda_{max}$ was unchanged in a reasonable extent, while the reduction of both the intensities soon made A collapse from the maximum initial value.

(e) While expected A values, calculated for instance with DeVoe's method, are as previously noted always greater than experimental ones, the *quantitative* agreement between calculated and experimental $\Delta\lambda_{max}$ values is quite satisfactory.

Conclusions

In this paper it has been demonstrated how the conformation in solution of 1,1′-binaphthyl derivatives substituted at 2 and 2′ with nonauxochromic groups can be assessed by means of a spectral parameter, namely the splitting $\Delta\lambda_{max}$ of the CD exciton couplet. The theoretical relation between $\Delta\lambda_{max}$ and the dihedral angle θ, calculated starting from the standard hypotheses of exciton model of optical activity of dimers, has in fact been shown to fit quite well the experimental values for a number of such derivatives (−CH$_2$− substituted); these values are simply calculated from CD spectra by a deconvolution procedure of the 220 nm couplet.

For the first time, then, an entirely quantitative relation between θ and CD parameters has proven to be sufficiently reliable; the substantially complete indipendence of $\Delta\lambda_{max}$ of experimental conditions (solvent, concentration) makes this method very versatile.

Experimental Section

(*R*)-(+)-2,2′-Bis(chloromethyl)-1,1′-binaphthalene[43] and (*R*)-(−)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]oxepine[15a] were prepared starting from (*R*)-(+)-2,2′-bis(hydroxymethyl)-1,1′-binaphthalene[44] according to standard literature methods and showed spectroscopic and physical data in accordance with predicted values.

UV and CD spectra were recorded with a UV−vis Varian CARY 4E spectrometer and a Jasco J-600 spectropolarimeter, respectively, using a 0.01 cm path length cell and spectropolarimetric grade acetonitrile as solvent.

The CD spectrum of **9** was recorded with Jasco J-710 spectropolarimeter interfaced to a Jasco PU-980 pump and a Jasco MD-910 detector. A racemic sample of **9** was used for the HPLC separation (CHIRALPAK OT, hexane/2-propanol 80:20, detector wavelength 230 nm, flow 0.5 mL/min; baseline resolution). The spectrum was recorded on-line on the first eluted (*S*)-(+) enantiomer (t_R = 11 min).

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(40) The anomalous appearance of the CD spectrum makes the conformational assessment for **4** not trivial: a sequence of four bands with alternating sign and similar amplitudes is apparent between 200 and 250 nm.[18b] Taking into account only the two in the middle, a negative couplet with $A \approx -100$ and $\Delta\lambda_{max}^{obs} \approx 14$ nm was recognized in the spectrum of (*S*)-**4**[18b] and related to a transoid ($\theta > 110°$) conformation.[1b,18d,20b] Such an assignment, on considering the large $\Delta\lambda_{max}^{obs}$ and A, would imply $\theta > 130°$, which seems extremely unlikely owing to steric repulsion; even with the most bulky 2,2′ substituents, namely two iodine atoms, 2,2′-substituted 1,1′-binaphthyls never exceed the critical angle of 110° for θ.[41] On the other hand, X-rays[42] and PM3 calculations also agree upon a quasiorthogonal arrangement for **4**.

(41) Pescitelli, G., Tesi di Laurea, Pisa, 1997.

(42) Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2747.

(43) Chong, J. M.; MacDonald, G. K.; Park, S. B.; Wilkinson, S. H. *J. Org. Chem.* **1993**, *58*, 1266.

(44) Rosini, C.; Tanturli, R.; Pertici, P.; Salvadori, P. *Tetrahedron: Asymm.* **1996**, *7*, 2971.

(45) Stará, I. G.; Starý, I.; Tichý, M.; Závada, J.; Fiedler, P. *J. Org. Chem.* **1994**, *59*, 1326.