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## Solution Conformation of Two $C_2$ -Symmetric Amino Derivatives of 1,1'-Binaphthalene by Circular Dichroism and Liquid Crystal Technique

Carlo Rosini, Livia Franzini, and Piero Salvadori\*

C.N.R. Centro Studi Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy

Gian Piero Spada

Dipartimento di Chimica Organica "A. Mangini", Universita' di Bologna, via S. Donato 15, 40127 Bologna, Italy

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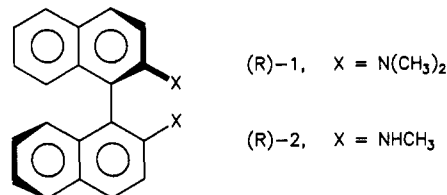
The solution conformation of two  $C_2$ -symmetric 1,1'-binaphthyl compounds (*N,N,N',N'*-tetramethyl-[1,1'-binaphthalene]-2,2'-diamine (1) and *N,N'*-dimethyl-[1,1'-binaphthalene]-2,2'-diamine (2) has been studied by MMX calculations, analysis of the absorption and CD spectra, and induction of cholesteric mesophases in nematic liquid crystals. All these methods indicate that 1 prefers a cisoid conformation and that 2 assumes a conformation where the two naphthyl moieties are quasi-perpendicular.

### Introduction

Studies aimed at determining the structure of  $C_2$ -symmetric 1,1'-binaphthyl compounds have received considerable attention in the past years. Such studies have been carried out by circular dichroism (CD) spectroscopy,<sup>1-3</sup> X-ray diffraction,<sup>4</sup> or liquid crystal techniques.<sup>5</sup>  $C_2$ -symmetric binaphthyl compounds play an important role as chiral auxiliaries in asymmetric organic reactions.<sup>6,7</sup> Conformational studies on these molecules deserve attention because the studies can help to explain the stereochemical outcome of the reactions in which these substances are employed as chiral auxiliaries.

It is the aim of this paper to present a detailed conformational study of two diamines with the  $C_2$ -symmetric binaphthyl structure, i.e., *N,N,N',N'*-tetramethyl-[1,1'-binaphthalene]-2,2'-diamine (1) and *N,N'*-dimethyl-[1,1'-binaphthalene]-2,2'-diamine (2) (Chart I). Optically active 1 has been recently introduced<sup>8</sup> as a chiral controller for the enantioselective addition of diethylzinc to aromatic aldehydes, and satisfactory enantiomeric excesses have been obtained. Although preliminary chiroptical data for 1 have been reported,<sup>1</sup> the CD spectrum of 1 has not been analyzed. No data about the chiroptical properties of 2 have appeared and to the best of our knowledge, it has

Chart I



been employed only as a chiral ligand for  $\text{LiAlH}_4$  in the asymmetric reduction of aromatic ketones.<sup>9</sup> Binaphthyls of a given absolute configuration, for example R, can have conformations with opposite helicities, depending on the dihedral angle ( $\psi$ ) (i.e., the angle  $\text{C}_9\text{--C}_1\text{--C}_1'\text{--C}_9'$ ) between the naphthyl rings (see Figure 1). For  $0 < \psi < 90$ , the helicity between the planes containing the naphthyl moieties is M, and for  $90 < \psi < 180$ , the helicity is P.

### Results and Discussion

**Synthesis.** The syntheses of compounds 1 and 2 require optically active [1,1'-binaphthyl]-2,2'-diamine as starting material. This compound was prepared and resolved into its antipodes according to the procedure of Miyano and co-workers.<sup>10</sup> The ee of the samples obtained was determined by HPLC analysis on a Pirkle (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine CSP column. (*R*)-1 was obtained from the reaction<sup>11</sup> of (*R*)-primary diamine with formaldehyde/formic acid (Eschweiler-Clarke reaction) and crystallization from toluene. The ee (>95%) of the product was established by  $^1\text{H}$ -NMR spectroscopy in the

(1) 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.

(2) Hanazaki, I.; Akimoto, H. *J. Am. Chem. Soc.* 1971, 94, 4102.

(3) (a) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* 1974, 30, 1671. (b) Harada, N.; Nakanishi, K. *Circular dichroic spectroscopy - Exciton coupling in organic stereochemistry*, Oxford University Press: Oxford, U.K., 1983.

(4) See, for instance; Harata, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* 1973, 46, 2747.

(5) Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladie, G.; Zimmermann, R. *J. Org. Chem.* 1988, 51, 589.

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

(7) Noyori, R. *Chem. Soc. Rev.* 1989, 18, 187.

(8) Rosini, C.; Franzini, L.; Iuliano, A.; Pini, D.; Salvadori, P. *Tetrahedron: Asymmetry* 1991, 2, 363.

(9) Kabuto, K.; Yoshida, T.; Yamaguchi, S.; Miyano, S. *J. Org. Chem.* 1985, 50, 3013.

(10) Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* 1984, 57, 2171.

(11) Benson, S. C.; Cai, P.; Colon, M.; Haiza, M. A.; Tokles, M.; Snyder, J. K. *J. Org. Chem.* 1988, 53, 5335.

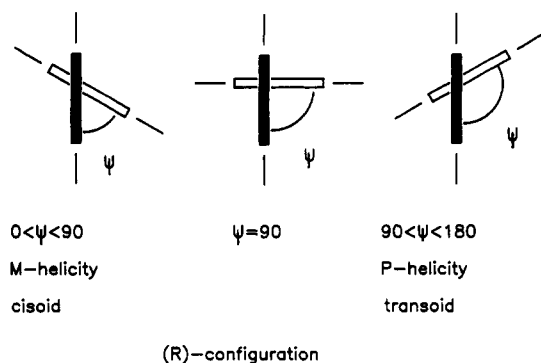


Figure 1.

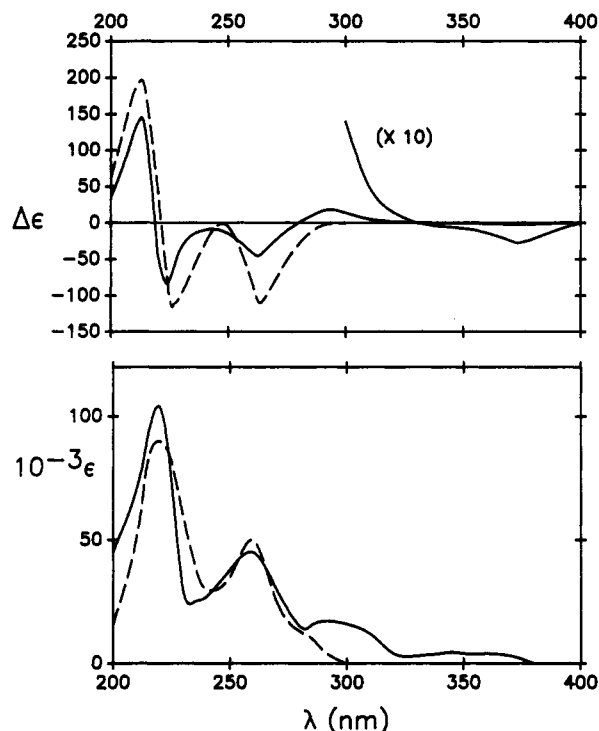


Figure 2. Circular dichroism (upper part) and absorption (lower part) spectra of (R)-1. Solid-line curves refer to the experimental spectra (in acetonitrile), and dashed-line curves refer to the calculated ones.

presence of an excess of (R)-mandelic acid as well as by chiral LC analysis by Chiralpack (+)-OT. (R)-2 was obtained from treatment of the (R)-primary diamine with ethyl chloroformate and subsequent LiAlH<sub>4</sub> reduction of the dicarbamate, according to the method of Miyano.<sup>10</sup> The ee was determined as in the case of (R)-1.

**Absorption and Circular Dichroism Spectra.** The absorption and circular dichroism spectra of (R)-1 and (R)-2, measured in acetonitrile solution, are reported in Figures 2 and 3, respectively. The electronic spectrum of (R)-1 shows four main region of absorption:  $\lambda$  370 nm ( $\epsilon$  4500 ca.),  $\lambda$  290 nm ( $\epsilon$  17 000 ca.),  $\lambda$  260 nm ( $\epsilon$  45 000 ca.), and  $\lambda$  220 nm ( $\epsilon$  105 000 ca.). A weak negative Cotton effect at 370 nm ( $\Delta\epsilon$  -3 ca.) is followed by two strong dichroic bands at 295 ( $\Delta\epsilon$  +16) and 264 nm ( $\Delta\epsilon$  -46). Corresponding to the intense absorption at 220 nm, a couplet-like feature (at 223 nm  $\Delta\epsilon$  -86 and at 213 nm  $\Delta\epsilon$  +146) is observable in the CD spectrum. The absorption spectrum of (R)-2 resembles that of (R)-1, although there are some significant differences. The absorption spectrum of (R)-2 also shows four regions of absorption: two moderate intensity bands at 365 and 290 nm followed by two stronger bands at 246 nm and 214 nm. There is an in-

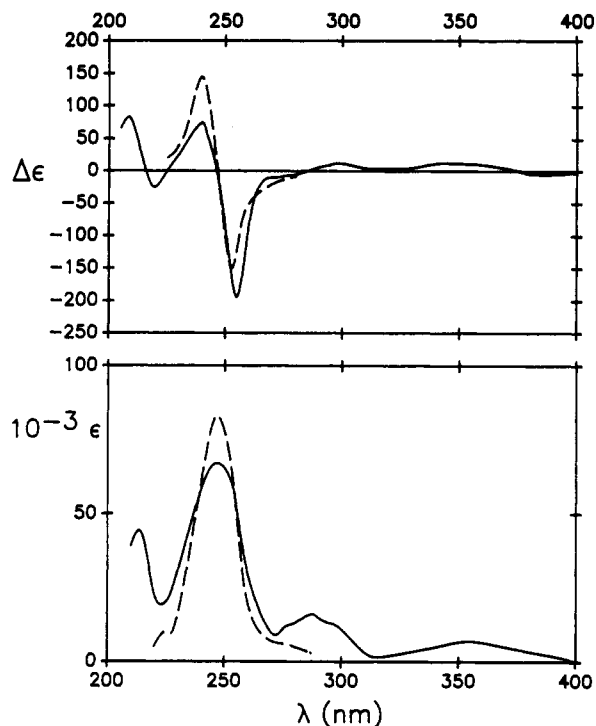


Figure 3. Circular dichroism (upper part) and absorption (lower part) spectra of (R)-2. Solid-line curves refer to the experimental spectra (in acetonitrile), and dashed-line curve refer to the calculated ones.

teresting difference between the spectrum of (R)-1 and that of (R)-2: in (R)-2 the 246-nm band is much stronger than the higher energy (215 nm) one, but the reverse trend is observed in the case of (R)-1. Furthermore, the two high-intensity bands of (R)-1 (260 and 220 nm) are red-shifted with respect to the two corresponding bands in (R)-2 (246 and 214 nm). The CD spectrum of (R)-2 presents relatively weak Cotton effects down to 270 nm, a very strong negative couplet at about 250 nm, and a less-intense couplet-like feature around 220 nm. The absorption and CD spectra of (R)-2 strictly resemble those of optically active [1,1'-binaphthyl]-2,2'-diamine, which has been analyzed by Mason<sup>3</sup> and co-workers. They correlate the sign of the couplet at 240 nm (originated by the coupling of long-axis polarized transitions of the 2-aminonaphthalene chromophores) with the molecular configuration.

The analysis of the spectra of 1 and 2 will be limited to the electrically allowed transitions that give rise to the intense couplets in the CD spectra; the sign and intensity of these effects can be calculated within the DeVoe model,<sup>12,13</sup> allowing a direct correlation between the CD spectrum and the conformation in solution. To carry out such calculations, two kinds of information are required: a knowledge of the structure of the molecule under investigation and a knowledge of the chromophores involved, in this case *N*-methyl-2-aminonaphthalene for 2 and *N*,*N*-dimethyl-2-aminonaphthalene for 1.

**Geometrical Information.** The molecular structure of 1 in the solid state has been recently determined.<sup>14</sup> The most interesting aspects of the structure are (a) the 71° dihedral angle ( $\psi$ ) between the two naphthalene rings (see

(12) DeVoe, H. *J. Chem. Phys.* 1965, 43, 3199.

(13) For some selected structural applications of CD calculations in the DeVoe frame, see for instance: Clericuzio, M.; Rosini, C.; Persico, M.; Salvadori, P. *J. Org. Chem.* 1991, 56, 4343 and references therein.

(14) Franzini, L.; Rosini, C.; Pasero, M. *Acta Crystallogr.* 1991, C47, 1259.

Table I. Absorption Data for Compounds 4-7

4 <sup>a,b</sup>		5 <sup>c</sup>		6 <sup>d</sup>		7 <sup>e</sup>	
$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$
348	2000	347	3100	340	2200	312	200
279	5000	295; 285	9300; 10 000	280	6300	280	5800
236	55 000	246	66 000	240	50 000	220	10 700
217	22 000	215	39 800				

<sup>a</sup>Reference 17. <sup>b</sup>Reference 18. <sup>c</sup>Reference 19. <sup>d</sup>Reference 20. <sup>e</sup>Reference 21.

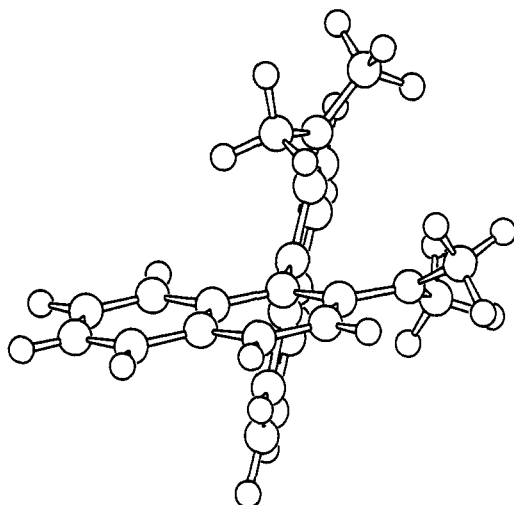


Figure 4. Structure of the minimum-energy conformation of (R)-1.

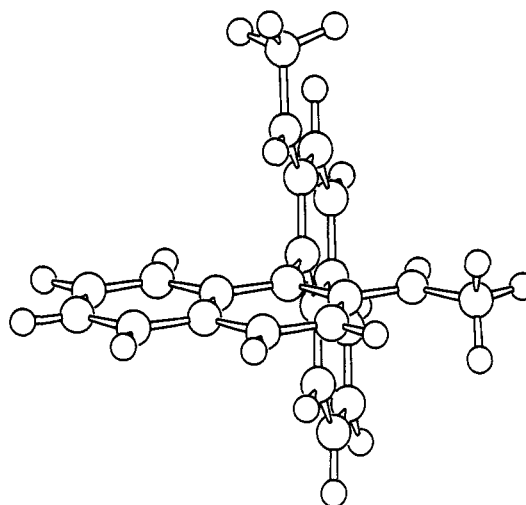


Figure 5. Structure of the minimum-energy conformation of (R)-2.

Figure 1) and (b) the 30° twist in the plane of the *N,N*-dimethyl groups with respect to the plane of the corresponding naphthalene ring. No crystal data are available for 2. In order to have homogeneous structural data for the CD computations, MMX<sup>15</sup> calculations on the preferred conformations of 1 and 2 have been performed. The minimum energy conformations found for 1 and 2 are reported in Figures 4 and 5, respectively. For 1 a dihedral angle of 75° between the naphthalene planes (cisoid conformation) and a twist angle of about 32° between a NMe<sub>2</sub> and the corresponding naphthalene ring were calculated. These values are very similar to those found in the solid state. The minimum-energy conformation of 2 is characterized by a dihedral angle of about 95° (transoid conformation). The NHMe fragment is perfectly coplanar with the naphthalene ring. This fact has the important consequence that in 2 the nitrogen lone pair is fully conjugated with the naphthalene ring; in 1 this conjugation is only partial. This structural difference is very important for understanding the differences in the absorption spectra of 1 and 2. A possible reason for this difference is the steric hindrance between the planar NMe<sub>2</sub> fragment and the naphthyl moiety when the naphthyl moiety is in an ortho-like position. This unfavorable steric interaction is absent in 2, which has only one Me group on the nitrogen atom.<sup>16</sup>

(15) MMX, Serena Software, P.O. Box 3076, Bloomington, IN 47402.

(16) This conformational preference around the C-N bond for compound 1 can be correlated with the well-known observation that the *o*-alkyl substituent of *N,N*-dimethylaniline causes extensive alteration of the absorption spectrum [Jaffé, H. H.; Orchin, M. *Theory and application of ultraviolet spectroscopy*; Wiley: New York, 1962; p 407]. Currently, the alteration is believed to be caused by the twist of the NMe<sub>2</sub> out of the plane of the phenyl ring. The same *o*-alkyl substitution in aniline and in *N*-methylaniline has little effect on the absorption spectra. Furthermore, the *pK<sub>BH</sub><sup>+</sup>* values observed for aniline derivatives support the role of an ortho substituent in inducing the twist around the C-N bond in the *N,N*-dialkyl system [Smith, J. W. In *The chemistry of the amino group*; Patai, S., Ed.; Wiley: London, 1968; Chapter 4].

(17) Suzuki, S.; Fuji, T.; Baba, H. *J. Mol. Spectrosc.* 1973, 47, 243.

**Spectroscopic Information.** Compounds 1 and 2 can be considered, from a spectroscopic point of view, as "dimers" of *N,N*-dimethyl-2-aminonaphthalene and *N*-methyl-2-aminonaphthalene, respectively. Absorption data for 2-aminonaphthalene (4), *N*-methyl-2-aminonaphthalene (5), *N,N*-dimethyl-2-aminonaphthalene (6), and naphthalene (7) are collected in Table I for easy comparison. From this table, it can be deduced that while the spectra of 4-6 are similar to each other, they are different from the spectrum of naphthalene. The reason for the difference can be found in a strong perturbation of the naphthalene chromophore due to the 2-amino substitution: the nitrogen lone pair strongly interacts with the  $\pi$ -electrons of the aromatic moiety modifying deeply its spectroscopic characteristics. In short, the most intense long-axis polarized transition at ca. 220 nm, which dominates the spectrum of naphthalene and the CD spectra of binaphthyls,<sup>3</sup> is red-shifted by the donating substituents. In derivatives 4, 5, 6, and 2 (i.e., compounds in which there is conjugation<sup>16</sup> between the nitrogen lone pair and the aromatic ring), a strong absorption is present at around 240 nm. In contrast, this strong absorption is at 220 nm for 1. The spectrum of 1 can be considered as that of a weakly perturbed naphthalene chromophore. The reduced perturbation finds its origin in the twist of the NMe<sub>2</sub> fragment of 1 with respect to its naphthalene ring; this twist significantly reduces conjugation and lessens the effect of the nitrogen lone pair on the naphthalene chromophore.<sup>21</sup> A qualitative interpretation of the main features of the CD spectra can be done in a straightforward way by considering the exciton coupling of the intense naphthalene long-axis polarized transition <sup>1</sup>B<sub>y</sub>. For 1, this

(18) Tanizaki, Y.; Kobayashi, M.; Hoehi, T. *Spectrochim. Acta* 1972, 28A, 2351.

(19) *Organic Electronic Spectral Data*; Phillips, J. P., Bates, D., Feuer, H., Thyagarajan, B. S., Eds.; Wiley: New York, 1980; Vol. XXII, p 163.

(20) Suck, E. A.; Ewing, G. *J. Am. Chem. Soc.* 1948, 70, 3397.

(21) Reference 3b, p 41.

transition is at ca. 220 nm, and for 2 it is red-shifted to ca. 250 nm by the conjugated methylamino substituents. In both the compounds with R absolute configuration, there is a negative couplet associated with this transition. This indicates that the dihedral angle between the naphthyl rings is smaller than the critical angle of the CD inversion. It must be pointed out that in the coupled oscillator approach,<sup>22</sup> this critical angle is not 90° but around 110°. Therefore, the CD spectra alone cannot distinguish between dihedral angles slightly larger or slightly smaller than 90°. In order to provide further support for this interpretation, CNDO/S-CI calculations of the spectroscopic properties of 5 and 6 (i.e., the "monomers" of 2 and 1, respectively) have been carried out, and these data have been used in a DeVoe computation. These calculations, the details of which are reported in the Appendix, lead to the calculated spectra reported in Figures 2 and 3, respectively. The agreement between the calculated and experimental CD spectra is more than satisfactory in both cases, supporting the structural hypothesis coming from the MMX calculations.

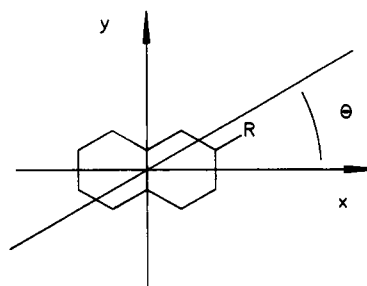
**Induced Cholesterics Analysis.** Recently, a simple technique for investigating the conformation of biaryls in solution has been proposed.<sup>5,23,24</sup> It is based on the measurement of the twisting powers of chiral compounds in nematic liquid crystal solvents. It has been known for a long time that traces of an optically active solute transform a nematic mesophase into a cholesteric one. The cholesteric phase has a helicoidal structure characterized by its handedness (P or M) and pitch; equal amounts of optical antipodes induce helical structures with identical pitch and opposite handedness. The ability of a chiral dopant to twist the nematic phase (helical twisting power, HTP) can be defined<sup>26</sup> as

$$\text{HTP} = (p\alpha r)^{-1}$$

where  $p$  is the pitch (in micrometers) of the cholesteric,  $c$  is the concentration of the solute (as molar fraction), and  $r$  is its optical purity. The sign (+) or (−) indicates right-handed (P) or left-handed (M) helicity, respectively. The phenomenon of cholesteric induction can be applied to the field of stereochemistry in several ways<sup>26</sup> ranging from configurational<sup>27,28</sup> and conformational<sup>5,23,24</sup> analysis to kinetic racemization studies<sup>29,30</sup> and to detection of small quantities of compounds<sup>32</sup> or compounds with low optical activity.<sup>31</sup>

When both the solute and the nematic solvent have a biaryl structure, right-handed cholesterics (P) are correlated to a P-skew of the two aryl groups of the dopant, and left-handed cholesterics (M) are correlated to the M-skew of the inducer.<sup>26</sup> Therefore, if the absolute configuration

Chart II



of the solute is known, it is possible to infer the helicity of the aryl groups from the handedness of the cholesteric. Furthermore, from the quantitative value of HTP, it is possible to get an indication of the value of the dihedral skew angle of the dopant. In the case of biphenyl derivatives, when this angle is zero or 90°, no helicity is related to the aromatic core (achiral conformation) and the twisting power is near zero. Similar considerations apply also to binaphthyl derivatives. The twisting powers of (R)-1 and (R)-2 in E7 (a solvent with a biphenyl core) are −5.9 and −1.1 μm<sup>−1</sup>, respectively. The negative HTP value for (R)-1 indicates an M-helicity of the binaphthyl moiety, which, for the R absolute configuration is connected to a cisoid conformation. Derivative (R)-2 has a smaller negative HTP value, which indicates an M skewness of the biaryl moiety and again a preferred cisoid conformation. This small absolute value is in keeping with the dihedral angle around 90° provided by the MMX and CD calculations.

## Conclusion

The different techniques employed indicate that 1 has a cisoid conformation with a dihedral angle markedly smaller than 90° and that 2 adopts a conformation with nearly perpendicular naphthyl rings. At first glance, it might seem surprising that the derivative with bulkier substituents is in a cisoid conformation, when the one with smaller substituents possesses a much larger  $\psi$ ; this is clearly due to the different conformation of the substituents around the C<sub>2</sub>-N bond. As already discussed in the Geometrical Information section, this conformational difference is due to the different steric requirements of 1 and 2 (relative hindrance caused by a NHMe group versus a NMe<sub>2</sub> group). Such different conformational behavior, indicated by the MMX calculation, has important experimental consequences because the absorption and CD spectra of 1 and 2 are deeply different.

## Experimental Section

**Preparations.** Compounds (R)-1 and (S)-2 were prepared according to the procedures of Snyder<sup>11</sup> and Miyano,<sup>10</sup> respectively.

**Spectroscopic Measurements.** Absorption spectra in the range 400–180 nm were obtained by means of a JASCO J 710 spectrophotometer; CD spectra, in the same spectral region, were carried out with a JASCO J 600 spectrometer. All the spectra were measured at room temperature in freshly prepared acetonitrile solutions.

**Calculations.** All the calculations reported in this paper were carried out by means of programs derived from the DeVoe treatment according to procedures described in previous papers.<sup>13</sup>

**Induced Cholesteric Measurements.** The nematic phase E7, a commercial product from BDH, is an eutectic mixture of cyanobiphenyl and cyanoterphenyl derivatives. Cholesteric pitch values were measured by means of the "lens" version of the Grandjean-Cano<sup>33</sup> method using a Standard 16 Zeiss microscope.

(22) Mason, S. F. *Molecular Optical Activity and the Chiral Discrimination*; Cambridge University Press: Cambridge, 1982; Chapter 6.

(23) Gottarelli, G.; Spada, G. P.; Seno, K.; Hagishita, S.; Kuriyama, K. *Bull. Chem. Soc. Jpn.* 1986, 59, 1607.

(24) Arnone, C.; Gottarelli, G.; Spada, G. P.; Spinelli, D. *J. Mol. Struct.* 1986, 147, 307.

(25) Friedel, G. *Ann. Phys. (Paris)* 1922, 18, 273.

(26) Gottarelli, G.; Spada, G. P.; Solladie, G. *Nouv. J. Chim.* 1986, 10, 691.

(27) Gottarelli, G.; Mariani, P.; Spada, G. P.; Samori, B.; Forni, A.; Solladie, G.; Hibert, M. *Tetrahedron* 1983, 39, 1344.

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

(29) Naciri, J.; Spada, G. P.; Gottarelli, G.; Weiss, R. G. *J. Am. Chem. Soc.* 1987, 109, 4352.

(30) Spada, G. P.; Tampieri, A.; Gottarelli, G.; Moretti, I.; Torre, G. *J. Chem. Soc., Perkin Trans. 2* 1989, 513.

(31) Gottarelli, G.; Samori, B.; Fuganti, C.; Grasselli, P. *J. Am. Chem. Soc.* 1981, 103, 471.

(32) Bertocchi, G.; Gottarelli, G.; Prati, R. *Talanta* 1984, 31, 138.

(33) Heppke, G.; Oestreich, F. *Z. Naturforsch.* 1977, A32, 899.

Helical handedness was obtained from the sign of the rotatory power<sup>34</sup> and from the sense of the spiral-like disclination observed under circular boundary condition.<sup>35</sup>

### Appendix

CNDO/S-CI calculations were carried out on **5** and **6** in order to characterize the absorption bands of **2** and **1**, respectively. For **5**, a planar structure was assumed; for **6**, a twist angle of about 30° between the NMe<sub>2</sub> and the naphthalene nucleus was used. (This angle was found in the solid state and in the MMX calculations.) In the following discussion,  $f$  is the calculated oscillator strength and  $\theta$  is the angle of polarization (defined as described in Chart II); an allowed transition will be considered to be one having  $f \geq 0.2$ . For **5**, the CNDO/S-CI calculations provide allowed transitions at 231 nm ( $f = 1.23$ ,  $\theta \approx 170^\circ$ ) and 229 nm ( $f = 0.54$ ,  $\theta \approx 16^\circ$ ), followed by another absorption at 207 nm ( $f = 0.55$ ,  $\theta \approx 110^\circ$ ). The total oscillator strength is 1.77 for the first absorption region and 0.55 for the second. When the same calculations are repeated for **6** (in the above described twisted geometry), a first region of absorption with transitions at 234 nm ( $f = 0.84$ ,  $\theta \approx 0^\circ$ ) and 227 nm ( $f = 0.27$ ,  $\theta \approx 139^\circ$ ) is followed by a second group of absorptions where four allowed transitions can be identified: 218 nm ( $f = 0.24$ ,  $\theta \approx 50^\circ$ ), 216 nm ( $f = 0.70$ ,  $\theta \approx 0^\circ$ ), 214 nm ( $f = 0.19$ ,  $\theta \approx 125^\circ$ ). The total oscillator strength of the first group is 1.11 and that of the second is 1.33. These results show that on changing from a planar system to a distorted system there is a decrease in the intensity of the low-energy band system (around 235 nm) and a parallel increase in the high-energy band system (around 210–200 nm). This is the trend experimentally observed. Calculations of the CD spectra of (*R*)-**1** and (*S*)-**2** have been carried out using the all-order coupled-oscillator model proposed by DeVoe. In this model, a chiral molecule is considered as an aggregate of interacting subsystems, the chromophores. (*R*)-**1** and (*S*)-**2** can be treated as "dimers" of chromophores **6** and **5**, respectively. These two chromophores have to be described in terms of electrically allowed transitions; each transition is represented by experimental data such as the polarization direction of absorption bands and by the ultraviolet spectrum of suitable model compounds. CD computations for (*S*)-**2** have been carried out only for the spectral range 300–220 nm, which is dominated by the intense positive couplet centered at about 245 nm. It is reasonable to identify the strong ab-

sorption at about 246 nm as due to the transitions at 231 and 229 nm obtained from the above-discussed CNDO/S-CI calculations. Therefore, in the DeVoe calculations, to describe the spectroscopic properties of *N*-methyl-2-aminonaphthalene in the 300–220-nm range, we employed two dipoles, located at the center of the naphthalene ring and directed as established by the MO calculations. In order to have a satisfactory reproduction of the UV spectrum, dipolar strengths of 30 and 12 D<sup>2</sup> were attributed to the dipoles. The geometry employed in the calculations was that found for **2** by the MMX calculations. As can be seen from Figure 3, the agreement between the calculated and experimental CD spectra is very good, supporting the structural hypothesis provided for **2** by the MMX calculations (presented in Figure 5).

CD calculations for (*R*)-**1** follow the guidelines established above. The spectroscopic information is taken from the CNDO/S-CI calculation as far as the polarization directions are concerned. The band at 260 nm in the experimental spectrum has been reproduced by two transition dipoles, to which polarization angles ( $\theta$ ) of 0° and 140° have been assigned, according to the results of the CNDO/S-CI calculations. Dipolar strengths of 21 and 4 D<sup>2</sup> have been attributed to the dipoles in order to have a good fit of the experimental absorption intensity in this range. The high-energy absorption region has been described by a set of three transitions centered at 220 nm, to which dipolar strengths of 12 ( $\theta = 50^\circ$ ), 36 ( $\theta = 0^\circ$ ), and 12 D<sup>2</sup> ( $\theta = 125^\circ$ ) have been attributed. From these parameters and the structure obtained from MMX analysis (Figure 4), the UV and CD spectra have been calculated. In this case also, the agreement between calculated and experimental spectra is more than satisfactory (Figure 2), considering that we have introduced in the DeVoe computations only the most intense transitions provided by the MO-CI calculations. Only the most intense transitions were used in order to avoid a great number of independent spectroscopic parameters. In addition, some uncertainty can affect the characteristics of the weakest transitions obtained by the CNDO/S-CI method. It is also noteworthy that the shape of the CD spectrum of (*R*)-**1** derives from the presence of two negative couplets (at 260 and 220 nm) having different amplitude: the tail of the high energy one (the most intense one) eliminates the positive branch of that present at a longer wavelength (the most weak one).

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