Anomalous CD/UV Exciton Splitting of a Binaphthyl Derivative: The Case of 2,2′-Diiodo-1,1′-binaphthalene

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Abstract: The UV and CD spectra of (*R*)-(+)-2,2′-diiodo-1,1′-binaphthalene show an unexpectedly large value of the wavelength splitting between the two main bands, resulting from the exciton coupling of ^1B_b transitions. An hypothesis is proposed on transition moments directions, making it possible to relate quantitatively the observed splitting to the orthogonal arrangement found in the solid state and calculated for the structure in solution.

Introduction

1,1′-Binaphthyl derivatives represent an important class of chiral auxiliaries,[1] thanks to a nonplanar arrangement of the two naphthalene moieties, which ensures a dissymmetric environment suitable for obtaining high degrees of stereoselectivity.[2]

Optical and chiroptical spectroscopies have been widely used in the past as a tool for the structural investigation of these compounds;[3,4] very recently, on the basis of the exciton coupling approach to the optical activity of dimers,[5] we pointed out the existence of a quantitative relation between the dihedral angle θ, defined by the two naphthyl planes, and the wavelength splitting $\Delta\lambda_{max}$ between the two resolved components of the 220 nm couplet, typical of the CD spectrum of these derivatives.[6] In particular, it was established that (1) unbridged derivatives ($-CH_2X$ substituted at 2,2′, X = H, OH, Cl), with $\theta \approx 90°$, have $\Delta\lambda_{max} < 10$ nm and (2) chain-bridged derivatives ($-CH_2-Y-CH_2-$ chain at 2,2′), with θ ranging from 55° (Y = O, NR) to 70° (Y = $SiMe_2$), have $\Delta\lambda_{max}$ varying from 12.5 to 14 nm. A useful quantitative distinction between the two classes of compounds is then possible, in addition to the evidence of the splitting of the main UV band,[3,7] so far observed only for bridged derivatives.[3,4,6,8]

Here we focus our attention on a first system bearing two auxochromic groups at 2 and 2′, 2,2′-diiodo-1,1′-binaphthalene (DIBN), which recently found application in an enantioselective synthesis.[9] DIBN features a large splitting of the main absorption and dichroic bands; we show how this molecule can fit into our model by correctly taking into account the distortion of the transition dipole orientation brought about by the presence of the iodine atoms.

Results

The UV and CD spectra of (*R*)-(+)-2,2′-diiodo-1,1′-binaphthalene (DIBN, **1**) are reported in Figure 1. In the UV spectrum the strongest band is split into two components, with maxima at 226 and 243 nm, of similar intensities, while the CD couplet, with zero-point at 231 nm, has the unpredictably[6] large $\Delta\lambda_{max}$ value of 19 nm. As for the conformation adopted by **1**, the following was observed:

(1) The absolute configuration of (*R*)-(+)-**1**, established by chemical correlation with (*R*)-2,2′-diamino-1,1′-binaphthalene, along with the negative sign of the couplet, indicates safely that θ does not exceed the critical value of 110°.[4]

(2) The molecular structure of (*R*)-(+)-**1** in the solid state, shown in Figure 2, possesses a pseudo-C_2 axis relating the two naphthyl moieties, which are rotated around the C(1)−C(11) bond by an angle $\theta = 91.5°$. The two iodine atoms of the molecule are removed from each other by 4.22 Å; a I···I distance slightly longer (4.33 Å) separates the iodine atoms of different molecules in the crystal packing. The C−I distances, 2.110 Å mean value, are in keeping with the value 2.09(1) Å averaged on 51 different aryl iodides.[10]

(3) The MNDO-PM3[11] optimized geometry for **1** has $\theta = 90°$ and a quite sharp potential energy well for the torsional

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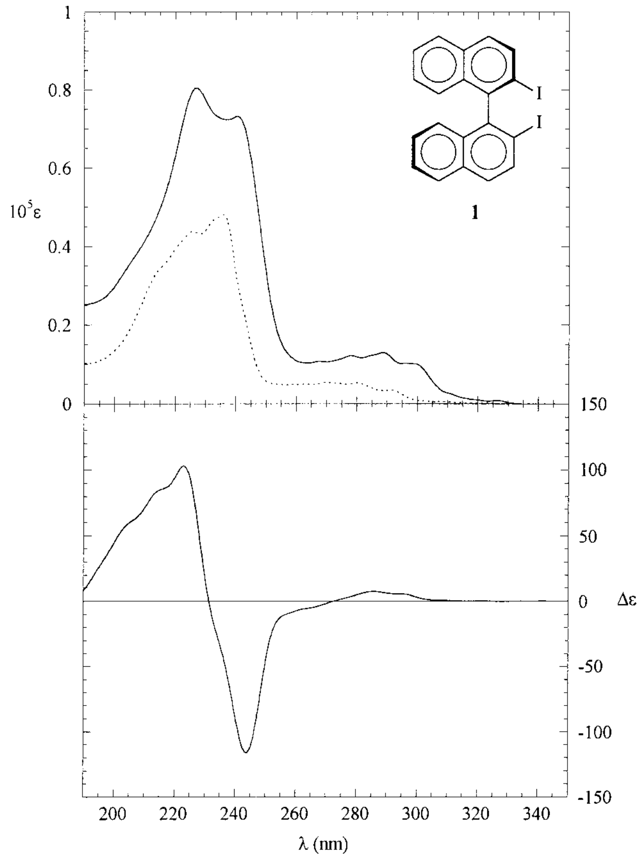

Figure 1. UV (top) and CD (bottom) spectra of (*R*)-(+)-2,2′-diiodo-1,1′-binaphthalene (**1**), 0.672 mM in CH_3CN, and UV spectrum (top, dashed line) of 2-iodonaphthalene, 1.44 mM in CH_3CN.

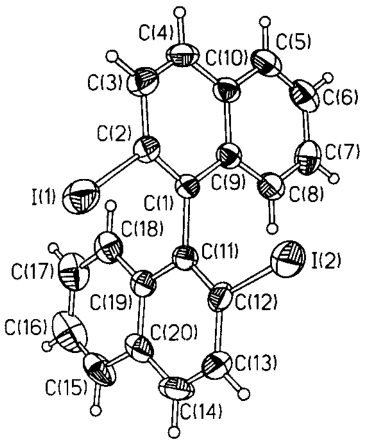

Figure 2. ORTEP view of 2,2′-diiodo-1,1′-binaphthalene (**1**).

mode of rotation about θ, as a consequence to the steric hindrance of iodine atoms.[12]

These observations strongly support a quasiorthogonal arrangment for **1**, with $\theta \approx 90°$. The anomalous appearance of UV and CD spectra of **1**, which would be in accordance with a considerably smaller θ, must then be explained.

Discussion

In the exciton coupling approach,[5] a spectroscopic description of the isolated chromophores present on the molecule is necessary. The absorption spectrum of 2-iodonaphthalene is apparently not available in the literature with a sufficient wavelength range, and the compound had to be synthesized. The UV spectrum of 2-iodonaphthalene (Figure 1, upper part, dashed line) shows itself an evident splitting of the band between 200 and 250 nm, in contrast to the spectrum of naphthalene, where only a shoulder is detectable on the high energy side of the ^1B_b band at 220 nm.[13] Despite some older hypotheses on the direct role of $n \rightarrow \sigma^*$ transitions localized on iodine atoms,[14] subsequent findings demonstrated that such contributions are negligible both in the absorption and in the circular dichroism of aryl iodides.[15] The origin of the splitting in the UV spectrum of 2-iodonaphthalene has then to be found in a vibrational structure. Second derivative analysis, in fact, resolves the spectrum into at least five bands, which can be arranged according to the tentative scheme of Table 1, i.e., two different vibrational progressions with spacings of about 2300 and 1000 cm^{-1}. A strong confirmation to this interpretation comes from the CD spectrum of (*R*)-(+)-**1**, where a progression with $\Delta\nu = 2300\ cm^{-1}$ (corresponding to $\Delta\lambda \approx 11$ nm) is likewise evident; indeed, this represents a case where the vibrational structuring of an exciton CD couplet strikingly appears, even at room temperature;[16] in the absorption, the summation, rather than the mutual cancellation, of the components, only leads to an unfeatured broadening of the peaks.

Table 1. Frequencies in kK (1 kK = $10^3\ cm^{-1}$) of Extrema of Spectra Reported in Figure 1 Resolved through the Second Derivative[a]

ν_{ext} (kK) UV DIBN	 CD (*R*)-DIBN	 UV Np-I
41.1 (243 nm)	**40.9** (244 nm)	42.1
		43.1
44.2 (226 nm)	**44.5** (225 nm)	44.3
	46.8	*45.3*
	49.1	46.7

[a] Bold text: main components of the couplet ($\Delta\lambda_{max} = 18 \pm 1$ nm, $\Delta\nu \approx 3.3$ kK). Light-face text: principal vibrational sequence ($\Delta\nu \approx 2.3$ kK). Italic text: secondary vibrational sequence ($\Delta\nu \approx 1.0$ kK).

The splitting between the two strongest components in the UV and in the CD spectrum of **1** is, however, sufficiently larger in frequency ($\Delta\lambda_{max} = 18$ nm, $\Delta\nu_{max} \approx 3300\ cm^{-1}$) than the vibrational separation, and it can be entirely ascribed to an exciton-type mechanism:[5] the very good agreement between the two wavelength splittings on the value $\Delta\lambda_{max} = 18 \pm 1$ nm supports this view and, as a consequence, the assignment of the two extrema at 225 and 244 nm in the CD spectrum to 0−0 components; the unexpectedly large value of $\Delta\lambda_{max}$, however, still remains to be interpreted.

In the formulation of the quantitative relation between θ and $\Delta\lambda_{max}$,[6] we used a model for 1,1′-binaphthyl derivatives describing $\pi \rightarrow \pi^*$ ^1B_b transitions, which mainly give rise to the 220 nm couplet, by means of transition dipole moments of defined position and direction, as prescribed by the coupled dipoles approach;[5] discarding the effects of substituents, we placed such moments in the center of each aromatic plane with a polarization parallel to the naphthalene long axis, as in the parent chromophore.[17] However, in the present case, the β-substitution with

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(12) PM3 calculations were executed with Gaussian 94, Gaussian Inc., Pittsburgh, PA.

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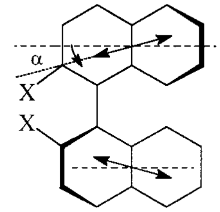

Figure 3. Geometrical model for the 1,1′-binaphthyl derivative showing deviation α of ^1B_b transition dipole moments from directions parallel to the naphthalene long axes (dashed lines).

iodine would account for a substantial deviation of ^1B_b moments toward the direction of the C−I bond. A direct access to the variable α (see Figure 3) is not available: the CNDO/S-CI method, commonly employed in calculations of transition moments polarization, is not parametrized for iodine; for a matter of comparison, it calculates $0 < \alpha < 6°$ for β-substituted naphthalene with X = OH, CH_3, CH_2OH.[18] As a consequence, we must resort to the qualitative description afforded by Platt's spectroscopic moments,[19] and the subsequent sum vector rule for the assessment of transition moment directions, which is indeed in keeping with the proposed picture: iodine has the very large moment value of 21 $(\text{cm}\cdot\text{mol/L})^{-1/2}$, to be compared to 7 for CH_3 and 3 for CH_2Cl; a similar, though less pronounced, trend is observed for Petruska's *q*-factors.[20]

The final question is: Can the transition dipole moment deviation account for the already discussed anomalies in the spectra of (*R*)-(+)-**1**? To answer that, we made the two following ultimate observations:

(1) Making use of the formula $\Delta\lambda_{max} = (2/hc)\lambda_0^2 V_{12}$,[6] (where $\lambda_0 = 236$ nm, from the spectrum of 2-iodonaphthalene) and evaluating the Coulombic coupling potential V_{12} for the model in Figure 3, a value of 18 nm is calculated for theoretical $\Delta\lambda_{max}$, with $\theta = 90°$, *if* α *has a value of about 15°*.

(2) Calculating UV and CD spectra of a generic 1,1′-binaphthyl derivative by means of the classical physics DeVoe's coupled oscillators approach,[21] with $\theta = 90°$ and $\alpha = 15°$, and even using the large experimental bandwidth of 2-iodonaphthalene ($\Delta\tilde{\nu}_{1/2} \approx 6$ kK), one obtains *an appreciable splitting of the UV main band, with two components of equal intensities* and a wavelength separation $\Delta\lambda_{max}$ of 18 nm.

We do not discuss here the role possibly played by transition dipoles positions, which in principle can be displaced from the center of each naphthalene. The effect of transition moments locations on exciton-type calculations is one of the most involved theoretical questions, yet not adequately debated in the literature.[22]

Conclusions

In this paper we reported for the first time the UV spectrum of an *unbridged* 1,1′-binaphthyl derivative characterized by a marked splitting of the 220 nm band. We modified the geometric model usually adopted in calculations of optical activity of this class of compounds,[4,6] introducing a substantial deviation of ^1B_b transition dipole moments toward C-2, justified by the presence of the auxochromic substituent. This allowed us to explain quantitatively the large value of the splitting on the basis of the standard hypotheses of the exciton model for dimers. It was also demonstrated that the vibronic structure, apparent in the UV spectrum of the isolated chromophore, negligibly affects the exciton splitting.

As a complementary remark, we want to point out that also in the case of (*R*)-(+)-2,2′-diiodo-1,1′-binaphthalene, a derivative with the most bulky substituents at 2 and 2′, the dihedral angle θ is far from the critical value of 110° where the sign of the couplet theoretically inverts,[4] in accordance with every other 2,2′-substituted 1,1′-binaphthyl derivative so far known,[6] with the only possible exception being $-CHBr_2$ disubstituted.[23]

Table 2. Selected Crystal Data and Structure Refinement for 2,2′-Diiodo-1,1′-binaphthalene (**1**)

empirical formula	$C_{20}H_{12}I_2$
formula weight	506.10
temperature	293(2) K
crystal system	orthorhombic
space group	$P2_12_12_1$
unit cell dimensions	$a = 10.439(1)$ Å $b = 12.054(1)$ Å $c = 13.318(3)$ Å
volume, *Z*	1675.8(4) Å^3, 4
goodness-of-fit on F^2	1.057
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0282$, $wR_2 = 0.0623$
R indices (all data)	$R_1 = 0.0364$, $wR_2 = 0.0659$

Experimental Section

Melting points were taken with a Kofler apparatus and are not corrected. ^1H NMR spectra were recorded with a Varian VXR 300 spectrometer at 300 MHz in $CDCl_3$ solution. Chemical shift values are expressed in ppm relative to tetramethylsilane. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra were obtained on a VG 7070E electron impact spectrometer with direct introduction of the sample. Optical rotatory power was measured with a Perkin-Elmer 142 spectropolarimeter with a 1 dm cell. UV and CD spectra were recorded using a UV−Vis Varian CARY 4E spectrometer and a Jasco J600 spectropolarimeter, respectively, with 0.01 or 0.02 cm cells in CH_3CN. The CD spectrum was recorded at room temperature with the following conditions: speed 10 nm/min, response 2 s, and bandwidth 1.0 nm. Enantiomeric excess was measured by HPLC on a Daicel CHIRALCEL OD column using a Jasco PU-980 chromatograph equipped with a Jasco UV-975 detector, with the following conditions: eluent hexane/2-propanol/formic acid 90:10:1, flow 0.5 mL/min, UV detector at $\lambda = 280$ nm.

X-ray diffraction measurements were executed by means of a Siemens P4 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), operating at room temperature ($T = 293$ K). The intensity data collection was obtained with a $\omega/2\theta$ scan mode, collecting a redundant set of data to check the diffraction symmetry and the reliability of the absorption correction procedure. Intensities were corrected for absorption by means of a ψ-scan method. The data reduction was done with the SHELXTL package[24] and structure solutions and refinements, based on full-matrix least-squares on F^2, were done with SHELX97 program.[25]

Pale yellow prismatic crystals of 2,2′-diiodo-1,1′-binaphthalene, obtained by recrystallization from 80% hexane/20% xylene, were found to have the lattice parameters listed in Table 2. The unit cell parameters

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[18] CNDO-CI calculations were executed with a CNDO/M program, according to Del Bene and Jaffé's formulation (Del Bene, J.; Jaffé, H. H. *J. Phys. Chem.* **1968**, *49*, 1221), with Mataga approximation of two-electron repulsion integrals. Up to 60 singly excited states, with maximum energy values of 7.0 eV, were included in the CI. The initial geometry was calculated as in ref 12.

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were calculated from the setting angles of 36 reflections having 5.0° $< \theta <$ 12.5°. The structure was solved by direct methods and completed by standard Fourier methods. The hydrogen atoms were introduced in calculated positions and were let ride on the connected carbon atoms. The final refinement cycle gave the reliability factors listed at the bottom of Table 2.

(*R*)-(+)-2,2′-diamino-1,1′-binaphthalene, ee ≥ 99.5%, and 2-bromonaphthalene were purchased from Aldrich. Acetonitrile for spectroscopy was purchased from Fluka and not further purified. THF was refluxed several hours on Na/K alloy and distilled immediately before use. The remaining reagents and solvents were commercial products and were purified according to standard procedures.

(*R*)-(+)-DIBN (1) was prepared from (*R*)-(+)-2,2′-diamino-1,1′-binaphthalene and purified according to the published procedure.[26] Mp = 220−222 °C. $[\alpha]_D^{23}$ +15.9 (*c* 2.16, py) [lit.[26] $[\alpha]_D^{23}$ +16.2 ± 0.2 (*c* 1.725, py)]. ^{1}H NMR: δ 7.05 (1H, d, J = 8.1 Hz, H8,8′), 7.27 (1H, t, J = 8.0 Hz, H7,7′), 7.49 (1H, t, J = 8.1 Hz, H6,6′), 7.70 (1H, d, J = 8.7 Hz, H4,4′), 7.91 (1H, d, J = 8.1 Hz, H5,5′), 8.04 (1H, d, J = 8.7 Hz, H3,3′). MS, *m*/*z* (rel intensity): 506 (M^+, 100%), 379 ($[M - I]^+$, 21%), 252 ($[M - 2I]^+$, 100%), 126 ($C_{10}H_6^+$, 86%).

(*R*)-(+)-1,1′-Binaphthyl-2,2′-dicarboxylic acid, obtained by reaction of **1** with (a) 2.2 equiv of *n*-butyllithium, 1.6 M in hexane, in THF at −78 °C for 4 h, under argon atmosphere and (b) gaseous CO_2 at −78 °C for 12 h and at −40 °C for 2 h with standard workup and recrystallization from toluene, showed molecular ion peak at *m*/*z* 314 and ee(HPLC) = 97%.

2-Iodonaphthalene was prepared by transhalogenation from 2-bromonaphthalene, according to the standard procedure,[27] and purified by recrystallization from absolute ethanol. Mp = 50−52 °C. ^{1}H NMR: δ 7.45−7.50 (2H, m, H6 and H7), 7.56 (1H, d, J = 8.5 Hz, H3), 7.70 (1H, d, J = 8.5 Hz, H4), 7.70 (1H, m, H5 or H8), 7.76−7.79 (1H, m, H5 or H8), 8.23 (1H, s, H1).

Supporting Information Available: Table of crystal data, structure solution and refinement, and bond lengths and angles for 2,2′-diiodo-1,1′-binaphthalene (**1**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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