

Occurrence of Strong Circular Dichroism during Measurement of CD Spectra Due to Intramolecular Cyclization

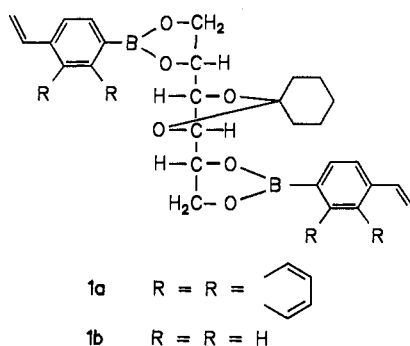
Günter Wulff,* Stephan Krieger, Bernd Kühneweg, and Alois Steigel

Institute of Organic Chemistry and
Macromolecular Chemistry
Heinrich-Heine-Universität Düsseldorf
Universitätsstrasse 1, D-40225 Düsseldorf, Germany

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During our investigations of optically active vinyl polymers with chirality in the main chain,^{1–3} we studied the chiroptical properties of the new monomer **1a** carrying two 4-vinylnaphthyl residues. On measuring the circular dichroism (CD) of **1a**, an



intensive exciton couplet at 231.8 nm was observed while using standard recording rates (5 nm/min).^{3c} More detailed studies on separate samples in each case now show that this effect is strongly dependent on the recording rate (see Figure 1). The circular dichroism increases with decreasing recording rates; with high recording rates (50 nm/min) or when measured only from 270 nm downwards, merely a small effect but with opposite sign of the couplet is seen. If the solution is scanned repeatedly from 270 nm downwards, a slow formation of the positive couplet is also observed. Further investigations established the surprising fact that even low-intensity light during UV or CD measurements results in an intramolecular [2 + 2] cycloaddition to a considerable extent (~10%). While the starting compound shows almost none, the product shows an extremely strong circular dichroism. This observation might give rise to a very sensitive method for information storage.

For isolation on a preparative scale, a solution of **1a** in methylene chloride (1.23 mmol / 250 mL) was irradiated with a mercury low-pressure emission lamp fitted with a 320-nm fluorescence filter. Optimum yields (62%) of the cyclization product **2** were obtained after 4 h of irradiation. On standing in solution, **2** decomposed slowly. Byproducts could be removed by precipitation with *n*-pentane. Product **2** remained in solution and was isolated by evaporation.

A [2 + 2] cycloaddition of **1a** should yield a cyclobutane ring with the formation of an 18-membered macrocycle. To prove this, **2** was hydrolyzed and the boronic acid groups were removed with Ag⁺/NH₃. In good yield the hitherto unknown *cis*-1,2-di-

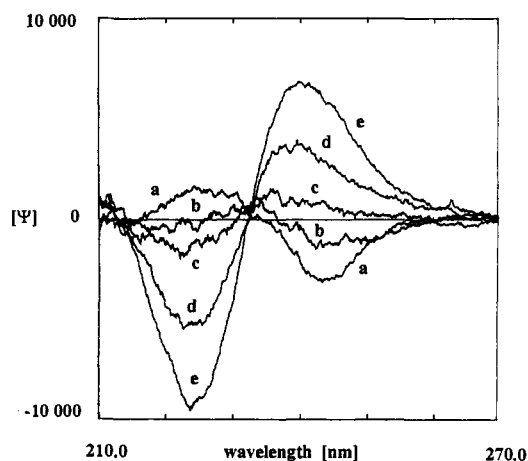
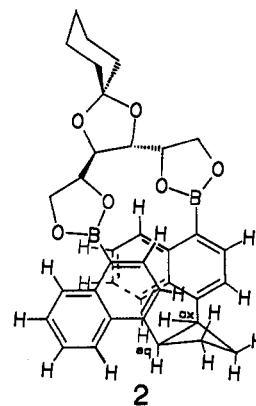
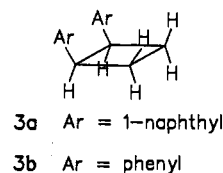


Figure 1. Dependence of the circular dichroism of **1a** on temperature and recording rate. Specific ellipticity ($[\psi]$) is given in $\text{deg}\cdot\text{cm}^2(100\text{ g})^{-1}$. Measured in tetrahydrofuran in a 0.1-mm cuvette with $c = 0.24\text{ g/L}$ with a JASCO J 600 spectropolarimeter. Curves a and b represent measurements starting at 270 nm, c, d, and e starting at 350 nm (downwards). Curve a was obtained at $-65\text{ }^\circ\text{C}$, all the others at room temperature ($22\text{ }^\circ\text{C}$). Recording rates were 5 nm/min in the cases of a, b, and d, 10 nm/min in the case of c, and 2 nm/min in the case of e. A fresh solution was prepared for each measurement.



(1-naphthyl)cyclobutane (**3a**) was obtained. The structure of **3a** could be ascertained by mass, ¹H NMR, and UV spectroscopy.



A more detailed picture of the structure of the cyclization product **2** was obtained by ¹H NMR, ¹³C NMR, and CD spectroscopic investigations.⁴ During cyclization the C₂-symmetrical monomer **1a** is transformed into a C₁-symmetrical **2**. Accordingly, all protons of the cyclobutane as well as of the naphthalene rings and the mannitol part are chemically and magnetically nonequivalent. 2D-COSY experiments allowed the assignment of these protons in the ¹H NMR spectrum of **2**.

The results of the structure elucidation were similar to those of Nishimura and co-workers,^{5,6} who prepared [2.*n*](1,4-naphthalenophanes) from α,ω -bis(4-vinylnaphthyl-1)alkanes by irradiation. NOE measurements unequivocally revealed that the

(4) Data are given in the supplementary material.

(5) Nishimura, J.; Dol, H.; Ueda, E.; Ohbayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 5293–5295.

(6) Nishimura, J.; Takeuchi, M.; Takahashi, H.; Ueda, E.; Matsuda, Y.; Oku, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3161–3166.

(1) (a) Wulff, G.; Zabrocki, K.; Hohn, J. *Angew. Chem.* **1978**, *90*, 567–568; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 535–536. (b) Wulff, G.; Hohn, J. *Macromolecules* **1982**, *15*, 1255–1261.

(2) Wulff, G.; Kemmerer, R.; Vogt, B. *J. Am. Chem. Soc.* **1987**, *109*, 7449–7457.

(3) For reviews, see: (a) Wulff, G. *Angew. Chem.* **1989**, *101*, 22–38; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 21–37. (b) Wulff, G. *Polym. News* **1991**, *16*, 167–173. (c) Wulff, G. *ChemTech* **1991**, 364–370.

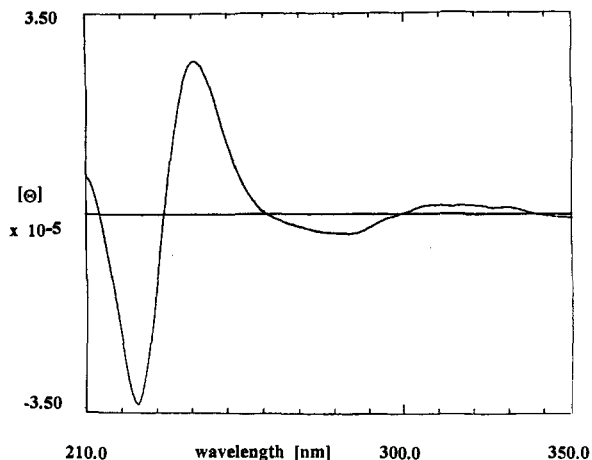


Figure 2. Circular dichroism of **2**. Molar ellipticity ($\theta = \text{deg}\cdot\text{cm}^2(10 \text{ mol})^{-1}$) is given; $c = 0.24 \text{ g/L}$ in tetrahydrofuran; recording rate 5 nm/min ; room temperature; 0.1-mm cuvette.

naphthalene rings in the existing rotamer are oriented *syn* (i.e., the annelated ring in both cases shows in the same direction). The rings are partially overlapping and shifted somewhat out of a parallel position (see structure **2**). The cyclobutane ring is *exo* oriented with respect to both naphthalene rings. COSY as well as NOE data confirm a puckered conformation of the cyclobutane ring.

As mentioned before, the cyclization product **2** gives rise to an extremely intensive exciton couplet at 231.8 nm (zero crossing) with a molar ellipticity of $[\theta] = -3.12 \times 10^5$ ($\lambda = 224.3 \text{ nm}$) and $[\theta] = +2.67 \times 10^5$ ($\lambda = 240.8 \text{ nm}$) corresponding to the 1B_b transition of naphthalene (Figure 2). This exciton couplet is caused by dipole-dipole interaction of the electric transition moments of the 1B_b transition of the neighboring naphthalene rings. The 1B_b transition is polarized along the long axis of the naphthalene chromophore. A second exciton coupling is situated at 301 nm (zero crossing), corresponding to the 1L_a transition, having an electric transition moment along the short axis of the chromophore. With the aid of the exciton chirality method of Nakanishi,⁷ the position of the naphthalene rings at the cyclobutane ring in **2** can be deduced (this is shown in Figure 4 of the supplementary material). Accordingly, with a positive couplet at 231.8 nm , the two naphthalene rings possess positive exciton chirality which results in the arrangement represented in structure **2**.⁴

In contrast, the starting monomer **1a** exhibits only a weak negative couplet at 241 nm (zero crossing) as shown in Figure 1 (shifted by 9 nm compared to **2** due to the additional double bonds). At lower temperature ($-65 \text{ }^\circ\text{C}$), the negative couplet becomes more intensive (Figure 1, curve a). From this it can be

(7) (a) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257–263. (b) Harada, N.; Nakanishi, K. *Circular dichroic spectroscopy: Exciton coupling in organic stereochemistry*; University Science Books: Oxford, U.K., 1983.

deduced that the two naphthalene rings in **1a** are on average not in a very close relationship to each other. This is in accordance with semiempirical calculations (MNDO) showing for **1a** a preferred conformation, in which by rotation around the C-2–C-3 and the C-4–C-5 bonds of the mannitol part the two vectors, spanned between the boron atoms and C-4 of the naphthalene ring, possess an angle of $\sim 30^\circ$. Such a conformation permits rotation of the naphthalene rings. The observed stereochemistry of the cyclization product **2** can be explained by the fact that 1-vinylnaphthalene derivatives for steric reasons react only in the *exo* position of the vinyl group and that the formation of 1,2-*cis*-disubstituted cyclobutanes is strongly favored.⁶

The corresponding phenyl derivative **1b** can also be intramolecularly cyclized by irradiation, but cyclization is not observed during UV or CD measurements. The cyclization product also shows a very intensive positive exciton couplet at 233 nm (zero crossing). Hydrolysis and deboronation furnishes *cis*-1,2-diphenylcyclobutane (**3b**).

On asymmetric cyclocopolymerization^{1–3} of **1a** and, e.g., methyl methacrylate and removal of the D-mannitol template, polymers are obtained containing asymmetric diads with two 4-boronynaphthyl-1 residues in (*S,S*) configuration. This polymer shows an exciton couplet in CD similar to that of the cyclization product **2**.

In conclusion, the monomer **1a** represents a system in which light of a defined wavelength can very sensitively be detected by analyzing the circular dichroism of the cyclization product. Another consequence is that, during conventional measurement of UV or CD spectra, cyclization easily could occur. This is true even if the quantum yield of this reaction at $\lambda = 320 \text{ nm}$ with $\phi = 0.27$ is not unusually high.⁸ In most cases a conversion of 5–10% during a UV measurement would not be striking, but the described system with almost no CD in the starting compound and an extremely high CD in the product clearly indicates even very small conversions.

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Supplementary Material Available: Characterization data for **2**, including a figure showing the numbering scheme, and a figure showing an application of the exciton chirality method of Nakanishi as described in ref 7 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(8) A Gränzel apparatus was used for determination of the quantum yield. The intensity of irradiation at $\lambda = 320 \text{ nm}$ was determined with an actinometer, potassium tris(oxalato)ferrate(III). With the aid of CD spectroscopy (measurement from 280 to 200 nm), the turnover of intramolecular cyclization of **1a** to **2** in methylene chloride was recorded at different times. From the inception slope the quantum yield of $\phi = 0.27$ could be obtained. For comparison, 2-vinylnaphthalene on irradiation at $\lambda = 334 \text{ nm}$ shows a quantum yield of $\phi = 0.23$ for the formation of the *cis*-cyclobutane (Shirota, Y.; Nishikata, A.; Aoyama, T.; Saimatsu, J.; Oh, S.-C.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1984**, 64–65).