Novel Chiral Bis-dipolar 6,6′-Disubstituted Binaphthol Derivatives for Second-Order Nonlinear Optics: Synthesis and Linear and Nonlinear Optical Properties

H.-J. Deussen,[†] E. Hendrickx,[‡] C. Boutton,[‡] D. Krog,[†] K. Clays,[‡] K. Bechgaard,[§] A. Persoons,*[,‡] and T. Bjørnholm*[,†]

Contribution from the Centre for Interdisciplinary Studies of Molecular Interactions, Department of Chemistry, University of Copenhagen, Symbion, Fruebjergvej 3, DK-2100 Copenhagen Ø, Denmark, Laboratory of Chemical and Biological Dynamics, Center for Research on Molecular Electronics and Photonics, Celestijnenlaan 200D, B-3001 Heverlee, Belgium, and Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark

Received January 10, 1996[⊗]

Abstract: A number of thermally and optically stable, bis-dipolar chiral molecules based on two geometries of the binaphthol (BN) system with different acceptors/substituents have been synthesized for the first time, and the synthetic routes are reported: optically pure 6,6′-disubstituted 2,2′-diethoxy-1,1′-binaphthyls {R, R′= −Br, −CHO, −CH═C(CN)(COOEt), −CH═C(CN)$_2$, −CH═CHCN, −CH═CH(*p*-NO$_2$Ph)} and optically pure 9,14-disubstituted dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepins {R, R′ = −Br, −CHO, −CH═C(CN)(COOEt), −CH═C(CN)$_2$, −CH═CHCN, −CH═CHSO$_2$CH$_3$, −CH═CHCHO, −CH═CHCH═C(CN)$_2$}. All molecules possess two equal donor−acceptor systems linked together to give a bis-dipolar system. Two mono-dipolar 6-substituted 2-butoxynaphthalene (R = −CH═C(CN)$_2$, −CH═C(CN)(COOEt)) donor−acceptor systems were prepared as references. The linear optical properties including solvatochromic shifts of absorption and fluorescence revealed strong charge transfer excitations in the new dipolar systems. The molecules show a high first hyperpolarizability β (up to (344−364) × 10^{-30} esu) as measured by electric-field-induced second-harmonic generation (EFISHG) and hyper-Rayleigh scattering (HRS). A model is developed to express the first hyperpolarizability of the bis-dipolar molecules in terms of the molecular geometry and the β of the monomeric donor−acceptor units. The tensor components were determined experimentally using this model and data from HRS and EFISHG. These techniques probe different combinations of the components of the molecular hyperpolarizability tensor. The results obtained are found to be in excellent mutual agreement.

Introduction

The field of nonlinear optics includes studies of second- and third-order nonlinear optical properties, such as electro-optic and photorefractive effects, second-harmonic generation, etc.[1] Due to high molecular hyperpolarizabilities organic molecular materials and polymers display a number of significant nonlinear optical properties and hence are emerging as possible materials for future technologies of next generation telecommunication technologies, optical information processing, and storage. The ultimate goal, the construction of devices for technological applications from organic chromophores, remains a challenge due to problems at the microscopic (molecular) and macroscopic (bulk) levels. On the microscopic side, it is well-known that the classical conjugated donor−acceptor substituted organic molecules[2] and the more recent octopolar[3] molecules have high molecular hyperpolarizabilities. Unfortunately, the trade-off that exists between the transparency and the nonlinearity has restricted the use of these molecules. On the macroscopic side, the ability to assemble these molecules in a noncentrosymmetric phase, such as noncentrosymmetric crystals, poled polymers, or Langmuir−Blodgett films is, in general, still unsatisfactory. The use of chiral molecules has been among the strategies to guarantee a noncentrosymmetric structure of dipoles in order to obtain a nonvanishing macroscopic susceptibility, $\chi^{(2)}$. However, depending on the nature of the chiral center, the D−π−A part of such optically active molecules is still able to orient in a pseudocentrosymmetric way. There are still no

* To whom correspondence should be addressed.
[†] University of Copenhagen.
[‡] Center for Research on Molecular Electronics and Photonics.
[§] Risø National Laboratory.
[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) (a) Prasad, N. P.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (b) *Materials for nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (c) Boyd, R. W. *Nonlinear optics*; Academic Press: New York, 1992. (d) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.

(2) (a) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631. (b) Cheng, L.-T.; Tam, W.; Marder, S. E.; Stiegman, A. E.; Rikken, G.; Sprangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10634.

(3) (a) Ledoux, I.; Zyss, J.; Siegel, J. S.; Brienne, J.; Lehn, J.-M. *Chem. Phys. Lett.* **1991**, *172*, 440. (b) Verbiest, T.; Clays, K.; Samyn, C.; Wolff, J.; Reinhoudt, D.; Persoons, A. *J. Am. Chem. Soc.* **1994**, *116*, 9320.

(4) (a) Bahl, A.; Grahn, W.; Stadler, S.; Feiner, F.; Bourhill, G.; Bräuchle, C.; Reisner, A.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *13*, 1485. (b) Bjørnholm, T.; Geisler, T.; Larsen, J.; Jørgensen, M.; Brunfeldt, K.; Schaumburg, K.; Bechgaard, K. *Synth. Met.* **1993**, *57* (1), 3813. (c) Bjørnholm, T.; Geisler, T.; Larsen, J.; Jørgensen J. *Chem. Soc., Chem. Commun.* **1992**, *11*, 815.

(5) (a) Nalwa, H. S.; Watanabe, T.; Miyata, S. *Adv. Mater.* **1995**, *7*, 754. (b) Kelderman E.; Derhaeg, L.; Heesink, G. J.; Verboom, W.; Engbersen, J. F.; Van Hulst, N. F.; Persoons, A.; Reinhoudt, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1075. (c) Watanabe, T.; Yamamoto, H.; Hosomin, H.; Miyata, S. in *Organic Molecules for Nonlinear Optics and Photonics*; Messier, J., et al., Eds.; NATO ASI Series; 1991, Vol. 194, p 151. (d) Tsunekawa, T.; Gotho, T.; Mataki, H.; Iwamoto, M. In *Nonlinear Optical Properties of Organic Materials III*; Khanarian, G., Ed.; Proc. SPIE; 1990, Vol. 1337, p 285. (e) Katz, H. E.; Schilling, M. L.; Holland, W. R.; Fang, T. In *Materials for Nonlinear Optics − Chemical Perspectives*; Marder, S. R., et al., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1991, Vol. 455, p 567.

S0002-7863(96)00076-5 CCC: $12.00

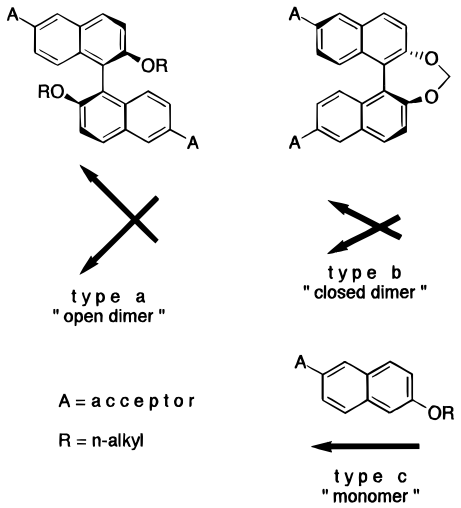


Figure 1. General structures of the bis-dipolar dimers, the monomers, and their dipole orientations.

accurate means of predicting the molecular packing in the crystalline state in order to guarantee deviation from antiparallel orientation of the dipoles in the bulk material. In order to overcome some of the above-mentioned obstacles, new strategies different from the classical one-dimensional (1D) charge transfer (CT) and octopolar molecules have been suggested. These include avoiding the direct conjugation between donor and acceptor using through space interactions,[4] and just recently, the use of two-dimensional (2D) charge-transfer molecules[5] has been reported.

The present paper deals with a bis-dipolar approach: two one-dimensional molecular units are connected together, leading to a three-dimensional V-shaped molecular structure.[6] In the dimeric binaphthol (BN) system (types a and b) (Figure 1), which is axially chiral with C_2 symmetry, two monomers of β-naphthol (type c) are connected at the 1,1′-positions. This leads for the 6,6′-diacceptor-substituted BN to a bis-dipolar molecule consisting of two donor−acceptor monomers of 6-acceptor-substituted β-naphthol.

In order to obtain further information, molecules based on this geometry, with strong acceptors and long conjugation lengths between donor and acceptor, were synthesized. We have prepared two types of chiral molecules: open chain BN-ethers (type a) with R = ethyl and closed bridge BN-acetals (type b). The latter was chosen in order to force the dipoles into the closest possible proximity to each other. Two of the corresponding monomers (type c) with R = *n*-butyl were prepared as references. According to X-ray diffraction on a racemic 6,6′-dicyano-substituted (type b) compound, the two naphthyl moieties display a dihedral angle of 54°. In the BN acetals this angle is mainly determined by the conformational energy of the heterocyclic ring, whereas in the open BN the angle between the two naphthyl moieties can vary, depending on packing effects in crystals, and solvent polarity and temperature in solution, as well as on dipole−dipole interactions in general.[7]

Unlike the classical dipolar molecules, the bis-dipolar compounds here possess two charge-transfer units within a molecule. For these nonplanar molecules, it can be anticipated that the second-order molecular hyperpolarizability tensor will have several significant tensor components. Since hyper-Rayleigh scattering (HRS) and electric-field-induced second-harmonic generation (EFISHG) assess different combinations of the components of the molecular hyperpolarizability tensor, we expect both techniques to give complementary information. The study of these molecules and the influence of their conformation on the second-order nonlinear optical response may provide an important step toward supramolecular engineering of nonlinear optical properties.

The synthesis is discussed in section I. In section II we present the linear optical properties and develop a model to express the ratio between the two main tensor components in terms of the dihedral angle between the two dipolar naphthyl units. The theory that is relevant for the analysis of the HRS and EFISHG measurements is also included in this section. In section III we present and discuss the experimental results obtained with these techniques. The conclusion is presented in section IV followed by section V, where the synthesis of all new compounds will be presented.

I. Synthesis

1. Introduction. Starting from optically pure 2,2′-dihydroxy-1,1′-binaphthyl **1**, the synthesis of all compounds proceeded by bromination in the 6,6′-positions followed by the alkylation of the hydroxy groups for the acetals (type b) or by reversed reaction order for the ethers (type a). By transformation of the dibromo compounds **4a** and **4b** to the formyl compounds **5a** and **5b**, the functionality, necessary for further reactions, was introduced. Reactions with the corresponding phosphonates by a Horner−Emmons reaction or by a Knoevenagel condensation yielded the desired enantiomeric push−pull (donor−acceptor-substituted) binaphthol derivatives.

The optical purity of the closed dimers (type b) was tested by ^{1}H-NMR (400 MHz) in the presence of the chiral alcohol (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol ((*R*)-(−)-TFAE from Aldrich): the methylene hydrogen signal of racemic 9,14-dibromodinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin (**4b**) was split 4−5 Hz due to the diastereomeric interaction with a large excess of (*R*)-(−)-TFAE. Only one optical isomer was found for all compounds tested. As a higher racemization barrier was found for open BN derivatives (type a),[8] their enantiomeric purity can be deduced from the results obtained for the closed dimers (type b), indicating that no racemization took place during the reactions.

2. Synthesis of the 6,6′-Dibromobinaphthol derivatives 4a and 4b. Optically pure binaphthol (BN) was obtained according to Kazlauskas.[9] The bromination of optically pure BN has been reported by Sogah and Cram,[10] and due to the difficulties with the purification of the dibromo diol **3a** the crude product was used as starting material. For the further synthetic steps dibromodiol **3a** could be alkylated with dibromomethane in boiling acetone and K_2CO_3 as a base, giving the acetal **4b** in nice yield (Scheme 1). In the latter reaction intramolecular ring closure took place exclusively. Direct alkylation of **1** with ethyl bromide using similar conditions gave **2** which could easily be brominated at room temperature to give **4a**. This reaction sequence, alkylation in the first step followed by bromination, was much more advantageous, as **2** was easy to purify by a single recrystallization. In comparison to the described methoxy

(6) (a) Wong, M. S.; Nicoud, J. F. *J. Chem. Soc., Chem. Commun.* **1994**, 249. (b) Wong, M. S.; Nicoud, J. F. *Nonlinear Opt.* **1995**, *9*, 181. (c) Andraud, C.; Brotin, T.; Garcia, C.; Pellé, F.; Goldner, P.; Bigot, B.; Collet, A. *J. Am. Chem. Soc.* **1994**, *116*, 2094.

(7) (a) Thorup, N.; Deussen, H. J.; Bjørnholm, T.; Bechgaard, K. Poster at ECM 16 Lund, 16th European Crystallographic Meeting, Aug 6−11, 1995, Lund, Sweden. (b) Suchod, B.; Renault, A.; Lajzerowicz, J.; Spada, G. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1839.

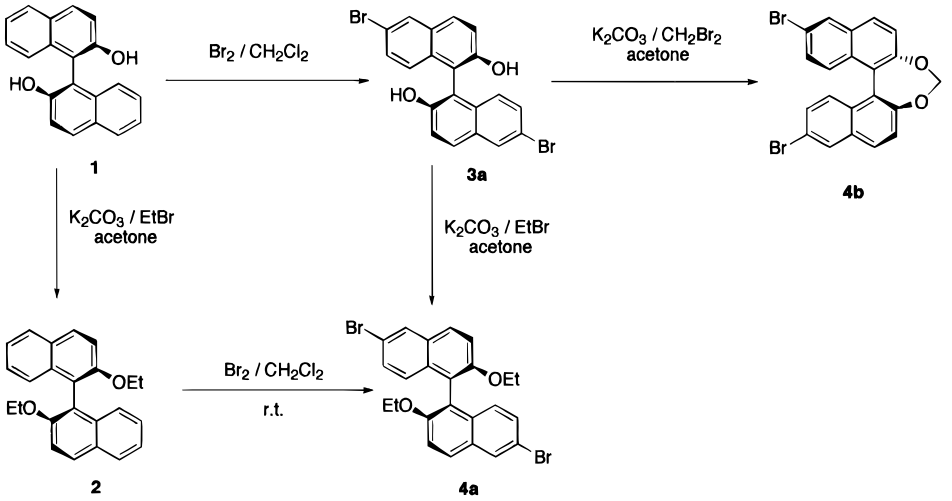
(8) Solladié, G.; Zimmermann, R. G. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 348.

(9) Kazlauskas, R. J. *Org. Synth.* **1992**, *70*, 60.

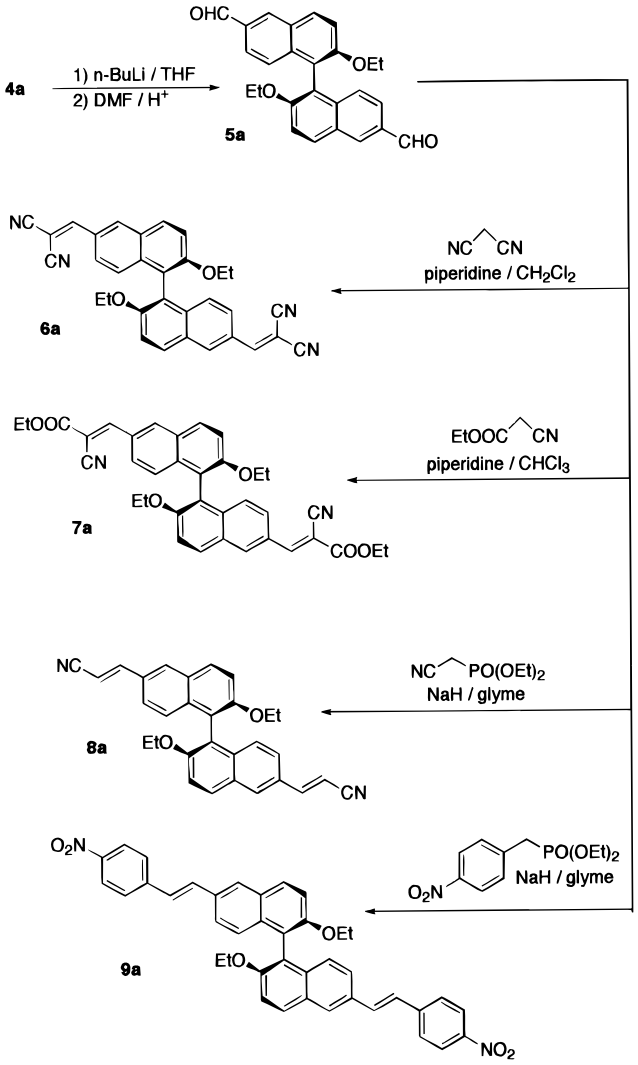
(10) Sogah, G. D. Y.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3035.

(11) (a) Gottarelli, G.; Spada, G. P. *J. Org. Chem.* **1991**, *56*, 2096 (b) Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628.

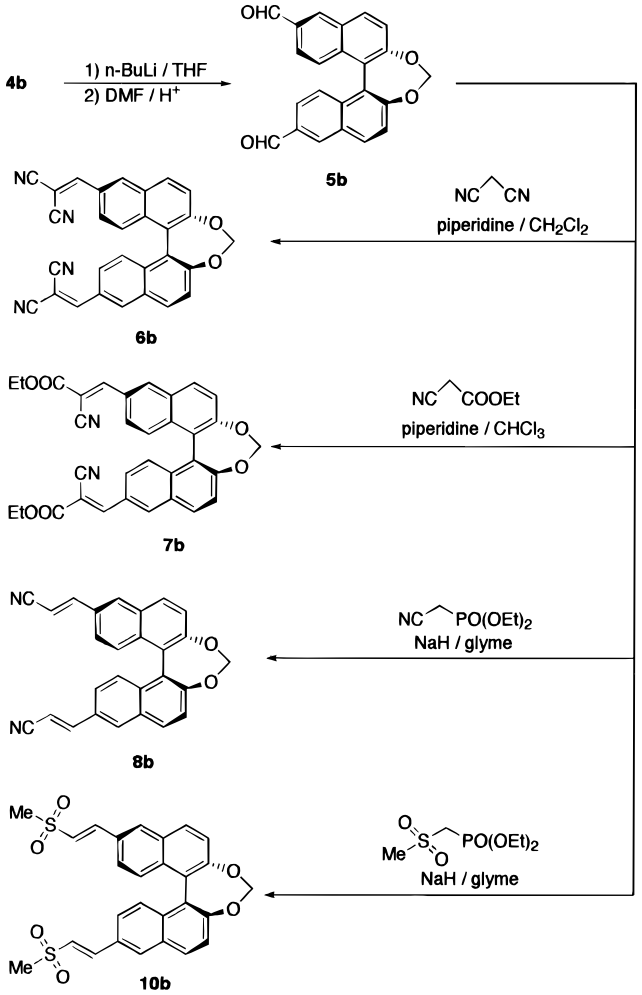
Scheme 1. Syntheses of **2**, **3a**, **4a**, and **4b**



Scheme 2. Syntheses of **5a**, **6a**, **7a**, **8a**, and **9a**



Scheme 3. Syntheses of **5b**, **6b**, **7b**, **8b**, and **10b**



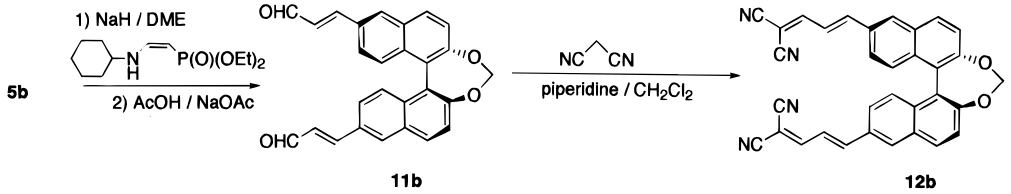
compounds,[11] the synthesized ethoxy compounds **2** and **4a** here were easier to crystallize and showed a significantly increased solubility, necessary in the subsequent synthetic steps.

3. Synthesis of the 6,6′-Diacceptor-Substituted Open BN Ethers 5a−9a. **4a** was lithiated in THF at −78 °C using an excess of *n*-BuLi. After 5−6 h an excess of DMF was added, and subsequent hydrolysis yielded the aldehyde **5a** (Scheme 2). The aldehyde was converted to the corresponding dicyanoethylene derivative **6a** by means of the Knoevenagel condensation[12] with malononitrile using a catalytic amount of piperidine as a base in methylene chloride. Compound **7a** was synthesized by condensation of the aldehyde **4a** with ethyl cyanoacetate under similar conditions as mentioned above, but using $CHCl_3$ as solvent. The (*E*)-configuration of **7a** was assigned on the basis

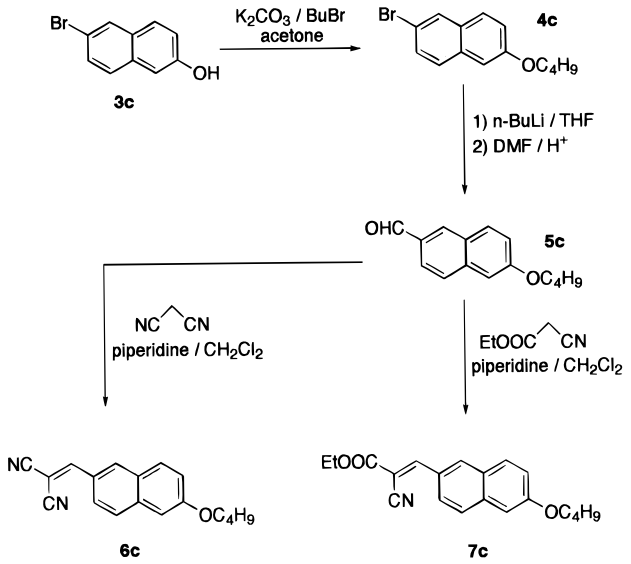
(12) *Org. React.* **1967**, *15*, 204.

(13) (a) Hesse, M.; Meier, B.; Zeh, B. *Spektroskopische Methoden in der organischen Chemie*, 3rd ed.; Stuttgart, 1987; p 115. (b) Zabicky, J. *J. Chem. Soc.* **1961**, 683.

Scheme 4. Syntheses of **11b** and **12b**



Scheme 5. Syntheses of **4c**, **5c**, **6c**, and **7c**



of the shift of the olefinic proton and was in accordance with a previous observation obtained for a benzene derivative.[13]

8a and **9b** were synthesized by the Horner−Emmons[14] reaction of the corresponding diethyl phosphonates in dimethoxyethane at room temperature using sodium hydride as a base. Diethyl (cyanomethyl)phosphonate was purchased (Merck); diethyl (4-nitrobenzyl)phosphonate was synthesized by the Arbuzov reaction of 4-nitrobenzyl chloride with triethyl phosphite which was superior to a procedure previously reported.[15]

4. Synthesis of the 6,6′-Diacceptor-Substituted Closed BN Acetals 5b−8b and 10b. The syntheses of the closed BN acetal derivatives **5b**−**8b** were analogous to the ones described above. **10b** and **11b** were synthesized by the Horner−Emmons reaction using conditions similar to those above. The diethyl [(methylsulfonyl)methyl]phosphonate used for the preparation of **10b** (Scheme 3) was prepared according to a known procedure.[16]

The vinylogous dialdehyde **11b** was synthesized by a two-step formylolefination using diethyl [2-(cyclohexylamino)vinyl]-phosphonate (Scheme 4).[17] The carbanion of the phosphonate was conveniently reacted with the aldehyde **5b**, giving the α,β-unsaturated aldimine. This was hydrolyzed in a two-layer system of CH_2Cl_2 and a buffer solution to give the unprotected dialdehyde **11b**. The aldehyde was converted to the corresponding dicyanoethylene derivative **12b** by means of the Knoevenagel condensation[12] as described earlier.

5. Synthesis of the β-Naphthol Derivatives 3c−7c. 3c was prepared according to a known method.[18] The subsequent reaction steps were similar to those for the binaphthol derivatives **4a**−**7a** (Scheme 5).

II. Linear and Nonlinear Optical Properties

1. Linear Optical Properties of Compounds 6a−6c and 7a−7c. The absorption spectra of the two types of BN dimers and of their corresponding references (double concentration) in $CHCl_3$ are shown in Figures 2 and 3 for two different acceptors. The tendency is the same for both acceptors 6 and 7: the absorption spectra of the type c and type a molecules are similar, whereas the closed type b compounds differ significantly from the others.

The differences of the type b compounds can be explained by the fact, as shown by X-ray diffraction, that the plane defined by the oxygen atoms and the carbon atom to which they both are bound does not coincide with the plane of the aromatic

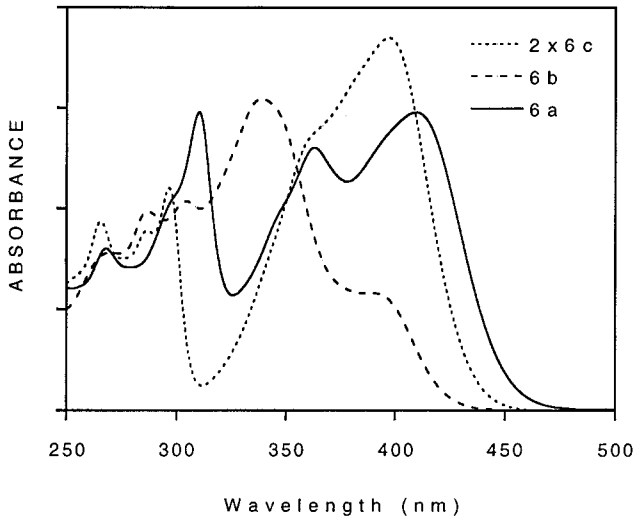


Figure 2. Absorption spectra of **6a**, **6b**, and **6c** (double concentration) in $CHCl_3$.

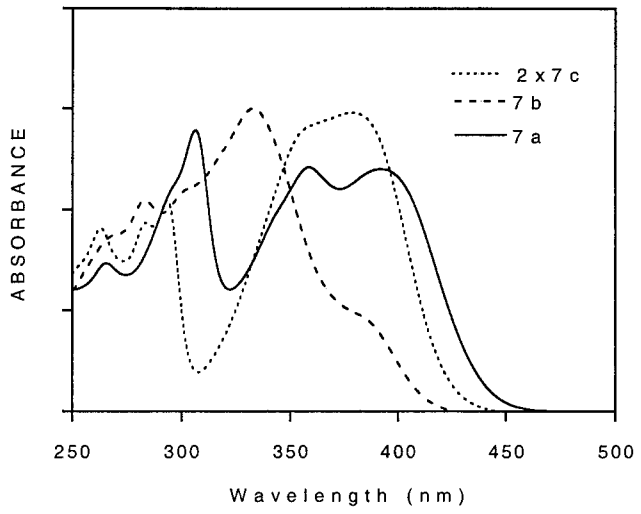


Figure 3. Absorption spectra of **7a**, **7b**, and **7c** (double concentration) in $CHCl_3$.

(14) Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733.

(15) Kagan, F.; Birkenmeyer, R. D.; Strube, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 3026.

(16) (a) Fillion, H.; Péra, M.-H.; Rappa, J.-L.; Luu-Duc, C. *J. Heterocycl. Chem.* **1978**, *15*, 753. (b) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1972**, *37*, 3547.

(17) Nagata, W.; Wakabayashi, D.; Hayase, Y. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 448.

(18) Koelsch, C. F. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 132.

Table 1. Solvatochromic Shifts of Absorption and Fluorescence Emission of Compounds **6a**−**6c** and **7a**−**7c**

compound	λ_{max} (nm) (*n*-hexane)	λ_{max} (nm) (CH_2Cl_2)	λ_{fluor} (nm) (*n*-hexane)	λ_{fluor} (nm) (CH_2Cl_2)	Stokes shift (eV) (*n*-hexane)	Stokes shift (eV) (CH_2Cl_2)
6a	399	407	442	494	0.302	0.537
6b	385	385	421	481	0.275	0.643
6c	389	394	421	459	0.242	0.446
7a	391	389	437	485	0.334	0.631
7b	377	378	418	470	0.323	0.642
7c	379	377	413	453	0.269	0.552

rings.[7a] Thus, the electron-donating lone pairs of the oxygen atoms are twisted out of conjugation with the aromatic system. This loss of donor strength is reflected in the hypsochromic shift of the absorption spectra.

The similarity between the spectra of 1,1′-binaphthyl and naphthalene has been attributed to the lack of coplanarity between the naphthyl moieties in 1,1′-binaphthyl due to steric hindrance.[19] The INDO/CI calculated potential energy curve of 1,1′-binaphthyl shows a broad minimum located around an angle between the two naphthalene units at 90°.[20] The minimum was found to be delimited by two steep walls at angles of 60° and 130° due to the strong steric interactions experienced by the molecule approaching planarity. At room temperature, the molecule is expected to oscillate around the perpendicular form. For the bis-dipolar BN, the similarity of the absorption spectra between the monomeric dipolar naphthol ethers (type c) and the open bis-dipolar BN ethers (type a) again demonstrates the lack of coplanarity. As the steric hindrance is not affected by the substitution, we still expect the potential energy curve to be delimited by the steric hindrance. Even though the dipolar interactions can introduce some asymmetry in the shape of the potential well since they favor antiparallel geometries, we do not expect that this effect is strong enough to prevent oscillation around the perpendicular form.

Still the absorption maxima at longer wavelengths of the type a BN are shifted bathochromicly by 10−15 nm in comparison to the monomers (type c). Since the two dipoles are oriented nearly perpendicular, the interaction energy between the two dipoles should be negligible. A possible explanation for the observed shifts could be the different interactions of the dipoles with the solvent. The effect of a solvent on a polar molecule can be described by Onsager's reaction field model.[21] In this model, the polar molecule is taken to occupy a spherical cavity and generates a reaction field directly proportional to and in the same direction as the molecular dipole moment. As the dipole moment of the type a BN will be larger than that of the monomeric units, the reaction field will also be larger for the type a BN, and consequently, the absorption maxima will be red-shifted for the type a BN. As the difference in dipole moment of the type a BN and their corresponding monomers will be even larger in the excited state, the bathochromic shift is even more significant if we look at the Stokes shifts (Table 1) of fluorescence emission, which are related to the change in dipole moment from the ground to excited state ($\Delta\boldsymbol{\mu}_{ge}$).[22]

It can be deduced from the solvatochroism of both absorption (the apparent discrepancy for **7a** and **7c** is due to the occurrence of a fine structure in *n*-hexane which is misleading) and fluorescence of **6a**−**c** and **7a**−**c**[23] that all the molecules display

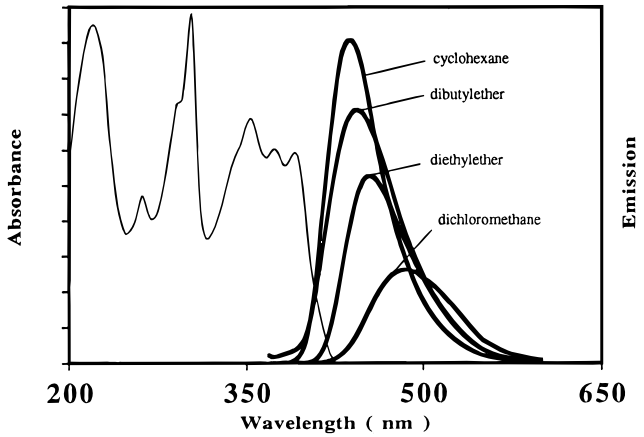


Figure 4. Absorption spectrum of **7a** in *n*-hexane and fluorescence emission in solvents of different polarity.

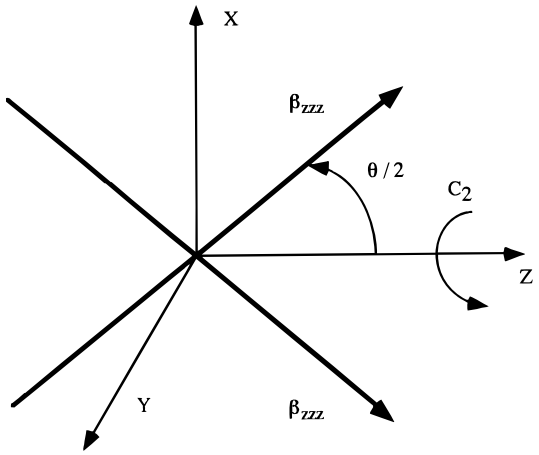


Figure 5. Model geometry of the coupled dipolar NLO units. Both β_{zzz} tensor components are lying in a plane parallel to the *ZX* plane and make an angle of $\theta/2$ deg with the 2-fold axis that is chosen as the *Z* axis of the reference frame of the dimer.

the necessary charge-transfer properties and thus fulfill the requirements for effective NLO materials according to the two-level model (Figure 4).[1]

2. Molecular Hyperpolarizability Tensor. A simple model can be used to express the ratio of the different molecular tensor components of the BN dimer in terms of the dihedral angle between the dipolar naphthyl units. As the two linked monomeric units each have dipolar symmetry, we further assume that their only significant tensor component is β_{zzz}, where *z* is in the direction of the charge transfer in the monomeric unit. Quantum chemical calculations[24] and depolarized HRS measurements[25] have shown that this approach is accurate within 10−15% for conjugated organic chromophores. If we also allow the angle between the two β_{zzz} tensor components to vary, these assumptions lead to the simplified geometry shown in Figure 5.[26]

(19) Friedel, R. A.; Orchin, M.; Reggel, L. *J. Am. Chem. Soc.* **1948**, *70*, 199.

(20) Baraldi, I.; Ponterini, G.; Momicchioli, F. *J. Chem. Soc., Faraday Trans, 2* **1987**, *83* 2139.

(21) Böttcher, C. J. P. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973.

(22) (a) Lippert, E. *Elektrochem.* **1957**, *61*, 962. (b) Suppan, P. *J. Photochem. Photobiol., A: Chem.* **1990**, *50*, 293.

(23) From the plot of the energy difference between the first fluorescence band and the first absorption band against the Onsager solvent polarity function in a series of solvents of different polarity, the changes in dipole moment from ground to excited state ($\Delta\boldsymbol{\mu}_{ge}$) were determined according to ref 22, to give the following values (D): **6a**,13; **6b**,14; **6c**, 10; **7a**, 16; **7b**, 14; **7c**, 8.

(24) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(25) Heesing, G. J. T.; Ruiter, A. G. T.; van Hulst, N. F.; Bölger, B. *Phys. Rev. Lett.* **1993**, *71*, 999.

(26) The choice of the model geometry and tensor components is furthermore justified by semiempirical calculations (PM3), which indicate that the two major tensor components are β_{ZZZ} and β_{ZXX}. The next significant component β_{ZYY} is less than 17% of the sum of β_{ZZZ} and β_{ZXX}.

According to this model, the tensor components of the dimer in the *XYZ* reference frame are given by

$$\beta_{IJK,\text{dimer}} = 2\cos_{I,z}\cos_{J,z}\cos_{K,z}\beta_{zzz,\text{monomer}} \quad (1)$$

Since the molecule has a 2-fold axis, the two monomeric tensor components have the same magnitude.

If *I*, *J*, or $K = Y$, then β_{IJK} will be equal to zero since $\cos_{Y,z} = \cos 90° = 0$. Furthermore, since the dimer in the model has C_{2v} symmetry, we are left with only four nonzero tensor components, β_{ZZZ}, β_{ZXX}, β_{XZX}, and β_{XXZ}. According to eq 1, the magnitude of these components is given by

$$\beta_{ZZZ} = 2\left(\cos\frac{\theta}{2}\right)^3\beta_{zzz,\text{monomer}} \quad (2)$$

$$\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ} = 2\left(\cos\frac{\theta}{2}\right)\left(\sin\frac{\theta}{2}\right)^2\beta_{zzz,\text{monomer}} \quad (3)$$

since $\cos(90 - \theta/2) = \sin(\theta/2)$. The fact that $\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ}$ can also be obtained assuming Kleinman[27] or intrinsic permutation symmetry, but here it simply follows from the model used.

Thus, if the angle $\theta/2$ can be determined by X-ray diffraction or semiempirical calculations, we can immediately calculate the ratio of the two independent tensor components according to

$$\frac{\beta_{ZXX}}{\beta_{ZZZ}} = \left(\tan\frac{\theta}{2}\right)^2 \quad (4)$$

We will use this model and eq 4 for the analysis of the hyper-Rayleigh scattering and electric-field-induced second-harmonic generation measurements. From symmetry considerations and vector addition it is also obvious that the dipole moment of the dimer is directed along the *Z* axis.

An additional conformational mobility is the flexibility of the vinyl- or styrylnaphthalene moiety. It was concluded earlier that 2-styrylnaphthalene exists in solution as an equilibrium mixture of two roughly isoenergetic conformers (in anti and synconformations) and that no steric factors impede the interconversion of the postulated conformers.[28] For 2-vinylnaphthalene the dominant conformation was found by NMR spectroscopy to be anti, with a dihedral angle α formed by the naphthyl and vinyl plane of 18.3° ± 3.1°. A 2-fold rotational barrier of 4.0 ± 0.4 kcal/mol was found for styrene.[29] However, the preferred vinyl and styryl conformations were found by PM3 calculations to be independent of the conjugate naphthalene framework (open chain BN ethers, closed BN acetals, and the β-naphthol monomers). This justifies ommiting the additional conformationally mobility in the above model, as these contributions will be the same for different dihedral angles θ between the naphthalene moieties.

3. Hyper-Rayleigh Scattering. As hyper-Rayleigh scattering (HRS) has so far not been applied to deduce numerical values for several tensor components, we find it useful to treat this technique in a more detailed fashion. An HRS measurement is performed by measuring the intensity of the second-order scattered light on focusing an intense laser beam, with frequency ω, on an isotropic solution.[30] For a detailed description of the experimental setup the reader is referred to ref 31.

For a liquid composed of noncentrosymmetric molecules the macroscopic polarization oscillating at the harmonic frequency 2ω will be equal to

$$\vec{P}(2\omega) = \mathbf{B}(-2\omega;\omega,\omega)\,\vec{E}(\omega)\,\vec{E}(\omega) \quad (5)$$

with $\mathbf{B}(-2\omega;\omega,\omega)$ the macroscopic nonlinear second-order susceptibility tensor for frequency doubling. Due to the orientational fluctuations of the molecules in solution it is only the average value of $\mathbf{B}(-2\omega;\omega,\omega)$ that is equal to zero. If the incident light travels in the *U* direction and is polarized in the *W* direction while the scattered light is observed in the *V* direction, the intensity of the HRS signal will be equal to

$$I(2\omega) = I_U(2\omega) + I_W(2\omega) = G(\langle B_{WWW}{}^2\rangle + \langle B_{UWW}{}^2\rangle)I_W{}^2(\omega) \quad (6)$$

$I(2\omega)$ is the intensity of the light at frequency 2ω, traveling in the *V* direction. Both the *U* and *W* polarized components of the harmonic light are measured. The angular brackets indicate orientational averaging and *G* is an instrumental factor that remains unchanged during a measurement. For a solution composed of noninteracting solvent (S) and solute (s) molecules, the macroscopic nonlinear susceptibility of the solution can be written as a function of the corresponding microscopic hyperpolarizabilities and number densities of the solvent and solute molecules:

$$\langle B_{WWW}{}^2\rangle + \langle B_{UWW}{}^2\rangle = f_\omega{}^4 f_{2\omega}{}^2 \sum_{p=\text{s,S}} N_p(\langle\beta_{WWW}{}^2\rangle + \langle\beta_{UWW}{}^2\rangle)_p \quad (7)$$

where f_ω and $f_{2\omega}$ are the local field correction factors at the fundamental and the harmonic frequencies, respectively.

If we define $\langle\beta_{\text{HRS}}{}^2\rangle$ by

$$\langle\boldsymbol{\beta}_{\text{HRS}}{}^2\rangle = \langle\beta_{UWW}{}^2\rangle + \langle\beta_{WWW}{}^2\rangle \quad (8)$$

this leads to the following equation for the intensity of the scattered field:

$$I(2\omega) = G f_\omega{}^4 f_\omega{}^2 (N_S\langle\boldsymbol{\beta}_{\text{HRS}}{}^2\rangle_S + N_s\langle\boldsymbol{\beta}_{\text{HRS}}{}^2\rangle_s) I_W{}^2(\omega) \quad (9)$$

For the analysis of the HRS results of the dimers, N_s is equal to the number density of the dimers. This implies that the harmonic fields of two monomeric units interfere if the monomeric units belong to the same dimer. There are no fixed phase relations between the harmonic fields of two dimers or two independent molecules in an isotropic solution. Thus, by performing the orientational average, we can link $\langle\boldsymbol{\beta}_{\text{HRS}}{}^2\rangle$ to the components of the molecular hyperpolarizability tensor. For the dimers, since N_s is equal to the number density of the dimers, $\langle\boldsymbol{\beta}_{\text{HRS}}{}^2\rangle$ is composed of the tensor components of the molecular hyperpolarizability tensor of the dimer. For a fully symmetrical tensor, i.e., assuming Kleinman and intrinsic permutation symmetry, this relation is given by

$$\langle\boldsymbol{\beta}_{\text{HRS}}{}^2\rangle = \frac{6}{35}\sum_i \beta_{iii}{}^2 + \frac{16}{105}\sum_{i\neq j}\beta_{iii}\beta_{ijj} + \frac{38}{105}\sum_{i\neq j}\beta_{iij}{}^2 + \frac{16}{105}\sum_{ijk,\text{cycl}}\beta_{iij}\beta_{jkk} + \frac{20}{35}\beta_{ijk}{}^2 \quad (10)$$

where the summations over $i \neq j$ contain six terms each, and the summation over *ijk*, cycl contains three terms ($\beta_{XXY}\beta_{YZZ}$, $\beta_{YYZ}\beta_{ZXX}$, $\beta_{ZZX}\beta_{XYY}$), as is also the case with the summation over

(27) Kleinman, D. A. *Phys. Rev.* **1962**, *126*, 1977.
(28) Haas, E.; Fischer, G.; Fischer, E. *J. Phys. Chem.* **1978**, *14*, 1638.
(29) Facchine, K. L.; Staley, S. W.; van Zijl, P. C. M.; Mishra, P. K.; Bothner-By, A. A. *J. Am. Chem. Soc.* **1988**, *110*, 4900.
(30) (a) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980. (b) Clays, K.; Persoons, A.; De Maeyer, L. *Adv. Chem. Phys.* **1994**, *85* (III), 455.
(31) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285.

i.[32] It is clear from this equation that HRS is sensitive to an isotropic average of all molecular tensor components.

For dipolar molecules such as *p*-nitroaniline, with only one significant β_{ZZZ} tensor component, eq 10 reduces to

$$\langle \boldsymbol{\beta}_{\mathrm{HRS}}{}^2 \rangle = \frac{6}{35}\beta_{ZZZ}{}^2 \tag{11}$$

For the BN dimers, according to the model presented above, there will only be two significant independent tensor components, β_{ZZZ} and $\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ}$. If we only take these components into account, we are left with

$$\langle \boldsymbol{\beta}_{\mathrm{HRS}}{}^2 \rangle = \frac{6}{35}\beta_{ZZZ}{}^2 + \frac{16}{105}\beta_{ZZZ}\beta_{ZXX} + \frac{38}{105}\beta_{ZXX}{}^2 \tag{12}$$

Equations 9, 11, and 12 are used to analyze the HRS measurements and to obtain an averaged value for the molecular hyperpolarizability. At low solute concentration, N_S in eq 9 can be taken as a constant, and the slope of a plot of the experimentally determined ratio $I(2\omega)/I_W{}^2(\omega)$ versus N_s will be equal to

$$\text{slope} = G f_\omega{}^4 f_\omega{}^2 \langle \beta_{\mathrm{HRS}}{}^2 \rangle \tag{13}$$

This slope is determined for a dilution series of *p*-nitroaniline in chloroform ($\boldsymbol{\beta} = 23 \times 10^{-30}$ esu)[30a] and for a dilution series of the molecule with the unknown hyperpolarizability. The ratio of the two slopes is proportional to

$$\frac{\text{slope}_{\mathrm{pna}}}{\text{slope}_x} = \frac{(6/35)(23)^2}{\langle \boldsymbol{\beta}_{\mathrm{HRS}}{}^2 \rangle_x} \tag{14}$$

From this equation the unknown averaged hyperpolarizability can easily be calculated. The estimated uncertainty of all experimental HRS results is ±10%.

4. Electric-Field-Induced Second-Harmonic Generation. The EFISHG technique is a standard technique for the determination of the first hyperpolarizability.[33] Unlike HRS, EFISHG uses a dc electric field to break the centrosymmetry of the solution. As there are three fields involved, the total contribution to the nonlinear polarization oscillating at the harmonic frequency is given by the microscopic second hyperpolarizability γ_0, which can be written as the sum of an electronic and an orientational contribution:

$$\gamma_0 = \gamma_{\mathrm{e}} + \mu_Z \beta_Z / 5kT \tag{15}$$

For conjugated organic molecules with a large first hyperpolarizability and dipole moment, it is usually assumed that γ_{e} can be neglected. The *Z* axis is in the same direction as the molecular dipole moment, and β_Z is given by

$$\beta_Z = \beta_{ZZZ} + (1/3)(\beta_{ZXX} + \beta_{ZYY} + \beta_{XZX} + \beta_{YZY} + \beta_{XXZ} + \beta_{YYZ}) \tag{16}$$

If we make the same assumptions for the molecular tensor components of the BN dimers as in section 2.2, this equation reduces to

$$\beta_Z = \beta_{ZZZ} + \beta_{ZXX} \tag{17}$$

Thus, EFISHG is sensitive to the sum of the two main tensor components of the BN dimers, while HRS is sensitive to the sum of the two main tensor components squared, each multiplied by a factor originating from the orientational average. The dipole moments were determined experimentally according to the procedure outlined in ref 34. As the *Z* axis of the dimer coincides with the 2-fold axis, the only component of the molecular dipole moment will be μ_Z. For EFISHG $\boldsymbol{\beta}$ values, the estimated uncertainties are ±15%.

III. Results and Discussion

The molecular hyperpolarizabilities ($\boldsymbol{\beta}$) have been determined using both EFISHG and HRS, and the results are shown in Tables 2−4. The obtained values are listed in units of 10^{-30} esu and were measured at 1064 nm in chloroform. Since fluorescence at 532 nm is known to artificially enhance the retrieved value for the first hyperpolarizability measured by HRS,[35] all the compounds were tested for fluorescence emission at this wavelength. No significant fluorescence at this wavelength was observed for any of the compounds.

We first focus our attention on the monomers (type c). For these simple dipolar molecules, it is obvious that β_{zzz}, where *z* is directed along the charge-transfer axis, is the largest component of the molecular hyperpolarizability tensor. As a result, both EFISHG and HRS measure the same value for the molecular hyperpolarizability. In good agreement with the position of the absorption band maxima, the hyperpolarizability of the molecule with the dicyanovinyl acceptor **6c** is larger than the hyperpolarizability of the molecule with the cyanocarboethoxyvinyl **7c** acceptor due to the higher acceptor strength of the dicyanovinyl acceptor (Table 2).

The results obtained for the dimers in the open form (type a) are listed in Table 3. To analyze the HRS results, a value of 45° for $\theta/2$ was introduced in eq 4 to calculate a ratio of 1 between β_{ZZZ} and β_{ZXX}, or $\beta_{ZZZ} = \beta_{ZXX}$. This average value was determined by semiempirical PM3 calculations.[36] Introducing this ratio into eq 12 gives

$$\langle \boldsymbol{\beta}_{\mathrm{HRS}}{}^2 \rangle = 0.686\beta_{ZZZ}{}^2 \tag{18}$$

Using eqs 18 and 14, the β_{ZZZ} tensor component of the dimer can easily be determined. Since $\beta_{ZZZ} = \beta_{ZXX}$, the other component is also known. Using eqs 2 and 3, these dimer tensor components can be linked to the tensor component of the dipolar monomeric units. EFISHG, on the other hand, is sensitive to the sum of the two tensor components of the dimer: to $\beta_{ZZZ} + \beta_{ZXX}$. As can be seen in Table 3, the EFISHG values ($\beta_{ZZZ} + \beta_{ZXX}$) are in excellent agreement with the sum of the two components determined by HRS ($\beta_{ZZZ} + \beta_{ZXX}$).

It is also clear that the $\boldsymbol{\beta}$ tensor components of the dipolar monomeric unit as well as the tensor components of the dimer increase with increasing acceptor strength and with increasing conjugation length. Furthermore, for the dimers with the dicyanovinyl and the cyanocarbethoxyvinyl acceptors (**6a** and **7a**), the calculated tensor components of the dipolar monomeric units are in good agreement with the hyperpolarizabilities of

(32) (a) Cyvin, S. J.; Rauch, J. E.; Decius, J. C. *J. Chem. Phys.* **1965**, *43*, 4083 (b) Bersohn, R.; Pao, Y.-H.; Frisch, H. L. *J. Chem. Phys.* **1966**, *45*, 3184.

(33) (a) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1975**, *63*, 2666. (b) Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572. (c) Meredith, G. R. *Rev. Sci. Instrum.* **1982**, *53*, 48.

(34) Nackaerts, R. Ph.D. Thesis **1983**, University of Leuven, Belgium, 1983.

(35) Hendrickx, E.; Dehu, C.; Clays, K.; Brédas, J.-L.; Persoons, A. *Polymers for Second-Order Nonlinear Optics*; ACS Symposium Series; American Chemical Society: Washington, Dc, 1995; Vol. 601.

(36) Simple vector calculation of the determined dipole moments of **6a**, **6c** and **7a**, **7c** assuming the V-shape model with C_{2v} symmetry (Figure 5) gives a calculated dihedral angle θ of 78° for **6a** and of 89° for **7a** in good agreement with the results of PM3 calculations.

Table 2. Molecular Hyperpolarizabilities (β) of **6c** and **7c** in Units of 10^{-30} esu (1064 nm, $CHCl_3$)

compound	β_{HRS}	β_{EFISHG}
6c	79	87
7c	64	64

Table 3. Molecular Hyperpolarizabilities (β) of **6a**, **7a**, **8a**, **9a**, and Their Hypothetical Monomers (See Text) in Units of 10^{-30} esu (1064 nm, $CHCl_3$)

com-pound	HRS: β_{zzz}	HRS: β_{zxx}	HRS: β_{mono}	HRS: $\beta_{zzz} + \beta_{zxx}$	EFISHG: $\beta_{zzz} + \beta_{zxx}$
6a	68	68	96	136	135
7a	59	59	83	118	103
8a	47	47	66	94	102
9a	182	182	255	364	344

Table 4. Molecular Hyperpolarizabilities (β) of **6b**, **7b**, **8b**, **10b**, **12b**, and Their Hypothetical Monomers (See Text) in Units of 10^{-30} esu (1064 nm, $CHCl_3$)

com-pound	HRS: β_{zzz}	HRS: β_{zxx}	HRS: β_{mono}	HRS: $\beta_{zzz} + \beta_{zxx}$	EFISHG: $\beta_{zzz} + \beta_{zxx}$
6b	54	14	37	68	65
7b	46	12	32	58	95
8b	27	7	19	34	34
10b	31	8	22	39	45
12b	193	50	132	243	219

the monomers **6c** and **7c** listed in Table 2. This indicates that a strong interaction exists between the electron donor and the electron acceptor and is in accordance with the proposed model (Figure 5).

Since the angle $\theta/2$ is not accurately known for the open BN (type a), the value for this angle will be determined using $\langle \boldsymbol{\beta}_{HRS}^2 \rangle$ and $\boldsymbol{\beta}_{EFISHG}$. From $\langle \boldsymbol{\beta}_{HRS}^2 \rangle$ (eq 12) and $\boldsymbol{\beta}_{EFISHG}$ (eq 17) we can easily calculate β_{ZZZ} and β_{ZXX}, which are related to $\theta/2$ by eq 4. If this is done using the measurement results of **6a**, **6c** and **7a**, **7c**, we find an average value of 46° ± 11° for $\theta/2$ in good agreement with the minimum of the calculated potential energy curve for 1,1′-binaphthyl[20] and of the dihedral angle calculated by PM3 calculations for these compounds.

The results obtained for the closed dimers (type b) are listed in Table 4. According to X-ray diffraction, the two naphthyl units display a dihedral angle of 54° in a racemic 6,6′-dicyano-substituted compound.[7a,37] For the analysis of the HRS results of the closed dimers (type b), a value of 27° for $\theta/2$ was introduced in eq 4 to calculate a ratio of 0.26 between β_{ZZZ} and β_{ZXX}, or $0.26\beta_{ZZZ} = \beta_{ZXX}$. Inserting this ratio into eq 12 gives

$$\langle \beta_{HRS}^2 \rangle = 0.234 \beta_{ZZZ}^2 \qquad (19)$$

Using eqs 19 and 14, the tensor components of the dimer can be determined. The sum of these two components is compared to the EFISHG $\beta_{ZZZ} + \beta_{ZXX}$ values. These EFISHG values ($\beta_{ZZZ} + \beta_{ZXX}$) are again in good agreement with the corresponding HRS values ($\beta_{ZZZ} + \beta_{ZXX}$).

If the tensor components of the dipolar monomeric units (of type b) are calculated using eqs 2 and 3 and a value of 27° for $\theta/2$, then these values are significantly lower than the values of the open monomers (type c), or of the calculated monomers of the corresponding open dimers (of type a). This can be attributed to the poor overlap between the electron lone pairs of the oxygen atom and the aromatic rings. As mentioned before, this loss of donor strength is also reflected in the hypsochromic shift of the absorption spectra. Again the tensor components of the dimer and the dipolar monomeric units increase with increasing acceptor strength and increasing conjugation length.

(37) PM3 calculations give an angle of 47° for this compound and all closed dimers (type b) independent of the substitution in the 6,6′-positions.

IV. Conclusion

In conclusion, we have prepared novel 6,6′-diacceptor-substituted chiral binaphthol derivatives for nonlinear optical applications based on two different molecular geometries displaying different acceptor strengths. A model was developed to account for the bis-dipolar character of the first molecular hyperpolarizability tensor. These components can be expressed in terms of the hyperpolarizabilities of the dipolar one-dimensional monomeric units and the dihedral angle between these monomers. The ratio between the two independent tensor components of the dimers was calculated using this model, and values for the dihedral angle from either X-ray diffraction or semiempirical PM3 calculations. This ratio is then used to analyze the results obtained by hyper-Rayleigh scattering.

By comparison of the tensor components determined using this model and the HRS measurements to the EFISHG measurements, the following conclusions can be drawn: (i) Results from EFISHG and HRS measurements are in excellent mutual agreement for the monomers, the open dimers, and the closed dimers. (ii) The values of the tensor components of the open dimers (type a) are significantly larger than the values of the tensor components of the corresponding closed dimers (type b) due to the bad conjugation between the electron donor and the aromatic system in the closed forms. (iii) For the open dimers an average value of 46° ± 11° has been calculated for $\theta/2$ using $\langle \boldsymbol{\beta}_{HRS}^2 \rangle$ and $\boldsymbol{\beta}_{EFISHG}$. (iv) The hyperpolarizability of the free monomers (type c) is equal to the hyperpolarizability of the dipolar monomeric units of the corresponding dimers (type a), indicating a strong electron donor−acceptor interaction in the open forms. (v) The values for the tensor components of the free monomers, open dimers, and closed dimers follow the expected increase in magnitude with increasing acceptor strength and increasing conjugation length.

Finally, we have presented a new approach to analyze the hyperpolarizability tensor of bis-dipolar molecules. We have demonstrated that EFISHG and HRS can be used to obtain complementary information on the molecular hyperpolarizability tensor. This approach is an important step toward a quantitative characterization of the nonlinear optical response of supramolecular systems where a large number of chromophores are assembled in a noncentrosymmetric manner.

The effect of the special expression of chirality in the BN systems on the intermolecular packing of the molecules and hence the overall dipolar nature of the resulting materials has not been addressed here, but will be presented in a forthcoming paper, including the crystal structures and the NLO properties of the crystals for a number of compounds.[38]

V. Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q, a Bruker AM-250, or a Varian Unity 400 as noted. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at 25 °C. Mass spectra were recorded on a VG Masslab12-250 and on a a Jeol JMS-HX/HX110A tandem mass spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument with a 5972 series detector, using a 30 m × 0.25 mm HP.5 MS (0.25 μm,

(38) Deussen, H. J., Thorup, N.; Boutton, C.; Geisler. T.; Persoons, A.; Bjørnholm, T.; Manuscript in preparation.

cross-linked 5% phenyl methyl silicone) column. IR spectra were recorded on a Perkin-Elmer FT-IR1760X spectrometer. Elemental analyses were performed at the Microanalysis Laboratory at the University of Copenhagen. Melting points were measured on a Büchi apparatus or on a homemade heating stage and are corrected. All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. THF was distilled under N_2 from Na/benzophenone, and DMF and DME were distilled from CaH_2. Dry acetone, CH_2Cl_2, and chloroform were of HPLC grade as well as all solvents used for spectrophotometry. K_2CO_3 and NaI were dried at 150 °C for one week prior to use. Silica and TLC plates were from Merck: Kieselgel 60, 0.063−0.200 mm, 70−230 mesh ASTM, and DC-Aluminiumfolien Kieselgel 60 F_{254}, $d = 0.2$ mm. The optical purity of the closed BN dimers (type b) was tested by ^{1}H NMR (400MHz) in the presence of the chiral alcohol (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol ((*R*)-(−)-TFAE from aldrich): the methylene hydrogen signals of racemic 9,14-dibromodinaphtho[2,1-*d*:1′,2′-*f*][1,3]-dioxepin (**4b**) were split 4−5 Hz due to the diastereomer interaction with a large excess of (*R*)-(−)-TFAE. Only one optical isomer was found for all compounds tested.

(*S*)-2,2′-Diethoxy-1,1′-binaphthyl (2). A mixture of 14.32 g of (*S*)-2,2′-dihydroxy-1,1′-binaphthyl (**1**) (0.05 mol), 32.69 g of bromoethane (0.30 mol), 28.0 g of dry potassium carbonate, and a catalytic amount of NaI in 75 mL of dry acetone was stirred magnetically and refluxed under anhydrous conditions ($CaCl_2$ tube) until the reaction was judged to be complete as monitored by TLC (usually 2−3 days). After cooling the reaction mixture was poured into water and extracted 3× with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, and the solvent was removed in vacuo after filtration. The remaining oil was recrystallized from ligroin (80/110 °C) to give 16.20 g (95%) of white needles after washing with light petroleum ether and drying in air: mp 139 °C; $[\alpha]^{25}_D = -85°$ ($c = 0.2$, $CHCl_3$); MS/FAB$^+$ *m*/*z* 343 (MH^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, 6H), 4.04 (m, 4H), 7.13 (br d, $J = 8$Hz, 2H), 7.20 (ddd, $J = 7$, 8, 1.5 Hz, 2H), 7.30 (ddd, $J = 7$, 8, 1.5 Hz, 2H), 7.42 (d, $J = 9$ Hz, 2H), 7.85 (d, $J = 8$ Hz, 2H), 7.93 (d, $J = 9$ Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.88, 65.10, 115.77, 120.58, 123.31, 125.40, 125.93, 127.68, 128.97, 129.15, 134.08, 154.22. Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.10; H, 6.46.

(*S*)-6,6′-Dibromo-2,2′-diethoxy-1,1′-binaphthyl (4a). A 17.2 g sample of (*S*)-2,2′-diethoxy-1,1′-binaphthyl (**2**) (0.05 mol) was dissolved in 150 mL of CH_2Cl_2 and stirred at 0 °C (ice bath). A 5.64 mL sample of bromine (0.11 mol) was added in one portion with stirring and a stream of nitrogen bubbling through the solution to remove the evolving HBr. The reaction mixture was stirred for an additional 5 h while the flask was allowed to warm to rt. The nitrogen flow was stopped and the yellow solution allowed to stand overnight. A 100 mL sample of 10% $NaHSO_3$ solution was added with vigorous stirring to destroy excess bromine. The colorless organic layer was separated, washed with 10% $NaHSO_3$ solution and water, and dried over $MgSO_4$ and the solvent removed in vacuo after filtration. The remaining oil was recrystallized from ligroin (80/110 °C) to give 22.27 g (89%) of fine white needles after washing with light petroleum ether and drying in air: mp 161−162 °C; $[\alpha]^{25}_D = -17.7°$ ($c = 0.2$, $CHCl_3$); MS/FAB$^+$ *m*/*z* 499 (MH^+), 501 (MH^+), 503 (MH^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, 6H), 4.03 (m, 4H), 6.95 (d, 2H), 7.26 (dd, $J = 2.0$, 9 Hz, 2H), 7.42 (d, 2H), 7.84 (d, $J = 9$ Hz, 2H), 8.00 (d, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.89, 64.96, 116.35, 117.16, 119.93, 126.98, 128.32, 129.34, 129.68, 130.11, 132.41, 154.42. Anal. Calcd for $C_{24}H_{20}Br_2O_2$: C, 57.63; H, 4.03; Br, 31.95. Found: C, 57.45; H, 4.01; Br, 31.75.

(*S*)-9,14-Dibromodinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin (4b). A mixture of 15.10 g of (*S*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl (**3a**) (34.0 mmol), 17.73 g of dibromomethane (102.0 mmol), 30.0 g of dry potassium carbonate, and a catalytic amount of NaI in 100 mL of dry acetone was stirred magnetically and refluxed under anhydrous conditions ($CaCl_2$ tube) until the reaction was judged to be complete as monitored by TLC (usually 40 h). After cooling, the reaction mixture was poured into water and extracted 3× with ether. The combined organic phases were washed with water. After drying over $MgSO_4$, the yellow solution was stirred with charcoal, and the solvent was removed in vacuo after filtration. The obtained white powder was washed with a small volume of cold MeOH and recrystallized from CH_2Cl_2/light petroleum ether. The fine crystals that formed in the freezer were filtered off using a glass frit. The filtrate was concentrated, and a second crop was obtained after cooling. The combined batches were dried under reduced pressure, giving 12.25 g (79%) of **4b**: mp 213−214 °C (ether); $[\alpha]^{25}_D = +600°$ ($c = 0.1$, $CHCl_3$); MS/EI *m*/*z* 456 (M^+); ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.68 (s, 2H), 7.30 (d, 2H), 7.38 (dd, $J = 1.9$, 9 Hz, 2H), 7.49 (d, 2H), 7.88 (d, $J = 9$ Hz, 2H), 8.09 (d, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 103.05, 119.05, 122.06, 125.75, 128.17, 129.48, 130.29, 130.38, 132.79, 151.45. Anal. Calcd for $C_{21}H_{12}Br_2O_2$: C, 55.30; H, 2.65; Br, 35.04. Found: C, 55.43; H, 2.74; Br, 35.14.

6-Bromo-2-butoxynaphthalene (4c). A mixture of 5.20 g of 6-bromo-2-naphthol (**3c**) (23.31 mmol), 0.95 g of sodium hydroxide (23.75 mmol) dissolved in a small volume of water, and 3.51 g of *n*-bromobutane (25.61 mmol) in THF was refluxed overnight. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and washed with water and brine. After drying over $MgSO_4$ and filtration, the solution was filtered through a pad of silica, and the solvent was removed in vacuo. The crude product was recrystallized from EtOH to give 6.03 g (93%) of a white solid: mp 56−57 °C; MS/EI *m*/*z* 278 (M^+); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.00 (t, $J = 7$ Hz, 3H), 1.52 (m, 2H), 1.82 (m, 2H), 4.05 (t, 2H), 7.08 (d, 1H), 7.15 (dd, $J = 2.4$, 9 Hz, 1H), 7.47 (dd, 1H), 7.58 (d, 1H), 7.63 (d, 1H), 7.90 (d, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.75, 19.19, 31.14, 67.67, 106.40, 116.75, 119.96, 128.22, 128.28, 129.41, 129.51, 129.82, 133.00, 157.33. Anal. Calcd for $C_{14}H_{14}BrO$: C, 60.23; H, 5.42; Br, 28.63. Found: C, 60.26; H, 5.32; Br, 28.62.

(*S*)-2,2′-Diethoxy[1,1′-binaphthyl]-6,6′-dicarbaldehyde (5a). A 5.0 g sample of (*S*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl (**4a**) (10.0 mmol) was dissolved in 120 mL of dry THF under an argon atmosphere. The magnetically stirred solution was cooled to −78 °C, and 17.6 mL of *n*-BuLi in *n*-hexane (2.5 M) (44.0 mmol) was added at such a rate in order not to allow the temperature to exceed −70 °C. After 5−6 h of stirring at this temperature, 5.1 mL of dry *N*,*N*-dimethylformamide (65.9 mmol) was added so that the temperature remained below −50 °C. After stirring for 45 min at this temperature, the reaction mixture was poured into HCl/ice (pH < 1) under vigorous stirring. It was allowed to reach rt overnight and extracted 3× with CH_2Cl_2. The combined organic phases were washed twice with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure after filtration to give an oil. The oil was recrystallized from a small volume of AcOEt/ligroin (60/80 °C). The white crystals that formed overnight in the freezer were filtered off and washed twice with light petroleum ether and dried in air to give 3.55 g of **5a** (89%). In order to obtain an analytical sample, the oil was submitted to chromatography on silica using a CH_2Cl_2 / AcOEt gradient as eluting agent prior to crystallization: mp 152 °C; $[\alpha]^{25}_D = +114°$ ($CHCl_3$, $c = 0.01$); MS /EI *m*/*z* 398 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 250 (52 800), 274 (57 500), 323 (24 300); IR (KBr) 1688 (s, −C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, 6H), 4.12 (m, 4H), 7.18 (d, 2H), 7.51 (d, 2H), 7.69 (dd, $J = 1.7$, 9 Hz, 2H), 8.13 (d, $J = 9$ Hz, 2H), 8.37 (d, 2H), 10.10 (s, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 14.62, 64.64, 115.50, 119.58, 123.12, 125.94, 127.88, 131.36, 132.05, 134.86, 137.15, 156.84, 191.85. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.42; H, 5.58.

(*S*)-Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-dicarbaldehyde (5b). A 4.56 g sample of (*S*)-9,14-dibromodinaphtho[2,1-*d*:1′,2′-*f*][1,3]-dioxepin (**4b**) (10.0 mmol) was dissolved in 100 mL of dry THF under an argon atmosphere. The magnetically stirred solution was cooled to −78 °C, and 17.6 mL of *n*-BuLi in *n*-hexane (2.5 M) (44.0 mmol) was added at such a rate so as not to allow the temperature to exceed −70 °C. After 5−6 h of stirring at this temperature, 5.1 mL of dry *N*,*N*-dimethylformamide (65.9 mmol) was added so that the temperature remained below −50 °C. After stirring for 45 min at this temperature, the reaction mixture was poured into HCl/ice (pH < 1) under vigorous stirring. It was allowed to reach rt and extracted 3× with CH_2Cl_2. The combined organic phases were washed twice with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure after filtration. The obtained residue was recrystallized from CH_2Cl_2/light petroleum ether and dried under reduced pressure to give 3.18 g (90%) of a white compound: mp 174−179 °C; $[\alpha]^{25}_D = +1045°$ ($c = 0.02$, $CHCl_3$); MS/FAB$^+$ *m*/*z* 355 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 251

(68 100), 278 (28 900); IR (KBr) 1697 (s, C═O) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.75 (s, 2H), 7.50 (d, 2H), 7.60 (d, 2H), 7.78 (dd, J = 1.7, 9 Hz, 2H), 8.18 (d, J = 9 Hz, 2H), 8.46 (d, 2H), 10.17 (s, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 103.21, 122.26, 123.38, 125.91, 127.41, 130.94, 132.29, 133.34, 134.51, 135.08, 153.83, 191.66. Anal. Calcd for $C_{23}H_{14}O_4$: C, 77.96; H, 3.98. Found: C, 77.81; H, 4.16.

6-Butoxynaphthalene-2-carbaldehyde (5c). A 4.03 g sample of 6-bromo-2-butoxynaphthalene (**4c**) (14.5 mmol) was dissolved in 150 mL of dry THF under an argon atmosphere. The magnetically stirred solution was cooled to −78 °C, and 6.4 mL of a solution of *n*-BuLi in *n*-hexane (2.5 M) (16.0 mmol) was added at such a rate so as not to allow the temperature to exceed −60 °C. After 6 h of stirring at this temperature, 3.0 mL of dry *N*,*N*-dimethylformamide (38.7 mmol) was added so that the temperature remained below −50 °C. After stirring for 30 min at this temperature, the reaction mixture was allowed to reach rt within 30 min. It was poured into HCl/ice (pH < 1) and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure after filtration. The compound was redissolved in 100 mL of ether and shaken with 100 mL of $NaHSO_3$ solution (40%) for 4 days. The water phase was washed 3× with ether, and the bisulfite addition product was destroyed by treatment with 25% sulfuric acid under reflux. After cooling, the mixture was extracted with ether. The combined organic phases were washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure after filtration. Recrystallization from EtOH gave 2.92 g (88%) of a white compound: mp 37 °C; MS/EI *m*/*z* 228 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 265 (28 100), 315 (16 700); IR (KBr) 1693 (s, C═O) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.00 (t, J = 7 Hz, 3H), 1.54 (m, 2H), 1.83 (m, 2H), 4.10 (t, 2H), 7.15 (d, J = 2.2 Hz, 1H), 7.21 (dd, J = 2.5, 9 Hz, 1H), 7.76 (d, 1H), 7.86 (d, 1H), 7.90 (dd, 1H), 8.22 (br s, 1H), 10.07 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.72, 19.15, 31.05, 67.84, 106.69, 120.12, 123.45, 127.57, 127.71, 130.93, 132.13, 134.14, 138.23, 159.73, 191.89. Anal. Calcd for $C_{15}H_{15}O_2$: C, 78.92; H, 7.07. Found: C, 78.90; H, 7.15.

(*S*)-3,3′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)bis(2-cyanopropenenitrile) (6a). A 800 mg sample of (*S*)-2,2′-diethoxy[1,1′-binaphthyl]-6,6′-dicarbaldehyde (**5a**) (2.0 mmol) and 291 mg of malononitrile (4.4 mmol) were dissolved in 40 mL of dry CH_2Cl_2. Two drops of piperidine were added, and the reaction mixture was refluxed under anhydrous conditions ($CaCl_2$ tube) for 20 h. The CH_2Cl_2 was removed in vacuo. After chromatography on silica gel (l = 11 cm, i.d. = 4 cm) using CH_2Cl_2 as an eluent, a yellow solid was obtained which was recrystallized from absolute ethanol (freezer). The yellow crystals were filtered off and washed twice with methanol, yielding 811 mg (82%): mp 225 °C; $[\alpha]^{25}_D$ = +1157° (c = 0.01, $CHCl_3$); MS/EI *m*/*z* 494 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 313 (31 500), 371 (51 500); IR (KBr) 2227 (s, CN), 1617 (s, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, 6H), 4.15 (q, 4H), 7.16 (d, 2H), 7.52 (d, 2H), 7.83 (s, 2H), 7.83 (dd, J = 1.8, 9 Hz, 2H), 8.09 (d, 2H), 8.34 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.63, 64.67, 80.31, 113.06, 114.22, 115.77, 118.99, 124.72, 126.35, 127.85, 131.97, 135.03, 136.63, 157.65, 159.28. Anal. Calcd for $C_{32}H_{22}N_4O_2$: C, 77.72; H, 4.48; N, 11.33. Found: C, 77.56; H, 4.48; N, 11.12.

(*S*)-3,3′-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-diyl)bis(2-cyanopropenenitrile) (6b). A mixture of 909 mg of (*S*)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3] dioxepin-9,14-dicarbaldehyde (**5b**) (2.57 mmol), 374 mg of malononitrile (5.66 mmol), and a catalytic amount of piperidine, in 50 mL of CH_2Cl_2, was refluxed under anhydrous conditions ($CaCl_2$ tube) for 39 h. The solvent was removed under reduced pressure. Column chromatography on silica (l = 12 cm, i.d. = 4 cm) using CH_2Cl_2 as eluent gave a yellow solid. The solid was dissolved in small volume of CH_2Cl_2, and petroleum ether was added. The precipitate was collected using a glass frit and dried under reduced pressure, giving 820 mg (71%) of a yellow solid: mp 233 °C; $[\alpha]^{25}_D$ = +1845° (c = 0.01, $CHCl_3$); MS/FAB$^+$ *m*/*z* 451 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 270 (25 300), 287 (32 000), 305 (33 700), 339 (50 300); IR (KBr) 2228 (s, CN), 1617 (s, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (s, 2H), 7.48 (d, 2H), 7.62 (d, 2H), 7.90 (dd, J = 1.9, 9 Hz, 2H), 7.90 (s, 2H), 8.15 (d, J = 9 Hz, 2H), 8.44 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 82.58, 103.37, 112.59, 113.70, 123.00, 124.87, 125.51, 127.68, 127.87, 130.88, 132.58, 134.38, 134.53, 154.56, 158.82. Anal. Calcd for $C_{29}H_{14}N_4O_2$: C, 77.33; H, 3.13; N, 12.44. Found: C, 77.27; H, 3.12; N, 12.59.

3-(6-Butoxy-2-naphthyl)-2-cyanopropenenitrile (6c). A 2.92 g sample of 6-butoxy-naphthalene-2-carbaldehyde (**5c**) (12.8 mmol) and 0.90 g of malononitrile (13.6 mmol) were dissolved in 100 mL of dry CH_2Cl_2. One drop of piperidine was added, and the reaction mixture was refluxed under anhydrous conditions ($CaCl_2$ tube) for 3 h. The CH_2Cl_2 was removed in vacuo, and the yellow compound was recrystallized from ethanol to give nice yellow needles. The mother liquid was concentrated to give a second crop: total yield 2.94 g (83%); mp 148 °C; MS/EI *m*/*z* 276 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 266 (15 200), 287 (14 400), 297 (17 900), 397 (30 100); IR (KBr) 2225 (s, CN) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.02 (t, J = 7 Hz, 3H), 1.56 (m, 2H), 1.86 (m, 2H), 4.12 (t, 2H), 7.15 (d, J = 2.3 Hz, 1H), 7.23 (dd, J = 2.5, 9 Hz, 1H), 7.78 (d, 1H), 7.80 (s, 1H), 7.82 (d, 1H), 8.04 (dd, 1H), 8.17 (d, J = 1.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.71, 19.14, 30.40, 68.04, 106.70, 113.16, 114.27, 120.82, 124.86, 126.24, 127.74, 128.03, 131.20, 134.36, 137.89, 159.46, 160.60. Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.23; H, 5.84; N, 10.13. Found: C, 78.07; H, 5.83; N, 9.96.

Diethyl (*S*)-(*E*,*E*)-3,3′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)bis-(2-cyanopropenate) (7a). A 800 mg sample of (*S*)-2,2′-diethoxy[1,1′-binaphthyl]-6,6′-dicarbaldehyde (**5a**) (2.0 mmol) and 498 mg of ethyl cyanoacetate (4.4 mmol) were dissolved in 40 mL of dry $CHCl_3$. Two drops of piperidine were added, and the reaction mixture was refluxed (Dean Stark trap) under anhydrous conditions ($CaCl_2$ tube) for 48 h. The $CHCl_3$ was removed in vacuo. The remaining oil was dissolved in a small volume of boiling absolute ethanol, and the solution was put in a freezer overnight. The light yellow crystals formed were filtered off and washed twice with ethanol and twice with methanol, giving 824 mg (70%) of **7a**: mp 168−169 °C; $[\alpha]^{25}_D$ = +695° (c = 0.01, $CHCl_3$); MS/EI *m*/*z* 588 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 265 (24 000), 306 (45 300), 359 (39 400), 392 (39 100); IR (KBr) 2222 (w, CN), 1724 (s, C═O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, 6H), 1.39 (t, 6H), 4.13 (m, 4H), 4.38 (q, 4H), 7.17 (d, 2H), 7.49 (d, 2H), 7.91 (dd, J = 1.8, 9 Hz, 2H), 8.08 (d, J = 9 Hz, 2H), 8.35 (s, 2H), 8.46 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.11, 14.70, 62.43, 64.70, 101.01, 115.63, 115.92, 119.26, 125.91, 126.08, 126.73, 128.17, 131.46, 134.49, 136.19, 154.83, 156.97, 162.87. Anal. Calcd for $C_{36}H_{32}N_2O_6$: C, 73.45; H, 5.48; N, 4.76. Found: C, 73.44; H, 5.53; N, 4.82.

Diethyl (*S*)-(*E*,*E*)-3,3′-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-diyl)bis(2-cyanopropenate) (7b). A mixture of 770 mg of (*S*)-dinaphtho[2,1-*d*:1′,2′-*f*] [1,3]dioxepin-9,14-dicarbaldehyde (**5b**) (2.17 mmol), 540 mg of ethyl cyanoacetate (4.77 mmol), and a catalytic amount of piperidine in 40 mL of $CHCl_3$ was refluxed (Dean Stark trap) under anhydrous conditions ($CaCl_2$ tube) for 51 h. The mixture was filtered through a pad of silica, and the solvent was removed under reduced pressure. Recrystallization from EtOH gave 888 mg (75%) of a bright yellow solid: mp 257 °C; $[\alpha]^{25}_D$ = +1365° (c= 0.01, $CHCl_3$); MS/FAB$^+$ *m*/*z* 545 (MH^+)l UV−vis ($CHCl_3$) λ_{max} (ϵ) = 283 (34 100), 323 (48 800)l IR (KBr) 2223 (s, CN), 1724 (s, C═O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (t, 6H), 4.41 (q, J = 7 Hz, 4H), 5.75 (s, 2H), 7.51 (d, 2H), 7.58 (d, 2H), 7.98 (dd, J = 1.9, 9 Hz, 2H), 8.13 (d, J = 9 Hz, 2H), 8.39 (s, 2H), 8.56 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.07, 62.64, 102.97, 103.29, 115.50, 122.43, 125.61, 126.12, 127.45, 128.39, 131.13, 132.21, 134.02, 153.88, 154.13, 162.45. Anal. Calcd for $C_{33}H_{24}N_2O_6$: C, 72.79; H, 4.44; N, 5.14. Found: C, 73.06; H, 4.26; N, 5.02.

Ethyl (*E*)-3-(6-Butoxy-2-naphthyl)-2-cyanopropenate (7c). A 1.50 g sample of 6-butoxynaphthalene-2-carbaldehyde (**5c**) (6.6 mmol) and 0.96 g of ethyl cyanoacetate (8.5 mmol) were dissolved in 30 mL of dry CH_2Cl_2. One drop of piperidine was added, and the reaction mixture was refluxed under anhydrous conditions ($CaCl_2$ tube) for 3 h. The CH_2Cl_2 was removed in vacuo, and the yellow compound was recrystallized from ethanol. The mother liquid was concentrated to give a second crop: total yield 1.88 g (88%); mp 115 °C; MS/EI *m*/*z* 323 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 263 (14 800), 284 (15 200), 293 (17 100), 379 (24 100); IR (KBr) 2220 (s, CN), 1713 (s, C═O), 1582 (s, C═C), 980 (m, ═C−H_{trans}) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.01 (t, J = 7 Hz, 3H), 1.41 (t, J = 7 Hz, 3H), 1.54 (m, 2H), 1.83 (m, 2H), 4.11 (t, 2H), 4.39 (q, 2H), 7.13 (d, J = 2.3 Hz, 1H), 7.20 (dd,

ArH, 1H), 7.76 (d, ArH, 1H), 7.82 (d, ArH, 1H), 8.16 (dd, ArH, J = 1.8, 9 Hz, 1H), 8.29 (br s, ArH, 1H), 8.34 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.72, 14.11, 31.05, 62.41, 67.90, 100.73, 106.55, 115.99, 120.31, 125.88, 126.69, 127.64, 127.97, 130.91, 134.12, 137.26, 154.95, 159.87, 162.87. Anal. Calcd for $C_{18}H_{16}N_2O$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.01; H, 6.47; N, 4.41.

(*S*)-(*E*,*E*)-3,3′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)dipropenenitrile (8a). A 1019 mg sample of (*S*)-2,2′-diethoxy[1,1′-binaphthyl]6,6′-dicarbaldehyde (**5a**) (2.56 mmol) and 1087 mg of diethyl cyanomethylphosphonate (6.14 mmol) were dissolved in 90 mL of dry DME under a nitrogen atmosphere. A 300 mg portion of sodium hydride (80% in mineral oil) (10.0 mmol) was added in small portions at 0 °C to the magnetically stirred mixture. The reaction mixture was slowly allowed to reach rt and stirred for 12 h. The mixture was hydrolyzed with 300 mL of dilute hydrochloric acid. The precipitate that formed was collected using a glass frit and washed thoroughly with water. After drying in air, it was recrystallized from a small volume of EtOH (freezer) to give 603 mg (53%) of **8a**: mp 155−158 °C; $[\alpha]^{25}_D$ = +455° (c = 0.01, $CHCl_3$); MS/FAB$^+$ m/z 445 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 260 (39 500), 288 (58 200), 334 (41 000); IR (KBr) 2215 (s, CN), 1616 (s, C═C), 966 (m, ═CH_{trans}) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, J = 7 Hz, 6H), 4.08 (m, 4H), 5.84 (d, J_{trans} = 16.5 Hz, 2H), 7.08 (d, 2H), 7.28 (dd, J = 1.8, 9 Hz, 2H), 7.45 (d, 2H), 7.51 (d, J_{trans} = 16.5 Hz, 2H), 7.88 (d, 2H), 7.98 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.76, 64.79, 94.87, 115.86, 118.45, 119.74, 122.47, 126.13, 128.44, 128.68, 129.91, 130.35, 135.18, 150.46, 155.83. Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.31; H, 5.68; N, 5.88.

(*S*)-(*E*,*E*)-3,3′-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-diyl)-dipropenenitrile (8b). A 1000 mg sample of (*S*)-dinaphtho)[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-dicarbaldehyde (**4b**) (2.82 mmol) and 1199 mg of diethyl (cyanomethyl)phosphonate (6.77 mmol) were dissolved in 40 mL of dry DME under a nitrogen atmosphere. A 305 mg portion of sodium hydride (80% in mineral oil) (10.17 mmol) was added in small portions at 0 °C to the magnetically stirred mixture. The reaction mixture was slowly allowed to reach rt and stirred for 24 h. It was hydrolyzed with 300 mL of dilute hydrochloric acid. The precipitate that formed was collected using a glass frit and washed thoroughly with water. After drying in air, the compound was dissolved in CH_2Cl_2 and filtered through a pad of silica. After evaporation of most of the solvent in vacuo, light petroleum ether was added, and the white precipitate was filtered off (glass frit) and dried in high vacuum to give 655 mg (58%) of **8b**: mp 324 °C; $[\alpha]^{25}_D$ = +1379° (c = 0.01, $CHCl_3$); MS/FAB$^+$ m/z 401 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 268 (71 200), 308 (58 200), 362 (6800); IR (KBr) 2216 (s, CN), 1620 (s, C═C), 963 (s, ═C−H_{trans}) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (s, 2H), 5.94 (d, J_{trans} = 16.5 Hz, 2H), 7.39 (dd, J = 1.8, 9 Hz, 2H), 7.43 (d, 2H), 7.54 (d, 2H), 7.55 (d, J_{trans} = 16.5 Hz, 2H), 7.96 (d, 2H), 8.02 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 96.64, 103.12, 118.10, 122.34, 122.61, 125.89, 127.59, 130.06, 130.36, 131.41, 131.48, 133.16, 149.95, 152.89. Anal. Calcd for $C_{27}H_{16}N_2O_2$: C, 80.99; H, 4.03; N, 7.00. Found: C, 80.79; H, 4.15; N, 6.71.

Diethyl (4-Nitrobenzyl)phosphonate. A mixture of 25.0 g of 4-nitrobenzyl bromide (Aldrich) (0.12 mol) and 39.88 g of triethyl phosphite (0.24 mol) was slowly heated over a 3 h period to 150 °C, and this temperature was maintained for 24 h. The ethyl bromide evolved was trapped with a condenser and a receiver cooled in an ice bath. The residual oil was fractionally distilled under high vacuum to give 23.4 g (71%) of an oil: bp 160−161 °C, 0.03 mmHg (lit.[14] bp 148−153 °C, 0.1 mmHg); GC 100%; MS/EI m/z 273(M^+); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.28 (t, J = 7 Hz, 6H), 3.32 (d, $J_{P,H}$ = 22.6 Hz, 2H), 4.08 (m, 4H), 7.50 (dd, 2H), 8.18 (dd, 2H); ^{31}P NMR (36.4 MHz, $CDCl_3$) δ 23, 79 (s).

(*S*)-(*E*,*E*)-2,2′-Diethoxy-6,6′-bis(4-nitrostyryl)-1,1′-binaphthyl (9a). A 882 mg sample of diethyl (4-nitrobenzyl)phosphonate (3.23 mmol) was dissolved in 50 mL of dry dimethoxyethane under an inert atmosphere. A 250 mg portion of sodium hydride (80% in mineral oil) (8.33 mmol) was added at 0 °C, and the suspension was stirred magnetically for 30 min at this temperature. To the suspension was added 500 mg (*S*)-2,2′-diethoxy-1,1′[binaphthyl]-6,6′-dicarbaldehyde (**5a)** (1.25 mmol) dissolved in 20 mL of dry dimethoxyethane, and the reaction mixture was allowed to warm slowly to rt while being stirred magnetically for 20 h. The mixture was hydrolyzed with 300 mL of dilute HCl. The precipitate that formed was collected by filtration (glass frit) and washed thoroughly with water. The obtained solid was dried, dissolved in CH_2Cl_2, and filtered through a pad of silica (1 cm). After evaporation of most of the solvent under reduced pressure, recrystallization from CH_2Cl_2/ether gave 700 mg (88%) of fine orange crystals: mp 273 °C; $[\alpha]^{25}_D$ = +776° (c = 0.002, $CHCl_3$); MS/FAB$^+$ m/z 637 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 253 (45 500), 297 (38 200), 397 (54 500); IR (KBr) 1618 (m, C═C), 966 (m, CH═CH_{trans}), 1515 (s, NO), 1338 (s, NO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, J = 7 Hz, 6H), 4.08 (m, 4H), 7.13 (d, J_{trans} = 16.3 Hz, 2H), 7.15 (d, 2H), 7.40 (d, J_{trans} = 16.3 Hz, 2H), 7.45 (d, 2H), 7.48 (dd, J = 1.7, 9 Hz, 2H), 7.62 (br d, 4H), 7.94 (d, 2H), 7.97 (d, J = 9 Hz, 2H), 8.20 (br d, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.87, 64.97, 115.92, 120.25, 123.49, 124.05, 125.38, 125.99, 126.57, 128.05, 129.05, 129.59, 131.29, 133.41, 134.20, 144.01, 146.48, 155.01. Anal. Calcd for $C_{40}H_{32}N_2O_6$: C, 75.46; H, 5.07; N, 4.40. Found: C, 75.29; H, 5.11; N, 4.20.

(*S*)-(*E*,*E*)-9,14-Bis[2-(methylsulfonyl)vinyl]dinaphtho[2,1-*d*:1′,2′-*f*] [1,3]dioxepin (10b). A 983 mg sample of diethyl [methylsulfonyl)-methyl]phosphonate (4.27 mmol) and 630 mg of (*S*)-dinaphtho)[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-dicarbaldehyde (**4b**) (1.78 mmol) were dissolved in dry DME (60 mL) under a nitrogen atmosphere. A 384 mg sample of sodium hydride (12.8 mmol) was added in portions at 0 °C to the magnetically stirred mixture. The reaction mixture was slowly allowed to reach rt and stirred for 3 days. The mixture was cautiously hydrolyzed with dilute hydrochloric acid (600 mL) and extracted 3× with CH_2Cl_2. The combined organic phases were washed with water and dried over $MgSO_4$, and most of the solvent was removed in vacuo after filtration. Ether was added, and the white precipitate that formed was collected using a glass frit and washed with a small volume of ether and dried in high vacuum to give 514 mg (57%) of a white powder: mp 206 °C dec; $[\alpha]^{25}_D$ = +980° (c = 0.01, $CHCl_3$); MS/FAB$^+$ m/z 507 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 263 (65 900), 300 (42 100); IR (KBr) 1620 (m, C═C), 1310 (s, −SO_2−), 1133 (s, −SO_2−), 970 (m, ═C−H_{trans}) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 6H), 5.73 (s, 2H), 6.98 (d, J_{trans} = 15.4 Hz, 2H), 7.43 (dd, J = 1.7, 9 Hz, 2H), 7.46 (d, 2H), 7.56 (d, 2H), 7.79 (d, J_{trans} = 15.4 Hz, 2H), 8.05 (d, J = 9 Hz, 2H), 8.07 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 43.27, 103.22, 122.22, 123.59, 125.78, 126.37, 127.51, 128.80, 131.35, 131.40, 133.15, 143.37, 152.86. Anal. Calcd for $C_{27}H_{22}O_3S_2$: C, 64.02; H, 4.38; S, 12.66. Found: C, 63.95; H, 4.31; S, 11.96.

(*S*)-(*E*,*E*)-3,3′-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-diyl) dipropenal (11b). A 610 mg sample of sodium hydride (80% suspension in mineral oil) (20.32 mmol) was added in portions to a mixture of 6.32 g of diethyl [2-(cyclohexylamino)vinyl]phosphonate (GC 84%) (20.32 mmol) and 3.00 g of (*S*)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-dicarbaldehyde (**4b**) (8.47 mmol) dissolved in 60 mL of dry dimethoxyethane under an inert atmosphere at 0 °C. The suspension was slowly allowed to reach rt and stirred for 24 h. The mixture was cautiously hydrolyzed with 500 mL of water and extracted 3× with CH_2Cl_2. The solvent of the combined organic phases was evaporated in vacuo. An oil was obtained, which was redissolved in 100 mL of CH_2Cl_2 and shaken with a 200 mL acetic acid−sodium acetate buffer (1 M) for 24 h. The organic phase was separated, washed 2× with 10% $KHCO_3$ solution and water, and dried over $MgSO_4$ and the solvent removed in vacuo after filtration. The obtained solid was purified by column chromatography on silica (l = 11 cm, i.d. = 4 cm) using a mixture of ligroin (60:80)/AcOEt (1:1, v:v) as eluent to give 2.10 g (61%) of a solid. An analytical sample was obtained after drying at 100 °C overnight: mp 152−155 °C; $[\alpha]_D$ = +1444° (c=0.02, $CHCl_3$); MS/EI m/z 406 (M^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 275 (47 500), 316 (52 300); IR (KBr) 1677 (s, C═O), 1621 (s, C═C), 978 (s, ═C−H_{trans}) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 2H), 6.80 (dd, J_{trans} = 15.9 Hz, 2H), 7.49 (d, 2H), 7.52 (dd, J = 1.8 Hz, 2H), 7.55 (d, 2H), 7.64 (d, J_{trans} = 15.9 Hz, 2H), 8.06 (d, J = 9 Hz, 2H), 8.11 (d, 2H), 9.77 (d, J = 8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 103.19, 122.08, 123.92, 125.85, 127.42, 128.79, 130.83, 130.83, 131.35, 131.50, 133.17, 151.91, 152.78, 193.34. Anal. Calcd for $C_{27}H_{18}O_4$: C, 79.79; H, 4.46. Found: C, 79.47; H, 4.48.

(*S*)-(*E*,*E*)-5,5′-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-diyl)bis-(2-cyanopenta-2,4-dienenitrile) (12b). A 519 mg sample of (*S*)-(*E*,*E*)-

3,3′-(dinaphtho[2,1-*d*:1′,2′-*f*][1,3]dioxepin-9,14-diyl)dipropenal (**11b**) (1.28 mmol) and 186 mg of malononitrile (2.82 mmol) were dissolved in 50 mL of dry CH_2Cl_2. A 7 mg portion of piperidine was added, and the reaction mixture was refluxed under anhydrous conditions ($CaCl_2$ tube) for 19 h. The CH_2Cl_2 was removed in vacuo. After chromatography on silica gel (l = 10 cm, i.d. = 4 cm) using CH_2Cl_2 as an eluent, the compound was dissolved in a small volume of CH_2Cl_2, and light petroleum ether was added. The precipitate was filtered off using a glass frit and dried under reduced pressure to give 420 mg (65%) of a bright orange powder: mp 185−187 °C; $[\alpha]^{25}_D = +3184°$ (c = 0.005, $CHCl_3$); MS/FAB$^+$ m/z 503 (MH^+); UV−vis ($CHCl_3$) λ_{max} (ϵ) = 313 (31 500), 371 (51 500); IR (KBr) 2226 (s, CN), 1603 (s, C═C), 980 (s, ═C−H_{trans}) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (s, 2H), 7.33 (dd, 2H), 7.44 (d, J_{trans} = 15.6 Hz, 2H), 7.46 (d, 2H), 7.56 (dd, J = 1.8, 9 Hz, 2H), 7.57 (d, 4H), 7.65 (d, J = 11.4 Hz, 2H), 8.07 (d, J = 9 Hz, 2H), 8.12 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 82.95, 103.28, 111.58, 113.40, 122.39, 122.62, 123.82, 125.83, 127.63, 130.84, 131.42, 131.49, 131.90, 133.48, 149.49, 153.31, 159.55. Anal. Calcd for $C_{33}H_{18}N_4O_2$: C, 78.87; H, 3.61; N, 11.15. Found: C, 78.75; H, 3.59; N, 11.17.

Acknowledgment. H.-J.D. thanks the Gottlieb Daimler- und Karl Benz-Stiftung for a Ph.D. Grant. E.H. is a research assistant and K.C. a senior research associate of the Belgian National Fund for Scientific Research. C.B. obtained a research grant from the Flemish Executive (IWT). We would like to express our gratitude to Professor E. W. Meijer for inspiring discussions. This work is partly supported by the Belgian Prime Minister's Office of Science Policy "InterUniversity Attraction pole in Supramolecular Chemistry and Catalysis" (Grant IUAP 16) and the Flemish Government's Grant GOA 95/1. We thank the Danish Material Research Program (MUP) for financial support.

JA960076O