New Chiral Bis(dipolar) 6,6′-Disubstituted Binaphthol Derivatives for Second-Order Nonlinear Optics

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Abstract: Several chiral molecules with C_2 symmetry derived from two geometries of the binaphthol (BN) system substituted with different acceptors have been synthesized in order to study the possibility of producing noncentrosymmetric crystals formed from these chiral structures. All the molecules possess two equal donor–acceptor (D–A) systems linked together to give a bis(dipolar) V-shaped system. The dihedral angle θ between the two connected D–A systems has been controlled by chemical methods; this leads to distinct changes in the optical spectra of the connected D–A chromophores, primarily changes caused by effective conjugation of the D–A system imposed by conformation constraints. The crystal structure of chiral (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarbaldehyde (**4a**) has been elucidated and indicates that the dipoles in the naphthyl moiety within the overall noncentrosymmetric crystal can cancel out exactly despite the noncentrosymmetry. The crystal structure of racemic 9,14-dicyanodinaphtho[2,1-d:1′,2′-f][1,3]-dioxepin (**2b**) was found to be centrosymmetric. The new compounds were investigated for second-harmonic generation (including BN derivatives reported earlier) by the Kurtz–Perry powder test to evaluate the second-order nonlinear optical (NLO) properties of polycrystalline samples. Although chirality ensures noncentrosymmetric crystals, only modest ($\approx$2-methyl-4-nitroaniline) or no nonlinearities were observed in the powder test. For a representative selection of the molecules, the first molecular hyperpolarizabilities β_z were shown to be very high (up to 888×10^{-30} esu for **14a**) by electric field induced second harmonic generation (EFISHG) measurements. Synthetic routes are reported for optically pure 6,6′-disubstituted-2,2′-diethoxy-1,1′-binaphthyls **2a**, **3a**, **6a**, **10a**, **11a**, **14a**, **15a** [acceptor = CN, SO_2CH_3, (*E*)-CH=CHSO$_2$CH$_3$, (*E*)-CH=CH(*p*-PhCN), (*E*)-CH=CH(*p*-PhSO$_2$CH$_3$), (*E*)-CH=CH(*p*-PhCH=C(CN)$_2$), (*E*)-CH=CHCH=C(CN)$_2$] and optically pure 9,14-disubstituted-dinaphtho[2,1-d:1′,2′-f][1,3]dioxepins **2b**, **3b**, **10b**, **11b**, **13b**, **14b**, **15b** [acceptor = CN (only racemic), SO_2CH_3, (*E*)-CH=CH(*p*-PhCN), (*E*)-CH=CH(*p*-PhSO$_2$CH$_3$), (*E*)-CH=CH(*p*-PhNO$_2$), (*E*)-CH=CH(*p*-PhCH=C(CN)$_2$), (*E*)-CH=CH-CH=C(CN)$_2$].

Keywords: atropisomerism · binaphthol derivatives · crystal structure · nonlinear optics · second-harmonic generation

Introduction

The field of nonlinear optics includes studies of second- and third-order nonlinear optical effects, such as electro-optic and harmonic generation.[1] Owing to their 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-generation telecommunication technologies and optical information processing and storage.[2]

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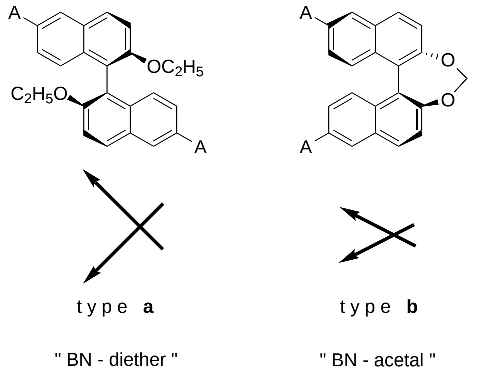
On the microscopic side, it is well established that the classical conjugated D–A-substituted organic molecules[2] and the more recent octopolar[3] molecules have high second-order molecular hyperpolarizabilities. However, for the observation of second-order nonlinear optical (NLO) phenomena from bulk materials, for example frequency doubling or electro-optic phase modulation, the material must be noncentrosymmetrically orientated. One of the strategies used to obtain noncentrosymmetric structures has explored the use of a chiral moiety attached to the nonlinear chromophore, since chiral molecules crystallize, a priori, in a noncentrosymmetric structure.[1,2a,b,f] If the NLO moiety and the chiral group are separated by a flexible σ bond, the donor–π–acceptor (D–π–A) units will still be able to align antiparallel. The noncentrosymmetry is hence limited to the chiral, linear optical part of the molecules.[2a,b,f,4] Still there are no 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.[5] Linking multiple units of a small chromophore together in larger macromolecular arrangements is among the new strategies investigated in NLO for the control of the alignment of the NLO chromophores on a molecular and a macroscopic level.[6]

We present the results concerning the generation of noncentrosymmmetric crystals by the use of bis(dipolar) molecules possessing two one-dimensional molecular units connected together to give a three-dimensional V-shaped molecular structure.[7] In the dimeric binaphthol (BN) system, types **a** and **b** (Figure 1) presented here, two monomers of 6-acceptor-substituted β-naphthol are connected at the 1,1′-positions. This leads to the 6,6′-diacceptor-substituted BN, a bis(dipolar) chiral molecule with C_2 symmetry possessing two charge-transfer units within a single molecule.[7c,d,e]

In the closed-bridge BN acetals (type **b**) the dipoles are forced into the closest possible proximity to each other, thereby minimizing the cancelation of dipole moments on a molecular level as the dihedral angle θ between the naphthol moieties is mainly determined by the conformational energy of the heterocyclic ring. In the open BNs (type **a**) the dihedral angle can vary depending on packing effects in crystals, solvent polarity, and temperature in solution, as well as on dipole–dipole interactions in general.[7e,8] For all these nonplanar molecules, the second-order molecular hyperpolarizability tensor has several significant tensor components. The model geometry of the coupled dipolar NLO units can be expressed in terms of the hyperpolarizabilities of the dipolar monomeric units and the dihedral angle between these monomers.[7e]



2 a , 2 b A = CN

3 a , 3 b A = SO_2CH_3

4 a , 4 b A = CHO

5 a , 5 b A = (*E*) CH=CHCN

6 a , 6 b A = (*E*) $CH=CHSO_2CH_3$

7 a , 7 b A = (*E*) CH=CHCHO

8 a , 8 b A = $CH=C(CN)_2$

9 a , 9 b A = (*E*) $CH=C(CN)(COOC_2H_5)$

10 a , 10 b A = (*E*) CH=CH(p-PhCN)

11 a , 11 b A = (*E*) $CH=CH(p\text{-}PhSO_2CH_3)$

12 a , 12 b A = (*E*) CH=CH(p-PhCHO)

13 a , 13 b A = (*E*) $CH=CH(p\text{-}PhNO_2)$

14 a , 14 b A = (*E*) $CH=CH(p\text{-}PhCHC(CN)_2)$

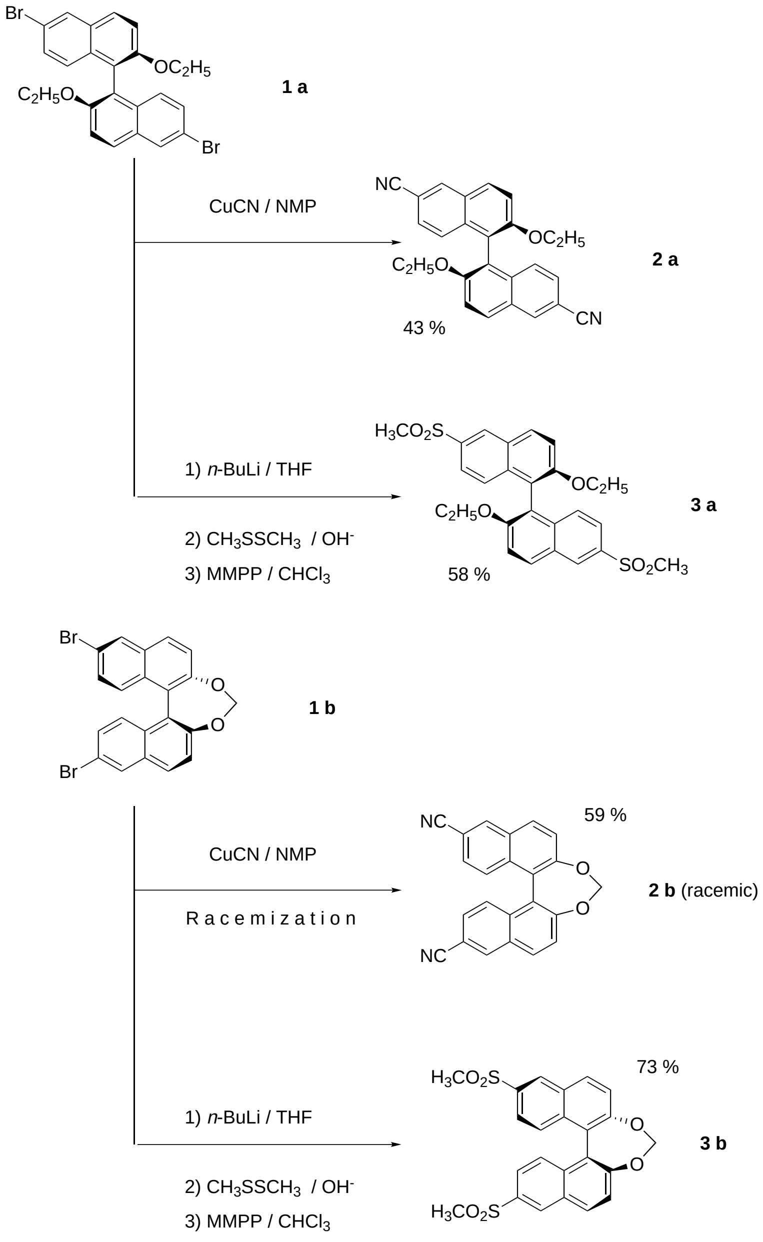
15 a , 15 b A = (*E*) $CH=CHCH=C(CN)_2$

Figure 1. General structures of the chiral bis(dipolar) binaphthol (BN) dimers (only **2b** racemic) and their dipole orientations.

In the case of chiral BNs presented here, π electrons instead of the usually proposed flexible σ bonds are involved in the induction of chirality. The introduction of chirality within the conjugated path could lead to a higher probability of obtaining active noncentrosymmetric crystals. Therefore, new chiral molecules based on this geometry (with strong acceptors and long conjugation lengths between donor and acceptor) were synthesized and the macroscopic susceptibilities $\chi^{(2)}$ of chiral **2a**,**b**–**15a**,**b** were estimated by the Kurtz–Perry powder test.[9] The microscopic hyperpolarizabilities (β_z) were additionally determined for the derivatives **10a**,**b**–**12a**,**b**, and **13b**, **14a**,**b**, **15a**,**b** by EFISHG measurements[10] and are shown together with some earlier results.[7e] For chiral **4a** (A=CHO) and racemic **2b** (A=CN) the crystallographic data were obtained by single-crystal X-ray analysis.

Results and Discussion

Synthesis: We have already reported the syntheses of the chiral compounds **1a**, **1b**, **4a**, **4b**, **5a**, **5b**, **6b**, **7a**,**b**–**9a**,**b**, **12a**, **12b**, **13b**, **14b**, **15a**, and **15b**.[7e,8c,11] Treatment of the dibromo compounds **1a** and **1b** with CuCN in boiling *N*-methylpyrrolidone at 202 °C for 5 h gave the nitriles **2a** and **2b** (Scheme 1).[12] Using optically pure **1b** as the starting compound, no optical rotation could be detected in the isolated compound **2b**. Thus complete racemization took



Scheme 1. Synthesis of **2a**, **3a**, **2b**, and **3b**.

place during the reaction. However, **2a** showed similar optical rotation to **1a**, indicating that racemization, if it took place, was only partial. Compounds **1a** and **1b** were lithiated as described in ref [7e]. The sulfenylation of the dilithium compounds with dimethyldisulfide[13] gave 6,6′-dimethylsulfides, which were not isolated. They were easily oxidized by means of hydrogenperoxide in acetic acid to give the corresponding sulfone **3b**, or by a large excess of magnesium monoperphthalate[14] in $CHCl_3$ to give **3a**. The use of the latter mild oxidant was preferable to that of H_2O_2 in glacial acetic acid for this compound, as the isolation of the product was made much easier (Scheme 1).

Compounds **6a, 10a**, **10b**, **11a**, **11b**, and **13a** were synthesized by the Horner–Emmons[15] reaction of the corresponding diethyl phosphonates in dimethoxyethane at room temperature with sodium hydride as a base. The phosphonates used were prepared according to known procedures.[7e,16] The configurations of the double bonds were established in all cases as (*E*) on the basis of the vinylic proton–proton coupling constants $J_{a,b}$. The aldehydes **7a**, **12a**, and **12b** were converted to the corresponding dicyanoethylene derivatives **14a**, **15a**, and **15b** by means of the Knoevenagel condensation[17] with malononitrile. The use of a catalytic amount of piperidine as a base in methylene chloride proved to be the best choice, as almost no side reactions could be traced on TLC. Furthermore, the use of the low-boiling methylene chloride ensured that optically purity was maintained. The mild conditions required rather long reaction times, which were necessary in order to obtain a quantitative conversion of the aldehydes. Thus the conjugation of the π system could easily be prolonged whilst simultaneously introducing a stronger acceptor.

The optical purity of the closed dimers 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): the methylene hydrogen signal of racemic 9,14-dibromodinaphtho[2,1-d:1′,2′-f][1,3]dioxepin (**1b**) was split by 4–5 Hz due to the diastereomeric interaction with a large excess of (*R*)-(−)-TFAE.[18] Only one optical isomer was found for all compounds tested, except for **2b**. As a higher racemization barrier was found for open BN derivatives,[19] their enantiomeric purity can be deduced (except for **2a**) from the results obtained for the closed BN dimers, indicating that no racemization took place during the reactions.

Kurtz–Perry powder test: The Kurtz–Perry powder method[9] at 1064 nm was used to determine the second-harmonic generation (SHG) efficiency of the materials in their crystalline forms. Urea, ammonium dihydrogen phosphate (adp), and 2-methyl-4-nitroaniline (MNA) were used as reference materials in the powder test. Given the broad range of sizes of crystalline particles in the samples and possible preferential orientation of the grains, the powder tests were not quantified. It can be seen from the results listed in Tables 1, and 2 that even though all the compounds (except **2b**) are chiral and thus crystallize in a noncentrosymmetric point group, no or only weak SHG signals were observed for many of the BN derivatives. The dipole orientation in the crystals of these compounds must thus be antiparallel or close to antiparallel. Compounds **5a**, **7a**, **9a**, **10a**, and **13a** show SHG effiencies comparable to MNA. Interestingly, racemic BN derivatives with substituents of comparable acceptor strengths have been shown to give similar powder efficiencies.[7c,7d]

Crystal structures: The chiral BNs were difficult to crystallize. Only crystals of the chiral aldehyde **4a** and the racemic nitrile **2b** were of sufficient quality to allow structure determination

Table 1. Dipole moments (Debye), hyperpolarizability tensor components and static hyperpolarizabilities of the type **a** bis(dipolar) binaphthol derivatives and their calculated dipolar monomeric units (10^{-30} esu, $CHCl_3$, 1064 nm), absorption maxima (nm, $CHCl_3$) and SHG powder efficiencies.

	Acceptor	μ_Z	$\beta_{ZZZ}+\beta_{ZXX}$	β_0	$\beta_{zzz,mono}$	$\beta_{0,mono}$	λ_{max} ($CHCl_3$)	powder test
2a	-CN						344	++ (≈urea)
3a	-SO_2CH_3						340	not visible
4a[a]	-CHO						323[b]	not visible
5a	-CH=CH(CN)	9.4	102		72		334[b]	+++ (>urea, <**13a**)
6a	-CH=CH(SO_2CH_3)						329[b]	not visible
7a	-CH=CH-CHO						343[b]	+++ (>urea, <**5a**)
8a	-CH=C$(CN)_2$	10.4	135	47	95	33	410	not visible
9a	-CH=C(CN)(COOEt)	10.4	103	41	73	29	392	+++ (>urea, ≈MNA)
10a	-CH=CH-Ph-CN	8.3	64	32	45	22	354[b]	+++ (>urea, ≈MNA)
11a	-CH=CH-Ph-SO_2CH_3	10.3	53		37		349[b]	+ weak (≈adp)
12a	-CH=CH-Ph-CHO	8.2	58	27	41	19	363[b]	not visible
13a	-CH=CH-Ph-NO_2	11.0	344	131	243	93	397	+++ (≈**9a**)
14a	-CH=CH-Ph-CH=C$(CN)_2$	8.7	888	233	628	165	440	visible white light
15a	-CH=CH-CH=C$(CN)_2$	16.5	283	80	200	56	433	not visible

[a] Crystal structure reported. [b] Shoulder at longer wavelength.

Table 2. Dipole moments (Debye), hyperpolarizability tensor components and static hyperpolarizabilities of the type **b** bis(dipolar) binaphthol derivatives and their calculated dipolar monomeric units (10^{-30} esu, $CHCl_3$, 1064 nm), absorption maxima (nm, $CHCl_3$), and SHG powder efficiencies.

	Acceptor	μ_Z	$\beta_{ZZZ}+\beta_{ZXX}$	β_0	$\beta_{zzz,mono}$	$\beta_{0,mono}$	λ_{max} ($CHCl_3$)	powder test
2b[a](racemic)	-CN						311[b]	not visible
3b	-SO_2CH_3						311[b]	+ (≈adp)
4b	-CHO						278[b]	(+) very weak
5b	-CH=CH(CN)	10.0	34		19		308[b]	+ (<adp)
6b	-CH=CH(SO_2CH_3)	8.5	45		25		300[b]	not visible
7b	-CH=CH-CHO						316[b]	not visible
8b	-CH=C$(CN)_2$	12.3	65	35	37	20	339[b]	+ weak (<<adp)
9b	-CH=C(CN)(COOEt)	11.4	58[c]	32	33	18	334[b]	+ very weak
10b	-CH=CH-Ph-CN	4.8	49	27	28	15	333[b]	not visible
11b	-CH=CH-Ph-SO_2CH_3	5.0	72		41		332[b]	not visible
12b	-CH=CH-Ph-CHO	3.8	33	17	19	10	346[b]	++ (<**13a**)
13b	-CH=CH-Ph-NO_2	6.5	166	80	94	44	364[b]	++ (=**12b**)
14b	-CH=CH-Ph-CH=C$(CN)_2$	9.3	379	126	214	71	415	visible white light
15b	-CH=CH-CH=C$(CN)_2$	12.6	219	99	123	55	371	not visible

[a] Crystal structure reported. [b] Shoulder at longer wavelength. [c] HRS value from ref. [7e].

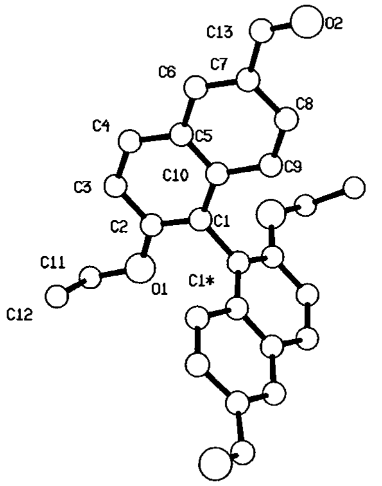


Figure 2. Molecular structure of **(*S*)-4a**. Selected torsion angles [°] (symmetry transformations used to generate equivalent atoms: #1 *y,x,−z*): C(10)−C(1)−C(1)#1−C(10)#1 −106.2(1.0), C(1)−C(2)−O(1)−C(11) 177.7(0.6), C(2)−O(1)−C(11)−C(12) −79.9(0.8), C(6)−C(7)−C(13)−O(2) 169.5(0.9).

by single-crystal X-ray diffraction. The huge nonplanar molecular shape of the large aromatic systems of the BNs and the high ground-state dipole moments seem to be the reasons for the rather poor crystal qualities obtained. This is also reflected in the weak intermolecular contacts found in the crystal structures.

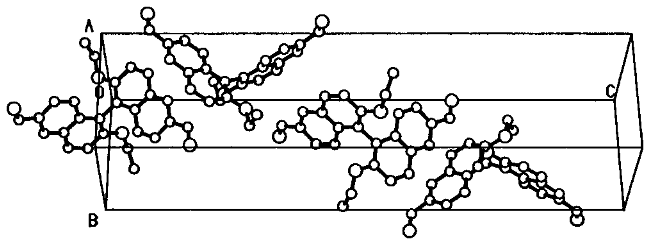


Figure 3. Unit cell of **(*S*)-4a**.

The molecular conformation of **4a** is given in Figure 2, and the unit cell is shown in Figure 3. The dihedral angle between the two naphthyl rings is 106.2(1.0)° corresponding to a transoid conformation. For this point group (422), all macroscopic nonlinear tensor coefficients vanish and $\chi^{(2)}$ is equal to zero: a crystallographic twofold axis runs through the central C−C bond and this axis coincides with any molecular dipole moment. In the crystalline phase, the dipole moments along the molecular twofold axis will cancel by symmetry, although the space group of the optically pure crystal is noncentrosymmetric. The macroscopic cancelation of all molecular dipole moments in the crystal is in full accordance with the negative result in the SHG powder test.[20] There are only weak intermolecular contacts in the crystal. It can be seen from the torsional angles that the ethoxy donor and the aldehyde acceptor are almost in plane with the aromatic π system (thus displaying their full donor strength); this is necessary in order to fulfil the requirements of a large molecular first hyperpolarizability.

For **2b** the molecular conformation is shown in Figure 4 and the unit cell is shown in Figure 5. Compound **2b** is a racemate (centrosymmetric space group) and can thus not exhibit macroscopic second-order nonlinearity. The structure consists of isolated molecules with no particularly close contacts. The dihedral angle between the two naphthyl rings is 54.6(0.8)°. Some ring distortion in the naphthol moieties due to the strain in the heterocyclic ring at C10 and C21 (both bonded to the O–C–O bridge) is observed. Furthermore, it can be seen from the alkoxy–naphthyl torsion angle C1–C10–O1–C23, which corresponds to 76.5(0.7)°, that the oxygen lone pairs of the donor are twisted out of conjugation with the aromatic π system. This loss of donor strength was predicted earlier by semiempirical calculations. The remaining donor strength was estimated to be equal to that of a methyl group.[21]

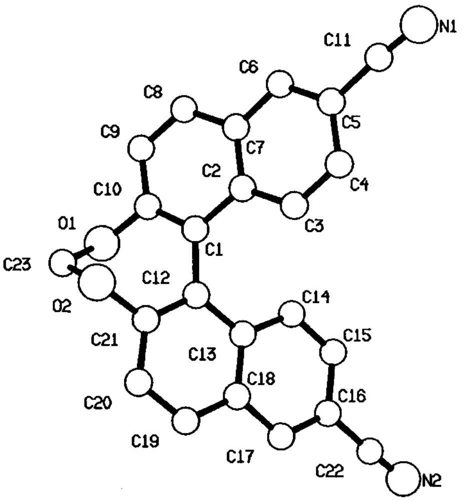


Figure 4. Molecular structure of racemic **2b**. Selected torsion angles [°]: C(2)–C(1)–C(12)–C(13) −54.6(0.8), C(1)–C(10)–O(1)–C(23) 76.5(0.7), C(12)–C(21)–O(2)–C(23) 76.9(0.7), C(10)–O(1)–C(23)–O(2) −45.2(0.7), C(21)–O(2)–C(23)–O(1) −46.5(0.7).

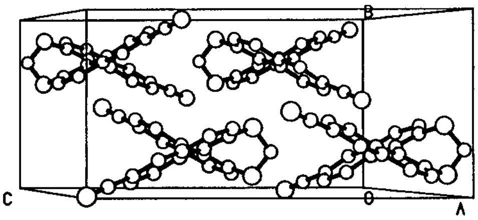


Figure 5. Unit cell of racemic **2b**.

Linear optical properties: The optical properties of the compounds listed in Tables 1 and 2 follow the expected tendencies. The wavelengths of the maximum absorptions shift bathochromically with increasing acceptor strength and conjugation length. In accordance with results obtained earlier,[7e,21] the absorption spectra of the open molecules differ significantly from those of the closed compounds with the same acceptors in the 6,6′-positions. This is shown in Figure 6 for **8a**, **8b**, **14a**, and **14b**. The differences between the two types of compounds can be explained by the fact (as shown by X-ray diffraction above for **2b**) that for the type **b** compounds the plane defined by the oxygen atoms and the carbon atom to which they are both bound does not coincide with the plane of the aromatic rings. 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. Furthermore, spectral shifts or splittings of the absorption bands in these dimeric molecules may appear for the component moieties owing to exciton splitting of excited states or intramolecular electronic interactions. As both are a function of the dihedral angle between the molecular planes, this will contribute to the observed differences in the absorption spectra of the **a** and **b** type BNs.[22]

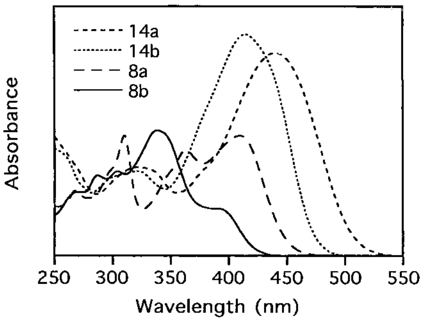


Figure 6. Absorption spectra of **8a**, **8b**, **14a**, and **14b** in $CHCl_3$.

Nonlinear optical properties (EFISHG) and dipole moments: For the determination of the microscopic nonlinear optical properties of **10a,b–12a,b**, **13b**, **14a**, **14b**, **15a**, and **15b**, EFISHG measurements were performed to obtain $\mu\beta_Z$.[10] The dipole moments were determined experimentally according to the procedure outlined in ref. [23]. As the Z axis of the dimer coincides with the twofold axis, the only component of the molecular dipole moment will be μ_Z. The results of the EFISHG measurements (in units of 10^{-30} esu, measured at 1064 nm in chloroform) and the dipole moments of the compounds are listed in Tables 1 and 2.

The ground-state dipole moments of the BN diethers (type **a**) and the BN acetals (type **b**) increase with increasing acceptor strength and conjugation length. In the closed BN acetals, the dihedral angle between the naphthol moieties is fixed and the dipole moments are a function of the donor and acceptor strength and the conjugation length only (if other conformational freedoms are neglected). For the open BN diethers, the rotation around the 1,1′-bond (changing the dihedral angle between the two naphthol moieties) represents an additional degree of freedom. The total dipole moment should therefore reach a maximum (if C_{2v} symmetry is assumed) when the dipoles of the monomeric units are pointing in the same direction ($\theta = 0°$) and be zero for $\theta = 180°$. Going from the closed BN acetal to the open BN diether, the better overlap between the oxygen lone pairs and the delocalized aromatic π system of the naphthol moieties will act to increase the total dipole moment, but this is counteracted by the increase in dihedral angle. Since we observe an increase in the dipole moment on going from the BN acetal to the BN diether, the former effect dominates.

The hyperpolarizability tensor of these bis(dipolar) compounds can be estimated by means of a vector model.[7e] We assume that the hyperpolarizability tensor of the dipolar subunits is dominated by $\beta_{zzz,\mathrm{mono}}$, where z is along the charge-transfer axis of the 2,6-naphthol push–pull system. If the Z axis is chosen parallel to the permanent dipole moment of the bis(dipolar) molecule, which coincides with the twofold axis, and the dipolar subunits lie in a plane parallel to the ZX plane, the four nonzero tensor components of the dimer can be expressed as shown in Equations (1) and (2). The ratio of the two independent tensor components is only a function of the dihedral angle θ [Eq. (3)]. EFISHG is sensitive to the sum of the two independent tensor components Equations (4) or (5), the latter being derived from Equations (2) and (3).

$$\beta_{ZZZ} = 2(\cos\theta/2)^3 \beta_{zzz,\mathrm{mono}} \tag{1}$$

$$\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ} = 2(\sin\theta/2)^2(\cos\theta/2)\ \beta_{zzz,\mathrm{mono}} \tag{2}$$

$$\beta_{ZXX}/\beta_{ZZZ} = (\tan\theta/2)^2 \tag{3}$$

$$\mu_Z\beta_Z = \mu_Z(\beta_{ZZZ} + \beta_{ZXX}) \tag{4}$$

$$\mu_Z\beta_Z = 2\mu_Z(\cos\theta/2)\beta_{zzz,\mathrm{mono}} \tag{5}$$

In a previous paper, we demonstrated the good accuracy of this vector model by comparing numerical values for the tensor components of similar BN derivatives, which were calculated from independent hyper-Rayleigh scattering (HRS), and EFISHG measurements.[7e]

$\beta_{zzz,\mathrm{mono}}$, β_{ZZZ} and β_{ZXX} were calculated with Equations (3)–(5), assuming a dihedral angle of 90° for the type **a** compounds (obtained from PM3 calculations) and an angle of 55° (from crystal structure of **2b**) for the type **b** compounds. Taking a dihedral angle of 106° for the type **a** compounds, as indicated by the crystallographic analysis of **4a**, increases $\beta_{zzz,\mathrm{mono}}$ by 17%. In general, the static hyperpolarizability of D–A-substituted molecules is calculated by means of the two-level approximation for β.[24,10b] The resonantly enhanced hyperpolarizability is given by Equation (6), where β_0 is the nonresonant value, and the resonance enhancement factor $R(\omega)$ is given by Equation (7), where ω_0 is the wavelength at which the maximum of the absorption occurs and ω corresponds to the wavelength of the laser.

$$\beta(\omega) = R(\omega)\beta_0 \tag{6}$$

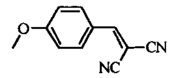
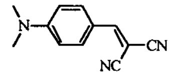
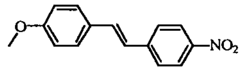
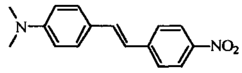
$$R(\omega) = \frac{\omega_0^4}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \tag{7}$$

As can be seen in Figure 6, several absorption maxima are present in the absorption spectra of the bis(dipolar) BN derivatives. According to the sum-over-states formalism, each of these transitions contributes to β and the two-level approximation is no longer valid. However, for the bis(dipolar) derivatives where the absorption spectrum is still dominated by an intense, low-lying charge-transfer transition, such as **14a** and **14b**, the static hyperpolarizability of the dipolar subunits was extrapolated by means of the two-level model.

Several tendencies can be observed. A strong increase in all the tensor components can be achieved by increasing the acceptor strength and the conjugation length. This increase is accompanied by a bathochromic shift of the absorption spectra. For the type **a** compounds, $\beta_{zzz,\mathrm{mono}}$ is 2.4 ± 0.7 times larger and $\beta_{0,zzz,\mathrm{mono}}$ is 1.7 ± 0.7 times larger than $\beta_{zzz,\mathrm{mono}}$ and the $\beta_{0,zzz,\mathrm{mono}}$ of the type **b** compounds, respectively. This can be attributed to the fact that the electron-donating lone pairs of the oxygen atoms are twisted out of conjugation with the aromatic system in the type **b** compounds. The experimental β_0 values of the monomeric units of **8** and **9** derived from ref. [7e] are 33×10^{-30} and 28×10^{-30} esu, respectively. Comparing these values with $\beta_{0,zzz,\mathrm{mono}}$ of **8a** and **9a,** and **8b** and **9b** supports our theory.

It has been shown that the static first hyperpolarizability of classic D–π–A molecules can be optimized by adequately tuning the aromaticity of the conjugated π system.[25] The naphthyl moiety has not found widespread use as a building block for chromophores for second-order nonlinear optics, because its resonance energy is too large for optimizing the hyperpolarizability. As can be seen from Table 3, the resonant ($\beta_{zzz,\mathrm{mono}}$) and two-level[24,10b] extrapolated hyperpolarizabilities and absorption maxima of the naphthyl type **a** derivatives with an ethoxy donor lie between those of similar benzene derivatives with methoxy and dimethylamino donors.

Table 3. Resonant (1064 nm) and two-level extrapolated hyperpolarizabilities (10^{-30} esu) and absorption maxima (nm) of the subunits of compounds **8a** ($CHCl_3$), **13a** ($CHCl_3$), and the related benzene ($CHCl_3$) and stilbene derivatives ($CHCl_3$).

	β	λmax	β_0
	38 [a]	352 [a]	19
8a	95	410	33
	130 [b]	431 [b]	37
	105 [a]	377 [a]	45
13a	243	397	93
	450 [b]	424 [b]	138

[a] Values from ref. [25a] ($CHCl_3$). [b] Value from ref. [25b] (acetone).

The type **a** bis(dipolar) materials are unique in the sense that they possess four large tensor components, while the hyperpolarizability tensor of the classic dipolar compounds is dominated by a single β_{ZZZ} tensor component. Depending on the symmetry of the macroscopic (bulk) medium and the ratio β_{ZXX}:β_{ZZZ}, the $\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ}$ tensor components can either increase, decrease or have no effect on the efficiency of frequency doubling.

For crystals, the relevant material parameters for frequency doubling are the molecular hyperpolarizability tensor, the symmetry of the crystal lattice, the phase-matching conditions, and the interaction length.[20a] For crystal classes 4, 4*mm*, 6, and 6*mm* the contribution from the molecular $\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ}$ tensor components cancel, while β_{ZXX} is directly proportional to one of the macroscopic susceptibility tensor components for crystal classes 1(b_{YXX}), 2(b_{YXX}), *m*(b_{XZZ}), *mm*2(b_{ZXX}), $\bar{4}$(b_{XYZ}), $\bar{4}2m$(b_{XYZ}), 23(b_{XYZ}) and $\bar{4}3m$(b_{XYZ}). Finally, according to ref. [20a], the macroscopic susceptibility tensor component b_{XXX} for crystal classes 3, 32, and $\bar{6}$, and b_{YYY} for 3*m* and $\bar{6}2m$ is proportional to $\beta_{ZZZ} - 3\beta_{ZXX}(\sin\alpha)^2$, where α is the angle between the molecular plane and the symmetry axis of the crystal. Therefore, if $(\sin\alpha)^2 = \beta_{ZZZ}/3\beta_{ZXX}$, both components will cancel. On the other hand, if $\beta_{ZZZ} \approx \beta_{ZXX}$ and $3(\sin\alpha)^2 > 2$, the absolute value of the macroscopic susceptibility tensor components will increase due to the presence of β_{ZXX}. Hence, depending on the crystal symmetry class and the orientation of the molecules in the unit cell, a positive, a negative, or no effect of the β_{ZXX} tensor component on the frequency doubling efficiency can be observed.

For poled polymer films, the analysis is more straightforward. The values of the macroscopic susceptibility tensor components induced by poling in an electric field are given by Equations (8) and (9), where E is the poling field, N the molecular number density, and $f(\omega)$ and $f(2\omega)$ the local field correction factors at frequency ω and 2ω, respectively.[1a]

$$\chi^{(2)}_{ZZZ} = \frac{N f^2(\omega) f(2\omega) \mu_Z (\beta_{ZZZ} + \beta_{ZXX}) E}{5kT} \tag{8}$$

$$\chi^{(2)}_{ZXX} = \frac{\chi^{(2)}_{ZZZ}}{3} \tag{9}$$

By expressing the dimer tensor components and the dipole moment in terms of the dipole moment and the hyperpolarizability of the monomeric unit and the dihedral angle Equation (8) can be rewritten as Equation (10).

$$\chi^{(2)}_{ZZZ} = \frac{4N f^2(\omega) f(2\omega) \mu_{mono} \beta_{zzz,mono} (\cos\theta/2)^2 E}{5kT} \tag{10}$$

If $\theta/2 < 45°$, the susceptibility tensor components of a poled film containing the bis(dipolar) BNs will be more than twice as large as the components of a film prepared with twice the concentration of the dipolar monomer.

Conclusions

The special expression of chirality (C_2 symmetry, atropisomerism) in the synthesized D–π–A BN derivatives leads to a relatively easy access towards optically pure molecules (and thus noncentrosymmetric materials). Although the bulk second-order nonlinearities of some chiral powders are high, the use of this stragegy in order to obtain NLO active crystals proved to be unsatisfactorily fulfilled. The general tendency of the powder measurements suggests a close to antiparallel orientation of the D–π–A conjugated systems in the crystals. In the specific case of the crystal structure of **4a**, the dipoles of the naphthol moieties tend to orient transoid (owing to free rotation around the $C_1-C_{1'}$ bond in the type **a** compounds) within the BN molecule, and thus cancel. This antiparallel dipole orientation on a molecular level should be even more pronounced in the type **a** derivatives with higher dipole moments. Favouring of antiparallel dipole orientation is also the trend on a macroscopic level as seen in unit cell of **4a** (and racemic **2b**). On the other hand in the type **b** compounds the dipole orientations with respect to each other within a BN molecule can be fixed on a molecular level. However, this leads to a significant loss of donor strength and to distortion of the aromatic π system and results in different absorption spectra for type **a** and type **b** BNs.

Nevertheless, the measured first hyperpolarizabilities (EFISHG) of the new compounds were very high (β_0 up to 233×10^{-30} esu, e.g. *p*-nitroaniline $\beta_0 = 12 \times 10^{-30}$ esu) and followed the expected tendencies (acceptor strengths, conjugations length, donor strength). In comparison to the diethoxy BNs, the corresponding BN acetals have lower molecular hyperpolarizabilities. This can again be explained by the loss of donor strength and the distortion of the aromatic π system.

The high $\mu\beta_0$ value of compound **14a** being 2000×10^{-48} esu, four times higher than for the classical dye disperse red 1, makes it of great interest for electro-optical (EO) poled polymers. Since the chromophores have a three-dimensional V-shaped conformation, the orientational stability of the induced alignment will be better than for conventional dipolar molecules in poled polymers. Furthermore, as the conjugated system is mainly aromatic, many of the compounds have high decomposition temperatures necessary for the fabrication of poled polymers with high glass transition temperatures that have long-term stability.[7b,d]

Experimental Section

^{1}H 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, δ, are reported relative to tetramethylsilane as an internal standard. UV-Vis spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer. Optical rotations were measured on a Perkin–Elmer 141 polarimeter at 25 °C. Mass spectra were recorded on a VG Masslab 12-250 and on a Jeol JMS-HX/HX 110 A Tandem Mass Spectrometer. IR spectra were recorded on a Perkin–Elmer FT-IR 1760X 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 DME was distilled from CaH_2. Dry CH_2Cl_2 and chloroform were of HPLC grade, as were all solvents used for spetrophotometry. 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 (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 by 4–5 Hz owing to the diastereomer interaction with a large excess of (*R*)-(−)-TFAE. Only one optical isomer was found for all compounds tested (except for 2b).

(*S*)-2,2′-Diethoxy-1,1′-binaphthyl-6,6′-dicarbonitrile (2a): A stirred mixture of (*S*)-2,2′diethoxy-6,6′-dibromo-1,1′-binaphthyl (**1a**, 2.0 g, 4.0 mmol), CuCN (1.1 g, 12.3 mmol), and *N*-methyl-2-pyrrolidone (60 mL) was

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refluxed for 5 h. The resulting brown mixture was cooled to RT, poured (residues are conveniently transferred with DMF) into a concentrated solution of $FeCl_3$ in water (100 mL), and stirred overnight. Dilute HCl (500 mL; 1:1, v/v) was added and the mixture was extracted with toluene (4 × 400 mL). Phase separation was difficult since the interface was obscured by dark colours. The combined organic layers were washed twice with diluted HCl (1:1, v/v) and twice with water. The organic layer was dried over $MgSO_4$ and filtered to remove the $MgSO_4$ and dark insoluble matter. After evaporation of the solvent in vacuo a brown oil was obtained, which was purified by column chromatography ($l = 15$ cm, $\varnothing = 4$ cm) with CH_2Cl_2 as eluting agent. The obtained solid was recrystallized from $CHCl_3$/petroleum ether 60/80 (freezer) to give 674 mg (43 %)of **2a** as fine white needles. M.p.: 192–193 °C; $[\alpha]_D^{25} = -35.2$ ($c = 0.01$, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.25$ (d, 2H, ArH^5), 8.02 (d, $J = 9$ Hz, 2H, ArH), 7.52 (d, 2H, ArH), 7.33 (dd, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.12 (d, 2H, ArH), 4.11 (m, 4H, $ArOCH_2$), 1.09 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 156.55$, 135.28, 134.26, 130.31, 127.64, 126.67, 125.98, 119.41, 118.97, 116.08, 106.65, 64.69, 14.64; MS (FAB$^+$): $m/z = 393$ [MH^+]; IR (KBr): $\tilde{\nu} = 2226$ cm^{-1} (s, CN); UV-Vis ($CHCl_3$): λ_{max} (ε) = 258 (90500), 307 (18500), 344 nm (8400); $C_{26}H_{20}N_2O_2$ (392.46): calcd C 79.57, H 5.14, N 7.14; found C 79.16, H 4.97, N 7.22.

(*R,S*)-Dinaphtho[2,1-d:1′2′-f][1,3]dioxepin-9,14-dicarbonitrile (**2b**): A stirred mixture of (*S*)-9,14-dibromodinaphtho[2,1-d:1′,2′-f][1,3]dioxepin (**1b**, 2.0 g, 4.38 mmol), CuCN (1.18 g, 13.2 mmol), and *N*-methyl-2-pyrrolidone (60 ml) was refluxed for 5 h. The resulting brown mixture was cooled to RT, poured (residues are conveniently transferred with DMF) into a concentrated solution of $FeCl_3$ in water (100 ml) and stirred overnight. Dilute HCl (500 ml; 1:1, v/v) was added and the mixture was extracted with toluene (4 × 400 mL). Phase separation was difficult since the interface was obscured by dark colours. The combined organic layers were washed twice with dilute HCl (1:1, v/v) and twice with water. The organic layer was dried over $MgSO_4$ and filtered to remove the $MgSO_4$ and dark insoluble matter. After evaporation of the solvent in vacuo a brown oil was obtained, which was purified by column chromatography ($l = 10$ cm, $\varnothing = 4$ cm) with CH_2Cl_2 as eluting agent. The obtained solid was recrystallized from abs. EtOH (freezer) to give 900 mg (59 %) of **2b** as white needles. M.p.: 289–291 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.35$ (br s, 2H, ArH^5), 8.08 (d, $J = 9$ Hz, 2H, ArH), 7.62 (d, 2H, ArH), 7.45 (br s, 4H, ArH), 5.75 (s, 2H, -CH_2-); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 153.82$, 134.62, 133.26, 131.35, 130.58, 127.37, 126.86, 125.47, 123.01, 118.68, 108.93, 103.33; MS (EI): $m/z = 348$ [M^+]; IR (KBr): $\tilde{\nu} = 2227$ cm^{-1} (s, CN); UV-Vis ($CHCl_3$): λ_{max} (ε) = 293 (13400), 311 nm (13300); $C_{23}H_{12}N_2O_2$ (348.36): calcd C 79.30, H 3.47, N 8.04; found C 79.28, H 3.44, N 8.18.

(*S*)-2,2′Diethoxy-6,6′-bis(methylsulfonyl)-1,1′binaphthyl (**3a**): **1a** (2.50 g, 5.0 mmol) was dissolved in dry THF (150 mL) under an argon atmosphere. The magnetically stirred solution was cooled to −78 °C and a solution of *n*BuLi (10.0 mL, 20.0 mmol) in hexane (2.0 M) was added at such a rate in order to keep the temperature below −70 °C. After 6 h of stirring at this temperature, dimethyl disulfide (2.4 mL, 26.6 mmol) was added whilst the temperature was maintained. After stirring for 1 h, the cooling bath was removed and the reaction hydrolyzed with 5 % KOH solution (100 mL). The reaction mixture was diluted with ether, and the organic phase was separated. The ethereal solution was washed twice with 5 % KOH solution and twice with water. The solution was dried ($MgSO_4$) and filtered, and the solvent removed under reduced pressure to give (*S*)-2,2′diethoxy-6,6′-dimethylthio-1,1′binaphthyl as an oil (1.9 g, 4.4 mmol) which was then dissolved in $CHCl_3$ (200 mL). Magnesium monoperoxyphthalate · $6H_2O$ (80 %, 62 g, 125.3 mmol) was added, and the mixture was refluxed for 5 h. After cooling the salt was filtered off on a glass frit and washed with $CHCl_3$ (3 × 150 mL). The combined filtrates were evaporated giving an oil which was purified by column chromatography ($l = 20$ cm, $\varnothing = 3$ cm) on silica gel with petroleum ether/AcOEt (60–80 °C, 1:1, v/v) as eluting agent. A glass was obtained, which was recrystallized from MeOH/water (freezer) to give 1.45 g (58 %) of **3a** as a white powder. M.p.: 125–126 °C; $[\alpha]_D^{25} = -8.3$ ($c = 0.01$, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.55$ (d, 2H, ArH^5), 8.13 (d, $J = 9$ Hz, 2H, ArH), 7.62 (dd, $J_{5,7} = 2.0$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.56 (d, 2H, ArH), 7.20 (d, 2H, ArH), 4.12 (m, 4H, -OCH_2-), 3.09 (s, 6H, SO_2Me), 1.10 (t, 6H, -CH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 156.82$, 136.01, 134.87, 131.31, 129.32, 127.42, 126.49, 122.51, 119.13, 116.28, 64.76, 44.49, 14.69; MS (FAB +): $m/z = 499$ [MH^+]; IR (KBr): 1305 (s, -SO_2-), 1147 cm^{-1} (s, -SO_2-); UV-Vis ($CHCl_3$): λ_{max} (ε) = 258 (44300), 282 (55300), 329 nm (32800); $C_{26}H_{26}S_2O_6$ (498.61): calcd C 62.63, H 5.26, S 12.86; found C 62.93, H 5.46, S 12.93.

(*S*)-9,14-Bis(methylsulfonyl)dinaphtho[2,1-d:1′2′-f][1,3]dioxepin (**3b**): Compound **1b** (2.50 g ,5.48 mmol) was dissolved in dry THF (100 mL) under an argon atmosphere. The magnetically stirred solution was cooled to −78 °C and a solution of *n*BuLi (14 mL, 28.0 mmol) in *n*-hexane (2.5 M) was added at such a rate as to keep the temperature below −70 °C. After 6 h of stirring at this temperature, dimethyl disulfide (2.2 mL, 42.2 mmol) was added whilst the temperature was maintained. After stirring for 1 h, the cooling bath was removed and the reaction hydrolyzed with 5 % KOH solution (100 mL). The reaction mixture was diluted with ether, and the organic phase was separated. The etheral solution was washed twice with 5 % KOH solution and twice with water. The solution was dried ($MgSO_4$) and filtered, and the solvent removed under reduced pressure to give (*S*)-9,14-dimethylthiodinaphtho[2,1-d:1′,2′-f][1,3]dioxepin (2.27 g, 5.8 mmol) as an oil, which was then dissolved in boiling AcOH (70 mL). Hydrogen peroxide (35 %, 5.0 g, 97.2 mmol) was added dropwise at this temperature under stirring and allowed to stir for a further 3 h at RT. The solution was heated again and water (35 mL) was added to the boiling solution. The white needles that formed overnight on cooling were filtered off, washed twice with cold water, and dried under reduced pressure to give 1.83 g (73 %) of **3b**. M.p.: 265 °C; $[\alpha]_D^{25} = 697$ ($c = 0.01$, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 8.65$ (d, $J_{5,7} = 1.8$ Hz, 2H, ArH^5), 8.20 (d, $J = 9$ Hz, 2H, ArH), 7.75 (dd, $J_{5,7} = 1.9$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.66 (d, 2H, ArH), 7.56 (d, 2H, ArH), 5.76 (s, 2H, -CH_2-), 3.15 (s, 6H, SO_2Me); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 154.04$, 136.96, 133.99, 132.32, 130.53, 129.62, 127.96, 125.60, 123.14, 122.72, 103.36, 44.40; MS (EI): $m/z = 454$ [M^+]; IR (KBr): $\tilde{\nu} = 1306$ (s, -SO_2-), 1145 cm^{-1} (s, -SO_2-); UV-Vis ($CHCl_3$): λ_{max} (ε) = 302 (13800), 340 nm (6300); $C_{23}H_{18}S_2O_6$ (454.52): calcd C 60.78, H 3.99, S 14.11; found C 60.90, H 3.92, S 14.15.

(*R*)-(*E,E*)-2,2′-Diethoxy-6,6′-bis[2-(methylsulfonyl)vinyl]-1,1′-binaphthyl (**6a**): Diethyl methylsulfonomethanephosphonate[16a,b] (1.60 g, 6.95 mmol) and (*R*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarbaldehyde (**4a**, 1158 mg, 2.91 mmol) were dissolved in dry DME (60 mL) under nitrogen. Sodium hydride (400 mg, 13.3 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 HCl (600 mL) and extracted with CH_2Cl_2 (3 × 250 mL). The combined organic phases were washed with brine and dried ($MgSO_4$), and the solvent removed in vacuo after filtration. The compound was redissolved in a small volume of CH_2Cl_2, and petroleum ether was added. The white precipitate that formed was collected on a glass frit and washed with petroleum ether to give 978 mg (61 %) of **6a**. M.p.: 169–172 °C (decomp.); $[\alpha]_D^{25} = -305$ ($c = 0.01$, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.00$ (d, 2H, ArH), 7.98 (d, 2H, ArH^5), 7.75 (d, $J_{trans} = 15.4$ Hz, 2H, =CH-), 7.46 (d, 2H, ArH), 7.33 (dd, $J_{5,7} = 1.8$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.11 (d, $J = 9$ Hz, 2H, ArH), 6.88 (d, $J_{trans} = 15.4$ Hz, 2H, =CH-), 4.09 (m, 4H, -OCH_2-), 3.03 (s, 6H, -SO_2Me), 1.09 (t, $J = 7$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 155.93$, 144.09, 135.29, 131.39, 130.40, 128.49, 127.09, 126.18, 124.79, 123.52, 119.71, 115.82, 64.78, 43.37, 14.75; MS (FAB +): $m/z = 551$ [MH^+]; IR (KBr): $\tilde{\nu} = 1618$ (s, C=C), 1310 (s, -SO_2-), 1133 (s, -SO_2-), 965 cm^{-1} (m, =C–H_{trans}); UV-Vis ($CHCl_3$): λ_{max} (ε) = 258 (44300), 282 (55300), 329 nm (32800); $C_{30}H_{30}O_6S_2$ (550.69): calcd C 65.43, H 5.49, S 11.64; found C 65.79, H 5.59, S, 11.81.

(*S*)-(*E,E*)-4,4′-[2,2′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)diethenyl]dibenzonitrile (**10a**): Diethyl(4-cyanobenzyl)phosphonate[16d] (629 mg, 2.48 mmol) was dissolved in dry 1,2-dimethoxyethane (monoglyme, 40 mL) under an inert atmosphere. Sodium hydride (80 % in mineral oil, 150 mg, 5.00 mmol) was added at 0 °C, and the suspension was stirred magnetically for 20 min. Compound **4a** (450 mg, 1.13 mmol) dissolved in dry monoglyme (20 mL) was added to the suspension, and the reaction mixture was stirred for 2 days at RT. The mixture was cautiously hydrolyzed with water (300 mL), saturated with NaCl, and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with water and dried ($MgSO_4$), and the solvent removed in vacuo after filtration. The solid obtained was refluxed in EtOH (200 mL) to dissolve impurities. The insoluble solid was filtered off on a glass frit after cooling to RT, washed with MeOH, and dried under reduced pressure to give 453 mg (67 %) of **10a**. M.p.: 274–275 °C; $[\alpha]_D^{25} = 611$ ($c = 0.01$, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.95$ (d, $J = 9$ Hz, 2H, ArH), 7.91 (d, 2H, ArH^5), 7.61 (br d, $J = 9$ Hz, 4H, ArH), 7.56 (br d, 4H, ArH), 7.46 (dd, ArH^7, $J_{5,7} = 1.7$ Hz, $J_{7,8} =$

9 Hz, 2H), 7.44 (d, 2H, ArH), 7.34 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 7.14 (d, 2H, ArH), 7.08 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 4.07 (m, 4H, -OCH$_2$-), 1.09 (t, $J = 7$ Hz, 6H, -CH$_3$); ^{13}C NMR (CDCl$_3$, 100.6 MHz): $\delta = 155.02$, 142.07, 134.19, 132.58, 132.44, 131.48, 129.59, 129.16, 127.85, 126.70, 126.04, 125.92, 123.60, 120.38, 119.05, 116.03, 110.30, 65.07, 14.97; MS (FAB+): $m/z = 597$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 2224$ (s, CN), 1600 (s, C=C), 965 cm^{-1} (m, =C–H$_{trans}$); UV-Vis (CHCl$_3$): λ_{max} (ε) = 302 (36600), 354 nm (49900); $C_{42}H_{32}N_2O_2$ (596.73): calcd C 84.54, H 5.41, N 4.69; found C 84.59, H 5.71, N, 4.59.

(*S*)-(*E,E*)-4,4′-[2,2′-(Dinaphtho[2,1-d:1′,2′-f][1,3]dioxepin-9,14-diyl)diethenyl]dibenzonitrile (**10b**): Diethyl (4-cyanobenzyl)phosphonate[16d] (785 mg, 3.10 mmol) was dissolved in dry monoglyme (40 mL) under an inert atmosphere. Sodium hydride (80% in mineral oil, 325 mg, 10.8 mmol) was added at 0 °C and the suspension was stirred magnetically for 30 min. (*S*)-Dinaphtho[2,1-d:1′,2′-f][1,3]dioxepin-9,14-dicarbaldehyde (**4b**, 500 mg, 1.41 mmol) was added to the suspension, and the reaction mixture was stirred overnight at RT. The mixture was cautiously hydrolyzed with dilute HCl (300 mL), and the precipitate that formed was collected by filtration (glass frit) and washed thoroughly with water. The solid obtained was dried in air, recrystallized from toluene/petroleum ether (80–110 °C, freezer). The fine crystals that formed were filtered off, washed with light petroleum ether, and dried in air to give 434 mg (56%) of **10b**. M.p.: 336–337 °C; $[\alpha]_D^{25} = 1246$ ($c = 0.01$, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.00$ (d, $J = 8$ Hz, 2H, ArH), 8.00 (d, 2H, ArH^5), 7.63 (m, 8H, Ar), 7.57 (dd, $J_{5,7} = 1.8$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.51 (d, 2H, ArH), 7.50 (d, 2H, ArH), 7.37 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 7.18 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 5.72 (s, 2H, -CH$_2$-); ^{13}C NMR (CDCl$_3$, 100.6 MHz): $\delta = 151.74$, 141.59, 132.93, 132.39, 131.95, 131.85, 130.53, 127.96, 127.26, 127.04, 126.73, 125.96, 123.43, 121.62, 118.84, 110.58, 101.13; MS (FAB+): $m/z = 553$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 2224$ (s, CN), 1601 (s, C=C), 963 cm^{-1} (m, =C–H$_{trans}$); UV-Vis (CHCl$_3$): λ_{max} (ε) = 333 nm (68200); $C_{39}H_{24}N_2O_2$ (552.63): calcd C 84.76, H 4.38, N 5.07; found: C 84.52, H 4.44, N 4.97.

(*S*)-(*E,E*)-2,2′-Diethoxy-6,6′-bis[4-(methylsulfonyl)styryl]-1,1′-binaphthyl (**11a**): Diethyl-4-(methylsulfonyl)benzylphosphonate (84%)[16c] (1300 mg, 3.56 mmol) was dissolved in dry monoglyme (60 mL) under an inert atmosphere. Sodium hydride (80% in mineral oil, 300 mg, 10.00 mmol) was added at 0 °C, and the suspension was stirred magnetically for 20 min. Compound **4a** (593 mg, 1.49 mmol) was added to the suspension, and the reaction mixture was stirred for 3 days at RT. The mixture was cautiously hydrolyzed with water (300 mL) and the precipitate that formed was collected by filtration (glass frit). The obtained solid was dried in air and recrystallized from a small volume of CH$_2$Cl$_2$/AcOEt (freezer) to give 827 mg (79%) of **11a**. An analytical sample was obtained after drying at 100 °C. M.p.: 335 °C; $[\alpha]_D^{25} = 517$ ($c = 0.01$, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.97$ (d, $J = 9$ Hz, 2H, ArH), 7.93 (d, 2H, ArH^5), 7.91 (m, 4H, ArH), 7.68 (m, 4H, Ar), 7.47 (dd, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.45 (d, 2H, ArH), 7.39 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 7.15 (d, 2H, ArH), 7.13 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 4.08 (m, 4H, -OCH$_2$-), 3.06 (s, 6H, -SO$_2$Me), 1.09 (t, $J = 7$ Hz, 6H, -CH$_3$); MS (FAB+): $m/z = 703$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 1592$ (s, C=C), 1303 (s, -SO$_2$-), 1148 (s, -SO$_2$-), 957 cm^{-1} (m, =C–H$_{trans}$); UV-Vis (CHCl$_3$): λ_{max} (ε) = 301 (41000), 349 nm (51900); $C_{42}H_{38}O_6S_2$ (702.88): calcd C 71.77, H 5.45, S 9.13; found C 72.07, H 5.54, S 9.42.

(*S*)-(*E,E*)-9,14-Bis[4-(methylsulfonyl)styryl]dinaphtho[2,1-d:1′2′-f][1,3]dioxepin (**11b**): Diethyl-4-(methylsulfonyl)benzylphosphonate (84%)[16c] (1043 mg, 2.86 mmol) was dissolved in dry monoglyme (60 mL) under an inert atmosphere. Sodium hydride (80% in mineral oil, 325 mg, 11.30 mmol) was added at 0 °C, and the suspension was stirred magnetically for 30 min. Compound **4b** (500 mg, 1.41 mmol) was added to the suspension, and the reaction mixture was stirred for 3 days at RT. The mixture was cautiously hydrolyzed with dilute hydrochloric acid (300 mL), saturated with NaCl and extracted with CH$_2$Cl$_2$ (4 × 100 mL) The combined organic phases were dried (MgSO$_4$), and the solvent removed in vacuo after filtration. The obtained solid was dissolved in a small amount of CH$_2$Cl$_2$, and ether was added. The white precipitate that formed was collected on a glass frit and washed with ether to give 610 mg (66%) of **11b** as a fine white powder. M.p.: >340 °C decomp.; $[\alpha]_D^{25} = 1045$ ($c = 0.01$, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.01$ (d, 2H, ArH^5), 8.01 (d, $J = 9$ Hz, 2H, ArH), 7.94 (br d, $J = 9$ Hz, 4H, ArH), 7.71 (br d, 4H, ArH), 7.59 (dd, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.52 (2d, 4H, ArH), 7.42 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 7.22 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 5.73 (s, 2H, -CH$_2$-), 3.08 (s, 3H, -SO$_2$Me); MS (FAB+): $m/z = 659$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 1593$ (s, C=C), 1304 (s, -SO$_2$-), 1148 (s, -SO$_2$-), 959 cm^{-1} (m, =C–H$_{trans}$); UV-Vis (CHCl$_3$): λ_{max} (ε) = 292 (44800), 332 nm (80500); $C_{39}H_{30}O_6S_2$ (658.79): calcd C 71.10, H 4.59, S 9.73; found C 70.97, H 4.57, S 9.95.

(*S*)-(*E*,*E*)-9,14-bis(4-nitrostyryl)dinaphtho[2,1-d:1′,2′-f][1,3]dioxepin (**13b**): Diethyl-4-nitrobenzylphosphonate[7e] (847 mg, 3.10 mmol) and **4b** (520 mg, 1.47 mmol) were dissolved in dry monoglyme (25 mL) under a nitrogen atmosphere. Sodium hydride (80% in mineral oil, 180 mg, 6.00 mmol) as suspension in DME (25 mL) was added at 0 °C, and the reaction mixture was stirred magnetically for 30 min at this temperature. The reaction mixture was stirred further for 16 h at RT and then cautiously hydrolyzed with dilute HCl (300 mL). The yellow precipitate that formed was collected on a glass frit and washed thoroughly with water. After drying in air, the compound was dissolved in boiling CH$_2$Cl$_2$. Ether was added to the cooled solution and the yellow precipitate that formed (freezer) was filtered off (glass frit), washed with a small volume of ether, and dried in air to give 671 mg (77%) of **13b.** M.p.: 302 °C; $[\alpha]_D^{25} = 1397$ ($c = 0.005$, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.24$ (m, 4H, Ar), 8.03 (d, 2H, ArH^5), 8.02 (d, $J = 8$ Hz, 2H, ArH), 7.67 (m, 4H, Ar), 7.59 (dd, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.53 (2d, 4H, ArH), 7.44 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 7.24 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 5.73 (s, 2H, -CH$_2$-); ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta = 151.90$, 146.79, 143.65, 132.89, 132.82, 132.10, 131.89, 130.65, 128.25, 127.36, 126.77, 126.67, 126.01, 124.12, 123.48, 121.72, 103.18; MS (FAB+): $m/z = 593$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 1593$ (s, C=C), 1342 (s, NO), 962 cm^{-1} (w, =C–H$_{trans}$); UV-Vis (CHCl$_3$): λ_{max} (ε) = 254 (42700), 292 (32000), 364 nm (58800); $C_{37}H_{24}N_2O_6$ (592.61): calcd C 74.99, H 4.08, N 4.73; found C 74.88, H 4.21, N 4.61.

(*R*)-(*E,E*)-3,3′-{4,4′-[2,2′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)diethenyl]diphenyl}bis(2-cyanopropenenitrile) (**14a**): (*R*)-(*E,E*)-4,4′-[2,2′-(2,2′-diethoxy-1,1′-binaphthyl-6,6′-diyl)diethenyl]dibenzaldehyde (**12a**, 518 mg, 0.86 mmol) and malononitrile (170 mg, 2.57 mmol) were dissolved in dry CH$_2$Cl$_2$ (40 mL). One drop of piperidine (7 mg) was added and the reaction mixture was refluxed under anhydrous conditions (CaCl$_2$ tube) for 14 h. The CH$_2$Cl$_2$ was removed in vacuo. After chromatography on silica gel ($l = 10$ cm, $\varnothing = 4$ cm) with CH$_2$Cl$_2$ as an eluent, the compound was dissolved in CH$_2$Cl$_2$, and light petroleum ether was added. An orange powder preticipated which was filtered off on a glass frit and dried under reduced pressure to give 467 mg (78%) of **14a**. M.p.: 271–273 °C; $[\alpha]_D^{25} = -1322$ ($c = 0.001$, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.98$ (d, $J = 9$ Hz, 2H, ArH), 7.95 (d, 2H, ArH^5), 7.91 (br d, $J = 8$ Hz, 4H, ArH), 7.70 (s, 2H), 7.65 (br d, 4H, ArH), 7.48 (dd, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH), 7.45 (d, 2H, ArH), 7.44 (d, $J_{trans} = 16{,}3$ Hz, 2H, ArH), 7.15 (d, 2H, ArH), 7.14 (d, $J_{trans} = 16{,}3$ Hz, 2H, =CH-), 4.09 (m, 4H, -OCH$_2$-), 1.10 (t, $J = 7$ Hz, 6H, -CH$_3$); ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta = 158.64$, 155.07, 144.08, 134.24, 133.53, 131.36, 129.64, 129.04, 128.22, 127.05, 126.00, 125.86, 123.50, 120.22, 115.90, 114.03, 112.92, 80.78, 64.93, 14.83; MS (FAB+): $m/z = 699$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 2227$ cm^{-1} (m, CN); UV-Vis (CHCl$_3$): λ_{max} (ε) = 322 (35500), 440 nm (81400); $C_{48}H_{34}N_4O_2$ (698.83): calcd C 82.50, H 4.90, N 8.02; found C 82.62, H 4.84, N 8.20.

(*S*)-(*E,E*)-3,3′-{4,4′-[2,2′-(Dinaphtho[2,1-d:1′,2′-f][1,3]dioxepin-9,14-diyl)-diethenyl]diphenyl}bis(2-cyanopropenenitrile) (**14b**): (*S*)-(*E,E*)-4,4′-[2,2′-(Dinaphtho[2,1-d:1′,2′-f][1,3]dioxepin-9,14-diyl)diethenyl]dibenzaldehyde (**12b**, 551 mg, 0.99 mmol) and malononitrile (151 mg, 2.29 mmol) were dissolved in dry CH$_2$Cl$_2$ (40 mL). One drop of piperidine (7 mg) was added and the reaction mixture was refluxed under anhydrous conditions (CaCl$_2$ tube) for 18 h. The CH$_2$Cl$_2$ was removed in vacuo. After chromatography on silica gel ($l = 12$ cm, $\varnothing = 4$ cm) with CH$_2$Cl$_2$ as an eluent, the compound was dissolved in a small volume of CH$_2$Cl$_2$, and light petroleum ether was added. A bright orange powder precipitated, which was filtered off on a glass frit and dried under reduced pressure to give 502 mg (77%) of **14b**. M.p.: 297–300 °C; $[\alpha]_D^{25} = 1601$ ($c = 0.001$, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 8.03$ (d, 2H, ArH^5), 8.02 (d, $J = 9$ Hz, 2H, ArH), 7.93 (br d, $J = 9$ Hz, 4H, ArH), 7.72 (s, 2H), 7.67 (br d, 4H, ArH), 7.59 (dd, $J_{5,7} = 1.8$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.52 (d, 2H, ArH), 7.51 (d, 2H, ArH), 7.47 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 7.22 (d, $J_{trans} = 16.3$ Hz, 2H, =CH-), 5.73 (s, 2H, -CH$_2$-); ^{13}C NMR (CDCl$_3$, 62.9 MHz): $\delta = 158.59$, 151.88, 143.60, 132.89, 132.81, 132.08, 131.85, 131.35, 130.65, 129.86, 128.35, 127.31, 127.19, 127.10, 125.96, 123.45, 121.70, 113.92, 112.83, 103.15, 81.17; MS (FAB+): $m/z = 655$ [MH$^+$]; IR (KBr): $\tilde{\nu} = 2227$ cm^{-1} (m, CN); UV-Vis (CHCl$_3$): λ_{max} (ε) = 322 (33900), 414 nm (88700); $C_{45}H_{26}N_4O_2$ (654.73): calcd C 82.55, H 4.00, N 8.56; found C 82.61, H 3.96, N 8.62.

(*R*)-(*E*,*E*)-5,5′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)bis(2-cyanopenta-2,4-dienenitrile) (**15a**): (*R*)-(*E,E*)-3,3′-(2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diyl)dipropenal (**7a**, 603 mg, 1.34 mmol) and malononitrile (195 mg, 2.95 mmol) were dissolved in dry CH_2Cl_2 (50 mL). One drop of piperidine was added and the reaction mixture was refluxed under anhydrous conditions ($CaCl_2$ tube) for 16 h. The CH_2Cl_2 was removed in vacuo. After chromatography on silica gel ($l = 11$ cm, $\varnothing = 4$ cm) with CH_2Cl_2 as an eluent, the compound was dissolved in CH_2Cl_2, and light petroleum ether was added. An orange powder precipitated which was filtered off on a glass frit and dried in high vacuum to give 505 mg (69 %) of **15a**. M.p.: 309–311 °C; $[\alpha]_D^{25} = -3289$ ($c = 0.005$, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta =$ 8.04 (d, 2H, ArH^5), 8.02 (d, $J = 9$ Hz, 2H, ArH), 7.61 (d, $J = 11.5$ Hz, 2H, =CH-), 7.48 (d, $J = 9$ Hz, 2H, ArH), 7.44 (dd, $J_{5,7} = 1.8$ Hz, $J_{7,8} = 9$ Hz, 2H, ArH^7), 7.41(d, $J_{trans} = 15.7$ Hz, 2H, =CH-), 7.26 (dd, 2H, =CH-), 7.12 (d, 2H, ArH), 4.12 (m, 4H, $-OCH_2-$), 1.07 (t, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 159.93$, 156.46, 150.56, 135.69, 132.12, 130.86, 129.20, 128.54, 126.30, 123.86, 121.38, 119.59, 115.72, 113.71, 111.86, 81.43, 64.72, 14.65; MS (FAB +): $m/z = 547$ [MH^+]; IR (KBr): $\tilde{\nu} = 2225$ (s, CN), 1587 (s, C=C), 981 cm^{-1} (m, $=C-H_{trans}$); UV-Vis ($CHCl_3$): λ_{max} (ε) = 321 (34400), 433 nm (62600); $C_{36}H_{26}N_4O_2$ (546.63): calcd C 79.10, H 4.79, N 10.25; found C 79.08, H 4.76, N 10.39.

EFISHG measurements: EFISHG is a standard technique for the determination of the first molecular hyperpolarizability. Since a static electric field is applied to break the centrosymmetry of the solution, EFISHG measures the second hyperpolarizability γ, which can be written as the sum of an electronic and an orientational contribution Equation (11), where $\gamma_{electronic}$ is assumed to be much smaller than the orientational contribution.

$$\gamma = \gamma_{electronic} + \mu_Z\beta_Z/5kT \tag{11}$$

For the bis(dipolar) compounds, the direction of the dipole moment coincides with the twofold axis and $\beta_Z = \beta_{ZZZ} + \beta_{ZXX}$. $\mu_Z\beta_Z$ was measured at 1064 nm and in chloroform. All compounds were checked to ensure that no or only insignificant absorption at the harmonic wavelength perturbed the EFISHG measurements. For EFISHG β_Z values, the estimated uncertainties are ± 15 %.

Dipole moment measurements: The dipole moments of the molecules were determined by capacitance measurements according to a procedure outlined in ref. [23]. All the molecules were dissolved in chloroform.

Kurtz–Perry powder test: The second-harmonic-generation efficiencies of the BNs were investigated by the Kurtz–Perry powder technique.[9] The powders were densely packed between two glass plates separated by a spacer ensuring control over the thickness of the powder sample. All the BN samples were made of ungraded powders. The samples were irradiated with 1064 nm radiation provided by a 10 nsec Q-switched Nd:YAG laser (Quanta-Ray, DCR). The beam spot size on the samples was larger than 2 mm. The samples were studied in reflection in order to eliminate effects of different transparencies of the samples. A filter was employed to avoid spurious signals due to multiphoton fluorescence. For purpose of calibration three standard samples were used: MNA, urea, and adp. For the last two the powder grain size grade was less than 140 µm.

X-ray diffraction: The crystals of **4a** and **2b** were studied by X-ray diffraction with an Enraf–Nonius CAD-4 diffractometer. Compound **4a** crystallizes in the tetragonal space group $P4_32_12$ with unit cell dimensions $a = b = 8.0232(7)$ and $c = 32.785(3)$ Å. Compound **2b** crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 12.495(2)$, $b = 8.388(1)$, $c = 17.228(7)$ Å and $\beta = 109.42(2)°$. The structures were solved with SHELXS-86[26] and refined with SHELXL-93.[27] Resultant residuals (R_1) were 0.0703 and 0.0696 for **4a** and **2b**, respectively. Hydrogen atoms were not included. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100673. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code + (44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Crystal structure figures were drawn with PLUTO.[28] For other details see Table 4.

Table 4. Crystal data and structure refinement of racemic **2b** and **(*S*)-4a**.

	(S)-4a	**2b** (racemic)
formula	$C_{26}H_{22}O_4$	$C_{23}H_{12}N_2O_2$
M_r	398.44	348.36
T [K]	293(2)	293(2)
λ [Å]	0.71073	1.54184
crystal system	tetragonal	monoclinic
space group	$P4_32_12$	$P2_1/c$
a [Å]	8.0232(7)	12.495(2)
b [Å]	8.0232(7)	8.3880(10)
c [Å]	32.785(3)	17.228(7)
β [°]		$\beta = 109.42(2)$
V [Å^3]	2110.4(3)	1702.9(8)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.254	1.359
absorption coefficient [mm^{-1}]	0.084	0.669
crystal size [mm]	0.08 × 0.08 × 0.28	0.35 × 0.10 × 0.005
transmission (min/max)	0.988/0.994	0.906/0.982
θ range for data collection [°]	2.48–29.96	3.75–65.97
scan mode	omega	omega
index ranges	$0 \leq h \leq 11$ $0 \leq k \leq 11$ $-46 \leq l \leq 46$	$-14 \leq h \leq 14$ $0 \leq k \leq 9$ $-20 \leq l \leq 20$
reflections collected	6892	5934
independent reflections	3071	2964
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	3071/0/136	2963/0/244
hydrogen atoms	ignored	ignored
goodness of fit on F^2	0.947	1.098
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0703$ w$R_2 = 0.1553$	$R_1 = 0.0696$ w$R_2 = 0.1783$
absolute structure parameter	−6(7)	
largest diff. peak/hole [e Å^{-3}]	0.303/−0.239	0.495/−0.295

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