1,8-Naphthalimides as Stereochemical Probes for Chiral Amines: A Study of Electronic Transitions and Exciton Coupling

J. Gawroński,*,† K. Gawrońska,† P. Skowronek,† and A. Holmén*,‡

Department of Chemistry, A. Mickiewicz University, 60-780 Poznań, Poland, and Department of Physical Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

Received August 27, 1998

The absorption and magnetic circular dichroism (MCD) spectra of 1,8-naphthalimide are analyzed in terms of the number of contributing electronic transitions and their polarization. The experimental results are supported by semiempirical INDO/S calculations. It is demonstrated that the strongly allowed, $\pi \rightarrow \pi^*$ naphthalene transition of the 1,8-naphthalimide chromophore located at 231 nm is perfectly suited for absolute configuration assignments of amine derivatives on the basis of the bichromophoric exciton coupling. Both degenerate (bis-1,8-naphthalimide) and nondegenerate (1,8-naphthalimide−phthalimide, 1,8-naphthalimide−phenyl, or 1,8-naphthalimide−benzoate) couplings were studied. In the latter case, the sign of the exciton Cotton effect was opposite to the sign of the degenerate exciton Cotton effect for the same absolute configuration. An extension of the application of the exciton coupling to the 264 nm $\pi \rightarrow \pi^*$ transition of 1,9-anthraimide is also shown.

Introduction

Aromatic imides in recent years have received wide attention for such diverse purposes as model compounds for photoinduced electron transfer in photophysical studies, fluorescent tags in molecular biology, and receptor antagonists in medicinal chemistry. Despite the many applications, excited states of aromatic imides have not been, in general, fully characterized and their chiroptical properties were not systematically studied.

Recently we have reported the results of our studies of electronic transitions of the phthalimide chromophore and the use of the electric-dipole allowed $\pi \rightarrow \pi^*$ transitions for the study of stereostructure of chiral amine derivatives by exciton coupling in homo- and heterochromophoric systems.[1−3]

Derivatives of 1,8-naphthalimide (benz[*d*,*e*]isoquinoline-1,3-dione, **1a**) (Chart 1) are of special interest, as they found applications as photoactivatable DNA-cleaving agents[4] and for the synthesis of palonosetron, a 5-HT$_3$ receptor antagonist[5] as well as inhibitors of antifolate thymidylate synthase.[6] 4-Amino-substituted 1,8-naphthalimides were used for the construction of rodlike molecules for photochemical charge separation[7] and as model compounds for the study of photoinduced electron transfer.[8] Compounds of this type are also known as fluorescent dyes[9] and fluorescent tags in molecular biology.[10]

Since the excited states are of importance in many of these applications, we have attempted the study of spectroscopic properties of 1,8-naphthalimides by means of magnetic circular dichroism (MCD) and circular dichroism (CD) measurements and semiempirical computations of electronic spectra. The CD technique was used to determine the nature of interchromophoric interactions of 1,8-naphthalimides within the exciton coupling mechanism and to develop a CD method for absolute configuration assignments.

Results and Discussion

Electronic Transitions of the 1,8-Naphthalimide Chromophore. In order obtain useful information when using the 1,8-naphthalimide chromophore in the CD experiments presented below, we first analyzed the electronic absorption spectrum in terms of the number of contributing transitions, their energy, and their polarizations. To this end we measured the electronic absorption and magnetic circular dichroism spectra of **1a** in acetonitrile (Figure 1).

The lowest energy absorption band (370−280 nm) is of medium intensity and displays some vibrational structure. It is plausible that more than one transition is responsible for this absorption. At about 275 nm there is a weak but distinct band. In the region 200−250 nm, the strongest absorption is found with a maximum (ϵ = 43 000 M^{-1} cm^{-1}) centered at 231 nm. At 213 nm there is shoulder, which probably corresponds to an isolated electronic transition.

[†] A. Mickiewicz University. E-mail: gawronsk@amu.edu.pl.

[‡] Chalmers University of Technology. E-mail: anders.holmen@hassle.se.astra.com.

(1) Kaźmierczak, F.; Gawrońska, K.; Rychlewska, U.; Gawroński J. *Tetrahedron: Asymmetry* **1994**, *5*, 527.

(2) Gawroński, J.; Kaźmierczak, F.; Gawrońska, K.; Skowronek, P.; Waluk, J.; Marczyk, J. *Tetrahedron* **1996**, *52*, 13201.

(3) Gawroński, J.; Kaźmierczak, F.; Gawrońska, K.; Rychlewska, U.; Holmén, A.; Nordén, B. Submitted for publication.

(4) (a) Saito, I.; Takayama, M.; Kawanishi, S. *J. Am. Chem. Soc.* **1995**, *117*, 5590. (b) Saito, I.; Takayama, M.; Sugiyama, H.; Nakatani, K.; Tsuchida, A.; Yamamoto, M. *J. Am. Chem. Soc.* **1995**, *117*, 6406. (c) Sugiyama, H.; Saito, I. *J. Am. Chem. Soc.* **1996**, *118*, 7063.

(5) (a) Kowalczyk, B. A.; Dvorak, C. A. *Synthesis* **1996**, 816. (b) Kowalczyk, B. A. *Heterocycles* **1996**, *43*, 1439. (c) Langlois, M.; Soulier, J. L.; Rampillon, V.; Gallais, C.; Bremont, B.; Shen, S.; Yang, D.; Giudice, A.; Sureau, F. *Eur. J. Med. Chem.* **1994**, *29*, 925.

(6) Costi, M. P.; Tondi, D.; Rinaldi, M.; Barlocco, D.; Cignarella, G.; Santi, D. V.; Musiv, C.; Pudu, I.; Vacca, G.; La Colla, P. *Eur. J. Med. Chem.* **1996**, *31*, 1011.

(7) Greenfield, S. R.; Svec, W. A.; Gosztola, D.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 6767.

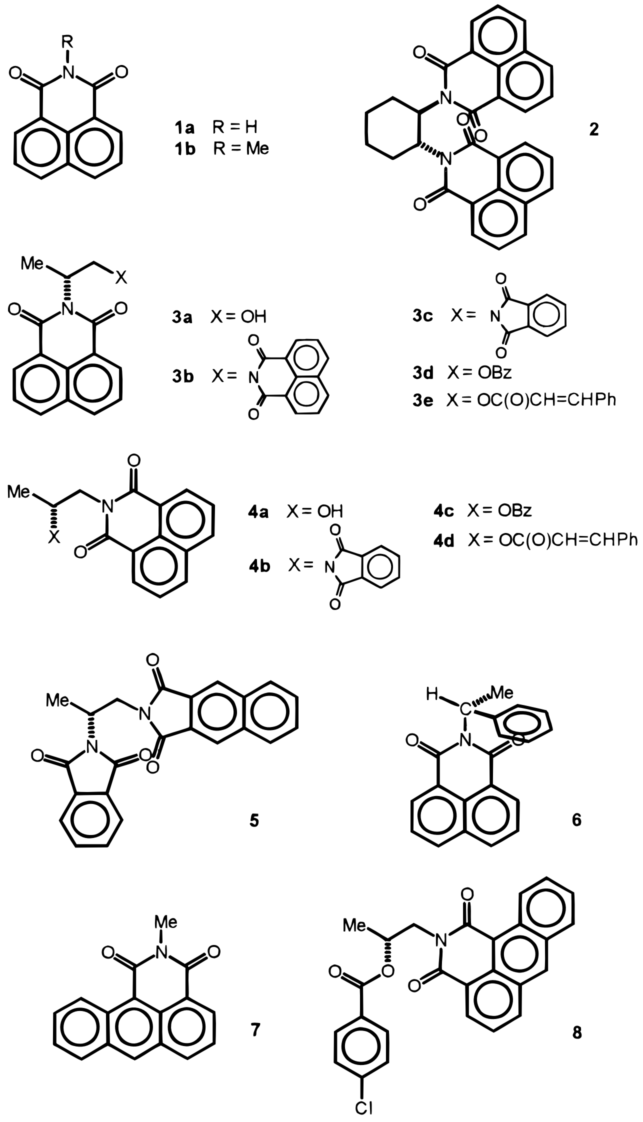
(8) Prasanna da Silva, A.; Nimal Gunaratne, H. Q.; Habib-Jiwan, J. L.; McCoy, C. P.; Rice, T. E.; Soumillion, J.-P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1728.

(9) Philipova, T. *J. Prakt. Chem.* **1994**, *336*, 587.

(10) Dubey, K. K.; Singh, R. K.; Misra, K. *Indian J. Chem.* **1995**, *B34*, 876.

10.1021/jo981760j CCC: $18.00

Chart 1



Since the 1,8-naphthalimide molecule has a nondegenerate ground state and also nondegenerate excited states, the magnetic circular dichroism (MCD) spectrum arises exclusively from the so-called *B*-term. In this case, we expect that consecutive orthogonally polarized transitions nearby in energy give rise to a sign reversal in the MCD signal.[11] With this in mind, we now turn to a closer look at the MCD spectrum of **1a** (Figure 1). First, we find the MCD spectrum to be bisignate over the lowest absorption band. This is a strong indication of two orthogonally polarized transitions in this region (I and II), presumably of $\pi \rightarrow \pi^*$ type as judged from their absorption strength.

The MCD spectrum is weak and negative over the absorption band at 275 nm, and the shape of the MCD is nearly identical to the shape of the absorption spectrum in this region which is expected for a relatively isolated transition (III). Over the strong absorption band at higher energy, we once again find a bisignate MCD spectrum indicative of at least two relatively strong orthogonally polarized $\pi \rightarrow \pi^*$ transitions located in this region. It is plausible to assume that one of them is mainly responsible for the intense sharp peak centered at 231 nm (IV) and the other one is responsible for the absorption shoulder at 213 nm (V).

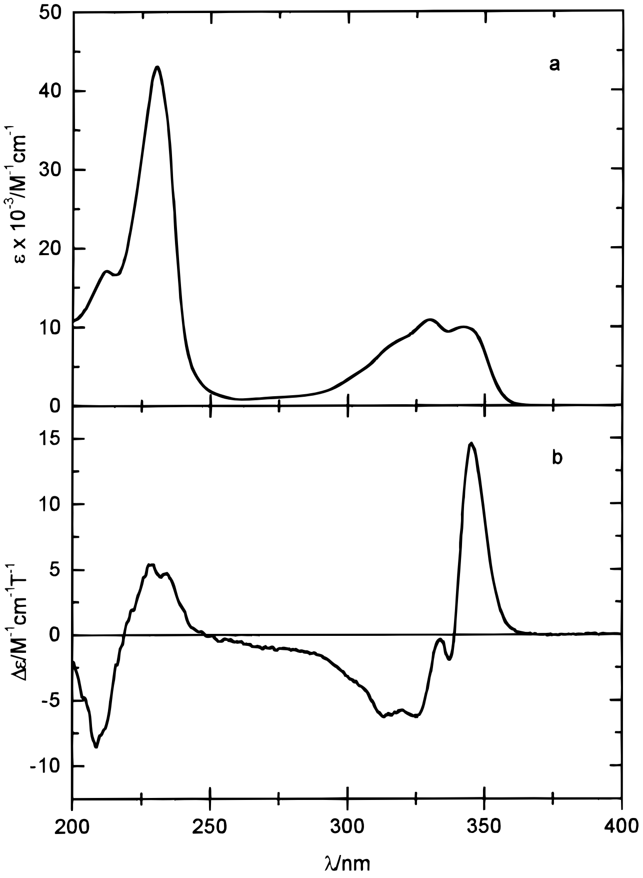


Figure 1. (a) Absorption spectrum and (b) magnetic circular dichroism (MCD) spectra of **1a** in acetonitrile.

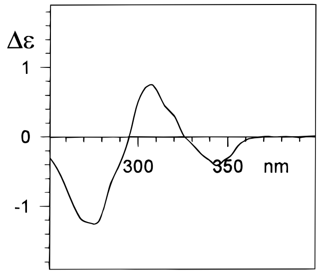


Figure 2. Circular dichroism spectrum of **3a** in acetonitrile.

Additional evidence for the assignment of the three lowest energy $\pi \rightarrow \pi^*$ transitions (I–III) comes from the CD spectrum of chiral 1,8-naphthalimide **3a** (Figure 2). The CD spectrum displays Cotton effects at 344, 307, and 276 nm corresponding to transitions I, II, and III.

In summary, from the analysis of the UV absorption and MCD spectra of **1a** we have found that at least five $\pi \rightarrow \pi^*$ transitions are needed to account for the observed spectral features. To shed further light on the detailed nature of these transitions and their absolute polarizations, we performed a semiempirical INDO/S calculation of the excited states of **1a**. The INDO/S method has been used extensively for the heterocyclic molecules[12] and

---

[11] Nordén, B.; Hokansson, R.; Pedersen, P. B.; Thulstrup, E. W. *Chem. Phys.* **1978**, 33, 355.

[12] (a) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta.* **1973**, *32*, 111. (b) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223. (c) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21. (d) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

Table 1. Calculated and Observed Electronic Transitions of 1,8-Naphthalimide (1a)

INDO/S[a]					experimental		
trans.	type	λ/ nm	f	pol.	trans.	λ/ nm	ϵ^b/M^{-1} cm^{-1}
$S_0 \rightarrow S_1$	$n \rightarrow \pi^*$	346	0.001	out-of-plane			
$S_0 \rightarrow S_2$	$n \rightarrow \pi^*$	330	0.000	forbidden			
$S_0 \rightarrow S_3$	$\pi \rightarrow \pi^*$	321	0.02	y	I	348	~5000
$S_0 \rightarrow S_4$	$\pi \rightarrow \pi^*$	306	0.46	z	II	330	~10000
$S_0 \rightarrow S_5$	$\pi \rightarrow \pi^*$	251	0.19	y	III	275	~1000
$S_0 \rightarrow S_6$	$\pi \rightarrow \pi^*$	234	0.02	z			
$S_0 \rightarrow S_7$	$\pi \rightarrow \pi^*$	231	0.63	y	IV	231	~40000
$S_0 \rightarrow S_8$	$\pi \rightarrow \pi^*$	219	0.34	z	V	213	~12000

[a] 105 singly excited configurations in CI. [b] Molar absorptivities at absorption maximum in acetonitrile. The numbers are crude estimates based on an analysis of the shapes of the absorption and MCD spectra.

proved to give excellent agreement with experiment in a recent study of the phthalimide chromophore.[3] The calculated and experimentally observed transitions are summarized in Table 1.

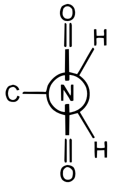
The two lowest calculated transitions are of $n \rightarrow \pi^*$ type, and the remaining transitions in the studied region are calculated to be of $\pi \rightarrow \pi^*$ type. Experimentally, we have no evidence for any $n \rightarrow \pi^*$ transition. In our previous study of the related phthalimide chromophore, we found evidence that the lowestlying transition is a very weak out-of-plane polarized $n \rightarrow \pi^*$ transition. This transition is responsible for the very weak absorption tail on the red side of the lowest absorption band of the phthalimide chromophore. A similar tail is not seen for the 1,8-naphthalimide chromophore. This indicates that the weak $n \rightarrow \pi^*$ transitions are obscured by the $\pi \rightarrow \pi^*$ transitions which make up the lowest energy band. Demeter et al.[13] studied the photophysical properties of *N*-methyl-1,8-naphthalimide in hexane and acetonitrile. In both solvents, this molecule has a quantum yield for intersystem crossing close to 1 and correspondingly very low quantum yields for fluorescence. Such a behavior has been found for many aromatic carbonyl compounds including phthalimide where the lowest state has been assigned to be an $n-\pi^*$ state.[14] Thus, it is plausible that the lowest energy transition in **1a** is an $n \rightarrow \pi^*$ transition, in agreement with the INDO/S result.

The first calculated $\pi \rightarrow \pi^*$ transition ($S_0 \rightarrow S_3$, L_b-type) has quite low intensity and is polarized in the molecular plane perpendicular to the C_2 axis of the molecule. At slightly higher energy a relatively strong $\pi \rightarrow \pi^*$ transition ($S_0 \rightarrow S_4$, L_a-type) is predicted. This transition is polarized in the plane and along the C_2 axis. We assign these two transitions to be the calculated counterparts of the experimentally observed transitions I and II. For the higher lying transitions, there is a high degree of conformity between experiment and theory and it is especially noteworthy that the INDO/S method predicts a weak transition ($S_0 \rightarrow S_5$) corresponding to the weak transition observed at about 275 nm. The strong $\pi \rightarrow \pi^*$ transition observed at 231 nm (IV) is predicted ($S_0 \rightarrow S_6$) to be polarized perpendicular to the C_2axis, and the next observed transition (V) is predicted ($S_0 \rightarrow S_7$) to be polarized orthogonally to transition IV.

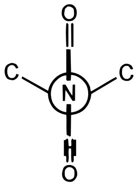
The predicted sequence of varying polarizations of transitions I, II, IV, and V is in harmony with the observed sign changes in the MCD spectrum. Furthermore, the absolute signs of the MCD bands are in accord with the rules developed by Michl for the *B*-term of cyclic π-electron systems.[15] The calculated energy splitting between the two highest occupied molecular orbitals (ΔHOMO) is smaller than the energy splitting between the lowest unoccupied molecular orbitals (ΔLUMO). Thus, for an odd-soft chromophore like naphthalene substituted with an electron-withdrawing imide group, the MCD signs of the L_b and L_a transitions should be + and −, respectively, which is what we observe.

Comparison with the Phthalimide Chromophore. In the phthalimide chromophore, the most intense $\pi \rightarrow \pi^*$ transition at ca. 220 nm is polarized along the long axis and the direction of the electric dipole transition moment is independent of any rotational equilibria around the C−N bond.[3] In the case of the 1,8-naphthalimide chromophore, we singled out the intense naphthalene $\pi \rightarrow \pi^*$ transition at 231 nm (ϵ ca. 43 000) as a candidate for efficient exciton coupling. According to the MCD measurements and INDO/S calculations (vide supra), the direction of the electric dipole transition moment for this transition is orthogonal to the C_2 axis. This means that when the 1,8-naphthalimide is coupled to another molecule via the imide nitrogen, the transition moment direction in the molecular framework depends on the rotational freedom around the connecting C−N bond. We find, however, that other structural characteristics of the 1,8-naphthalimide chromophore make the problem of rotational dependence of the transition moment direction far less critical.

Notably, as it is also well-documented in the case of phthalimides,[1] there is a clear-cut rotational energy minimum for the C−N bond. For the 1,8-naphthalimide chromophore attached to a primary alkyl group, both semiempirical (AM1) and molecular mechanics (PC MODEL 5.0) calculations of *N*-ethyl-1,8-naphthalimide (**1c**) assign the rotational energy minimum to the conformer with the Me−CH_2 bond perpendicular to the imide plane (rotamer A). The rotational barrier calculated by either of the two methods is 3.2 kcal/mol for the Me−C bond coplanar with the imide plane (Figure 3) and is ca. 1.5 kcal/mol higher compared to the rotational barrier calculated for *N*-ethylphthalimide.



A



B

Rotamers defined as having the R−CH_2−N plane approximately perpendicular to the 1,8-naphthalimide plane have been found in the solid state by X-ray diffraction studies of RCH_2-substituted 1,8-naphthalimides,[16,17] including **1c**.[18a]

---

(13) Demeter, A.; Bérces, T.; Biczók, L.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Phys. Chem.* **1996**, *100*, 2001.

(14) Becker, R. S. *Theory and interpretation of fluorescence and phosphorescence*, Chapter 12; Wiley: New York, 1969.

(15) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6819.

(16) Clark, R. G.; Hall, S. B. *Acta Crystallogr.* **1989**, *C45*, 67.

(17) Baughman, R. G.; Chang, S.-C.; Utecht, R. E.; Lewis, D. E. *Acta Crystallogr.* **1995**, *C51*, 1189.

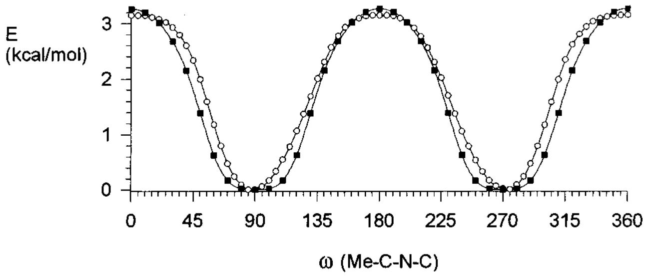
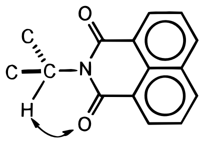


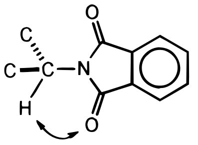
Figure 3. Steric energy of **1c** as a function of angle of rotation of the N−Et bond: □−□−□−□, AM-1; ○−○−○−○, PC MODEL 5.0.

In the case of the 1,8-naphthalimide chromophore attached to a secondary carbon atom, the preferred rotamer has coplanar arrangement of the imide ring and the vicinal C−H bond (rotamer B).

The reason for the higher rotational barrier in 1,8-naphthalimides compared to phthalimides becomes obvious on inspection of molecular structures. In 1,8-naphthalimides the interaction between the *syn*-hydrogen atom and the imide oxygen atom is more significant due to the larger (O)C−N−C(O) angle in these imides (C), ca. 125° in *N*-phenyl-1,8-naphthalimide, when compared to phthalimides (D), ca. 111° in *N*-phenyl-2,3-naphthalimide.[18b] This should result in significant differences in shielding of protons *syn* to the carbonyl groups. Comparison of the experimental chemical shifts of the C*H*-N protons in 1,8-naphthalimides **2**−**5** with the shifts of the corresponding protons in phthalimides reveals additional 0.7−1.0 ppm downfield shift in the former cases, providing support for the smaller distance between the imide carbonyl group and the α-hydrogen atom.



C



D

Consequently, rotation of the 1,8-naphthalimide chromophore attached to a secondary carbon atom in bis-imides **2**, **3b**, and **3c** is severely slowed, resulting in broadening of the resonance signals of 1,8-naphthalimide protons in the NMR spectra recorded at ambient temperature. Signals of protons of 1,8-naphthalimides appear in the following ranges: 2H, 7H 8.4−8.6; 3H, 6H 7.6−7.8; 4H, 5H 8.0−8.2 ppm. Signal broadening is most significant for the pairs of protons 2,7 and 3,6. In the case of C_2-symmetrical imide **2**, separate signals of the symmetry-related aromatic protons are observed with the following $\delta\nu$ values: 2H, 7H 40.7 Hz; 3H, 6H 21.4 Hz; 4H, 5H 5.1 Hz. This indicates very slow, concerted rotation of the two 1,8-naphthalimide groups in **2** at ambient temperature.

Degenerate Exciton Coupling in the Circular Dichroism Spectra. The CD spectrum of bis-1,8-naphthalimide **2** (Figure 4) represents the case of degenerate exciton coupling due to the allowed naphthalene $\pi \rightarrow \pi^*$ transitions at 231 nm. The observed Cotton effect, $A = -205$, is very strong while Cotton effects due to other transitions are relatively weak.

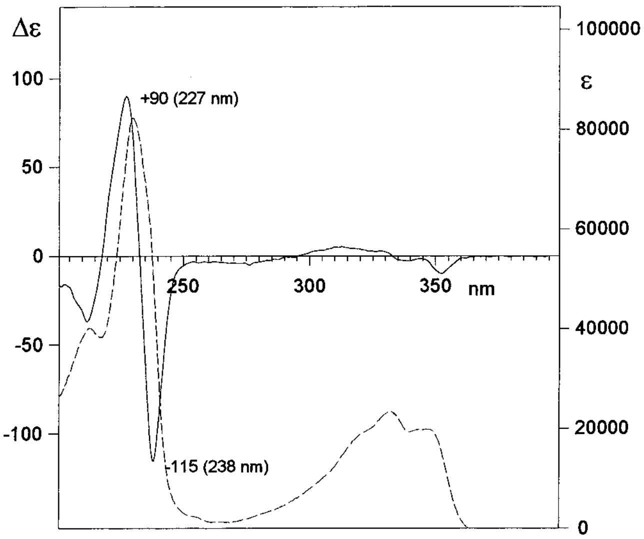
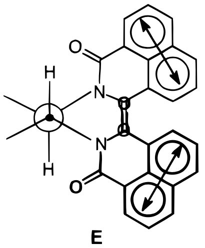
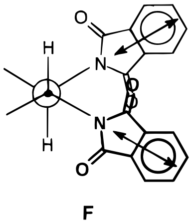


Figure 4. CD and UV spectra of **2** in acetonitrile.

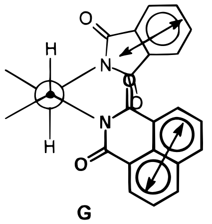
The transition at 231 nm is polarized perpendicularly to the direction of the C−N bond connecting the imide and the cyclohexane moieties, and high amplitude of the exciton Cotton effect is the result of restricted rotation of the naphthalimide chromophores. The exciton Cotton effect is negative (Δϵ −115 at 238 nm and +90 at 227 nm) and is of the same sign as the 220 nm exciton Cotton effect of the corresponding bis-phthalimide,[3] despite the fact that in the latter case the electric dipole transition moments are colinear with the C−N bonds. This apparent paradox is readily explained by the rotation of the electric dipole transition moments in *each* of the two chromophores by 90° when substituting the phthalimide chromophores by 1,8-naphthalimide chromophores. Orthogonality of the polarization direction of the most intense $\pi \rightarrow \pi^*$ transitions in the 1,8-naphthalimide and phthalimide chromophores results in reversal of *both* the handedness and the energy order of the exciton-coupled Cotton effects (structures E and F).



E



F



G

Thus, in the case of degenerate exciton coupling represented by **2**, a negative N−C−C−N torsional angle of the bis-naphthalimide system leads to a negative exciton Cotton effect within the exciton-split 231 nm $\pi \rightarrow \pi^*$ transition.

---

[18] (a) Easton, C. J.; Gulbis, J. M.; Hoskins, B. F.; Scharfbilling, I. M.; Tiekink, R. T. *Z. Kristallogr.* **1992**, *199*, 249. (b) Dromzée, Y.; Kossanyi, J.; Wintgens, V.; Valat, P.; Biczók, L.; Demeter, A.; Bérces, T. *Z. Kristallogr.* **1995**, *210*, 760.

Table 2. Short-Wavelength (300−210 nm) Cotton Effects of Naphthalimides 2−6 and 8 and the Corresponding UV Maxima (in Acetonitrile)

no.	CD, $\Delta\epsilon$ (nm)			UV, ϵ (nm)	
2		−115.0 (238)	+90.0 (227)	81000 (230)	
3b		−61.0 (238)	+65.0 (227)	81000 (231)	
3c	−24.2 (242)	+52.2 (230)	−58.6 (219)	50400 sh (233)	61200 (221)
3d		+35.0 (236)	−21.5 (223)	57500 (231)	
3e		+2.5 (260)		26100 (277)	51200 (233)
4b	−44.2 (242)	+34.0 (229)	−53.9 (220)	50000 sh (233)	60000 (221)
4c		+27.0 (236)	−44.6 (224)	53200 (230)	
4d		+2.6 (283)	−16.8 (232)	23800 (277)	50800 (233)
5		−51.2 (243)	+32.2 (211)	61500 (259)	60000 (217)
6		−15.0 (235)	+7.5 (214)	46700 (233)	28900 (212)
8		+13.8 (264)	−24.4 (237)	86500 (264)	39600 (243)

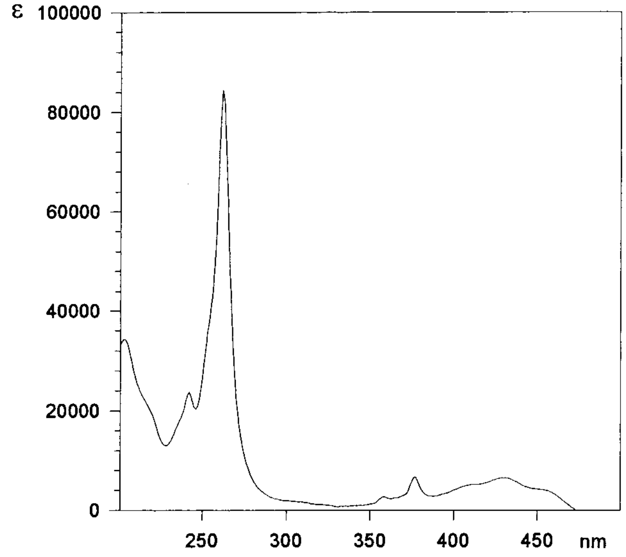


Figure 5. UV spectrum of **7** in acetonitrile.

Acyclic bis-1,8-naphthalimide **3b** represents another case of the degenerate bichromophoric system. Its exciton Cotton effect due to the 231 nm transition ($A = -126$, Table 2) is less intense compared to that of **2**, most probably due to the contribution of other conformers of **3b**, yet it is of the same sign as the corresponding Cotton effects of **2**. Since the sense of helicity of the N−C−C−N bond system in **2** and in the most stable *trans* conformer of **3b** is negative, we conclude that in degenerate bis-1,8-naphthalimide systems the sign of the 231 nm $\pi \rightarrow \pi^*$ exciton-split Cotton effect corresponds to the helicity of the N−C−C−N bond system connecting the two imide chromophores.

Nondegenerate Exciton Coupling. We have studied the coupling of the two electric dipole transition moments in nondegenerate bis-imide systems, **3c**, **4b**, and **5**. In **3c**, **4b**, and **5** the phthalimide 220 nm $\pi \rightarrow \pi^*$ transition is polarized along the C−N bond as is the 256 nm $\pi \rightarrow \pi^*$ transition in **5**. The 1,8-naphthalimide 231 nm $\pi \rightarrow \pi^*$ transition in **3c** and **4b** is polarized perpendicularly to the direction of the imide C−N axis (structure G).

In bis-imides **3c** and **4b**, only one electric dipole transition moment is perpendicular to the C−N bond axis and the helicity of the interacting electric dipole system is reversed. This results in a positive exciton Cotton effect, observed as a positive band at 229−230 nm and a negative one at 219−220 nm. There is also a negative CD band observed at 242 nm in the CD spectra of **3c** and **4b**, and this is due to the coupling of the short-axis polarized $\pi \rightarrow \pi^*$ transition in the phthalimide at 240 nm[3] with the 233 nm transition in the 1,8-naphthalimide (both handedness and energy order are reversed).

In contrast, the CD spectrum of bis-imide **5** displays a negative exciton Cotton effect, as expected for the bis-imide chromophoric system in which the two transition moments are colinear with the C−N bonds.

Benzoates **3d** and **4c** also belong to the category of bichromophoric systems with nondegenerate exciton coupling. Their CD spectra show positive exciton Cotton effects due to the coupling of the 1,8-naphthalimide 233 nm transition with the 227 nm $\pi \rightarrow \pi^*$ benzoate transition. Since the benzoate transition is polarized approximately in the direction of the C−O bond, this bichromophoric system behaves similarly to the 1,8-naphthalimide−phthalimide system (**3c**, **4b**).

The cinnamates **3e** and **4d** display much weaker Cotton effects than the corresponding benzoates **3d** and **4c**. This is due to the large energy gap separating the excited states of the two chromophores, the cinnamate (λ_{max} 277 nm) and the 1,8-naphthalimide (λ_{max} 231 nm). Consequently, the cinnamate chromophore is not well-suited for coupling with the 1,8-naphthalimide chromophore.[19]

Still another example of nondegenerate exciton coupling is represented by the CD spectrum of imide **6**. The coupling of the 1,8-naphthalimide 231 nm transition with the phenyl group ^1L_a transition (long-axis polarized) results in a negative exciton Cotton effect (Table 1). A negative Cotton effect is expected for a preferred conformer of **6** in which the 1,8-naphthalimide plane bisects the Ph−C−Me angle in the substituent attached to the nitrogen atom. It should be noted that only a weak, nonexciton Cotton effect could be measured for the phthalimide analogue of **6**, in which the two transition moments are coplanar.[1]

1,9-Anthraimide Chromophore. It was anticipated that the imide moiety fused to the anthracene ring would produce a chromophore with even more intense aromatic $\pi \rightarrow \pi^*$ transition and with effective exciton coupling resulting in larger Cotton effects.

N-Methyl-1,9-anthraimide (**7**) was obtained from the known 1,9-anthracenedicarboxylic anhydride,[20−22] and its UV spectrum (Figure 5) indeed shows an intense band,

---

(19) Cinnamate **4d** displays additional Cotton effect, $\Delta\epsilon$ −4.6 at 316 nm, apparently due to the coupling of the cinnamate $\pi-\pi^*$ transition (λ_{max} 277 nm) with the 1,8-naphthalimide $\pi-\pi^*$ transition at 330 nm, polarized along the direction of the C−N axis.

(20) Liebermann, C.; Zsuffa, M. *Ber.* **1911**, *44*, 202.

(21) Bergmann, E. D.; Ikan, R. *J. Org. Chem.* **1958**, *23*, 907.

(22) Neugebauer, W.; Clark, T.; von Ragué Schleyer, P. *Chem. Ber.* **1983**, *116*, 3283.

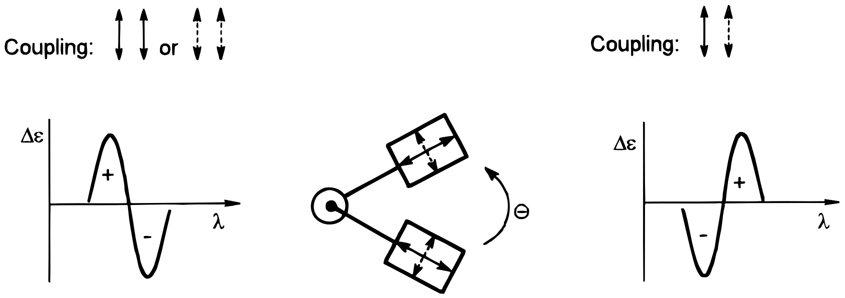


Figure 6. Exciton Cotton effects resulting from coupling of orthogonaly polarized electric dipole transition moments.

$\epsilon = 84\,500$, at 262 nm, presumably due to the $\pi-\pi^*$ transition polarized along the molecule's long axis. Compound **7** shows λ_{max} in fluorescence spectra at 495 and 522 nm, in acetonitrile solution.

We were unable to prepare the bis-imide from (1*R*,2*R*)-1,2-diaminocyclohexane and 1,9-anthracenedicarboxylic anhydride; however imide **8** was synthesized from (*R*)-1-amino-2-propanol and its CD spectrum (Table 1) displays typical exciton-split Cotton effects located at approximately absorption maxima of the 1,9-anthraimide and *p*-chlorobenzoate chromophores. The sign of the Cotton effect is positive, as expected for the chromophoric system analogous to that in the 1,8-naphthalimidobenzoate **4c**. However, contrary to expectation, the amplitude of the exciton Cotton effect is smaller than that for **4c**. This, combined with more troublesome preparation of 1,9-anthraimides and their low solubility, makes 1,9-anthraimides less attractive as chromophoric derivatives of amines, compared to 1,8-naphthalimides.

Conclusions

From the analysis of the absorption, MCD, and CD spectra of mono-1,8-naphthalimides in combination with INDO/S calculations, we have assigned five $\pi \rightarrow \pi^*$ transitions that are mainly responsible for the observed UV−vis spectra. The strong absorption at 231 nm was found to be due to a transition polarized perpendicular to the C_2 axis of the 1,8-naphthalimide chromophore. For bischromophoric 1,8-naphthalimide derivatives, this transition can be used effectively for absolute configuration assignments based on exciton coupling. Both degenerate and nondegenerate coupling are applicable, in the latter case the sign of the exciton Cotton effect resulting from the coupling of the 1,8-naphthalimide 231 nm transition with the allowed $\pi \rightarrow \pi^*$ transitions of the phthalimide (220 nm) or benzoate (228 nm) chromophores is opposite to the sign of the degenerate exciton Cotton effect.

Figure 6 is a generalized picture of exciton coupling of the electric dipole transition moments in the case of degenerate and nondegenerate bichromophoric systems linked by a gauche bond pattern. The sign pattern of the Cotton effects reflects unequivocally the helicity of the gauche bond system and, thus, the absolute configuration of any chiral center included in the bond system.

Experimental Section

General Methods. CD measurements were made on a Jobin-Yvon III dichrograph, in acetonitrile solution, ^{1}H NMR were recorded on a 300 MHz spectrometer in $CDCl_3$ with TMS as internal reference, and IR spectra were taken in KBr pellets. HRMS were taken with an AMD 402 spectrometer. MCD measurements were made on a JASCO 720 spectropolarimeter equipped with a permanent horse shoe magnet. The magnetic field was calibrated to be 1.1 T by using the MCD signal at 510 nm of a 1 M solution of $CoSO_4$ ($\Delta\epsilon_{510} = -1.88 \times 10^{-2}$ M^{-1} cm^{-1} T^{-1}).[23] The MCD was measured for **1a** in acetonitrile.

The molecular orbital (MO) calculations of electronic absorption spectra were performed with the INDO/S model Hamiltonian.[12] The two-center electron repulsion integrals were calculated using the Mataga−Nishimoto scheme.[24]

Materials. Phthalimide, 2,3-naphthalimide, 1,8-naphthoic anhydride, and 1,8-naphthalimide (**1a**), as well as (*R*)-2-amino-1-propanol and (*R*)-1-amino-2-propanol, were purchased from Aldrich.

N-Methyl-1,8-naphthalimide (**1b**) was prepared according to a published procedure:[25] mp 209−210 °C; ^{1}H NMR ($CDCl_3$) δ 3.56 (s, 3H), 7.50 (dd, $J = 8.3$, 7.3 Hz, 2H), 8.20 (dd, $J = 8.3$, 1.1 Hz, 2H), 8.60 (dd, $J = 7.3$, 1.1 Hz, 2H).

1,9-Anthracenedicarboxylic anhydride was synthesized from anthracene by Friedel−Crafts reaction with oxalyl chloride (as a solvent dichloromethane was used instead of carbon disulfide)[20] and hydrogen peroxide oxidation of the resulting aceanthrenequinone.[21] 1,9-Anthracenedicarboxylic acid forms the anhydride on heating, mp 297−299 °C.[22]

(1*R*,2*R*)-1,2-Bis(1′,8′-naphthalimido)cyclohexane (2). A solution of (1*R*,2*R*)-1,2-diaminocyclohexane (114 mg, 1 mmol) in DMF (1 mL) was added to a hot solution of 1,8-naphthalic anhydride (396 mg, 2 mmol) in DMF (5 mL). The mixture was refluxed for 6 h and diluted with water and the precipitate filtered off. Column chromatography (silicagel, CH_2Cl_2−2% MeOH) afforded uncreated anhydride, followed by product **2**, yield 80 mg (17%). Product **2** crystallized from benzene with a half molar equivalent of the solvent, but no solvent was included from dioxane: mp 324−326 °C; $[\alpha]^{20}_D$ −141 ($c = 1$, $CHCl_3$); IR (KBr) 1695, 1662, 1625, 1585, 1377, 1340, 1236, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 2H), 1.96 (m, 4H), 2.69 (m, 2H), 6.40 (m, 2H), 7.56 (dd, $J = 8.2$, 7.3 Hz, 2H), 7.64 (dd, $J = 8.2$, 7.3 Hz, 2H), 8.03 (dd, $J = 8.2$, 1.0 Hz, 2H), 8.05 (dd, $J = 8.2$, 1.0 Hz, 2H), 8.42 (dd, $J = 7.3$, 1.0 Hz, 2H), 8.55 (dd, $J = 7.3$, 1.0 Hz, 2H). Anal. Calcd for $C_{30}H_{22}N_2O_4$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.61; H, 4.82; N, 5.72.

(*R*)-*N*-(1′,8′-Naphthaloyl)-2-aminopropanol (3a). A mixture of (*R*)-2-amino-1-propanol (225 mg, 3 mmol), 1,8-naphthoic anhydride (595 mg, 3 mmol), and dioxane (5 mL) was refluxed under argon for 6 h. After purification by short-column chromatography, product **3a** was obtained in a yield of 610 mg (80%): mp 199−201 °C (dioxane−diethyl ether); $[\alpha]^{20}_D$ −14.5 ($c = 1$, $CHCl_3$); IR (KBr) 1690, 1650, 1620, 1585, 1350, 1240, 1050, 775 cm^{-1}; UV$_{max}$ (MeCN) 234 nm (ϵ 45 400); ^{1}H NMR ($CDCl_3$) δ 1.55 (d, $J = 7.1$ Hz, 3H), 3.25 (dd, $J = 9.2$, 3.2 Hz, OH), 3.98 (dt, $J = 12.0$, 3.3 Hz, 1H), 4.17 (ddd, $J = 12.0$, 9.2, 7.3 Hz, 1H), 5.49 (dq, $J = 7.2$, 3.3 Hz, 1H), 7.76 (dd, $J = 8.3$, 7.3 Hz, 2H), 8.22 (dd, $J = 8.3$, 1.1 Hz, 2H), 8.60 (dd, $J =$

---

[23] McCaffery, A. J.; Stephens, P. J.; Schatz, P. N. *Inorg. Chem.* **1967**, *9*, 1614.

[24] Nishimoto, K.; Mataga, N. *Z. Phys. Chem.* **1957**, *12*, 335.

[25] Somich, C.; Mazzochi, P. H.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 3614.

7.3, 1.1 Hz, 2H); HRMS *m/e* (M^+) calcd for $C_{15}H_{13}NO_3$ 255.089, obsd 255.090.

(*R*)-1,2-Bis(1′,8′-naphthalimido)propane (3b). A solution of triphenylphosphine (157 mg, 0.6 mmol) in DMF (2.5 mL) was cooled to 0 °C, and diethyl azodicarboxylate (0.1 mL, 0.6 mmol) was added. Stirring was continued for 15 min, followed by addition of 1,8-naphthalimide (99 mg, 0.5 mmol) and **3a** (128 mg, 0.5 mmol). After 2 days of stirring at room temperature, the mixture was subjected to extractive workup (AcOEt−2 M HCl, then H_2O) and column chromatography (silica gel, CH_2Cl_2−2%AcOEt). Product **3b** was obtained in a yield of 76 mg (35%): mp 286−289 °C (from AcOEt); $[\alpha]^{20}_D$ −173 (*c* = 0.8, $CHCl_3$); IR (KBr) 1695, 1660, 1625, 1585, 1377, 1340, 1236, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.79 (d, *J* = 7.3 Hz, 3H), 4.57 (dd, *J* = 13.4, 3.9 Hz, 1H), 5.18 (dd, *J* = 13.6, 8.0 Hz, 1H), 5.69 (m, 1H), 7.66 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.6−7.8 (broad m, 2H), 8.15 (dd, *J* = 8.3, 1.0 Hz, 2H), 8.15−8.17 (broad d, 2H), 8.47 (dd, *J* = 7.3, 1.0 Hz, 2H), 8.3−8.7 (broad m, 2H). Anal. Calcd for $C_{27}H_{18}N_2O_4$: C, 74.65; H, 4.18; N, 6.45. Found: C, 74.44; H, 3.99; N, 6.44.

(*R*)-1-Phthalimido-2-(1′,8′-naphthalimido)propane (3c). Bis-imide **3c** was obtained from **3a** and phthalimide according to the procedure described for **3b**. **3c**: yield 54%; mp 165−166 °C (AcOEt−MeOH); $[\alpha]^{20}_D$ −224 (*c* = 0.9, $CHCl_3$); IR (KBr) 1772, 1710, 1652, 1587, 1390, 1240, 777, 725, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (d, *J* = 7.1 Hz, 3H), 4.08 (dd, *J* = 14.1, 4.2 Hz, 1H), 4.68 (dd, *J* = 14.1, 9.0 Hz, 1H), 5.58 (m, 1H), 7.63 (m, 2H), 7.73 (m, 2H), 7.6−7.8 (broad m, 2H), 8.19 (dd, *J* = 8.3, 1.0 Hz, 2H), 8.54 (broad m, 2H). Anal. Calcd for $C_{23}H_{16}N_2O_4$: C, 71.87; H, 4.20; N, 7.29. Found: C, 71.80; H, 4.34; N, 6.98.

(*R*)-*O*-Benzoyl-*N*-(1′,8′-naphthaloyl)-2-aminopropanol (3d). Imide **3a** (150 mg, 0.59 mmol), pyridine (0.5 mL), benzoyl chloride (0.15 mL), and DMAP (10 mg) were stirred overnight at room temperature and then heated at 100 °C for 1 h. Extraction (AcOEt−2 M HCl, then 10% $NaHCO_3$, then H_2O) followed by short-column chromatography (silica gel, CH_2Cl_2) gave 178 mg (84%) **3d**: mp 96−98 °C (AcOEt−hexane); $[\alpha]^{20}_D$ −50 (*c* = 1, $CHCl_3$); IR (KBr) 1720, 1690, 1640, 1585, 1270, 780, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69 (d, *J* = 7.0 Hz, 3H), 4.77 (dd, *J* = 11.1, 5.8 Hz, 1H), 5.00 (dd, *J* = 11.1, 8.2 Hz, 1H), 5.72 (m, 1H), 7.34 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.48 (m, 1H), 7.76 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.93 (m, 2H), 8.21 (dd, *J* = 8.3, 1.0 Hz, 2H), 8.60 (dd, *J* = 7.3, 1.0 Hz, 2H); HRMS *m/e* (M^+) calcd for $C_{22}H_{17}NO_4$ 359.115, obsd 359.112.

(*R*)-*O*-Cinnamoyl-*N*-(1′,8′-naphthaloyl)-2-aminopropanol (3e) was prepared from **3a** and cinnamoyl chloride according to the procedure described for **3d**. **3e**: yield 68%; mp 143−145 °C (AcOEt−hexane); $[\alpha]^{20}_D$ −129 (*c* = 1, $CHCl_3$); IR (KBr) 1710, 1700, 1655, 1590, 1380, 1243, 1180, 785, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (d, *J* = 7.0 Hz, 3H), 4.68 (dd, *J* = 11.2, 5.7 Hz, 1H), 4.90 (dd, *J* = 11.2, 8.3 Hz, 1H), 5.64 (m, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 7.32 (m, 3H), 7.42 (m, 2H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.76 (dd, *J* = 8.2, 7.3 Hz, 2H), 8.22 (dd, *J* = 8.2, 1.0 Hz, 2H), 8.61 (dd, *J* = 7.3, 1.0 Hz, 2H); HRMS *m/e* (M^+) calcd for $C_{24}H_{19}NO_4$ 385.131, obsd 385.131.

(*R*)-*N*-(1′,8′-Naphthaloyl)-1-amino-2-propanol (4a). Imide **4a** was obtained from (*R*)-1-amino-2-propanol and 1,8-naphthalic anhydride according to the procedure described for **3a**. **4**a: yield 72%; mp 146−148 °C (from dioxane−diethyl ether); $[\alpha]^{20}_D$ +10.4 (*c* = 1, $CHCl_3$); IR (KBr) 1700, 1645, 1620, 1590, 1385, 1350, 1235, 1055, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (d, *J* = 6.2 Hz, 3H), 2.75 (d, *J* = 5.8 Hz, OH), 4.23 (m, 1H), 4.32 (m, 2H), 7.77 (dd, *J* = 8.3, 7.3 Hz, 2H), 8.23 (d, *J* = 8.3 Hz, 2H), 8.61 (d, *J* = 7.3 Hz, 2H);. HRMS *m/e* (M^+) calcd for $C_{15}H_{13}NO_3$ 255.089, obsd 255.090.

(*R*)-1-(1′,8′-Naphthalimido)-2-phthalimidopropane (4b). Bis-imide **4b** was obtained from *N*-phthaloyl-D-alaninol[1] and 1,8-naphthalimide according to the procedure described for **3b**. **4b**: yield 68%; mp 185−187 °C; $[\alpha]^{20}_D$ −242 (*c* = 1, $CHCl_3$); IR (KBr) 1770, 1700, 1660, 1590, 1380, 1370, 1335, 1240, 1070, 780, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (d, *J* = 7.2 Hz, 3H), 4.32 (dd, *J* = 13.0, 3.1 Hz, 1H), 4.85 (m, 1H), 5.00 (dd, *J* = 13.0, 9.5 Hz, 1H), 7.6−7.8 (m, 6H), 8.19 (dd, *J* = 8.3, 1.0 Hz, 2H), 8.46 (dd, *J* = 7.3, 1.0 Hz, 2H). Anal. Calcd for $C_{23}H_{16}N_2O_4$: C, 71.87; H, 4.20; N, 7.29. Found: C, 71.61; H, 4.25; N, 7.03.

(*R*)-*O*-Benzoyl-*N*-(1′,8′-naphthoyl)-1-amino-2-propanol (4c) was prepared from **4a** according to the procedure described for **3d**. **4c**: yield 78%; mp 117−119 °C (AcOEt−hexane); $[\alpha]^{20}_D$ −132 (*c* = 1, $CHCl_3$); IR (KBr) 1710, 1695, 1660, 1595, 1270, 1110, 780, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51 (d, *J* = 6.4 Hz, 3H), 4.29 (dd, *J* = 13.5, 3.4 Hz, 1H), 4.77 (dd, *J* = 13.5, 8.9 Hz, 1H), 5.59 (m, 1H), 7.36 (m, 2H), 7.49 (m, 1H), 7.73 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.96 (m, 2H), 8.19 (dd, *J* = 8.3, 1.0 Hz, 2H), 8.58 (dd, *J* = 7.3, 1.0 Hz, 2H); HRMS *m/e* (M^+) calcd for $C_{22}H_{17}NO_4$ 359.115, obsd 359.113.

(*R*)-*O*-Cinnamoyl-*N*-(1′,8′-naphthaloyl)-1-amino-2-propanol (4d) was prepared from **4a** and cinnamoyl chloride according to the procedure described for **3d**. **4d**: yield 82%; mp 116−117 °C (AcOEt−hexane); $[\alpha]^{20}_D$ −223 (*c* = 1, $CHCl_3$); IR (KBr) 1696, 1647, 1632, 1590, 1235, 1050, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (d, *J* = 6.4 Hz, 3H), 4.25 (dd, *J* = 13.5, 3.5 Hz, 1H), 4.68 (dd, *J* = 13.5, 8.6 Hz, 1H), 5.53 (m, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 7.35 (m, 3H), 7.45 (m, 2H), 7.55 (d, *J* = 16.0 Hz, 1H), 7.74 (dd, *J* = 8.3, 7.3, Hz, 2H), 8.20 (dd, *J* = 8.3, 1.1 Hz, 2H), 8.60 (dd, *J* = 7.3, 1.1 Hz, 2H); HRMS *m/e* (M^+) calcd for $C_{24}H_{19}NO_4$ 385.131, obsd 385.131.

(*R*)-1-(2′,3′-Naphthalimido)-2-phthalimidopropane (5). Bis-imide **5** was prepared from *N*-phthaloyl-D-alaninol[1] and 2,3-naphthalimide according to the procedure described for **3b**. **5**: yield 64%; mp 226−228 °C; $[\alpha]^{20}_D$ −301 (*c* = 1, $CHCl_3$); IR (KBr) 1760, 1705, 1375, 1100, 1045, 765, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (d, *J* = 7.3 Hz, 3H), 3.97 (dd, *J* = 13.9, 3.7 Hz, 1H), 4.46 (dd, *J* = 13.9, 9.7 Hz, 1H), 4.73 (m, 1H), 7.67 (m, 4H), 7.78 (m, 2H), 8.00 (m, 2H), 8.25 (s, 2H). Anal. Calcd for $C_{23}H_{16}N_2O_4$: C, 71.87; H, 4.20; N, 7.29. Found: C, 71.84; H, 4.12; N, 7.08.

(*R*)-*N*-(1′,8′-Naphthaloyl)-α-methylbenzylamine (6) was prepared from (*R*)-α-methylbenzylamine according to the procedure described for **2**. **6**: yield 69%; mp 157−160 °C (from methanol); $[\alpha]^{20}_D$ +222 (*c* = 1, $CHCl_3$); IR (KBr) 1695, 1655, 1585, 1380, 1240, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.99 (d, *J* = 7.1 Hz, 3H), 6.56 (q, *J* = 7.1 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 7.8, 7.3 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.74 (dd, *J* = 8.3, 7.3 Hz, 2H), 8.20 (d, *J* = 8.3 Hz, 2H), 8.56 (d, *J* = 7.3 Hz, 2H). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.61; H, 5.13; N, 4.40.

***N*-Methyl-1,9-anthraimide (7).** A mixture of 1,9-anthracenedicarboxylic anhydride (1.24 g, 5 mmol) and formamide (10 mL) was refluxed for 30 min. After cooling to room temperature, 1,9-anthraimide was filtered-off and recrystallized from DMF: yield 0.8 g, mp 282−285 °C. This product (0.25 g) was heated with potassium carbonate (0.28 g) in DMF (5 mL) at 100 °C for 3 h. After cooling to room temperature, the solution was stirred overnight with methyl iodide (0.2 mL) and the solution was diluted with methanol. The product was filtered off and purified by column chromatography (silica gel, CH_2Cl_2). Product **7** (0.17 g, 64%) was crystallized from dioxane: mp 226−230 °C; IR (KBr) 1690, 1650, 1560, 1280, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (s, 3H), 7.64 (m, 1H), 7.74 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.84 (ddd, *J* = 8.2, 6.6, 1.4 Hz, 1H), 8.12 (ddd, *J* = 8.5, 1.4, 0.7 Hz, 1H), 8.35 (ddd, *J* = 8.5, 1.4, 0.8 Hz, 1H), 8.77 (dd, *J* = 7.1, 1.4 Hz, 1H), 8.83 (s, 1H), 9.99 (m, 1H). Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 77.93; H, 4.25; N, 5.04.

(*R*)-*O*-(4-Chlorobenzoyl)-*N*-(1′,9′-anthrayl)-1-amino-2-propanol (8). A mixture of (*R*)-1-amino-2-propanol (76 mg, 1 mmol) and 1,9-anthracenedicarboxylic anhydride (248 mg, 1 mmol) was refluxed in dioxane (5 mL) for 10 h. The solvent was removed in vacuo, and the product was purified by column chromatography on silica gel: yield 225 mg (74%), mp 178−180 °C. This product (61 mg, 0.2 mmol) was stirred overnight with *p*-chlorobenzoic acid (50 mg), DMAP (5 mg), and DCC (65 mg) in dioxane (3 mL). The solvent was evaporated, and product **8** was purified by column chromatography (silica gel, CH_2Cl_2): yield 23 mg (26%), mp 202−203 °C (from AcOEt−ethanol); $[\alpha]^{20}_D$ −238 (*c* = 0.1, $CHCl_3$); IR (KBr) 1718, 1682, 1650, 1562, 1270, 758, 740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.55 (d, J = 6.6 Hz, 3H), 4.40 (dd, J = 13.5, 3.3 Hz, 1H), 4.87 (dd, J = 13.5, 8.8 Hz, 1H), 5.64 (m, 1H), 7.27 (d, J = 8.8 Hz, 2H), 7.64 (m, 1H), 7.72 (m, 1H), 7.83 (m, 1H), 7.89 (d, J = 8.8 Hz, 2H), 8.10 (dd, J = 8.4, 0.7 Hz, 1H), 8.34 (dd, J = 7.8, 0.7 Hz, 1H), 8.73 (dd, J = 7.1, 1.4 Hz, 1H), 8.82 (s, 1H), 9.93 (dd, J = 9.0, 0.8 Hz, 1H); HRMS *m*/*e* (M$^+$) calcd for $C_{26}H_{18}ClNO_4$ 443.092, obsd 443.090.

Acknowledgment. We thank H. Kolbon, M.Sc., and A Pieta for technical assistance. Support by the Committee for Scientific Research, Grant 3 T09A 079 08 is gratefully acknowledged.

JO981760J