Steady-State Photolyses. Typically, nitrogen-saturated acetonitrile-d_3 solutions (ca. 10^{-2} M) in a Pyrex NMR tube were irradiated through an appropriate filter. The photolyses were monitored by ^{1}H NMR spectroscopy. Product yields were calculated from integrations of unique peaks in the spectrum with 1,4-dichlorobenzene as internal standard.

9-Acetyl-10-ethoxyanthracene was isolated and characterized after photolysis on a larger scale in CH_3CN with a 1000-W Hg-Xe lamp with a 420-nm cutoff filter for 2 h. Evaporation of the solvent and elution of the residue through a silica gel column with 10% ethyl acetate in hexane afforded the product as a yellow solid along with a small amount of 9-acetylanthracene. ^{1}H NMR (CD_3CN): δ 1.64 (t, 3 H, J = 6.9 Hz), 2.80 (s, 3 H), 4.30 (q, 2 H, J = 6.9 Hz), 7.56 (m, 4 H), 7.87-7.90 (m, 2 H), 8.38-8.41 (m, 2 H). GC/MS *m/e* (rel intensity): 264 (100), 235 (92), 221 (98), 207 (74), 163 (43), HRMS (EI, 70 eV) calcd for $C_{18}H_{16}O_2$: 264.1150, found 264.1135.

General Procedure for Transient Absorption Spectra. The solution to be irradiated was placed in a 1-cm path length stopcock-fitted quartz or Pyrex cell equipped with a Teflon-coated magnetic stir bar. The solution, in most cases, was air-saturated and stirred during the irradiation. The concentration of the electron acceptor was kept constant (0.16-0.17 M), but the concentration of the electron donor was adjusted in such a way that an optical density of 2 (±5%) across the cell was achieved. Transient absorption spectra were generated by monitoring the change in absorption at various wavelengths. To avoid the photolysis of sample with probe light, a cutoff filter (WG-345; <400 nm) was placed in the probe beam. The analysis of the mixed-order kinetic decay for acetylanthracene-sensitized irradiation of $DEBP^{2+}$ was made with the assumption that the second-order component arises from annihilation of the acetylanthracene radical cation and the DEBP radical cation, which are formed in identical initial concentration.

Study of Formation of Charge-Transfer Complexes. In a typical procedure, 2 mL of a 0.16-0.17 M solution of *N*-(4-cyanophenoxy)-pyridinium tetrafluoroborate in CH_3CN was prepared, and the UV absorption spectrum was recorded. To this solution were added electron donors in small increments, and the UV absorption spectra of the mixtures recorded. These data were analyzed according to the Benesi-Hildebrand equation.[17]

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Enantioselective Catalysis of the Triplex Diels-Alder Reaction: A Study of Scope and Mechanism

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Abstract: Irradiation of the chiral sensitizers 1,1'-bis(2,4-dicyanonaphthalene) and 1,1'-bis(2,10-dicyanoanthracene) catalyzes the triplex Diels-Alder reaction of *trans*-β-methylstyrene with 1,3-cyclohexadiene to form the [4 + 2] cycloadducts *endo-trans*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-ene. When the sensitizer is optically active and the irradiation is performed at low temperature in ether or toluene solution, the [4 + 2] cycloadducts are formed enantioselectively. The mechanism of the enantioselective triplex Diels-Alder reaction was examined by chemical and spectroscopic means. Interaction of the chiral sensitizer with the prochiral styrene forms diastereomeric exciplexes. The equilibration of these exciplexes is fast at room temperature but not at low temperature. The exciplexes react with diene to form a triplex. This reaction leads to cycloadduct formation. Enantioselection is a consequence of different trapping efficiencies for the diastereomeric exciplexes by diene.

Introduction

The predictable regiochemistry and stereochemistry of the Diels-Alder reaction are two factors that make it an important process for synthesis of compounds having six-membered rings.[1] The rate and regiochemical outcome of normal Diels-Alder reactions are thought to be determined by the interaction of frontier orbitals: the LUMO of the dienophile and the HOMO of the diene. Consequently, the reaction proceeds rapidly when an electron-poor dienophile reacts with an electron-rich diene. Correspondingly, the reaction of electron-rich dienes and electron-rich dienophiles normally proceeds slowly if at all. Attempts to overcome this limitation have focused on the discovery of catalysts. Chief among these are Lewis acids which are believed to function by forming a complex with the dienophile.[1] Transfer of electron density from the dienophile to the Lewis acid in the complex is thought to play the key role in the catalysis. In addition to the rate enhancement, the use of chiral Lewis acids as catalysts in the Diels-Alder reaction provides a means for controlling the stereochemistry of the adducts formed.

Excited states have unique electronic properties that may be used to influence reactions. In particular, singlet excited states of electron-deficient arenes often form exciplexes with electron-rich alkenes. Exciplex formation results in a transfer of electron density from the alkene to the excited arene. This fact suggests the possibility that exciplexes and Lewis acid complexes of dienophiles may undergo similar reactions. This similarity was demonstrated experimentally with the discovery of the triplex Diels-Alder reaction.[2]

The triplex Diels-Alder reaction is the photocatalyzed [4 + 2] cycloaddition of an electron-rich diene and an electron-rich dienophile carried out in a nonpolar solvent initiated by irradiation of an electron-deficient arene. For example, irradiation of a benzene solution containing tetracyanoanthracene (TCA), 1,3-cyclohexadiene (CHD), and *trans*-β-methylstyrene (tBMS) leads to the efficient formation of *endo-trans*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-ene (**1**), eq 1.[3] Other examples of the triplex Diels-Alder reaction that have been investigated provide evidence for its scope, utility, and mechanism.[3]

The mechanism of the triplex Diels-Alder reaction has been examined by chemical, stereochemical, and spectroscopic means,[2,3] These experiments are consistent with a two-step reaction se-

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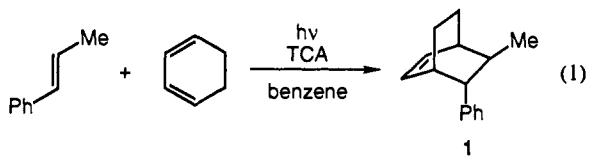


(1)

1

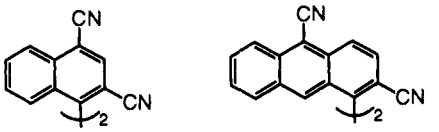
quence. In the first step, the electronically excited arene forms an exciplex with the electron-rich dienophile. In some cases emission from this exciplex allows its thorough characterization. In the second step, the exciplex reacts with the diene. Kinetic analysis of the reaction reveals the necessity of a termolecular complex, [sens···dienophile···diene]*[1], but does not discriminate between its participation as an intermediate or a transition state. Whichever role the triplex plays, reaction of the dienophile and the diene in the triplex gives their [4 + 2] cycloadduct with retention of dienophile stereochemistry and regenerates the arene catalyst. Side reactions become significant when the excited arene is quenched by diene, when the sens···dienophile (or sens···diene) exciplex is consumed irreversibly, and when the triplet of the sensitizer has a higher energy than that of the diene.

Exciplexes of electron-deficient arenes and electron-rich alkenes are well-known.[4] In general these intermediates are formed by the intimate overlap of π-molecular orbitals and are stabilized, relative to the locally excited state, by charge and exciton resonance. Close contact between the exciplex components and the important role of the frontier orbitals mean that the lifetime and stabilization of an exciplex will be strongly dependent on both steric and electronic factors.[5] On this basis we reasoned that the diastereomeric exciplexes formed from a chiral sensitizer and a prochiral dienophile might have different properties. Reaction of a diastereomeric exciplex with a diene in the triplex Diels–Alder reaction could lead to the catalytic, enantioselective formation of the [4 + 2] cycloaddition products.

The discovery of enantioselective photophysical processes has been an elusive goal. In 1967 Grossman and Wilkins unsuccessfully sought evidence of the influence of a chiral environment on the rate of the photochemical redox reaction between pairs of optically active organometallic complexes.[6] Similarly, Kane-Maguire and co-workers[7] found no evidence for stereoselectivity in an electron-transfer reaction of (+)-D-$[Co(phen)_3]^{3+}$ in the presence of (+)- or (−)-$[Cr(phen)_3]^{3+}$. However, experiments recently reported by Porter and co-workers show that the rates of electron transfer between an optically active Ru complex and chiral Co complexes, monitored by circular dichroism spectroscopy, differ by ca. 4% according to the diastereomeric pair reacting.[8]

Diastereoselectivity during energy-transfer processes has also been observed. Brittain[9] showed that the rates of energy transfer from Tb(III) complexes with chiral ligands to Eu(III) complexes differ by 23%. In this case, however, a charge-transfer complex of the ground states rather than collisional, dynamic quenching of excited states is thought to be responsible for the stereoselectivity. De Schryver and co-workers studied chiral discrimination in the formation of intermolecular excimers from stereoisomeric *N*-acetyl-3-(1-pyrenyl)alanine methyl esters.[10] The results revealed no difference in the rates of excimer formation but a ca. 20% difference in the rates of excimer dissociation. This observation led to the suggestion that the two diastereomeric excimers have different stabilization energies and different lifetimes.

Chart I



[BDCN] [BDCA]

The discovery of enantioselective photochemical sensitization reactions also has had limited success.[11] In this process an achiral reagent reacts with a chiral sensitizer to give optically active products. All of the enantioselective sensitization reactions reported to date are isomerizations. The first successful attempt,[12] and the most important example of photoasymmetric induction, was described by Hammond and Cole in 1965. An optically active naphthalene-containing ester was used to sensitize the isomerization of *trans*- and *cis*-1,2-diphenylcyclopropane. At the photostationary state, a 7% enantiomeric excess (ee) of the trans isomer was obtained. The asymmetric induction was proposed to proceed through diastereomeric exciplexes having different lifetimes. Since this initial report, a number of other workers have described attempts to improve and understand this asymmetric induction.[13] In a recent example of photoasymmetric induction, Inoue reported photoisomerization of cyclooctene with chiral aromatic ester sensitizers.[14] This reaction gives a 12–53% ee of the trans isomer and shows a complex temperature dependence. Inoue suggests that the mechanism for this asymmetric induction is controlled by differences in the rates of relaxation of diastereomeric exciplexes.

Herein we report[15] the application of chiral sensitizers to the triplex Diels–Alder reaction. For example, irradiation of toluene solutions containing CHD, tBMS, and either of the optically active sensitizers 1,1′-bis(2,4-dicyanonaphthalene) (BDCN) or 1,1′-bis(2,10-dicyanoanthracene) (BDCA) (see Chart I) at low temperature gives [4 + 2] cycloadducts **1** enriched in one enantiomer. Examination of the mechanism of this reaction suggests that the ee arises as a consequence of dissimilar properties of the diastereomeric exciplexes formed from BDCN, or BDCA, and tBMS.

Results

(1) Synthesis of Chiral Sensitizers for the Triplex Diels–Alder Reaction. The optically active sensitizers BDCN and BDCA were selected for synthesis and investigation on the basis of three criteria. First, previous examination of the triplex Diels–Alder reaction has shown that nitrile-substituted aromatic hydrocarbons are the most useful sensitizers for this reaction.[2,3] Second, BDCN was chosen because emission is often observed from the exciplex formed between cyano-substituted naphthalene sensitizers and tBMS. BDCA was selected specifically because its triplet energy is below that of either CHD or tBMS. This fact prevents, in part, the [2 + 2] dimerization reactions that result from formation of the triplet dienophile or diene. Third, both BDCN and BDCA are C_2-symmetric biaryls, and therefore, the number of possible conformationally derived diastereomeric exciplexes is limited. Ad-

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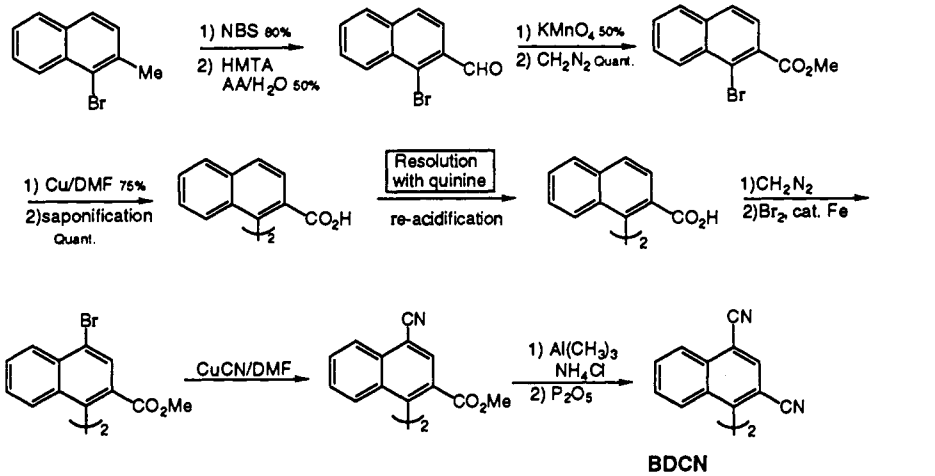
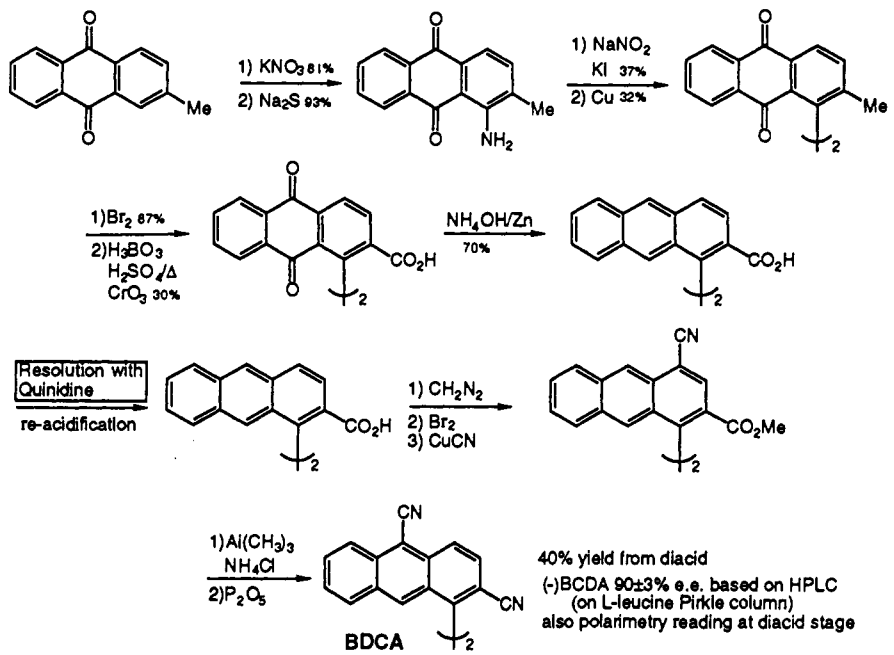
Scheme I

Synthesis of BDCN



Synthesis of BDCA



ditionally, studies of related compounds have revealed that their aryl rings are nearly perpendicular in the ground state[16] and that there is a substantial barrier to racemization.[17] Thus these sensitizers are likely to be conformationally stable when irradiated, and their diastereomeric exciplexes with dienophiles are expected to have significantly different properties.

BDCN and BDCA were prepared as shown in Scheme I and described in detail in the Experimental Section. The synthesis and resolution of the dicarboxylic acids follow previous reports.[18] Conversion of the diacids to BDCN and BDCA was accomplished without racemization. The optical purity of (-)-BDCN was determined spectroscopically by application of the chiral shift reagents Yb(hfbc)$_3$ and Ag(fod).[19] Addition of these reagents to $CDCl_3$ solutions of BDCN caused all of the proton resonances to shift upfield. The most upfield resonances, assigned to the 8 and 8′ protons, were completely resolved. Integration of these absorptions shows that the optical purity of (-)-BDCN is 77 ± 5%. The optical purity of (-)-BDCA was determined chromatographically on a Pirkle column to be 91 ± 2%.

It is of some significance that, despite their same sense of rotation [both (-)], the bis(naphthalene) and bis(anthracene) dicarboxylic acids are known to have opposite absolute configu-

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Table I. Temperature Dependence of Enantiomeric Excess in the Endo [4 + 2] Cycloadduct Formed between tBMS and CHD

temp (°C)	ee (%)[a]	ee (%)[b]
25	1 ± 1	
−15	9 ± 2	14 ± 2
−35	5 ± 2[c]	15 ± 2
−65	15 ± 3	19 ± 2

[a] Catalyzed with (−)-BDCN in toluene: [tBMS] = 0.13 M, and [CHD] = 0.03 M. [b] Catalyzed with (−)-BDCA in toluene: [tBMS] = 0.14 M, and [CHD] = 0.032 M. [c] This reaction was carried out at slightly different concentrations of substrates: [tBMS] and [CHD] = 0.13 M.

rations. On this basis, (−)-BDCN is assigned as the *S* enantiomer and (−)-BDCA is expected to be the *R* enantiomer.[20]

The utility of BDCN and BDCA as chiral sensitizers in the triplex Diels–Alder reaction requires that they resist racemization under both thermal and photochemical conditions. It was previously reported that related axially chiral biaryls have relatively high barriers to thermal racemization.[17] In contrast, it is known that 1,1′-binaphthyl racemizes rapidly when irradiated.[21] We showed that neither (−)-BDCN nor (−)-BDCA racemizes measurably under the conditions of the triplex Diels–Alder reaction. However, irradiation of these sensitizers in the presence of tBMS causes their slow, irreversible consumption. Photochemical addition reactions of alkenes and dienes to arenes have been reported previously.[22] We presume that this path accounts for the consumption of BDCN and BDCA during the triplex Diels–Alder reaction.[3]

(2) Enantioselective Triplex Diels–Alder Reaction of CHD and tBMS. Irradiation of a toluene solution of (±)-BDCN containing CHD (0.12 M) and tBMS (0.12 M) gives their [4 + 2] cycloaddition products, dimers of CHD, and a trace of a [2 + 2] cycloadduct of tBMS and CHD. This finding is precisely analogous to that reported previously for 1,4-dicyanonaphthalene (DCN) sensitization of this reaction.

The endo trans cycloadducts **1** can be resolved into enantiomers by gas chromatography on a capillary GC column coated with 3-(trifluoroacetyl)-2,6-dimethyl-β-cyclodextrin.[23] Sensitization with (±)-BDCN gives the expected 1:1 mixture of the two enantiomers. When this reaction is sensitized with (−)-BDCN (tBMS = 0.13 M; CHD = 0.03 M) at room temperature, the two enantiomers of **1** are formed in essentially equal amounts. However, irradiation of an identical mixture at −65 °C gives a 15 ± 2% enrichment of the enantiomer of endo trans cycloadduct **1** having the shorter retention time. As a control experiment we showed that sensitization with (+)-BDCN under these conditions gives a 12 ± 2% enrichment of the other enantiomer of **1**.

The effect of temperature on the enantioselectivity of the (−)-BDCN-sensitized triplex Diels–Alder reaction of tBMS and CHD was examined. The results, shown in Table I, show that the ee obtained is inversely related to temperature.

The triplex Diels–Alder reaction of tBMS and CHD sensitized with (±)-BDCA gives results analogous to those previously reported for sensitization with 9,10-dicyanoanthracene (DCA).[3] With these anthracene-based sensitizers the yields of endo trans cycloadducts **1** increase, and the yield of dimers of CHD and tBMS decreases. Sensitization of this reaction with (−)-BDCA (CHD = 0.03 M; tBMS = 0.03 M) in toluene solution at −65 °C gives a 23 ± 2% enrichment of the enantiomer of endo trans cycloadduct **1** with longer retention time. This is the highest level of enantioselectivity observed to date for the photocatalyzed cycloaddition reaction. It is worth noting that sensitization with (−)-BDCN or (−)-BDCA leads to enrichment of opposite enantiomers of endo trans cycloadduct **1**. This observation reveals that enantioselection in the cycloaddition reaction is sensitive to the absolute configuration of the sensitizer.

Table II. Summary of Low-Temperature Photolysis Results with CHD and *p*-Substituted Methylstyrenes[a]

methylstyrene	E_{ox} (V)[b]	ee (%) (−)-BDCN[c]	ee (%) (−)-BDCA[d]
p-CF_3	2.30	15	na
p-F	2.05	16	9.2
tBMS	1.94	15	23
p-CH_3	1.77	14	12
p-OCH_3 (anethole)	1.45		

[a] All studies were perfomed in toluene solution at −65 °C: [CHD] = 0.03–0.07 M, and [methylstyrene] = 0.12 M. [b] Cyclic voltammetry measurements were carried out in acetonitrile with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. E_{ox} is reported from the peak potential vs Ag/Ag^+ since the oxidation waves were irreversible (referenced to ferrocene, 0.55 V). [c] The product is enriched in the enantiomer with shorter retention time. [d] The product is enriched in the enantiomer with longer retention time, and the yield of cycloadducts ranged from 5 to 45%.

Table III. Diene Concentration Dependence of Enantiomeric Excess in the [4 + 2] Adduct between tBMS and CHD[a]

[CHD] (M)	ee in [4 + 2] (%)
0.005	21
0.05	17
0.11	15
0.16	14

[a] (−)-BDCA was used as the sensitizer with [tBMS] = 0.14 M.

(3) The Triplex Diels–Alder Reaction of CHD and Substituted *trans*-β-Methylstyrenes. As an aid to the investigation of the mechanism for asymmetric induction in the triplex Diels–Alder reaction and to examine the range of useful reagents, we investigated the effect of substituents on the dienophile. Para substituents can affect electronic properties of the styrenes without significantly changing their steric properties. For example, there is a large difference in oxidation potential between *p*-CH_3-β-methylstyrene and *p*-CF_3-β-methylstyrene but only a small difference in their steric natures. Although the substituted styrenes used contained small amounts of the cis isomers, we examined only the yield and enantioselectivity of the endo trans cycloadducts.

Irradiation of (±)-BDCN in solution with CHD (0.05 M) and various substituted *trans*-β-methylstyrenes gives related sets of [4 + 2] and [2 + 2] cycloadducts. The endo trans [4 + 2] cycloadducts were identified by coinjection with independently prepared samples and comparison of retention times and mass spectra. Sensitization of these reactions with (−)-BDCN was carried out at −65 °C; under these conditions the yield of the endo trans cycloadducts ranged from 5 to 30%. It appears that as the oxidation potential of the dienophile decreases, the yield of endo trans cycloadduct at first increases and then decreases. However, the enantioselectivity of the reaction is unaffected by the substituent (15 ± 2% ee). This observation suggests that steric rather than electronic effects control asymmetric induction in the triplex Diels–Alder reaction. The data are summarized in Table II.

(4) Effect of Diene Concentration on the Enantioselective Triplex Diels–Alder Reaction. Photophysical studies to be described later show that the likely first step in the triplex Diels–Alder reaction is formation of an exciplex of the sensitizer and the dienophile. Subsequently, this exciplex reacts with the diene to give the observed cycloadducts. We examined the effect of the concentrations of the diene and dienophile on the yield and enantioselectivity of this reaction.

The relationship between enantioselectivity and the concentrations of CHD and tBMS was determined for reaction in toluene solution with (−)-BDCA at −65 °C. In the first set of experiments, the concentration of CHD was maintained at 0.14 M and the concentration of tBMS was varied from 0.005 to 0.16 M. Analysis

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(23) Schurig, V.; Nowotny, H.-P.; Schmalzing, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 6.

of the product mixture shows that the enantioselectivity for the endo trans cycloadducts **1** is independent (15 ± 2% ee) of tBMS concentration over this range. A similar experiment was carried out with the concentration of tBMS held constant at 0.14 M and the concentration of CHD varied over the range 0.005–0.16 M. Gas chromatographic analysis shows that the enantioselectivity of cycloadduct **1** formation ranged from 14 to 21% inversely with the concentration of CHD. The data are summarized in Table III. These findings suggest that differential reaction of diastereomeric exciplexes of the sensitizer and tBMS with CHD leads to the enantioselectivity of the triplex Diels–Alder reaction.

(5) Effect of Solvent on the Enantioselective Triplex Diels–Alder Reaction. Solvent properties, particularly polarity and polarizability, greatly affect the nature of exciplex intermediates.[24] If diastereomeric exciplexes are formed in the enantioselective triplex Diels–Alder reaction, they may possess different dipole moments, for example, and therefore respond differently to a change of solvent. This issue was explored by examining the yield and ee of cycloadducts **1** formed by sensitization with (−)-BDCA at −65 °C (CHD = 0.08 M; tBMS = 0.13 M) in toluene and diethyl ether solutions.

The yield of cycloadducts **1** is unaffected by the change in solvent, but the enantioselectivity of the reaction increases from 8% in toluene to 14 ± 2% in diethyl ether. When (−)-BDCN is the sensitizer, the enantioselectivity of the reaction is also greater in ether solution (12%) than it is in toluene under comparable conditions. These results suggest that differential stabilization of diastereomeric exciplexes by solvent affects the enantioselectivity of the triplex Diels–Alder reaction.

To probe further for the involvement of exciplexes in the asymmetric induction, the triplex Diels–Alder reaction of tBMS and CHD was carried out in acetonitrile solution, where exciplexes (if they are formed at all) are known to dissociate rapidly to ionic intermediates. Sensitization with (−)-BDCN gives racemic endo trans cycloadduct **1** under all conditions examined. This result, too, supports participation of exciplex intermediates in the asymmetric induction observed in toluene and ether solutions and further distinguishes the triplex and radical cation[25] Diels–Alder reactions.

(6) Photophysical Studies of the Triplex Diels–Alder Reaction. Exciplex emission is often observed when nitrile-substituted arenes are excited in the presence of electron-rich alkenes in nonpolar solvents. This emission provides an important means for monitoring the rate of formation and the reaction of the exciplexes. The reduction potential of the arene acceptor and the oxidation potential of the alkene donor provide guides to the stabilization of the exciplex. The chiral sensitizers studied in this work, (±)-BDCN and (±)-BDCA, have reversible reduction potentials in CH_3CN solution of −1.5 and −0.9 V vs SCE, respectively. Oxidation of the dienophiles by cyclic voltammetry show irreversible waves with peak potentials ranging from 1.15 to 2.0 V. These values indicate that the efficiency of formation and the stabilization of exciplexes formed between these sensitizers and dienophiles will vary significantly.

The fluorescence of BDCN in benzene solution (λ_{max} = 400 nm; τ_s = 6 ns) is quenched by tBMS. Stern–Volmer analysis of the data reveals a quenching rate constant that is close to the diffusion-controlled limit (4.0×10^9 M^{-1} s^{-1}). As the concentration of tBMS is increased, the fluorescence of BDCN is quenched and a new, broad emission at longer wavelength ($\lambda_{max} \approx 490$ nm) assigned to the exciplex grows into the spectrum, Figure 1. At room temperature, the lifetime of the BDCN···tBMS exciplex is 26 ± 2 ns. Under these conditions, kinetic analysis of the BDCN fluorescence and exciplex emission shows that exciplex formation is essentially irreversible. Related results are obtained for the quenching of BDCN by *p*-CH_3-β-methylstyrene in toluene solution (λ_{max} = 510 nm; τ_s = 32 ns), Figure 1.

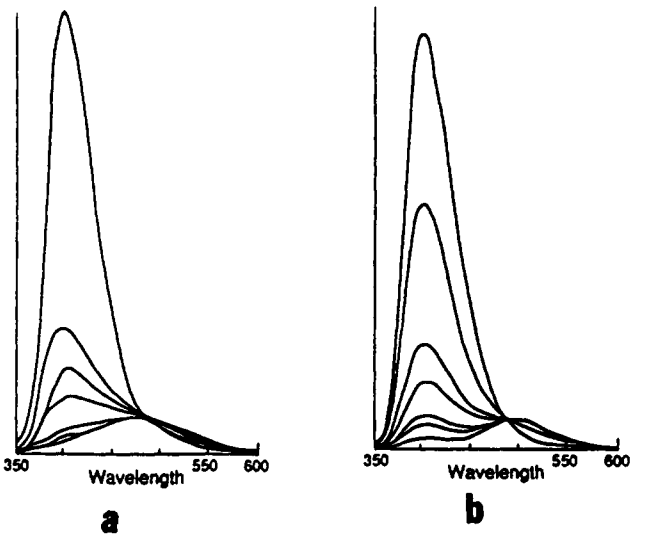


Figure 1. Emission spectra of BDCN in the presence of (a) tBMS and (b) *p*-methyl-β-methylstyrene.

Table IV. Summary of Photophysical Results[a]

methylstyrene	$k_q\tau$	k_q (s^{-1} M^{-1})[b]	λ_{em} (nm)	τ_{exc} (ns)[c]	k_q^{exc} (s^{-1} M^{-1})[d]
p-CF_3	16	2.7×10^9	none		
p-F	60	1.1×10^{10}	480–490	22	2×10^9
tBMS	84	1.4×10^{10}	480–490	26	4×10^9
p-CH_3	102	1.7×10^{10}	500–510	32	5×10^8
CHD	100	1.7×10^{10}	none		
tBMS[e]	3	3.0×10^8	500–520[f]		

[a] All studies were carried out with BDCN in benzene with the exception of the last entry. [b] The Stern–Volmer quenching rates were calculated with τ(BDCN) = 6 ns. [c] The lifetime of the exciplex was measured after quenching approximately 94% of BDCN*[1]. [d] CHD was used as the quencher of the exciplexes. [e] BDCA*[1] was quenched and the quenching rate was calculated with τ(BDCA) = 10 ns. [f] A weak and broad emission from the exciplex of BDCA and tBMS in toluene was observed at −65 °C. The exciplex lifetime and the exciplex quenching rate by CHD were not measured.

The fluorescence of BDCN in diethyl ether solution is quenched by *p*-CH_3-β-methylstyrene ($k_q = 2.3 \times 10^{10}$ s^{-1} M^{-1}) with the formation of an exciplex emitting with a maximum at ca. 520 nm and a lifetime at room temperature of 34 ns. This exciplex is quenched by CHD with a rate constant of 2×10^9 s^{-1} M^{-1}. The fluorescence of BDCA in benzene solution is quenched by tBMS ($k_q = 2.3 \times 10^9$ s^{-1} M^{-1}), but no exciplex emission is detected at room temperature. However, in toluene at −65 °C a very broad and weak exciplex emission is observed at ca. 510 nm. These data and those for the other dienophiles examined are summarized in Table IV.

It is of interest to compare the emission spectra of the locally excited singlet state and the tBMS-containing exciplexes of DCN and BDCN. The dihedral angle between the naphthalene rings in 1,1′-binaphthyl is ca. 95° in the ground state. This angle is smaller in the excited singlet state of this compound. This conclusion is based on a shift in the fluorescence spectrum of 1,1′-binaphthyl compared with an isolated naphthalene chromophore.[26] BDCN similarly consists of two identical chromophores joined by a single bond. The absorption and emission spectra and lifetimes of BDCN are virtually identical with those of the isolated chromophore. This suggests that there is little difference between the conformations of ground- and excited-state BDCN and that there is only a small electronic interaction between the naphthalene rings of this compound.

In contrast, the emission spectra of the exciplexes of DCN and BDCN with tBMS are considerably different. The emission maximum of the BDCN···tBMS exciplex is found at ca. 490 nm

(24) Beens, H.; Weller, A. *Chem. Phys. Lett.* **1968**, 140. Mimura, T.; Itoh, M.; Ohta, T.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1665.

(25) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. Reynolds, D. W.; Lorenz, K. T.; Chiou, H.-S.; Bellville, D. J.; Pabon, R. A.; Bauls, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 4960.

(26) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971.

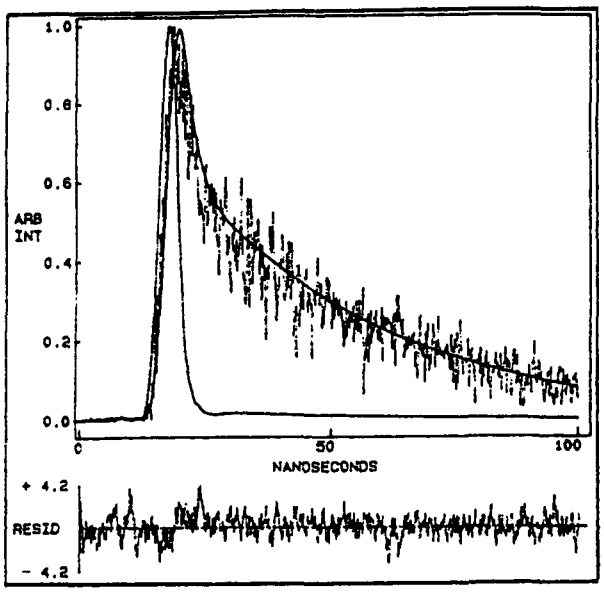


Figure 2. Exciplex emission from BDCN and tBMS in toluene fitted to a biexponential decay function at −65 °C.

while the maximum of the DCN···tBMS exciplex occurs at ca. 450 nm. Thus there is a large shift in emission for the exciplexes of DCN and BDCN, but there is virtually no change in the emission spectra of their locally excited states. This finding indicates a special stabilization of the exciplex that is possibly due to a change in the conformation of BDCN.

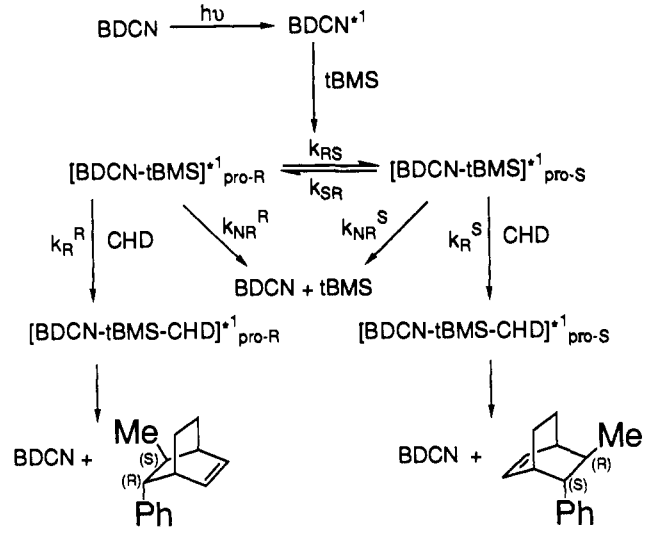
The second step in the mechanism proposed for the triplex Diels–Alder reaction is the formation of a triple complex by reaction of the exciplex of sensitizer and dienophile with diene. Direct evidence for this step is provided by the quenching of the emission of the BDCN···tBMS exciplex with CHD. At room temperature the rate constant for this reaction, obtained by monitoring the lifetime of the exciplex, is 5×10^{10} M^{-1} s^{-1}. No new emission assignable to the triplex is observed.

(7) A Physical Basis for Enantioselectivity in the Triplex Diels–Alder Reaction. Since BDCN is chiral and tBMS has two prochiral faces, the BDCN···tBMS exciplex is able to exist in diastereomeric forms. The asymmetric induction observed in the triplex Diels–Alder reaction may arise from differences inherent to the exciplexes or to differences in their reactions with CHD. These limiting options were examined by photophysical methods.

The emission from the BDCN···tBMS exciplexes was monitored at room temperature and at −65 °C in toluene solution under conditions where more than 94% of excited singlet BDCN is quenched by the dienophile. At room temperature, the exciplex emission decay monitored at 490 nm fits a single-exponential function with a lifetime of 26 ± 2 ns. This behavior is consistent with either the existence of only one emitting species or rapid equilibration among several emitters. At −65 °C the exciplex emission decay is best described by a biexponential function. The data, analyzed by using a nonlinear least squares algorithm, reveals two exciplex components with lifetimes of 37 and 22 ns. The longer-lived component contributes 70% to the initial emission intensity at 490 nm. The data are shown in Figure 2 along with the best statistical fits. These results indicate that at low temperature there is more than one species responsible for the exciplex emission. We attribute this to diastereoisomerism of the BDCN···tBMS exciplex. Similar results are obtained with BDCN and the other dienophiles studied.

The difference found for the lifetimes of the diastereomeric exciplexes at low temperature suggests that they may also have different emission spectra. The BDCN···tBMS exciplex was monitored at three different wavelengths and the emission from each wavelength fitted to a biexponential decay function. This procedure gives two lifetimes and two population coefficients at each wavelength. The results show that the contribution of the two components depends on wavelength, indicating that the diastereomeric exciplexes have different emission spectra as well as different lifetimes.

Scheme II



Discussion

The objectives of this work were to search for an enantioselective triplex Diels–Alder reaction and to probe the mechanism of this process. An enantioselective reaction was discovered. In the best example found to date, endo trans cycloadduct **1** is formed in 23% ee by sensitization with (−)-BDCA in toluene solution at −65 °C. This is the first report of an enantioselective, catalytic photochemical cycloaddition reaction. The mechanism for this process was probed by chemical and spectroscopic means. These experiments indicate that the enantioselectivity originates predominantly in differential lifetimes of diastereomeric exciplexes of the sensitizer and the dienophile.

The proposed reaction mechanism outlined in Scheme II is based on previous examinations of the triplex Diels–Alder reaction and on the results reported in this work. Only the key reaction steps leading to [4 + 2] cycloadducts are shown in Scheme II. For example, radiative and nonradiative relaxation reactions of BDCN*1 must occur under some conditions, but they are not shown. Similarly, quenching of BDCN*1 by CHD or of the BDCN···tBMS exciplex by tBMS and intersystem crossing of the exciplex may take place, but they are not shown in Scheme II. There are two key issues concerning the enantioselection that will be discussed here: (i) the existence and equilibration of diastereomeric exciplexes of BDCN and tBMS and (ii) the attempt to decide whether enantioselection originates from different formation efficiencies, or different lifetimes, of the diastereomeric exciplexes, or if it is a consequence of differential rates of reaction of these exciplexes with CHD.

(1) Diastereomeric Exciplexes of BDCN and tBMS: The Temperature Dependence of Enantioselectivity and Exciplex Emission. The fluorescence of BDCN is quenched rapidly by tBMS, providing direct evidence for the interaction of these compounds. In nonpolar solvents, this interaction gives rise to a new emission readily characterized as due to the [BDCN··· tBMS] exciplex. Kinetic analysis of the emissions from BDCN and the exciplex shows that this reaction is irreversible at room temperature. Once the excited singlet state of BDCN is quenched by tBMS, the locally excited state of the sensitizer is never reformed. This behavior is typical of exciplexes formed between good electron acceptors and good electron donors.[4] In these cases, stabilization by exciplex formation is typically 5–10 kcal/mol and dissociation of the exciplex cannot compete successfully with the other radiative and nonradiative reactions of the exciplex. This observation is potentially in conflict with our findings that both the enantioselectivity of the triplex Diels–Alder reaction and the exciplex lifetimes are temperature dependent.

At room temperature, no enantioselectivity is observed in the triplex Diels–Alder reaction and the emission of the [BDCN···

tBMS] exciplex shows a single-exponential decay. The enantioselectivity of cycloadduct formation increases as the temperature is lowered, and at −65 °C two exciplexes formed from BDCN and tBMS with distinct lifetimes and different spectra are observed.

Since BDCN is chiral and tBMS is prochiral, the exciplexes they form must be diastereomeric. The biexponential decay of the exciplex emission at −65 °C strongly supports a separate existence for the diastereomeric exciplexes. However, the single-exponential decay observed at room temperature indicates that there is only one emitting species under these conditions. These observations can be reconciled with the fact that the exciplexes are formed irreversibly, even at room temperature, if the diastereomeric exciplexes can equilibrate without dissociation to the locally excited state of BDCN.

Our experiments do not reveal precisely the structural differences between the diastereomeric exciplexes. However, it is reasonable to assume that they arise by complexation of the different prochiral faces of tBMS with the chiral surface of BDCN. In Scheme II these exciplexes are labeled pro-R and pro-S to indicate their selectivity in forming the (*R*,*S*)- and (*S*,*R*)-enantiomers of the endo trans adducts **1**. We suggest that at room temperature the pro-R and pro-S exciplexes of BDCN and tBMS equilibrate without dissociation. This may occur, for example, by a "slithering" motion of the tBMS along the surface of BDCN that converts pro-R to pro-S exciplex without complete loss of π-overlap. At low temperature, where enantioselectivity is observed, interconversion of the diastereomeric exciplexes must be slow compared with their reaction with CHD, whereas at room temperature this equilibration is rapid compared with both the reaction with CHD and the lifetime of the exciplex.

(2) Enantioselection in the Triplex Diels–Alder Reaction: A Question of Differential Trapping. The detection of nonequilibrating diastereoselective exciplexes at low temperature provides a basis for understanding the enantioselectivity of the triplex Diels–Alder reaction but does not pinpoint the origin of this phenomenon. Three limiting cases may be considered: (i) Unequally formed diastereomeric exciplexes are trapped with equal efficiency by CHD. (ii) A difference in exciplex lifetimes results in their unequal capture by CHD. (iii) Enantioselection occurs because the pro-R and pro-S [BDCN···tBMS] exciplexes have different rate constants for reaction with CHD. The kinetics of exciplex formation and the effect of CHD concentration on enantioselectivity were examined to distinguish these possibilities. The experimental results are more compatible with limiting case ii.

As is generally observed,[6-10,13,14] photophysical measurements in this system indicate that the diastereomeric exciplexes of BDCN and tBMS are formed in equal amounts. In particular, the fluorescence of BDCN is quenched by tBMS at approximately the diffusion-limited rate, and detailed analysis of the quenching behavior reveals a linear Stern–Volmer plot. These findings indicate that there is no detectable difference in rate constants for formation of the pro-R and pro-S exciplexes. On this basis, it seems unlikely that limiting case i can be the exclusive explanation for the observed enantioselection in the triplex Diels–Alder reaction.

The emission of the [BDCN···tBMS] exciplex is quenched by CHD. This observation confirms an interaction of the exciplex with CHD that, according to the proposed mechanism,[2] generates a triplex of sensitizer, dienophile, and diene with the structure [BDCN···tBMS···CHD]. This triple complex has never been detected directly in the triplex Diels–Alder reaction, so its precise participation remains uncertain. Nevertheless, according to the mechanism outlined in Scheme II, enantioselection is controlled in the step leading to formation of the triplex with CHD and its subsequent conversion to cycloadducts. If the lifetime difference of the diastereomeric exciplexes controls this process, then the ee should increase inversely with CHD concentration, as is shown analytically in eq 2. On the other hand, if different rate constants for reaction within the diastereomeric triplex cause the enantioselection, then the ee should be independent of CHD concentration. The experimental results, shown in Table III, show that the ee obtained in the triplex Diels-Alder reaction follows from eq 2 and supports control by differential exciplex lifetimes. In contrast, neither the concentration of the dienophile nor the presence of substituents on the dienophile affects the ee of the reaction.

$$ee^R = \frac{k_{NR}^S k_R^R - k_{NR}^R k_R^S}{2k_R^S k_R^R[CHD] + k_{NR}^S k_R^R + k_{NR}^R k_R^S} \quad (2)$$

Conclusions

Resolved chiral sensitizers catalyze the triplex Diels–Alder reaction with modest enantioselectivity. This reaction proceeds through diastereomeric exciplexes of the sensitizer and the dienophile that equilibrate rapidly at room temperature but more slowly at low temperature. Differences in lifetime of the diastereomeric exciplexes results in their selective trapping by diene. These findings point again to similarities between the Lewis acid catalyzed Diels–Alder reaction and the triplex Diels–Alder reaction.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded with either a General Electric QE-300 or GN-500 spectrometer referenced to the residual proton resonance in the deuteriated solvent. Yield analyses by gas chromatography were performed on a Hewlett-Packard 5890A OV-1 megabore column. Analyses of optical purity (enantiomeric excess, ee) were carried out with a Varian 3700 gas chromatograph equipped with a 25-m capillary chiral column coated with modified β-cyclodextrin [3-(trifluoroacetyl)-2,6-dimethyl-β-cyclodextrin].[23] GC/MS analyses were carried out on a Hewlett-Packard 5890A gas chromatograph with a Hewlett-Packard 5970 mass selective detector (EI, 70 eV). Product identification was made by coinjection of an authentic sample of the compound and comparison of GC retention times and GC/MS fragmentation patterns. Fluorescence spectra were recorded on either a Farrand I spectrofluorimeter or a SPEX Fluorolog. Emission lifetimes were measured with a Photon Technology International LS1000-16. IR spectra were recorded on an IBM FT-IR 32. High-resolution electron impact mass spectra (HR/EI) were recorded on a Varian 731 mass spectrometer. Optical rotations were determined with a Jasco 360 polarimeter at room temperature. Elemental analyses were performed by the microanalysis laboratory of the University of Illinois.

Materials. 1,3-Cyclohexadiene (Aldrich) was distilled from sodium borohydride immediately before use. Toluene was dried with CaH_2 and then distilled from sodium. *trans*-β-Methylstyrene (Wiley Organics) and 9,10-dicyanoanthracene (Kodak) were used without further purification. 1,4-Dicyanonaphthalene[27] was purified by sublimation and recrystallization from $CHCl_3$. 2-Methylanthraquinone (Aldrich) was recrystallized from ethanol. 1-Bromo-2-methylnaphthalene (Aldrich) was fractionally distilled under vacuum.

Typical Procedure for Triplex Diels–Alder Reaction with Optically Active Sensitizer. Air-saturated toluene solutions of the diene (ca. 0.1 M), the dienophile (ca. 0.1 M), a sensitizer (saturated, ca. 10^{-3} M, for room temperature experiments, adjusted to an absorbance of 2.0 for low-temperature experiments), and an internal standard were irradiated in Pyrex test tubes equipped with stirring bars. DCN-, BDCN-, or benzophenone-sensitized experiments were carried out in a Rayonet photoreactor equipped with 350-nm lamps. BDCA- and DCA-sensitized photolyses were carried out with a 450- or a 1000-W Hg lamp equipped with a cutoff filter selected to insure that only the sensitizer absorbed the light. The photoproducts were analyzed by GC and GC/MS and compared with authentic samples.

The determination of optical purity (ee) was accomplished by gas chromatography on an optically active column typically after ca. 45 min of irradiation. The samples were concentrated by evaporation and chromatographed on silica gel with hexane as the eluent to remove the sensitizer and its decomposition products. The response factors for the enantiomers of **1** on the chiral capillary column coated with modified β-cyclodextrin were determined with racemic **1**. The two enantiomers were completely resolved (retention times = 40.7 and 41.7 min) isothermally at 109 °C. The normalized areas of the peaks for the two enantiomers were 1.04 and 0.96, respectively. The response factors of the other compounds studied were similarly determined. The experimental error reported in the ee determinations is random errors from repeated injections.

Control experiments validated the analytical method. When racemic sensitizer was used in experiments carried out at −65 °C, GC analysis of **1** showed the two enantiomers in equal amounts: ee = 2 ± 2%.

(27) Newman, M. S. *Org. Synth.* **1941**, *21*, 89.

Sensitization with (+)-BDCN and (−)-BDCN gave comparable enrichments of opposite enantiomers of **1**.

Synthesis of 1,1′-Bis(2,4-dicyanonaphthalene) (BDCN). The synthesis of dimethyl 1,1′-bis(2-naphthoate) from 1-bromo-2-methylnaphthalene was performed according to the procedures reported by Weber and Hall[18] with slight modification.

1-Bromo-2-(bromomethyl)naphthalene. A suspension in 70 mL of CCl_4 was prepared containing 11.0 g (50 mmol) of 1-bromo-2-methylnaphthalene (Aldrich 90%, purified by distillation), 8.9 g of *N*-bromosuccinimide (50 mmol, freshly recrystallized from water and dried under vacuum), and a catalytic amount of dibenzoyl peroxide (31.5 mg, 0.13 mmol). The suspension was heated at reflux for 4 h and then filtered while still hot. The precipitate was digested twice with 50 mL of hot CCl_4. The filtrates were combined, and the solvent was removed, leaving a beige solid. Recrystallization from hexane yielded 12.0 g (40 mmol) of 1-bromo-2-(bromomethyl)naphthalene (80% yield): mp 102–104 °C (lit.[18] mp 106–108 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.34 (d, J = 8.6 Hz, 1 H), 7.83–7.78 (m, 2 H), 7.62–7.605 (m, 1 H), 7.56–7.51 (m, 2 H), 4.87 (s, 2 H); GC/MS 301.95 (10), 299.95 (M^+, 20), 297.95 (10).

1-Bromo-2-naphthaldehyde was prepared essentially as previously described starting with 9.0 g of 1-bromo-2-(bromomethyl)naphthalene (30 mmol). The workup of the reaction mixture was modified. The hexamethylenetetramine–bromonaphthalene salt was not filtered; instead, the solvent ($CHCl_3$) was evaporated, leaving a white solid, which was used directly in subsequent reactions. Recrystallization from hexane yielded 3.5 g (15 mmol, 50%) of the aldehyde: mp 116 °C (lit.[18] mp 118–119 °C); ^{1}HMR ($CDCl_3$, 500 MHz) δ 10.66 (s, 1 H), 8.50–8.48 (m, 1 H), 7.93–7.92 (m, 1 H), 7.88–7.83 (m, 2 H), 7.70–7.66 (m, 2 H); GC/MS 235.95 (72), 233.95 (73).

1-Bromo-2-naphthoic acid was prepared from 1-bromo-2-naphthaldehyde. A 17-mmol (4.0 g) portion of the aldehyde was dissolved in 5 mL of acetone and heated at reflux (bath 60–70 °C). A hot solution of potassium permanganate (29 mmol, 4.58 g) in a mixture of 2 mL of water and 14 mL of acetone was added dropwise to the aldehyde solution over a period of 10 min. The solution was heated for 10 min, and the mixture was filtered while hot to remove manganese dioxide. The precipitate was washed with acetone, the filtrates were combined, and the solvent was evaporated, leaving a white solid, which was added to 10 mL of water. The mixture was cooled in an ice/water bath and acidified slowly by dropwise addition of concentrated HCl. The precipitate isolated by filtration was thoroughly washed with water and dried under vacuum to afford 2.13 g (8.5 mmol, 50% yield) of the acid: mp 177–179 °C (lit.[18] mp 189–191 °C); ^{1}H NMR ($CDCl_3$) δ 10.68 (s, 1 H), 8.53 (d, J = 8 Hz, 1 H), 7.89 (d, J = 8 Hz, 1 H), 7.70–7.63 (m, 4 H); MS (EI, 70 eV) 252 (85), 250 (84).

Methyl 1-bromo-2-naphthoate was prepared directly from the acid by reaction with diazomethane prepared from Diazald (Aldrich).[28] The bromonaphthoic acid (2.13 g, 8.5 mmol) was dissolved in ether and cooled in an ice/water bath. An ether solution of diazomethane was added to the acid solution until the acid solution remained greenish-yellow, indicative of excess diazomethane. Evaporation of the solvent gave 2.25 g (8.5 mmol, 100%) of the ester: mp 55–57 °C (lit.[18] mp 53–55 °C or 58–59 °C); ^{1}H NMR ($CDCl_3$) δ 8.61 (br s, 1 H), 8.05 (d, J = 7.0 Hz, 1 H), 7.94 (d, J = 7.7 Hz, 1 H), 7.87 (d, J = 8.6 Hz, 1 H), 7.59–7.55 (m, 2 H), 3.97 (s, 3 H); GC/MS 263.95 (85, M − 1), 265.95 (84, M + 1).

Dimethyl 1,1′-Bis(2-naphthoate). Placed in a three-neck flask under a N_2 atmosphere were 1.7 g of Cu (26.8 mmol, Aldrich, fine powder) and 795 mg of methyl bromonaphthoate (3 mmol) in 12 mL of dry DMF (freshly distilled from CaH_2). The mixture was heated at reflux for 7 h and then filtered. The precipitate obtained was thoroughly washed with hot toluene. The combined filtrates were extracted four times with 10% HCl to remove DMF, washed with water, and dried ($MgSO_4$). The solvent was removed, leaving a white solid, which was recrystallized from methanol to afford 830 mg (2.7 mmol) of the bis-naphthoate ester (75%): mp 154–156 °C (lit.[18] mp 156–158 °C); ^{1}H NMR ($CDCl_3$) δ 8.195 (d, J = 9 Hz, 2 H), 8.015 (d, J = 9.0 Hz, 2 H), 7.96 (d, J = 9.0 Hz, 2 H), 7.54–7.49 (m, 2 H), 7.26–7.21 (m, 2 H), 7.08 (d, J = 9.0 Hz, 2 H), 3.49 (s, 6 H); GC/MS 370.2 (M^+, 100), 311.2 (25), 339.2 (24).

Dimethyl 1,1′-Bis(4-bromo-2-naphthoate). A 1.85-g (5 mmol) portion of dimethyl 1,1′-bis(2-naphthoate) in 10 mL of CCl_4 was added dropwise to a stirred, refluxing CCl_4 solution (50 mL) of Br_2 (1.81 g, 11.3 mmol) and Fe (33 mg, 0.6 mmol). After the addition was complete, the mixture was heated at reflux for 10 min and then filtered to remove iron. The organic layer was washed sequentially with aqueous $NaHCO_3$ and water and then dried with $MgSO_4$. The solvent was evaporated to yield 2.45 g (4.65 mmol) of an off-white solid (93%), which was purified by chromatography: mp 180–184 °C; ^{1}H NMR ($CDCl_3$) δ 8.53 (s, 2 H), 8.36 (d, J = 8.4 Hz, 2 H), 7.64 (dd, 2 H), 7.30 (dd, 2 H), 7.07 (d, J = 8.5 Hz, 2 H), 3.56 (s, 6 H).

Dimethyl 1,1′-Bis(4-cyano-2-naphthoate). A solution of dimethyl 1,1′-bis(4-bromo-2-naphthoate) (2.45 g, 4.65 mmol) and CuCN (1.19 g, 13.3 mmol) in 50 mL of dry DMF was heated at reflux overnight and then quenched with 10% HCl. Benzene (300 mL) was added to the reaction mixture. The organic layer was washed with water (3 × 25 mL) and then with aqueous $NaHCO_3$ and dried ($MgSO_4$). Removal of the solvent gave 1.86 g of a white solid (4.42 mmol, 95%): IR (KBr), 2226 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.69 (s, 2 H), 8.35 (d, J = 8.6 Hz, 2 H), 7.73 (dd, J = 8.0, 7.7 Hz, 2 H), 7.39 (dd, J = 8.0, 7.3 Hz, 2 H), 7.07 (d, J = 8.5 Hz, 2 H), 3.58 (s, 6 H); HR/MS calcd 420.111 60, found 420.111 01.

1,1′-Bis(2,4-dicyanonaphthalene) (BDCN). Methylchloroaluminum amide was prepared according to Weinreb.[29] A 66-mL portion (44 mmol, 0.67 M) of the methylchloroaluminum amide solution was added slowly via a cannula to a benzene solution containing 1.86 g of dimethyl 1,1′-bis(4-cyano-2-naphthoate) (4.42 mmol). The solution was heated at reflux for 4 h, and then the temperature was lowered to 55 °C, and the reaction mixture was stirred overnight. The mixture was carefully quenched with 5% HCl, and the organic layer was separated. The aqueous layer was extracted three times with ethyl acetate, and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated to yield 1.5 g of amide (3.85 mmol, crude yield 87%), which was used directly in the next step.

The crude amide was placed in a flask containing 80 mL of dry benzene and an excess (ca. 2 g) of P_2O_5. The mixture was heated at reflux for 3 h. The solvent was evaporated, and the crude product was chromatographed on silica gel eluted with a benzene/chloroform mixture. BDCN was further purified by recrystallization from chloroform to yield 939 mg (2.65 mmol, 60%): mp 316–320 °C; ^{1}H NMR ($CDCl_3$) δ 8.51 (d, J = 8.4, 2 H), 8.30 (s, 2 H), 7.96 (dd, 2 H), 7.66 (dd, 2 H), 7.23 (d, J = 8.6 Hz, 2 H); UV (benzene) λ_{max} (log ϵ) 315 (3.90), 342 (3.70), 350 (3.45); HR/MS calcd 354.090 76, found 354.090 55.

Synthesis of Optically Active BDCN. 1,1′-Bis(2-naphthalenecarboxylic acid) was prepared by saponification of the dimethyl bis(2-naphthoate). The diester (5 mmol, 1.85 g) was dissolved in 50 mL of methanol containing 10 g (0.18 mmol) of KOH. The solution was heated at reflux for 14 h, and the solvent was removed. Approximately 5 g of ice was added to the residual off-white solid, and the mixture was carefully acidified by dropwise addition of concentrated HCl. Filtration gave a white solid, which was washed with cold water until the filtrate was no longer acidic. The procedure gave 1.54 g (4.5 mmol, 90%) of the diacid: mp 270–274 °C (lit.[3] mp 272–274 °C); ^{1}H NMR (acetone-d_6) δ 10.89 (s, 2 H), 8.2 (d, J = 8.7 Hz, 2 H), 8.11–8.02 (m, 4 H), 7.54 (dd, J = 7.8, 7.5 Hz, 2 H), 7.27 (dd, J = 7.8, 7.6 Hz, 2 H), 7.01 (d, J = 8.6 Hz, 2 H).

Resolution of 1,1′-Bis(2-naphthalenecarboxylic acid). The procedure reported by Hall[18] was followed with 3.06 g (8.94 mmol) of the diacid. A 300-mg sample (0.88 mmol) of the less soluble diastereomeric salt of the bis-naphthoic acid and quinine gave (−)-diacid after reacidification: $[\alpha]$ = −74.5° (acetone) corresponding to an enantiomeric enrichment of 73%. The more soluble diastereomeric salt (900 mg, 2.63 mmol) gave (+)-diacid after acidification: $[\alpha]$ = +36° (acetone) corresponding to an enantiomeric enrichment of 35%.

Optically active BDCN was prepared from the resolved acids by means of the procedure described above for the racemic compound. The optical purity of BDCN was determined by NMR spectroscopy with the aid of chiral shift reagents (CSR).[19] A solution of 170 mg of (+)-Yb(hfbc)$_3$ (0.14 mmol) and 52.4 mg of Ag(fod) (0.13 mmol) was prepared in 2.6 mL of $CDCl_3$ under nitrogen in the dark and filtered through a small plug of Celite. Approximately 0.6 mL of this solution was added to a capped NMR tube containing 3 mg of optically active BDCN (0.014 M). Addition of the CSR caused all of the proton resonances of BDCN to shift upfield. The most upfield doublet was resolved into two resonances centered at δ 7.162 and 7.097. Integration of these peaks using a delay time of 5 μs, a pulse angle of ca. 90°, and zero-filling with base-line correction gave an 88.5:11.5 ratio for (−)-BDCN, which corresponds to an enantiomeric excess of 77 ± 5%. Similar experiments with (±)-BDCN as a control gave an integration ratio of 100:98.2. (−)-BDCN, 75 ± 5% ee: $[\alpha]_D$ −18.0° (0.5, toluene). Anal. Calcd for $C_{24}H_{10}N_4$: C, 81.34; H, 2.84; N, 15.81. Found: C, 81.24; H, 2.85; N, 15.65.

Synthesis of 1,1′-Bis(2,10-dicyanoanthracene) (BDCA). The synthesis of 1,1′-bis(2-anthracenecarboxylic acid) was repeated by methods already described.[18] Previously unreported spectral data for the compounds on that route are presented here.

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1-Nitro-2-methylanthraquinone: mp 270 °C (lit.[30] mp 265–267 °C); ^{1}H NMR ($CDCl_3$) δ 8.38 (d, J = 6 Hz, 1 H), 8.31–8.25 (m, 2 H), 7.85–7.82 (m, 2 H), 7.77 (d, J = 6 Hz, 1 H), 2.44 (s, 3 H).

1-Amino-2-methylanthraquinone: mp 201–203 °C (lit.[30] mp 202–203 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.31–8.23 (m, 2 H), 7.76–7.71 (m, 2 H), 7.61 (d, J = 9 Hz, 1 H), 7.39 (d, J = 9 Hz, 1 H), 7.05 (br s, 2 H, exchanged with D_2O), 2.28 (s, 3 H); MS (EI, 10 eV) 237.0 (100, M^+), 238 (17).

1-Iodo-2-methylanthraquinone: mp 169–171 °C (lit.[30] mp 169–169.5 °C); ^{1}H NMR ($CDCl_3$) δ 8.33–8.22 (m, 3 H), 7.83–7.76 (m, 2 H), 7.64 (d, J = 8.1 Hz, 1 H), 2.68 (s, 3 H).

1,1′-Bis(2-methylanthraquinone): mp 364–366 °C (lit.[30] mp 366–367 °C); ^{1}H NMR (C_6D_6) δ 8.47 (d, J = 8.3 Hz, 2 H), 8.14 (dd, J_1 = 1 Hz, J_2 = 6.9 Hz, 2 H), 7.82 (dd, J = 0.9 Hz, J_2 = 7.9 Hz, 2 H), 7.17 (d, J = 7.9 Hz, 2 H), 6.89 (dd, J_1 = 1.3 Hz, J_2 = 8.5 Hz, 2 H), 6.82 (dd, J_1 = 1.0 Hz, J_2 = 7.4 Hz, 2 H), 1.58 (s, 6 H); MS/FAB 442 (M^+) and metastable 222.

1,1′-Bis[2-(bromomethyl)anthraquinone]: mp 332–334 °C (approximately 300 °C);[31] ^{1}H NMR (C_6D_6) δ 8.29 (d, J = 8.4 Hz, 2 H), 8.13 (d, J = 8.4 Hz, 2 H), 8.05 (dd, J_1 = 7.5, J_2 = 4.6, 2 H), 7.76 (d, J_1 = 7.1, J_2 = 4.4, 2 H), 6.89–6.86 (m, 2 H), 6.82–6.79 (m, 2 H), 5.92 (s, 2 H); ^{1}H NMR ($CDCl_3$) δ 8.70–8.61 (m, 4 H), 8.31 (d, J = 7.7 Hz, 2 H), 7.95 (d, J = 7.5 Hz, 2 H), 7.80–7.75 (m, 2 H), 7.71–7.68 (m, 2 H), 6.04 (s, 2 H).

1,1′-Bis(2-anthraquinonecarboxylic acid): mp 330 °C, browned slightly at 266 °C (lit.[30] mp 330 or 334–337 °C); ^{1}H NMR (acetone-d_6) δ 8.51–8.44 (dd, J_1 = 11 Hz, J_2 = 3.0 H≤ 4 H), 8.27 (d, J = 7.6 Hz, 2 H), 7.93–7.81 (m, 6 H); IR (KBr) 1680, 1700 cm^{-1}; MS/EI 502.1 (35, M^+), 503.1 (4), 458.0 (–CO_2, 23), 414 (–2CO_2, 13).

1,1′-Bis(2-anthracenecarboxylic acid): mp 293–303 °C (lit.[32] mp 305 °C); ^{1}H NMR (acetone-d_6) δ 8.70 (s, 1 H), 8.32 (d, J = 9.0 Hz, 1 H), 8.22 (d, J = 9.0 Hz, 1 H), 8.09 (d, J = 8.5 Hz, 1 H), 7.82 (s, 1 H), 7.61 (d, J = 8.6 Hz, 1 H), 7.50–7.45 (m, 1 H), 7.34–7.28 (m, 1 H); MS (EI, 70 eV) 442.1 (100, M^+), 443.1 (40), 354.1 (–2CO_2H, 11).

Dimethyl 1,1′-Bis(2-anthracenecarboxylate). Diazomethane was prepared from Diazald (Aldrich). A 1.78-g (4 mmol) portion of the bis-anthracene diacid was dissolved in a large amount of ether and cooled in an ice/water bath. An ether solution of diazomethane was added to the diacid solution until the reaction mixture remained green. The solvent was evaporated to yield 1.89 g (4 mmol) of the diester: ^{1}H NMR ($CDCl_3$) δ 8.56 (s, 2 H), 8.22 (d, J = 2.1 Hz, 4 H), 8.00 (d, J = 8.6 Hz, 2 H), 7.73 (s, 2 H), 7.54 (d, J = 8.5 Hz, 2 H), 7.44 (t, J = 7.4 Hz, 2 H), 7.29 (d, J = 7.5 Hz, 2 H).

Dimethyl 1,1′-Bis(9-bromo-2-anthracenecarboxylate). To a stirred, refluxing solution of 1.76 g (11.0 mmol) of Br_2 and a catalytic amount (16.5 mg, 0.3 mmol) of Fe in 50 mL of CCl_4 was added dropwise 2.36 g (5 mmol) of the bis-anthracene diester dissolved in 20 mL of CCl_4. When the addition was complete, the mixture was heated at reflux for 10 min and filtered to remove iron. The organic layer was washed with aqueous $NaHCO_3$ and water and dried ($MgSO_4$). The solvent was evaporated, and the resulting solid was recrystallized from $CHCl_3$ to yield 1.92 g (3.05 mmol) of yellow solid (61%): ^{1}H NMR ($CDCl_3$) δ 8.82 (d, J = 9.4 Hz, 2 H), 8.50 (d, J = 8.8 Hz, 2 H), 8.35 (d, J = 9.3 Hz, 2 H), 7.74 (s, 2 H), 7.60–7.52 (m, 4 H), 7.32 (t, J = 7.5 Hz, 2 H), 3.54 (s, 6 H); MS (EI, 10 eV) 599.9 (100, M^+), 579.9 (51), 601.9 (54).

Dimethyl 1,1′-Bis(9-cyano-2-anthracenecarboxylate). To a dry DMF solution (50 mL) of the bis-bromoanthracene diester (3.15 g, 5.0 mmol) was added a 2.68-g (30 mmol) portion of CuCN. The mixture was flushed thoroughly with N_2 and heated at reflux for 5 h. The reaction mixture was diluted with 200 mL of benzene, and the organic layer was extracted with 10% HCl, with water (3 × 20 mL), and with $NaHCO_3$ (aqueous). The organic layer was dried ($MgSO_4$), and the solvent was evaporated, leaving 1.56 g of a yellow solid (3 mmol, 60% yield): ^{1}H NMR ($CDCl_3$) δ 8.73 (d, J = 9.2 Hz, 2 H), 8.51 (d, J = 9.1 Hz, 2 H), 8.39 (d, J = 8.6 Hz, 2 H), 7.99 (s, 2 H), 7.67 (d, J = 8.2 Hz, 4 H), 7.42 (dd, J_1 = 6.8 Hz, J_2 = 8.2 Hz, 2 H), 3.56 (s, 6 H); MS (EI, 10 eV) 520.3 (81, M^+), 521.3 (30); IR)KBr) 2215 cm^{-1} (CN stretch).

1,1′-Bis(2,4-dicyanoanthracene) (BDCA). To a benzene solution containing 522 mg (1 mmol) of the bis-cyanoanthracene diester cooled in an ice bath (ca. 5 °C) was added 15 mL of a 0.67 M solution (10 mmol) of methylchloroaluminum amide via a cannula. The reaction mixture was heated at reflux for 4 h, then the temperature was lowered to 55 °C, and the reaction mixture was stirred overnight. The reaction was quenched with 5% HCl, and the layers were separated. The aqueous layer was extracted three times with ethyl acetate, and the organic layers were combined and dried ($MgSO_4$). The solvent was evaporated, and the crude product (characterized by the disappearance of the methyl ester resonance at δ 3.6) was added to 40 mL of dry benzene and an excess (ca. 2 g) of P_2O_5. The mixture was heated gently at reflux for 5 h and then filtered while hot. The benzene layer was extracted with $NaHCO_3$ (aqueous) and dried ($MgSO_4$). The solvent was evaporated, and the product was recrystallized from benzene to yield 272 mg of yellow solid (0.6 mmol, 60%): mp 396 °C; ^{1}H NMR ($CDCl_3$) δ 8.83 (d, J = 8.8 Hz, 2 H), 8.63 (s, 2 H), 8.41 (d, J = 8.2 Hz, 2 H), 8.34 (d, J = 9.0 Hz, 2 H), 7.96–7.89 (m, 4 H), 7.61 (t, J = 7.6 Hz, 2 H); MS (EI, 10 eV) 454.3 (100, M^+); HR/MS calcd 454.122 02, found 454.121 85; UV (benzene) λ_{max} (log ϵ) 376 (4.04), 400 (4.11), 420 (4.2).

Resolution of 1,1′-Bis(2-anthracenecarboxylic acid) and Synthesis of (–)-BDCA. The procedure reported by Hall[18] was followed closely for preparation of the optically active diacid. A 1.0-g (2.25 mmol) portion of racemic diacid was suspended in 40 mL of ethanol and heated to boiling on a steam bath. Finely powdered quinidine [365 mg, 1.125 mmol, $[\alpha]_D$ = +256° (1, alcohol), from Sigma] was slowly added to the mixture. The solution immediately became brownish-red. Addition of a second equivalent of quinidine caused precipitation. The mixture was heated for an additional 10 min. Upon cooling, the small crystals of the diastereomeric salt were isolated by filtration and washed with ethanol to give 1.2 g (1.56 mmol) of salt: $[\alpha]_{5461}$ = –509°. The salt was decomposed by being warmed on a steam bath for 30 min in a 1.5% NaOH solution. The mixture was filtered, and the red filtrate was acidified with concentrated HCl. The resolved diacid was isolated by filtration to give 250 mg (0.563 mmol, 50% yield) of a bright yellow crystalline solid: $[\alpha]_{5461}$ = –384° (0.44, acetone) [lit.[18] $[\alpha]_{5461}$ = –440° (0.8, acetone)]. Optically active BDCA was prepared from the (–)-bis-anthracene diacid by means of the procedure described for the racemic compound. The optical purity of (–)-BDCA was determined by HPLC. An L-leucine covalent Pirkle column was used to separate the enantiomers of BDCA with hexane/isopropyl alcohol (90:10, v/v) as eluent (flow rate of 2 mL/min). The enantiomers of BDCA have retention times of 18.6 and 19.3 min. The optical purity of (–)-BDCA was determined to be 91% on the basis of the integration of these peaks. Anal. Calcd for $C_{32}H_{14}N_4$: C, 83.18; H, 3.39; N, 11.76. Found: C, 83.14; H, 3.38; N, 11.40.

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