tempted due to the lack of suitable empirical increment parameters.

The analysis of the ^{13}C resonances of *exo*- and *endo*-DCP present in EPDM rubbers (see Figures 2) has been done in the manner presented above. However, no copolymers containing only E–*exo*-DCP or E–*endo*-DCP have been made. In the analysis, we followed the line of reasoning explained for terpolymer C; we used the same empirical increments as used for ENB (Table III) but did not add Grant and Paul increments to the ^{13}C resonances C_8, C_9, and C_{10} of 5,6-dihydro-*endo*- and -*exo*-DCP. The results of the calculations are given in Table VI, where it is assumed that the calculations hold for the respective ethylene–*exo*- or *endo*-DCP copolymers. Only the results for exo–exo additions are given, together with the experimental chemical shifts of terpolymers D and E. The following conclusions can be drawn with respect to terpolymer D and E:

endo- and *exo*-DCP are present in the same 5-exo–6-exo configuration in these polymers.

No isomerization of *endo*-DCP in *exo*-DCP or the reverse takes place for these terpolymers. This result is in agreement with results from IR measurements on similar systems.[16] Cesca et al.[16] have reinterpreted earlier work from our laboratory.[17]

endo- and *exo*-DCP are adjoined by long (δ^+) methylene sequences.

Accidental coincidence of ^{13}C resonances is noted for the C_3 and C_6 resonances in terpolymer D (*endo*-DCP).

Appreciable shift inaccuracies occur for the C_5 and C_6 resonances for both terpolymers.

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Registry No. A, 25038-37-3; B, 26521-87-9; C, 25038-36-2; D, 26589-66-2; E, 26589-67-3; *trans*-5-methyl-2-hexene, 7385-82-2; *cis*-5-methyl-2-hexene, 13151-17-2; (*E*)-ENA, 39173-91-6; (*Z*)-ENA, 39173-92-7; 5,6-dihydro-*endo*-DCP, 1755-01-7; 5,6-dihydro-*exo*-DCP, 933-60-8; 5-*exo*-6-*exo*-dimethyl-2-norbornanone, 51154-52-0; 5-*exo*-6-*endo*-dimethyl-2-norbornanone, 15925-44-7; 5-*endo*-6-*exo*-dimethyl-2-norbornanone, 15780-43-5; 5-*endo*-6-*endo*-dimethyl-2-norbornanone, 27141-85-1; E-*cis*-HEX, 83468-45-5; E-*trans*-HEX, 83815-98-9.

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Intramolecular Photocyclomerization and Excimer Emission of 1,1′-Di(1-naphthyl)diethyl Ethers: Model Systems of Poly(1-vinylnaphthalene)

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ABSTRACT: Temperature-dependent fluorescence spectra and intramolecular excimer decay curves of *meso*- and *rac*-1,1′-di(1-naphthyl)diethyl ether (D1NEE) show the existence of at least two excimers in both diastereomers. Broadening of the ^{13}C NMR absorptions at low temperatures of *meso*- and *rac*-D1NEE and the model compound 1-(1-naphthyl)ethyl methyl ether (1NEME) indicates that hindering of rotations occurs. Photoreaction yields for both isomers an intramolecular exo cycloadduct. Cleavage of the cycloadducts reveals that the hypsochromic excimer in *meso*-D1NEE can be correlated with the exo configuration. The data are interpreted on the basis of hindering of the rotation around the 1-naphthyl carbon–methine carbon bond in combination with steric interactions between the peri H_8, $H_{8'}$ hydrogens and the methyl substituents.

Introduction

The intramolecular photocyclomerization of nonconjugated dinaphthyl compounds with different chains can lead to several possible isomeric photoisomers[1-7] (Figure 1). Todesco et al. have reported a direct correlation between the excimer emission in solution and the configuration of the cyclomers of di(1-naphthyl)dimethyl ether (D1NME).[7] Photocleavage of the endo and exo cyclomer of D1NME in an ethanol matrix at 77 K yields for both products an emission spectrum identical with the excimer emission in solution. Todesco et al. conclude that the excimer precursors of the cyclomers have an identical but not complete sandwich overlap.

In a number of intramolecular excimer-forming systems in solution the spectral distribution and time-dependent fluorescence intensities have been analyzed as derived from one excimer species.[8] In the case of poly(*N*-vinylcarbazole), however, two spectral different intramolecular complexes

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Table I
Quantum Yields of Fluorescence of the Local Excited State (φ_{FM}), the Excimer (φ_{FD}), and Photoreaction (φ_R) of *meso*- and *rac*-D1NEE and D1NME in Isooctane at 293 K

	$\varphi_{F_{tot}}$	φ_{FM}	φ_{FD}	φ_R	λ_{max}, nm	fwhm, cm^{-1}
meso-D1NEE	0.017	0.003[a]	0.014[a]	0.010	385	6500
rac-D1NEE	0.095	0.030	0.065	0.004	405	4800
D1NME[7]	0.043	0.006	0.037	0.032	413	4200

[a] Because of the large overlap between the excimer and the local excited state emission, it is difficult to evaluate the exact contribution.

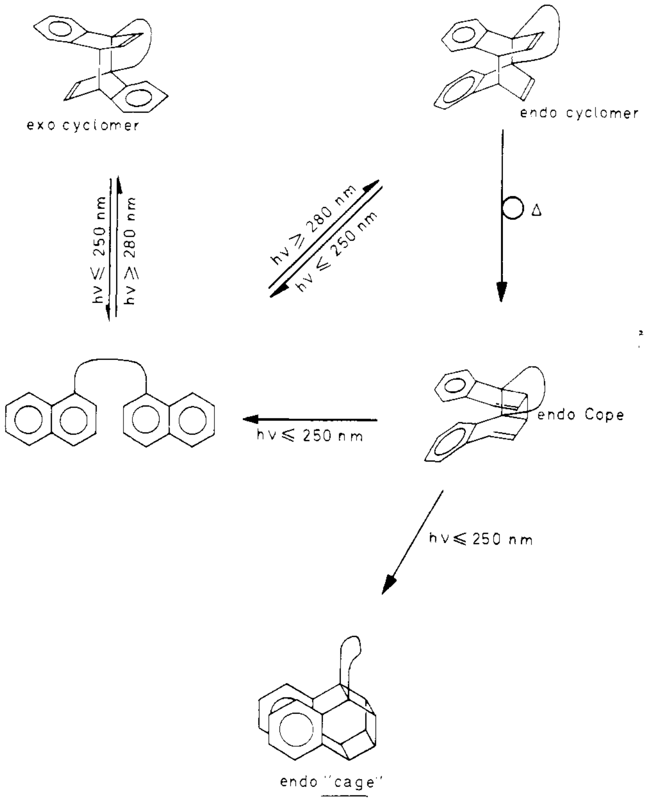


Figure 1. Possible photoproducts formed after light excitation of di(1-naphthyl) compounds with short chains.

are detected.[9] A study on the diastereomeric bichromophoric model molecules of poly(N-vinylcarbazole) revealed that these two types of excimer emission are related to the isotactic and syndiotactic sequences in the polymer chain.[9c]

The dual excimer emission observed in the fluorescence spectra of 1,3-bis[1-(4-methoxynaphthyl)]propane and 1,3-bis[1-(4-hydroxynaphthyl)]propane has been ascribed to two different excimer geometries caused by bulky substituents and intramolecular hydrogen-bond formation, respectively.[10] In the case of 1,3-di(9-anthryl)-1,1,3,3-tetramethyldisiloxane also two spectral different excimers exist simultaneously in solution.[11]

For several 2-substituted dinaphthyl compounds and poly(2-vinylnaphthalene), a two-exponential decay part of the time-dependent excimer fluorescence intensities has been reported.[12a,b] Phillips et al. have also reported a poor fit as a difference of two exponentials for the excimer decay of poly(1-vinylnaphthalene)–methyl methacrylate copolymers.[12c] Because the 2-substituted di and polynaphthyl systems are not photoreactive, no correlation could be made with the nonstationary data and the excimer configurations using cleavage experiments on the photoproducts.

In this study, temperature-dependent fluorescence spectra and time-dependent fluorescence intensities at different wavelengths of *meso*- and *rac*-1,1′-di(1-naphthyl)diethyl ether (D1NEE) were recorded. Temperature-dependent ^{13}C NMR spectra of *meso*- and *rac*-D1NEE and the model compound 1-(1-naphthyl)ethyl methyl ether (1NEME) were obtained. Furthermore, the photocyclomers of the pure diastereomers of D1NEE were synthesized and their structure was characterized using 360-MHz ^{1}H NMR, UV spectroscopy, and mass spectrometry. Emission spectra of the cleaved photoproducts in a 3:1 MCH/IP matrix at 77 K were compared with the spectral data of *meso*- and *rac*-D1NEE in dilute solution. Finally, additional information was obtained from molecular models of *rac*- and *meso*-D1NEE.

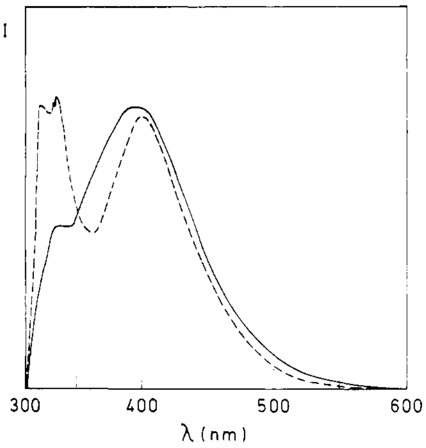


Figure 2. Fluorescence spectra of *meso*-D1NEE (—, ×5) and *rac*-D1NEE (---) at 298 K in isooctane (10^{-4} M).

Experimental Results

Fluorescence Data of *meso*- and *rac*-D1NEE in Dilute Isooctane Solutions. The fluorescence spectra of *rac*- and *meso*-D1NEE in 10^{-4} M isooctane solutions at 298 K show a striking difference between the two diastereomers (Table I and Figure 2). *meso*-D1NEE has a much lower $\varphi_{F_{tot}}$ and a relative much larger excimer contribution with respect to *rac*-D1NEE. Furthermore, the excimer of *meso*-D1NEE is more hypsochromic and broader than *rac*-D1NEE and D1NME.

Temperature-dependent fluorescence spectra of *meso*-D1NEE, especially at temperatures lower than 230 K (Figure 3) reveal that the broad excimer emission at 293 K originates from at least two intramolecular complexes with different spectral distributions. The bathochromic complex (λ_{max} = 420 nm) dominates at lower temperatures, while the hypsochromic emission (λ_{max} = 385 nm) is already predominant at room temperature.

The temperature-dependent fluorescence spectra of *rac*-D1NEE show no such effects. They can be compared with the spectral characteristics of the classic intramolecular excimer-forming systems[8] (Figure 4).

The time-dependent fluorescence intensity of *meso*-D1NEE analyzed in the excimer region at 298 K in isooctane cannot be deconvoluted as a difference between two exponentials; the growing in excimer luminescence is within the resolution of the apparatus. Furthermore, there is a clear influence of analysis wavelength on the decay

Table II
^{13}C NMR Chemical Shifts (ppm), Signal Broadening $\omega_{1/2}$ (Hz), and Percentages of Conformers as a Function of Temperature Derived from the Methyl and Methine Carbons of *meso*- and *rac*-D1NEE and 1NEME[a]

	T, K	CH_3	%	$\omega_{1/2}$	CH	%	$\omega_{1/2}$	OCH_3	%	$\omega_{1/2}$
1NEME	298	23.3	100		77.7	100		56.6	100	
	223	23.7	100		77.2	100		56.7	100	
	183	24.1	100	9	76.8	100	20	56.8	100	3
meso-D1NEE	298	23.3	100		72.5	100				
	223	23.4	100		71.6	100				
	183	23.5	100	12	72.1	100	20			
rac-D1NEE	298	24.2	100		73.8	100				
	213	24.4	100	4	72.8	100	25			
	183	23.4	15		78.0	15				
		24.7	85		71.9	85				

[a] Solvent: CD_2Cl_2, Me_4Si.

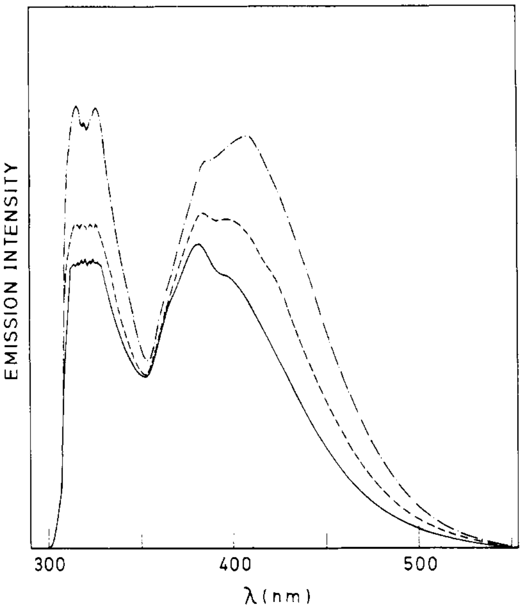


Figure 3. Fluorescence spectra of a 10^{-4} M solution of *meso*-D1NEE in isooctane at low temperatures: (–·–) 196 K; (- - -) 212 K; (—) 232 K.

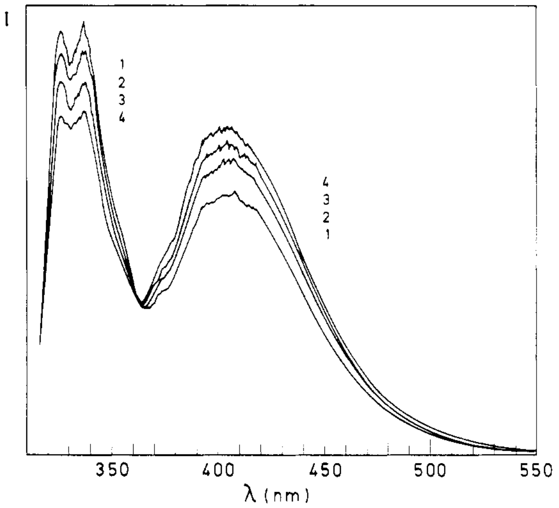


Figure 4. Fluorescence spectra of a 10^{-4} M solution of *rac*-D1NEE in isooctane at low temperatures: (1) 190 K; (2) 201 K; (3) 222 K; (4) 239 K.

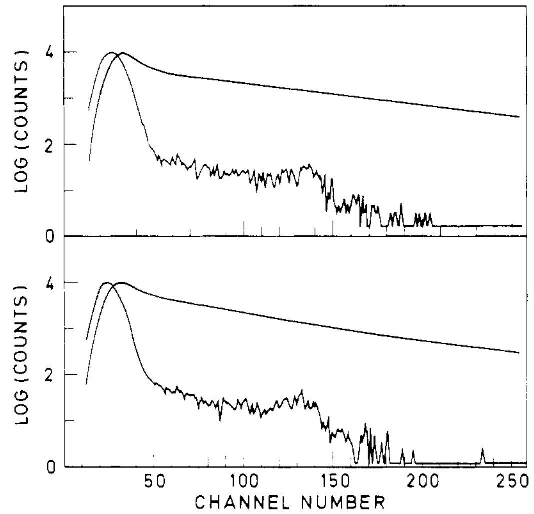


Figure 5. Time-dependent excimer fluorescence intensities of the *meso*-D1NEE excimer at 420 (upper) and 385 nm (lower) (10^{-4} M, isooctane, 298 K).

curve. Analysis at 385 nm (Figure 5) emphasizes the more slowly decaying species.

Analysis of the excimer decay curves of *rac*-D1NEE shows the same complexity without the dependence of the analysis wavelength. These curves are analogous to those of the excimers of some 2-naphthyl-substituted bichromophores.[12] A detailed kinetic study of the photophysics of D1NEE is still in progress.

NMR Data of *meso*- and *rac*-D1NEE. In ^{1}H NMR as in ^{13}C NMR, there is a difference between the chemical shifts of the methine and methyl resonances (see Table II and Experimental Section) of *meso*- and *rac*-D1NEE.

For 2,4-diarylpentanes, where meso and racemic isomers are easily identified, thanks to the absorption pattern of the central methylene protons, the methine and methyl *carbons* of the meso isomer absorb upfield and the methine and methyl *protons* absorb downfield with respect to the racemic isomers.[9c,13]

In the case of D1NEE, where the coupling information in ^{1}H NMR is lost, the chemical shift data can be used for a provisional assignment of the meso and racemic isomers. At low temperatures (183 K), special attention was paid to the broadening in the methyl and methine carbon absorptions (Table II). For *meso*-D1NEE and 1NEME, only a broadening of the signals has been observed. The absorptions in *rac*-D1NEE split into two signals, indicating the existence of two groups of conformers that cannot interconvert within the NMR time scale.

Photocyclomerization of *meso*- and *rac*-D1NEE. Irradiation at λ >280 nm of 10^{-3} M isooctane solutions of, respectively, *meso*- and *rac*-D1NEE leads to intramolecular photocyclomerization. The quantum yield of photoreaction at 298 K of *meso*-D1NEE is higher than for *rac*-D1NEE (Table I). No absorption above 300 nm was observed for either cyclomer. A slow spontaneous back-re-

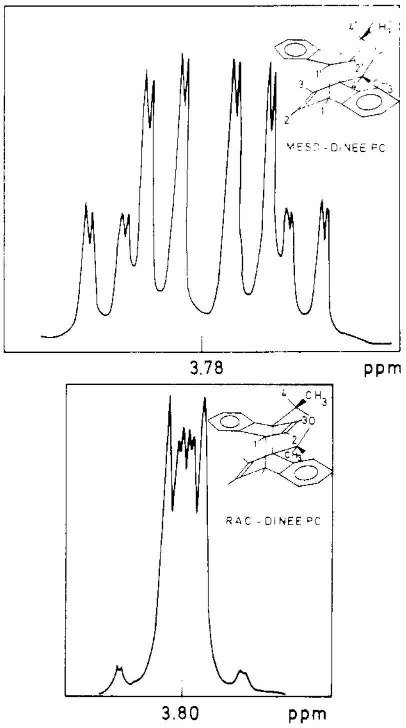


Figure 6. 360-MHz absorptions of the H_1 and $H_{1'}$ protons of *meso*-D1NEEPC (upper) *rac*-D1NEEPC (lower) in $CDCl_3/Me_4Si$.

action to the original *meso*- and *rac*-D1NEE occurs on storage (260 K). The value of the molecular ions (m/e 376) is identical with those of *meso*- and *rac*-D1NEE, confirming the intramolecular reaction.

In order to clear up the configuration of the cyclomers, a ^1H NMR spectrum was recorded at 360 MHz. In contrast to the ^1H NMR spectra of the starting diastereoisomers D1NEE, there is a striking difference between the photoisomers of *rac*- and *meso*-D1NEE. The cyclomer obtained by irradiation of the *rac*-D1NEE is highly symmetric and its ^1H NMR shows only *nine* different protons: four aromatic, two vinyl, and two aliphatic CH and 1 CH_3. As a consequence of this symmetry, only a few coupling constants can be extracted by analysis of the spectrum and virtual coupling is observed in the pattern of protons H_1 and H_2 (Figure 6).

The cyclomer obtained by irradiation of *meso*-D1NEE is not symmetric at all: one can observe two CH_3, four aliphatic CH, 4 vinyl protons, and a complex absorption in the aromatic region. Protons H_1 and $H_{1'}$ absorbs as the AB part of an ABXY pattern (two ddd: $\Delta\nu_{AB} = 25$ Hz, $\Delta\delta = 0.07$ ppm (Figure 6). Proton H_4 (0.9 ppm upfield from $H_{4'}$) is a sharp quartet ($\omega_{1/2} = 1$ Hz), where $H_{4'}$, as well as H_4 in the racemic cyclomer, is broadened ($\omega_{1/2} = 2$ Hz) by a long-range coupling with the vinyl proton $H_{2'}$ in a zigzag path.[14]

In Table III, it should be noted that the primed protons have almost the same chemical shifts as the protons in the racemic cyclomer. This provides information on the respective position of H_4 and CH_3 in the molecule. Finally, the chemical shifts of the aromatic protons in both cyclomers are typical for the exo configuration (ref 7 and references therein).

Emission of the Cleaved Photoproducts of D1NEE in a Matrix at 77 K. Cleavage of *rac*- and *meso*-D1NEE at 77 K in a 3:1 MCH/IP matrix with 250-nm light yields, apart from the emission of the naphthalene chromophore of residual *rac*- and *meso*-D1NEE, an unstructured fluorescence spectrum with a maximum of emission at 390 nm for *meso*-D1NEEPC and 410 nm for *rac*-D1NEEPC. These emissions can be related with the hypsochromic isomer of *meso*-D1NEE and the excimer of *rac*-D1NEE, respectively (Figure 7). The emission of *meso*- and *rac*-D1NEE under the same experimental conditions gives for both isomers a spectrum similar to the emission spectrum of a 1-alkylnaphthyl chormophore.

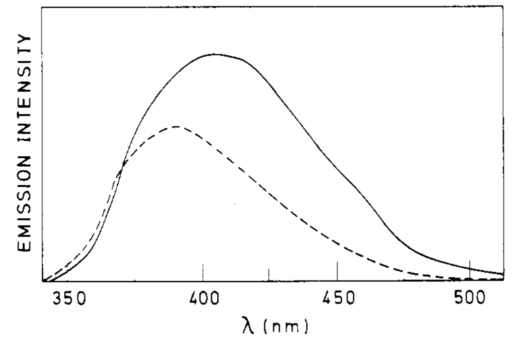


Figure 7. Excimer emission of the cleaved D1NEEPC in a 3/1 MCH/IP matrix at 77 K: (---) meso; (—) rac.

Table III

A. 360-MHz ^1H NMR Data of *meso*-D1NEEPC in $CDCl_3/Me_4Si$

chem shift, ppm	multiplicity	J, Hz	I	H
7.10-7.65	m		8	Ar
6.12	d of d (sh)	$^3J_{H_2-H_3} = 9.0$ $^3J_{H_2-H_1} = 6.8$	1	H_2
5.87	d of d	$^3J_{H_3-H_2} = 9.0$ $^4J_{H_3-H_1} = 1.3$	1	H_3'
5.78	d of d (br)	$^3J_{H_2'-H_1'} = 6.8$ $^5J_{H_2'-H_4'} \leqslant 2$	1	H_2'
5.36	d of d	$^4J_{H_3-H_1} = 1.3$	1	H_3
4.95	q (br)	$^3J_{H_4'-CH_3} = 6.8$	1	H_4'
4.04	q (sh)	$^3J_{H_4-CH_3} = 6.8$	1	H_4
3.82	m	$\Delta\nu_{H_1-H_1'} = 25$ Hz	1	H_1 and/or
3.75		$^3J_{H_1-H_1'} =$ 10.0	1	H_1'
1.52	d		3	CH_3
1.52	d		3	CH_3
1.37	d		3	CH_3'

B. 360-MHz ^1H NMR Data of *rac*-D1NEEPC in $CDCl_3/Me_4Si$

chem shift, ppm	multiplicity	J, Hz	I	H
7.10-7.40	m		8	Ar
5.97	filled m	$^3J_{H_2-H_3} = 8.5$	2	H_2
5.81	d		2	H_3
5.03	q	$^3J_{H_4-CH_3} = 6.5$	2	H_4
3.80	filled d		2	H_1
1.40	d		6	CH_3

Discussion

rac- and *meso*-D1NEE are the first short-chain bisnaphthalenes forming only exo cycloadducts at room temperature. The elucidation of the cyclomer geometry confirmed the previous assignments of "meso" and "racemic" to D1NEE. These assignments were based on the analogy of the ^1H and ^{13}C NMR of D1NEE with other 2,4-diarylpentanes.[13]

The fluorescence spectra of *meso*-D1NEE clearly show the existence of at least two excimer emissions. This is confirmed by the wavelength dependence of the decay curves in the excimer region of *meso*-D1NEE. For *rac*-D1NEE, there is only an indication of the possible existence of two excimers from the excimer decay curves. Cleavage in a matrix of the photocyclomer of *rac*-D1NEE gives the same excimer emission as observed in solution.

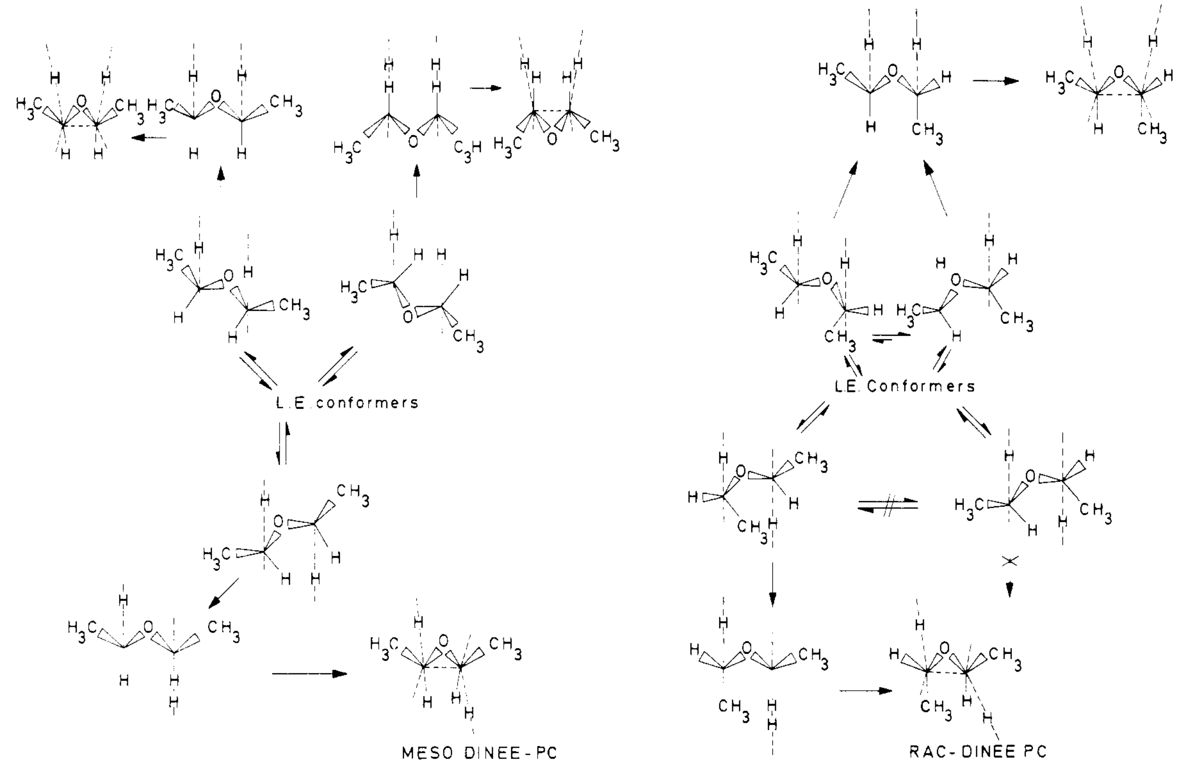
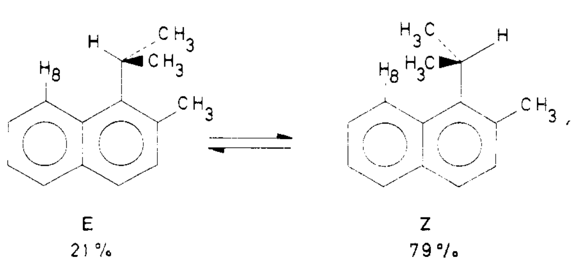


Figure 8. Top view of the possible excimer geometries and related photoproducts of *meso*-D1NEE (left) and *rac*-D1NEE (right) derived from molecular models.

For *meso*-D1NEE the cleavage of the photocyclomer results in a hypsochromic (exo) excimer emission. The bathochromic emission in solution of *meso*-D1NEE is not photoreactive at room temperature.

The temperature-dependent ^{13}C NMR spectra indicate for all products, the model compound included, a high activation energy between two conformers or group of conformers. This means that even at room temperature these conformations cannot interconvert in the *nano*second scale of single photon counting. For the intramolecular exciplex forming α,ω-phenyl(*N*,*N*-dimethylamino)alkanes, it has been shown that these conformations can be correlated with distinct chain conformations.[15] Although the influences of chain conformations are also possible for D1NEE, one has in addition to consider the rotation around the 1-naphthyl carbon and the methine carbon bond. It is well-known that for 1-substituted naphthalene, this rotation is hindered by the steric interaction with the H_8 peri hydrogen.[16a] The activation energy of rotation increases from 8.5 to 14 kJ mol^{-1} on going from 1-methylnaphthalene to 1-ethylnaphthalene.[16b,c] Mannschreck et al. reported an activation energy of 53 kJ mol^{-1} for 1-isopropyl-2-methylnaphthalene, resulting in the existence of two conformers at low temperatures.[16d]



For 1NEME, the steric hindrance of this rotation is weaker due to the absence of the 2-methyl group. In the bichromophoric systems, however, one of the CH_3 substituents of the isopropyl group of isopropyl-2-methylnaphthalene has to be replaced by a very bulky 1-(1-naphthyl)ethoxy group. Using molecular models, one can hardly form an exo overlap excimer from an endo overlapping excimer. Therefore, the NMR data support the complexity of the photophysical data caused by the hindered rotation of the sp^2 1-naphthyl carbon and the sp^3 methine carbon bond.

The photophysical and photochemical properties of D1NEE are quite different from those of D1NME.[7] Using molecular models, one can easily show that the overall steric hindrance in *rac*- and *meso*-D1NEE is much higher than in D1NME. Furthermore, the introduction of the methyl groups gives rise to the existence of more excimer isomers with respect to D1NME.

Figure 8 gives an impression of the most realistic possible excimer geometries of D1NEE, starting from the excimer geometry proposed by Todesco et al., followed by the cyclomer precursor overlap and the cyclomer itself. Note that for *meso*-D1NEE, there are two not directly interconverting types of endo overlaps. This is also the case for two types of exo overlap in *rac*-D1NEE. One of the exo overlap geometries of *rac*-D1NEE is totally prohibited from forming a cyclomer, due to the inevitable steric hindrance between the H_8 peri hydrogen and a methyl substituent.

According to Figure 8, the photoreactivity of a certain LE-state conformer is determined by its ability to form excimer, followed by the probability of closer encounter of the naphthyl moieties leading to the photoreaction. This close-encounter geometry is to a large extent governed by the repulsion between the methyl groups and the peri H_8 hydrogens. In order to explain the photoreactivity of D1NEE, detailed conformational maps are necessary.

A recent conformational study on poly(1-vinylnaphthalene) and poly(2-vinylnaphthalene) ascribes the large difference in steric interactions between these two polymers to the same type of steric interactions as described here.[17] The high steric hindrance imposed by the methyl groups explains the lower reactivity of *meso*- and *rac*-D1NEE with respect to D1NME. From Figure 8 one cannot reject the possibility of photoreaction of the endo overlap excimers. Figure 8 clearly shows that these effects originate at the methyl substituents. For *meso*-D1NEEPC, the asymmetry of the ^{1}H NMR spectra indicates a highly asymmetric excimer with a relative weak overlap. This results in a more hypsochromic emission. Omission of the methyl substituents reduces the amount of possible excimer isomer geometries and steric hindrance. Therefore, with these data of D1NEE, the hypothesis of Todesco et al. concerning the geometry of exo and endo overlap of the D1NEE excimer is not contradicted. Finally, these bichromophoric D1NEE molecules can serve to a certain extent as model compounds of poly(1-vinylnaphthalene) (P1VN).

A complex decay in the monomer and excimer region of poly(1-vinylnaphthalene) and copolymers[12c] due to the described steric effects and the superpositions of isotactic and syndiotactic sequences cannot be excluded. On the other hand, replacing the central oxygen by a methylene group causes additional steric interactions. As a consequence, some conformations of the local excited state and the excimer of D1NEE, especially the exo excimer, can be absent in P1VN.

Experimental Section

Synthesis of *meso*- and *rac*-D1NEE and 1NEME. *meso*- and *rac*-D1NEE were synthesized according ref 18. The reaction mixture was first purified on a silica column with toluene as eluent. Further separation of the diastereomers was accomplished on a Lichrosorb SI60 10-μm MPL column with 60:40 toluene/dichloromethane as eluent. ^{1}H NMR ($CDCl_3$, $(CH_3)_4Si$): *meso*, δ 7.30–8.10 (m, 14 H), 5.40 (q, 2 H), 1.66 (d, 6 H); *rac*, δ 7.30–8.10 (m, 14 H), 5.06 (q, 2 H), 1.60 (d, 6 H).

1NEME was synthesized according a modified Williamson synthesis with iodomethane, 1-(1-naphthyl)ethanol, and sodium hydride as reactants. 1-(1-Naphthyl)ethanol was obtained from the reduction of 1-acetylnaphthalene with $LiAlH_4$ in dry ether. Purification of 1NEME was accomplished in the same way as for D1NEE. ^{1}H NMR (CD_2Cl_2, $(CH_3)_4Si$): δ 7.30–8.2 (m, 7 H), 4.95 (q, 1 H), 3.20 (s, 3 H); 1.55 (d, 3 H).

Intramolecular Photocyclomerization of *meso*- and *rac*-D1NEE. Solutions (10^{-3} M) of, respectively, *meso*- and *rac*-D1NEE, previously bubbled with dry nitrogen, were irradiated at 300 nm during 3 days using a Rayonet with 3000-Å RUL lamps. The cyclomers precipitated and residual D1NEE was removed on a silica plate with toluene as eluent.

Instrumentation. 360-MHz ^{1}H NMR spectra were taken on a Bruker WH 360 at the Rijksuniversiteit Gent and temperature-dependent ^{13}C NMR spectra were recorded at 20 MHz, using a Bruker WP 80. Fluoresecence spectra were obtained from a Fica 55 spectrofluorimeter absolute and a Spex Fluorolog. Time-dependent fluorescence intensities were obtained from a single-photon-counting apparatus from Applied Photophysics with Canberra and Ortec modules. Decay curves were deconvoluted with a PDP11 using the nonlinear least-squares method.[19] Quantum yields of photocyclomerization were determined using a Bausch and Lomb monochromator and hexamethylene bis(maleimide) as actinometer.[20] Preparative cyclomerization was accomplished with a Rayonet equipped with 3000-Å RUL lamps.

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Registry No. *rac*-D1NEE, 83815-95-6; *meso*-D1NEE, 83815-97-8; P1VN, 25135-12-0; 1NEME, 83815-96-7.

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