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Fluorescence of the Diastereoisomers of 2,4-Di(*N*-carbazolyl)pentane and the Two Excimers Observed in Poly(*N*-vinylcarbazole)

F. C. De Schryver,* J. Vandendriessche, S. Toppet, K. Demeyer, and N. Boens

Department of Chemistry, Universiteit Leuven, Celestijnenlaan 200 F, B-3030 Heverlee, Belgium. Received July 20, 1981

ABSTRACT: The two diastereoisomers of 2,4-di(*N*-carbazolyl)pentane were synthesized and characterized by NMR. Their respective emission in the excimer region, at 420 nm for the meso isomer and 370 nm for the racemic isomer, can be related to the two excimers observed in poly(vinylcarbazole).

A recent publication[1] proposing an interpretation of the excimer kinetics of poly(*N*-vinylcarbazole) in solution prompts us to report preliminary results on the emission properties of 2,4-di(*N*-carbazolyl)pentanes. We have already shown[2] that the classical kinetic scheme for intermolecular complex formation could not be extended to systems where substantial barriers prevent fast conformational equilibrium. The role of conformational equilibrium upon intramolecular excimer formation was also suggested by Morawetz.[3] As was pointed out by Bovey,[4] one should, in the case of polymers such as polystyrene, consider configurational aspects. Monnerie[5] has shown that the excited-state properties of 2,4-diphenylpentane are substantially different for the meso and the racemic diastereoisomers, especially their capacity to form the excimer.[5b] The nonvalidity of the classical kinetic scheme of intermolecular excimer formation in poly(2-vinylnaphthalene)[6] could also be related to differences in excited-state properties of meso and racemic model systems.[6b]

Table I
^{1}H NMR Data of Diastereoisomers of 2,4-Di(*N*-carbazolyl)pentane in CD_2Cl_2 at 313 K

δ	multiplicity	group of protons	J, Hz
	Sample B (meso)		
1.58	d	CH_3	
2.76 (A), 2.90 (B)	ABX_2	H_ACH_B	$^2J_{AB} = -14.2$
4.53	ABX_2, q	CH	$^3J_{AX} = 7.8$, $^3J_{BX} = 7.6$
6.9–7.4	m		
7.98–8.05	m	carbazolyl	
	Sample A (*dd*,*ll*)		
1.39	d	CH_3	
3.02	$AA'XX'$	$CH_{2AA'}$	$^2J = -14.85$
4.40	$AA'XX'$, q	$CH_{XX'}$	$^3J_{AX} = 4.45$, $^3J_{AX'} = 10.80$
6.2–7.6	hump		$J_{XX'} = 0$
7.9–8.05	m	carbazolyl	

Poly(vinylcarbazole) has, however, in the realm of the polyvinyl aromatic systems a particular aspect: dual excimer emission is observed, one excimer emitting at 380 nm (high-energy excimer, trap II) and the other (low-energy excimer) at 420 nm.[7] Attempts to interpret the fluorescence properties of poly(vinylcarbazole) were made on the basis of a scheme in which an equilibrium between the two excimers is included.[1,8] It had, however, been noted[9] that "the intensity of the high-energy excimer in-

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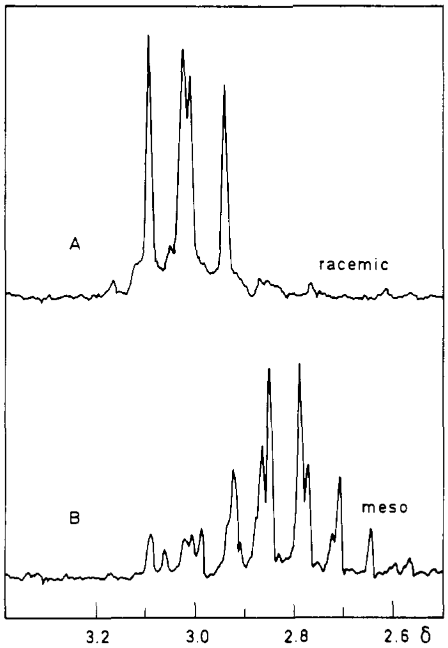
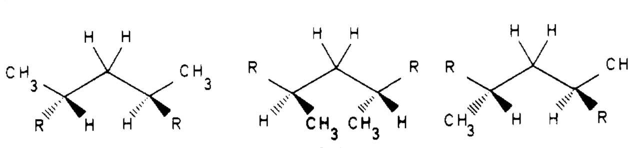


Figure 1. ^{1}H NMR spectra of samples A and B: (A) CH_2 group of the racemic diastereoisomer under identical experimental conditions (the meso isomer still contains ±20% of the racemic compound); (B) CH_2 group of *meso*-2,4-di(*N*-carbazolyl)pentane in CD_2Cl_2 at room temperature.

creased with an increase in the content of the syndiotactic sequences" in the polymer. To contribute to the elucidation of this problem 2,4-di(*N*-carbazolyl)pentane was synthesized. Two fractions were isolated by high-performance liquid chromatography, both having an $M^{+}\cdot$ of *m*/*z* 402. ^{1}H NMR data, reported in Table I, characterize sample B as consisting of more than 80% *meso*-2,4-di(*N*-carbazolyl)pentane (**1**) and sample A as consisting of more than 95% of racemic (*dd*,*ll*)-2,4-di(*N*-carbazolyl)pentane (**2**). Indeed, the CH_2 group of sample A (Figure 1) shows no difference in shift for both protons while the same group of protons in sample B shows a $\Delta\nu_{AB}$ of 14.5 Hz (Figure 1).

In view of the influence of the aromatic groups on the absorption of the methine and methylene protons in comparison with 2,4-diphenylpentane[11] and on the basis of the ^3J coupling constant, it can be proposed that TG/GT is the most stable conformation of **1** while TT and GG conformations are present at room temperature for **2**. A calculation equivalent to the one reported by Bovey[10] indicates a distribution of 82% TT and 18% GG for **2** at 313 K in CD_2Cl_2.



2 TT 2 GG 1 TG/GT

R= carbazolyl

Especially noteworthy is the important splitting of the shift of the aromatic protons of **2** at 233 K (Table II) while at 313 K only proton 4 can be distinguished from the other coalescing protons.

For **1** under the same experimental conditions only the splitting of proton H_1 (δ 7.48 and 6.64) and proton H_4 (δ 8.08 and 8) can be followed at 100 MHz, H_2 and H_3 absorbing in the narrow range δ 7–7.4. This further supports the TG/GT conformation for **1** and the TT conformation for **2** as being the more stable. In both compounds the carbazolyl groups are no longer able to rotate at that temperature.[12] In **2** two carbazole groups are lying in such a spatial arrangement that one phenyl moiety is on top of that of the other carbazole group. The coalescence temperature is approximately 273 K for H_4. Temperature dependence of the NMR signals of proton H_4 indicate that the rate constant for exchange at 273 K equals 42 s^{-1} while the activation free enthalpy at that temperature equals 58 kJ·mol^{-1}. The quantity of pure **1** and **2** necessary for emission spectroscopy was obtained by repeated thin-layer chromatography on silica with 30/70 toluene–hexane as eluent. The absorption spectra of **1** and **2** at room temperature in isooctane show a band pattern analogous to the one reported for *N*-isopropylcarbazole.[13] The emission spectra of **1** and **2** in isopentane are reported in Figure 2. The emission spectrum of **1** at room temperature shows, besides carbazole emission, an excimer band with its maximum at 420 nm and a bandwidth of 3350 cm^{-1}. The maximum of this excimer, the so-called low-energy excimer, shifts to 425 nm at 197 K. This excimer decays as a single exponential with a decay parameter obtained by single-photon counting, varying from 46.5 ns at 223 K to 34.9 ns at 350 K. The relative intensity of the excimer over the carbazole emission increases by a factor of 2 from 173 to 293 K, while the carbazole emission decreases by a factor of 12 in the same temperature domain. The emission spectrum of **2** at room temperature shows, besides carbazole emission, a new band at longer wavelengths. A new maximum is observed at 370 nm with a bandwidth of 2600 cm^{-1} upon spectral deconvolution. When the sample is cooled to 133 K, the latter emission is almost the sole contributor to the spectrum (Figure 2). The decay parameter of this excimer, the so-called high-energy excimer, which also decays monoexponentially, equals 17 ns at 300

Table II
^{1}H NMR Shifts of the Aromatic Protons of **2** and *N*-Isopropylcarbazole at 233 K in CD_2Cl_2

proton	downfield	upfield	*N*-isopropyl-carbazole
H_1	7.65	5.87	7.4-7.5
H_2	7.4	6.59	7.4-7.5
H_3	7.2	6.87	7.20
H_4	8.09	7.9	8.10

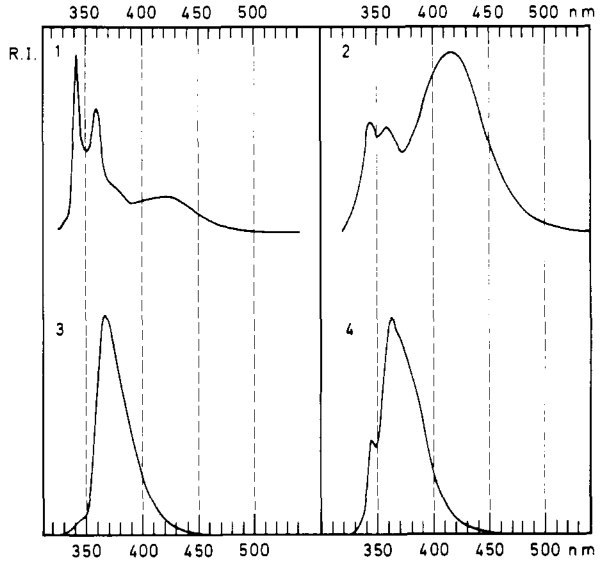


Figure 2. Emission spectra of (1) the meso isomer in isooctane at 197 K, (2) the meso isomer in isooctane at 293 K, (3) the racemic isomer in isopentane at 133 K, and (4) the racemic isomer in isopentane at 293 K. Excitation wavelength: 320 nm.

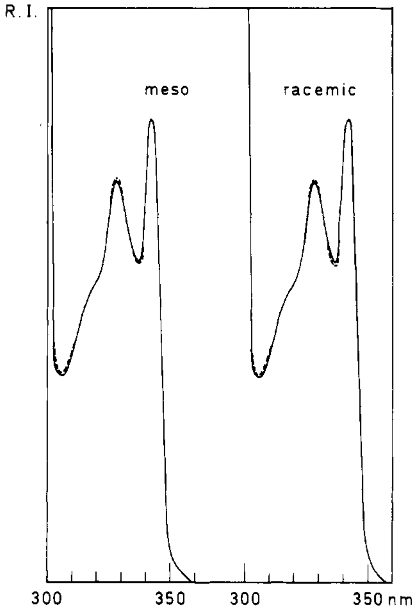


Figure 3. Excitation spectra at room temperature of the racemic isomer in isopentane at (- - -) 400 and (—) 365 nm and of the meso isomer in isooctane at (- - -) 410 and (—) 370 nm.

K and 17.8 ns at 200 K.

The emission maximum of both excimers is not dependent upon solvent polarity since no variation of the respective values was observed in acetonitrile.

The excitation spectra of **1** and **2** are identical in the monomer and excimer region (Figure 3) and identical with the lowest transition of *N*-isopropylcarbazole. This clearly establishes the origin of the two excimers in poly(vinylcarbazole) as being related to the isotactic (meso) and syndiotactic (racemic) sequences. It further rules out the probability that excimer II and excimer I are in equilibrium via a direct pathway as proposed in the above-mentioned schemes.[1,8] Combining the NMR data and the emission data furthermore substantiates the suggestion by Johnson[7c] and Itaya[9a] that the high-energy excimer has an only partially overlapping structure. A detailed NMR study and kinetic and thermodynamic aspects of excimer formation in 2,4-di(*N*-carbazolyl)pentane will be reported later.

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