

Rotational barriers in perylene fluorescent dyes

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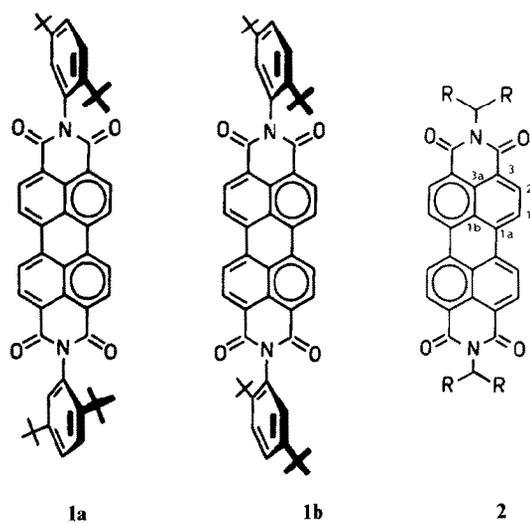
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(Received 4 March 1988; in final form 20 April 1988; accepted 26 April 1988)

Abstract—Rotational barriers in *N*-substituted perylene dyes have been determined. Phenyl substituents with *tert*-butyl groups in the *o*-position give rigid systems, whereas secondary alkyl groups cause low rotational barriers. In spite of that, fluorescent quantum yields are high in both cases. Conformations in solution are discussed.

INTRODUCTION

Conformational mobility plays an important role in deactivation processes of fluorescent dyes ('loose bolt effect' [1]). In perylene fluorescent dyes with high fluorescent quantum yields and photostabilities [2] the *N*-substituent can rotate around the terminal C–N single bond. The height of barrier of this rotation is dependent on the substituents and should be determined.



EXPERIMENTAL

Chemicals

The synthesis of dyes 2 Nos. 1–4 (Table 1) and Nos. 8–11 has been described in a previous paper [3]. The dyes Nos. 5–7 have been prepared and purified according to literature procedure [3].

N,N'-bis(3-heptyl)-3,4:9,10-perylenebis(dicarboximide) (2, No. 5)

1.00 g (2.55 mol) perylenetetracarboxylic-3,4:9,10-bis-anhydride and 0.69 g (6.0 mol) 3-heptylamine give 1.01 g (67%). —m.p. > 360°C— R_f (silica gel/CHCl₃)=0.40.—i.r. (KBr): ν =2959 cm⁻¹s, 2931s, 2872m, 1698s, 1658s, 1594s, 1579s, 1508w, 1485w, 1460m, 1435m, 1406s, 1380m, 1338s, 1253s, 1209m, 1193m, 1177w, 1125w, 1097m, 962w, 940w, 852m, 810s, 792w, 783w, 747s, 617w.—u.v.-vis (CHCl₃): λ_{max} (ϵ)=457 nm(18480), 488(50650), 524.5(83860)—u.v.-

vis (*n*-heptane): λ_{max} (ϵ)=448 nm(19270), 478(52720), 513.5(89500)—Fluorescence (CHCl₃): λ_{max} =536 nm, 575—Fluorescence (heptane): λ_{max} =519 nm, 559—¹H-NMR (CDCl₃): δ =0.95(m, 12H), 1.33(m, 8H), 2.10(m, 8H), 5.08(m, 2H), 8.42(q, 8H)—C₃₈H₃₈N₂O₄ (586.7) calcd. C 77.79 H 6.53 N 4.77 found C 77.51 H 6.56 N 4.65.

N,N'-bis(3-nonyl)-3,4:9,10-perylenebis(dicarboximide) (2, No. 6)

1.00 g (2.55 mmol) perylenetetracarboxylic-3,4:9,10-bis-anhydride and 0.85 g (6.0 mmol) 3-nonylamine give 0.55 g (33%).—m.p. 269–270°C— R_f (silica gel/CHCl₃)=0.46.—i.r. (KBr): ν =2956 cm⁻¹m, 2928m, 2857m, 1698s, 1658s, 1595s, 1579m, 1507w, 1484w, 1460w, 1435w, 1406m, 1379w, 1339s, 1253m, 1210w, 1176w, 1125w, 1102w, 961w, 852w, 810m, 804w, 793w, 783w, 746m.—u.v.-vis (CHCl₃): λ_{max} (ϵ)=458 nm(18240), 488.5(49690), 525(82290)—u.v.-vis (*n*-heptane): λ_{max} (ϵ)=448.5 nm(19490), 478(54090), 514(92810)—Fluorescence (CHCl₃): λ_{max} =534 nm, 575—Fluorescence (*n*-heptane): λ_{max} =519 nm, 558.5—¹H-NMR (CDCl₃): δ =0.86(m, 12H), 1.23(m, 16H), 2.05(m, 8H), 5.03(m, 2H), 8.48(q, 8H)—C₄₂H₄₆N₂O₄ (642.8) calcd. C 78.47 H 7.21 N 4.36 found C 78.77 H 7.24 N 4.20.

N,N'-bis(3-undecyl)-3,4:9,10-perylenebis(dicarboximide) (2, No. 7)

1.00 g (2.55 mmol) perylenetetracarboxylic-3,4:9,10-bis-anhydride and 1.24 g (6.0 mmol) 3-undecylamine give 0.33 g (18%).—m.p. 249–250°C— R_f (silica gel/CHCl₃)=0.57.—i.r. (KBr): ν =2957 cm⁻¹s, 2926s, 2854m, 1698s, 1658s, 1595s, 1579m, 1508w, 1484w, 1459w, 1435w, 1406m, 1379w, 1339s, 1253m, 1209w, 1175w, 1124w, 1103w, 962w, 852w, 810m, 802w, 792w, 782w, 746m.—u.v.-vis (CHCl₃): λ_{max} (ϵ)=457.5 nm(18790), 488(51100), 525(84450)—u.v.-vis (*n*-heptane): λ_{max} (ϵ)=448 nm(18850), 478(52540), 514(89580)—Fluorescence (CHCl₃): λ_{max} =536 nm, 575—Fluorescence (heptane): λ_{max} =520 nm, 559—¹H-NMR (CDCl₃): δ =0.91(m, 12H), 1.29(m, 24H), 2.10(m, 8H), 5.08(m, 2H), 8.52(q, 8H)—C₄₆H₅₄N₂O₄ (698.9) calcd. C 79.05 H 7.79 N 4.01 found C 78.86 H 7.68 N 3.99.

Measurements

The rate constants of the internal rotation are obtained by NMR line form analysis [4] using a Bruker WP 80 DS spectrometer (20.151 MHz) with an ASPECT 2000 computer. The spectrum parameters are 2.0 s pulse delay, 1.6 s acquisition time, and 3 μ s pulse width corresponding to a flip angle of 30°. The rate constants and line positions obtained are given in Table 1.

RESULTS AND DISCUSSION

The perylene fluorescent dye 1 has bulky *tert*-butyl groups in the *o*-position of the phenyl substituents and

Table 1. Rotational barriers and ^{13}C -NMR chemical shifts in ppm of perylene dyes 2 in CDCl_3

No.	Substituent*	T^\ddagger [$^\circ\text{C}$]	ΔG^\ddagger [$\text{kJ K}^{-1} \text{mol}^{-1}$] (4^\ddagger [s^{-1}])	$\text{C}=\text{O}$ ($b_{1/2}$ [Hz]) \S	C_3	C_2	C_{3a}	C_{1a}	C_{1b}	C_1
1	3-Pentyl-	32	56.76 (1200)	164.1 (3.6)	134.5	131.4	129.6	126.4	123.6	123.0
		-2			134.2	131.6	129.4	126.2	122.9	122.9
		-45	56.80 (0.47)	164.9 163.4 (1.45)	134.13	131.79	129.2	125.9	123.1	122.9
2	4-Heptyl-	32	59.13 (480)	164.1 (6.1)	134.06 134.4	130.95 131.4	129.5	126.4	123.6	122.9
3	5-Nonyl-	32	61.00 (230)	163.9 (10)	134.2	131.0	129.4	126.2	123.5	122.8
4	6-Undecyl-	48	63.28 (340)	164.0 (5.8)	134.5	131.4	129.6	126.5	123.7	122.9
		32	62.78 (110)	164.0 (15)	134.5	131.5	129.6	126.4	123.6	123.0
		-2	62.97 (4.2)	164.6 163.5 (2.6)	134.3	131.82	129.4	126.2	123.6	122.9
		-45	(58.85) \parallel (0.16) \parallel	164.7 163.5 (1.4)	134.21	131.94	129.2	126.0	123.2	122.5
5	7-Tridecyl-	32	63.31 (93)	163.9 (18)	134.2	131.3	129.4	126.2	123.5	122.8
6	3-Heptyl-	32	60.02 (340)	164.0 (4.1)	134.3	131.3	129.5	126.3	123.6	122.0
		-2	60.52 (12)	164.3 163.4 (5.30)	134.2	131.7	129.3	126.1	123.5	122.9
7	3-Nonyl-	32	58.89 (530)	164.1 (4.1)	134.5	131.4	129.6	126.4	123.6	123.0
		-3	61.07 (8.8)	164.7 163.5 (4.1)	134.3	131.82	129.4	126.2	123.6	123.0
		-39	56.21 (1.4) \parallel	164.8 163.5 (1.8)	134.3	131.85	129.2	126.0	123.28	122.6
8	3-Undecyl-	32	59.90 (360)	164.1 (6.6)	134.5	131.04	129.6	126.5	123.6	123.0
		-3	63.00 (3.7)	164.8 163.5 (2.5)	134.4	131.82	129.4	126.3	123.6	123.0

9	Cyclododecyl-	32	¶	164.1	134.5	131.5	126.2	123.8	123.0
10	Cyclotetradecyl-	32	58.99 (510)	164.0 (2.2)	134.4	131.4	129.5	126.4	123.0
		-2	¶	¶	134.9		129.9	126.7	123.5
		-40	¶	165.1 164.5	134.9		130.1	129.6	123.68
11	Cyclopentadecyl-	32	61.80 (170)	163.9 (4.0)	134.4	131.3	129.5	126.4	123.7 123.42 122.9

* Substituent R in 2.

† Temperature.

‡ ^{13}C -NMR spectroscopically determined rate constant for the rotation of the groups R around the R-N bond; natural linewidth: 1.3 Hz.

§ Halfwidth of the lines.

|| Temperature near by coalescence and therefore very broad lines.

¶ Lines with nearly natural linewidth and therefore large uncertainties in the determination ΔG^\ddagger and k .

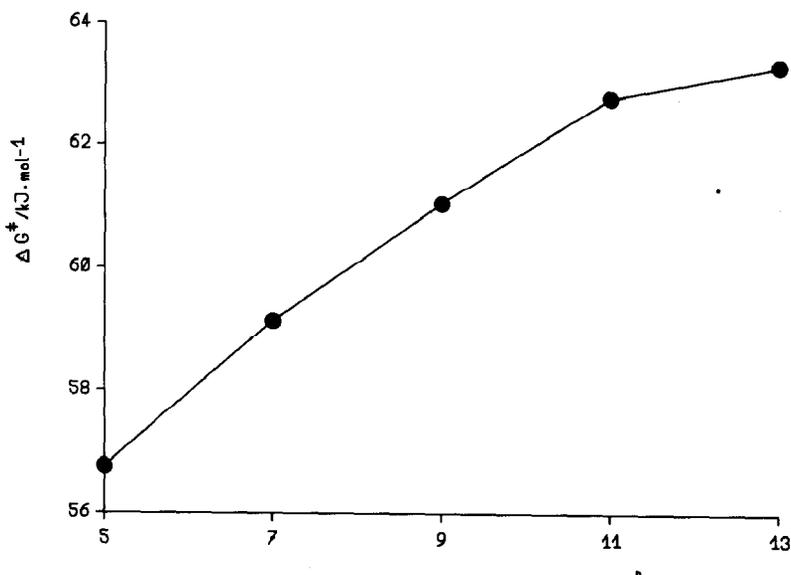


Fig. 1. Rotational barriers of the perylene fluorescent dyes **2** with R = secondary alkyl at 32°C in CDCl₃ solution as a function of the chain length *n*. Substitution in position (*n* + 1)/2.

can be obtained in the two atropisomeric forms **1a** and **1b** [2]. Both isomers are stable at 220°C in quinoline solution for more than 4 h without any interconversion (¹H-NMR detection limit 1%). Therefore, the rotational barrier for the interconversion of the isomers must be more than 180 kJ/mol. In accordance with the rigid structure of dye **1** the fluorescent quantum yield of **1** is about unity in most solvents, e.g. in CHCl₃.

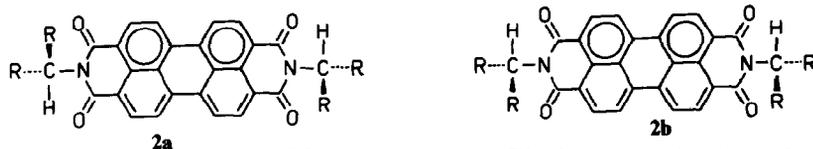
The perylene fluorescent dyes **2** with secondary alkyl substituents are expected to be less rigid than **1**. Indeed, rotational barriers of the alkyl groups can be obtained by ¹³C-NMR spectroscopy. The chemical shifts of the carbonyl C-atoms are markedly dependent on the conformations of the *N*-substituent, but only little on chain length and temperature. Therefore, the carbonyl signals are specially prone for the determination of rotational barriers of the terminal secondary alkyl groups. At low temperature two carbonyl signals with nearly the same intensity are observed

the buttressing effect is less pronounced (Nos. 6–8). In each of these dyes the less bulky ethyl group can move along the oxygens of the perylene chromophore.

These results are confirmed by measurements of rotational barriers of dyes with cycloalkyl groups which can be regarded as secondary alkyl groups with two long chains in which the ends of the chains are tied together. The rotational barriers in the cyclotetradecyl and the cyclopentadecyl derivative (Nos. 9 and 10) are in the same order as in the long chain derivatives.

For the rotation in the 6-undecyl derivative (No. 4) the parameters of the Eyring equation are determined using the rate constants at 48, 32 and –2°C (the rate constant at –45°C has lower accuracy, because nearly natural linewidth is observed). Values of $H^{\ddagger} = 62$ kJ/mol and $S^{\ddagger} = -4$ J K⁻¹ mol⁻¹ are obtained. They are in accordance with a rotation with $G^{\ddagger} = 63$ kJ/mol.

The conformations with lowest energies will probably be **2a** and **2b**, in which the plane formed by the groups R and the C-atom is perpendicular to the plane



at about 163.5 and 164.5 ppm. Higher temperature causes coalescence and at even higher temperatures only one signal at about 164.0 ppm appears.

For the 3-pentyl derivative (No. 1) the rate constant corresponds to a free enthalpy of activation of 57 kJ/mol. With longer alkyl chains the rotational barrier is increased by a buttressing effect up to 63 kJ/mol as shown in Fig. 1. If each of the secondary alkyl groups has one long chain and an ethyl group,

of the aromatic system. This is supported by the rather high difference in chemical shifts of 1 ppm between the ¹³C-carbonyl resonances at low temperature, for in either of the two conformations **2a** and **2b** two of the carbonyl C-atoms are near by the R–C single bonds, whereas the two other ones are near by the hydrogens.

The fluorescent quantum yields of the dyes **2** with R = alkyl are about unity in most solvents though the rotational barrier is rather low. Obviously, the mobility does not lead to a deactivation of the electronically

excited state. HMO-calculations with usual heteroatomic parameters [5] show that the wavefunctions have nodes in the π -orbitals at the nitrogens not only in HOMO and LUMO, but also in the orbital above LUMO and in the orbital below HOMO. These nodes are experimentally supported by the fact that both u.v.-vis absorption and fluorescent spectra are only little influenced by the electronic properties of the substituents at the nitrogens [6]. They might explain that the coupling between the electronic state and the rotation is very weak and so it is not relevant for fluorescent deactivation.

Acknowledgement—This work was supported by Stiftung Volkswagenwerk and Fonds der Chemischen Industrie.

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