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Synthesis and Properties of Fluorescent Bis-Quaternized Perylene Dyes

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ABSTRACT

A series of perylene dyes containing aliphatic trialkylamino and quaternary ammonium groups has been prepared. Perylene dyes containing trialkylamino groups were virtually nonfluorescent Quaternization of the trialkylamino groups with alkyl iodide resulted in an increase in the fluorescence ($Q_f = 0{\cdot}8$–$0{\cdot}9$)*; the same phenomenon was observed by protonation of the trialkylamino groups in acid media.*

1 INTRODUCTION

In recent years there has been considerable interest in perylene dyes, in view of their high photostability and high fluorescence quantum yield. Perylene dyes are also well established as very stable organic pigments,[1] and have more recently received attention in the context of 'hi-tech' applications. The application of perylene dyes in fluorescent solar collec-

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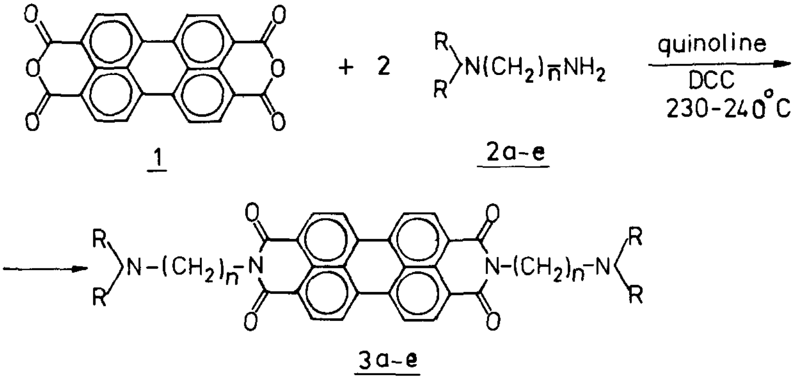
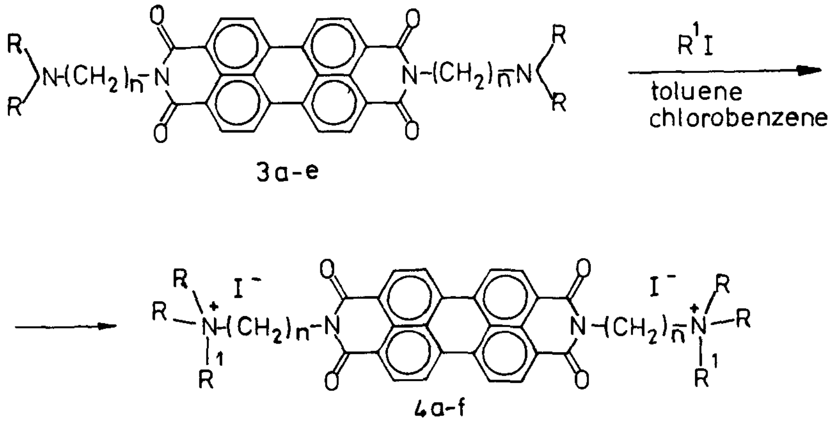


DCC=1,3-dicyclohexylcarbodiimide ; n=2,3 ; R=CH_3, C_2H_5 or RR=C_2H_4O C_2H_4 ;

Scheme 1

tors[2,3] is illustrative of this and their use as laser dyes has also been described.[4,5] High sensitivity analytical,[6] as well as a fluorescent application[7] have also been reported, as has their use in Xerographic processes of these dyes as organic photoconductive materials.[8]

The properties of perylene dyes containing aliphatic trialkylamino groups and quaternary ammonium salts have not been previously reported and this present paper deals with the synthesis and properties of N,N'-bis(2-N,N-dialkylaminoethyl)-3,4,9,10-perylenebis(dicarboximides), N,N'-bis(3-N,N-dialkylaminopropyl)-3,4,9,10-perylenebis(dicarboximides) and their quaternary salts.



R=CH_3; C_2H_5 or RR= C_2H_4O C_2H_4 ; n= 2,3 ; R^1=CH_3 , C_2H_5 .

Scheme 2

2 RESULTS AND DISCUSSION

The perylene dyes were prepared using the method of Rademacher *et al.*[9] by reaction of perylenetetracarboxylic-3,4,9,10-bisanhydride (**1**) and the corresponding 2-N,N-dialkylaminoethylenediamine or 3-N,N'-dialkylaminopropylenediamine (**2a–e**) in quinoline as solvent in the presence of dicyclohexylcarbodiimide at 230–240°C (Scheme 1). Dyes **3a–e** were thus obtained and these were then quaternized with methyl or ethyl iodide in toluene or chlorobenzene to give the quaternary ammonium derivatives (**4a–f**) (Scheme 2).

Data for dyes **3a–e** and **4a–f** are given in Table 1; some quaternized dyes contained water of crystallization. All the perylene dyes are also very thermostable.

TABLE 1

Substituents, Melting point, Yield and Elemental Analysis for Dyes **3a–e** and **4a–f**

Dye	*R*	*R*	*R¹*	*n*	*Melting point (°C)*	*Yield (%)*	*Molecular formulae*	*Analysis (%) found/calculated*		
								C	*H*	*N*
3a	CH_3	CH_3	—	2	>350	92	$C_{32}H_{28}N_4O_4$	72·5	5·7	—
								72·2	5·3	
3b	CH_3	CH_3	—	3	>350	94	$C_{34}H_{32}N_4O_4$	72·9	6·0	—
								72·8	5·7	
3c	C_2H_5	C_2H_5	—	2	>350	97	$C_{36}H_{36}N_4O_4$	73·4	6·1	—
								73·5	6·2	
3d	C_2H_5	C_2H_5	—	3	>350	92	$C_{38}H_{40}N_4O_4$	73·8	6·8	—
								74·0	6·5	
3e	C_2H_4O	C_2H_4	—	3	>350	97	$C_{38}H_{36}N_4O_4$	71·5	5·6	—
								70·8	5·6	
4a	CH_3	CH_3	CH_3	2	>350	90	$C_{34}H_{34}N_4O_4I_2 . 3H_2O$	47·1	4·1	6·0
							46·9	46·9	4·6	6·4
4b	CH_3	CH_3	CH_3	3	>350	91	$C_{36}H_{38}N_4O_4I_2 . 5H_2O$	46·2	4·8	5·7
								46 2	5·2	6·0
4c	CH_3	CH_3	C_2H_5	3	>350	93	$C_{38}H_{42}N_4O_4I_2 . 2H_2O$	50·3	4·8	5·4
								50·2	4·8	6·1
4d	C_2H_5	C_2H_5	C_2H_5	2	>350	93	$C_{40}H_{46}N_4O_4I_2 . 7H_2O$	46·7	6·4	5·0
								46·8	5·9	5 4
4e	C_2H_5	C_2H_5	CH_3	3	>350	91	$C_{40}H_{46}N_4O_4I_2 . 2H_2O$	51·4	5·4	5·1
								51 3	5·3	5·6
4f	C_2H_4O	C_2H_4	CH_3	3	>350	91	$C_{40}H_{42}N_4O_4I_2 . H_2O$	50·6	5·2	5·5
								50·7	4 7	5·9

3a–e were recrystallized from quinoline; **4a–f** were recrystallized from acetic acid : water 95 : 5.

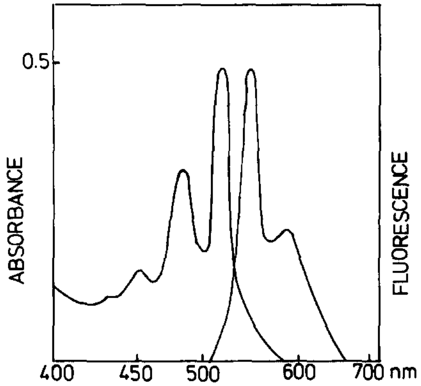


Fig. 1. The absorption and fluorescence spectra of dye in **4e** in acetonitrile at 293 K.

The absorption and fluorescence spectra of compound **4e** in acetonitrile at 293 K are shown in Fig. 1. The fluorescence spectrum is given in arbitrary units. The absorption and fluorescence spectra of all the compounds studied (Table 2) are similar both in the shape of the curves and of the absorption maxima to those of compound **4e**.

The absorption spectra of the perylene dyes studied showed three bands of high intensity, with a well defined vibrational structure in the region 440–520 nm (Fig. 1, Table 2). The molar absorptivities of the longest wavelength absorption maximum in acetonitrile and in chloroform were between 70 000 and 80 000 mol^{-1} cm^{-1}. The presence of alkyl substituents on the N-atoms of the amino group as well as quaternization of the N-atoms, did not significantly influence the absorption maxima. Increase in the polarity of the solvent (acetonitrile–DMSO) gave a slight bathochromic shift of the bands, by about 10–20 nm (Table 2).

The compounds studied fluoresced in solution at room temperature in the 520–580 nm region. Their fluorescence spectra also showed a well defined vibrational structure (Fig. 1, Table 2). There was a significant difference between the fluoresence quantum yields of the quaternized and nonquaternized compounds in acetonitrile (see Table 2). The quaternized perylene derivatives have Q_f = 0·8–0·9, while for the nonquaternized derivatives, Q_f was 0·001, with the exception of compound **3e**, for which Q_f in acetonitrile was 0·06.

Most probably the reason for the low fluorescence quantum yield of the nonquaternized compounds is rotation around the C–N bond between the dialkylamino and the methylene group, leading to an enhanced non-radiative deactivation of their excited $S_1(\pi - \pi^*)$ states. The possibility for such rotation in perylene dyes has been discussed by Langhals *et al.*,[10]

TABLE 2

Experimental Spectral Characteristics of the Perylene Dyes **3a–e**, **4a-f**; λ_{abs}, λ_{fl}-Absorption and Fluorescence Maximum; Q_f-Fluorescence Quantum Yields; (—) No Measurement

Dye	Acetonitrile			Acetonitrile + $HClO_4$			DMSO	
	λ_{abs} *nm*	λ_{fl} *nm*	Q_f	λ_{abs} *nm*	λ_{fl} *nm*	Q_f	λ_{abs} *nm*	λ_{fl} *nm*
3a	452, 472, 515	526, 562	0·001	454, 478, 515	530, 570	0·86	455, 491, 529	530, 570
3b	451, 472, 510	530, 570	0·001	456, 480, 520	535, 575	0·79	455, 491, 528	540, 580
3c	451, 471, 511	525, 565	0·001	455, 485, 522	535, 570	0·80	460, 487, 527	540, 580
3d	452, 480, 513	520, 560	0·001	455, 483, 518	535, 575	0·81	460, 484, 522	540, 580
3e	455, 475, 510	530, 570	0·06	455, 478, 518	536, 580	0·84	455, 487, 520	540, 580
4a	453, 473, 520	530, 570	0·84	—	—	—	460, 488, 529	545, 585
4b	452, 480, 520	530, 570	0·88	—	—	—	455, 483, 520	540, 580
4c	447, 476, 514	530, 570	0·80	—	—	—	455, 488, 520	540, 580
4d	452, 473, 519	540, 570	0·76	—	—	—	460, 492, 529	545, 585
4e	451, 483, 518	530, 570	0·84	—	—	—	455, 488, 526	545, 585
4f	448, 477, 514	530, 570	0·86	—	—	—	455, 487, 521	540, 580

who showed that in N,N'-disubstituted perylenes with branched alkyl (pentyl-undecyl) or cycloalkyl groups, the rotation barrier is in the range of 57–65 kJ mol^{-1} and increases with the length of the alkyl chain. Although the rotational barrier is rather low, it does not lead to a radiationless deactivation of the electronically excited state, and the fluorescence quantum yield of these compounds is close to 1.

The perylene dyes investigated here have shorter and nonbranched amino alkyl chains as substituents (Scheme 1), which favours rotation around the C–N bond and the radiationless deactivation of the excited $S_1(\pi - \pi^*)$ states of the molecules. This is, most probably, the reason for the extremely low fluorescence quantum yield (of about 0·001) of the nonquaternized compounds **3a–3d** (Table 2). The Q_f value of compound **3e** is much higher (0·06), and we conclude that this is due to the cycloalkylamino character of the substituent, which hinders rotation around the C–N bond. This assumption for the nonradiative deactivation due to rotation around the C–N bond is supported by the considerable enhancement of the fluorescence quantum yield of the compounds which occurs on their protonation (see Table 2). In this case, rotation around the C–N bond is almost impossible and the fluorescence quantum yield becomes 0·8–0·9 (Table 2) (viz. approximately 1000 times higher than that of the nonquaternized and nonprotonated dyes). Further investigations are needed to confirm this assumption, and the result of these will be reported later.

3 EXPERIMENTAL

3.1 General

Melting points were determined on a Koffler apparatus. The absorption spectra were taken on a Specord M 40 (Carl Zeiss, Jena) spectrophotometer. The fluorescence spectra were recorded on a Perkin Elmer MPF 44 spectrofluorimeter. The fluorescence quantum yield (Q_f) was determined relative to 3-aminophthalamide (Q_f = 0·6 in ethanol[11]). The solvents used were of spectral grade.

3.2 General procedure for preparation of perylene dyes 3a–e

Perylenetetracarboxylic-3,4,9,10-bisanhydride (2g) (5 mm), quinoline 15 ml, and the appropriate diamine 20 mmol and dicyclohexylcarbodiimide 0·7 g (3·4 mmol) were refluxed with stirring in an inert atmosphere at 230–240°C for 3–4 h. After cooling to room temperature, the reaction mixture was poured into 200 m ethanol and the precipitate filtered and dried.

3.3 General procedure for preparation of quaternized perylene dyes 4a–f

The appropriate perylene dye (**3a–e**) 2·5 mmol, toluene (80 ml) (or chlorobenzene) and methyl or ethyl iodide (10 mmol) were refluxed with stirring for 90 min. After cooling to room temperature, the precipitate was filtered, washed with ether and dried.

Data pertaining to m.p., yield and elemental analysis for dyes **3a–e** and **4a–f** are shown in Table 1.

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