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Synthesis and Properties of *N,N'*-Unsymmetrical Dialkyl-3,4:9,10-Perylenebis(dicarboximide)s

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SUMMARY

N,N'-*Unsymmetrical dialkyl-3,4:9,10-perylenebis(dicarboximide)s (in which alkyl = methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl and octyl) were prepared by the condensation of* N-*alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide with the appropriate alkylamines. The properties of these derivatives as pigments were tested and their thermal stability measured.*

1. INTRODUCTION

Symmetrical 3,4:9,10-perylenebis(dicarboximide)s (**2** and **3**) are readily prepared from 3,4:9,10-perylenetetracarboxylic dianhydride (**1**), and some of them are used as dyes or pigments. Recently there have been reported several studies on their application as organic conductors or photoconductors in electroreprography[1–4] in addition to their utilization for the colouration of plastics.

Previous studies[5–7] have described the preparation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**4**) and of *N*-alkyl-*N'*-aryl-3,4:9,10-perylenebis(dicarboximide)s, and both the properties of these derivatives as pigments and also their thermal decomposition characteristics have been investigated. Recently, the

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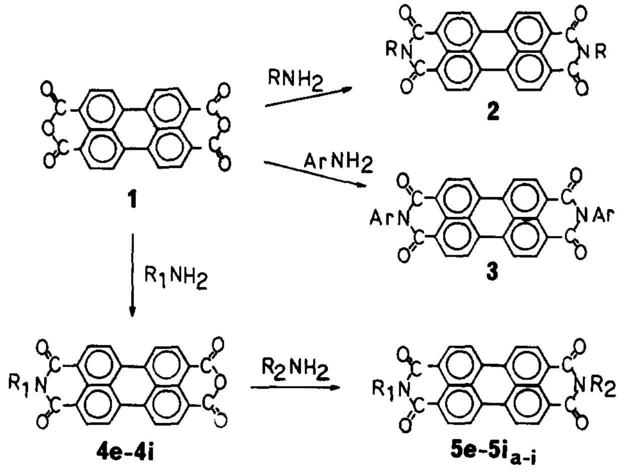

Compound	*R_1 or R_2*
a	H
b	CH_3
c	CH_2CH_3
d	$(CH_2)_2CH_3$
e	$(CH_2)_3CH_3$
f	$CH_2CH(CH_3)_2$
g	$(CH_2)_4CH_3$
h	$(CH_2)_5CH_3$
i	$(CH_2)_7CH_3$

Scheme 1

synthesis in high yield of some *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides has been reported.[8]

In this present paper the preparation of *N*,*N'*-unsymmetrical dialkyl-3,4:9,10-perylenebis(dicarboximide)s in which the alkyl groups are methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl and octyl (**5e–5i$_{a-i}$**) Scheme 1,† by the condensation of alkylamines R_2NH_2 with the *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides (**4e–4i**), is described. The properties of these derivatives as pigments have been evaluated and their thermal decomposition measured.

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† *Editors note:* See ref. 7 for format previously used in numbering, with subscripts.

2. RESULTS AND DISCUSSION

2.1. Preparation of 3,4:9,10-perylenebis(dicarboximide) (5e–5i$_{a-i}$)

The *N*,*N*′-unsymmetrical dialkyl substituted 3,4:9,10-perylenebis-(dicarboximide)s (**5e–5i$_{a-i}$**) prepared by the condensation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides (**4e–4i**) with alkylamines (R_2NH_2) are listed in Table 1. Their structures were confirmed by elemental analysis, absorption spectra, and IR or MS spectra. Relevant data are given in Table 2. In many cases the reaction of **4e–4i** with alkylamines gave higher yield of imides **5** than reaction with ammonia, presumably because of their high basicity.

In the visible spectra recorded in 95 % conc. sulphuric acid solution, the bis-imides containing one alkyl residue (**5e–5i$_a$**) absorbed at slightly lower wavelength (λ_{max}596–597 nm) than the bis-alkylimides (**5e–5i$_{b-i}$**), which had λ_{max} in the range 597–600 nm. Infrared spectra of the compounds showed $\nu_{c=0}$ at 1684–1695 cm^{-1} and 1645–1654 cm^{-1} and no discernible differences in the position of $\nu_{c=0}$ due to changes in the alkyl group were observed. Mass spectra showed the appropriate molecular ion peak for all the pigments synthesized.

2.2. Properties of 3,4:9,10-perylenebis(dicarboximide) derivatives

The properties of 3,4:9,10-perylenebis(dicarboximide) derivatives as pigments were tested by methods similar to those previously described.[7] Figure 1 shows a typical spectral reflectance curve. All compounds showed great reflectance in the long wavelength region indicative of

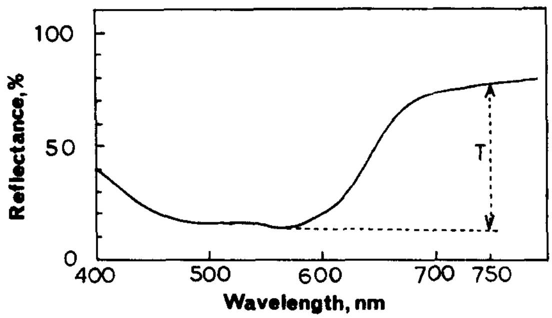

Fig. 1. Spectral reflectance curve of *N*-hexyl-*N*′-propyl-3,4:9,10-perylenebis(dicarboximide) (**5h$_a$**).

TABLE 1
Reaction Conditions for the Preparation of 3,4:9,10-Perylenebis(dicarboximide)s

Starting compound R_1	*Amine* R_2	*Product*	*Yield* (%)
4e $(CH_2)_3CH_3$	H	**5e**$_a$	56
	CH_3	**5e**$_b$	90
	CH_2CH_3	**5e**$_c$	98
	$(CH_2)_2CH_3$	**5e**$_d$	89
4f $CH_2CH(CH_3)_2$	H	**5f**$_a$	80
	CH_3	**5f**$_b$	95
	CH_2CH_3	**5f**$_c$	89
	$(CH_2)_2CH_3$	**5f**$_d$	89
	$(CH_2)_3CH_3$	**5f**$_e$	85
4g $(CH_2)_4CH_3$	H	**5g**$_a$	76
	CH_3	**5g**$_b$	52
	CH_2CH_3	**5g**$_c$	41
	$(CH_2)_2CH_3$	**5g**$_d$	64
	$(CH_2)_3CH_3$	**5g**$_e$	99
	$CH_2CH(CH_3)_2$	**5g**$_f$	84
4h $(CH_2)_5CH_3$	H	**5h**$_a$	70
	CH_3	**5h**$_b$	90
	CH_2CH_3	**5h**$_c$	76
	$(CH_2)_2CH_3$	**5h**$_d$	84
	$(CH_2)_3CH_3$	**5h**$_e$	82
	$CH_2CH(CH_3)_2$	**5h**$_f$	74
	$(CH_2)_4CH_3$	**5h**$_g$	70
	$(CH_2)_7CH_3$	**5h**$_i$	54
4i $(CH_2)_7CH_3$	H	**5i**$_a$	70
	CH_3	**5i**$_b$	82
	CH_2CH_3	**5i**$_c$	90
	$(CH_2)_2CH_3$	**5i**$_d$	91
	$(CH_2)_3CH_3$	**5i**$_e$	80
	$CH_2CH(CH_3)_2$	**5i**$_f$	87
	$(CH_2)_4CH_3$	**5i**$_g$	92

Reaction mixture contained 1·0 g **4**; mole ratio amine: **4** was 20:1; vol. H_2O 25 ml; temp. 200 °C; time 10 h.

TABLE 2—*contd.*

Compound		*Analysis (%) found (calculated)*			$\lambda_{max}^{H_2SO_4}$ (*nm*)	*IR (KBr)* $\nu_{C=O}$ (*cm*$^{-1}$) *Imide*		*MS (m/e)* (M^+)
R_1	R_2	*C*	*H*	*N*				
5i$_{a-g}$ $(CH_2)_7CH_3$	H	75·54 (76·48	5·13 5·21	5·30 5·57)	597	1 685	1 648	502
	CH_3	77·00 (76·73	5·53 5·46	5·25 5·42)	598	1 685	1 649	516
	CH_2CH_3	77·75 (76·96	5·81 5·70	5·18 5·28)	598	1 690	1 647	530
	$(CH_2)_2CH_3$	77·20 (77·19	6·00 5·92	4·90 5·14)	599	1 690	1 647	544
	$(CH_2)_3CH_3$	76·63 (77·39	6·01 6·13	5·02 5·01)	599	1 690	1 650	558
	$(CH_2CH(CH_3)_2$	78·09 (77·39	6·20 6·13	5·38 5·01)	599	1 691	1 650	558
	$(CH_2)_4CH_3$	77·29 (77·60	6·28 6·34	4·82 4·89)	599	1 689	1 652	572

a reddish colour. *T* values (reflectance maximum – minimum) were calculated from reflectance curves. The differences of the *T* values of the compounds were found to be in agreement with the observed tinting strength and *T* values can therefore be used as a convenient parameter for the evaluation of tinting strength. The lightfastness of the compounds was determined by light exposure in a fade meter.

The colour, tinting strength (expressed as *T* %) and lightfastness values obtained are shown in Table 3 for the unsymmetrical perylenebis-(dicarboximide)s (**5e–5i$_{a-i}$**) and Table 4 for the symmetrical compounds (**2**). These compounds gave a variety of reddish hues and the nature of the alkyl groups (R_1 or R_2) thus affects the colour of these compounds to a noticeable degree. The unsubstituted and the methyl substituted unsymmetrical compounds (**5e–5i$_{a-b}$**) ($R_2 = H$ and CH_3) (Table 3) gave higher tinting strengths than the analogous unsubstituted and methyl substituted symmetrical compounds (**2**) ($R = H$ and CH_3) (Table 4). The lightfastness of both the unsymmetrical compounds and the symmetrical compounds was excellent.

The initial temperatures of thermal decomposition of the pigments are shown in Table 3 for **5e–5i$_{a-i}$** and the values obtained were in a range between those of the higher alkyl and the lower alkyl symmetrically substituted compounds (**2**).[7]

TABLE 3
Properties of 3,4:9,10-Perylenebis(dicarboximide)s

Compound		*Colour*	*Tinting strength, T(%)*	*Lightfastness (Blue Scale)*	*Thermal decomposition temp. (°C)*
R_1	*R_2*				
$5e_{a\text{–}d}$ $(CH_2)_3CH_3$	H	Reddish violet	54	8	360
	CH_3	Reddish brown	64	8	360
	CH_2CH_3	Reddish brown	65	8	365
	$(CH_2)_2CH_3$	Reddish violet	64	8	342
$5f_{a\text{–}e}$ $CH_2CH(CH_3)_2$	H	Reddish violet	59	8	338
	CH_3	Reddish brown	56	8	355
	CH_2CH_3	Dark violet	59	8	350
	$(CH_2)_2CH_3$	Dark violet	68	8	317
	$(CH_2)_3CH_3$	Dark violet	65	8	346
$5g_{a\text{–}f}$ $(CH_2)_4CH_3$	H	Dark violet	49	8	320
	CH_3	Reddish brown	58	8	300
	CH_2CH_3	Dark violet	54	8	286
	$(CH_2)_2CH_3$	Dark violet	50	8	300
	$(CH_2)_3CH_3$	Reddish violet	60	8	335
	$CH_2CH(CH_3)_2$	Reddish violet	66	8	310
$5h_{a\text{–}g}$, 5i $(CH_2)_5CH_3$	H	Dark violet	68	8	353
	CH_3	Reddish brown	72	8	325
	CH_2CH_3	Reddish violet	77	8	350
	$(CH_2)_2CH_3$	Reddish violet	63	8	340
	$(CH_2)_3CH_3$	Reddish violet	59	8	330
	$CH_2CH(CH_3)_2$	Reddish brown	63	8	290
	$(CH_2)_4CH_3$	Reddish violet	62	8	315
	$(CH_2)_7CH_3$	Reddish violet	62	8	320
$5i_{a\text{–}g}$ $(CH_2)_7CH_3$	H	Dark violet	70	8	340
	CH_3	Reddish violet	65	8	340
	CH_2CH_3	Reddish violet	61	8	360
	$(CH_2)_2CH_3$	Reddish violet	64	8	375
	$(CH_2)_3CH_3$	Reddish violet	64	8	340
	$CH_2CH(CH_3)_2$	Reddish brown	69	8	305
	$(CH_2)_4CH_3$	Reddish violet	55	8	330

3. EXPERIMENTAL

3.1. Materials and measurements

Compounds **2** and **4e–4i** were prepared by the methods previously described.[5,6]

Mass spectra were recorded on a Hitachi RMU-7M mass spectrometer. Visible spectra were recorded on a Hitachi 124 spectrometer from

TABLE 4
Properties of Symmetrical 3,4:9,10-Perylenebis(dicarboximide)s

Compound **2** *R*	*Colour*	*Tinting strength,* *T(%)*	*Lightfastness* *(Blue Scale)*
H	Dark violet	44	8
CH_3	Reddish brown	49	8
CH_2CH_3	Reddish brown	70	8
$(CH_2)_2CH_3$	Dark violet	65	8
$(CH_2)CH_3$	Dark violet	55	8
$CH_2CH(CH_3)_2$	Reddish brown	73	8
$(CH_2)_4CH_3$	Reddish brown	65	8
$(CH_2)_5CH_3$	Reddish violet	63	8
$(CH_2)_7CH_3$	Reddish violet	54	8

solutions in conc. sulphuric acid, and IR spectra on a Nippon Bunko IR-E spectrometer. All samples for analysis were obtained by sublimation at 300–350 °C/3–5 mmHg. Thermal decomposition was measured with a Shinku-Riko TGD-300RH Differential Thermal Micro Balance at a heating rate of 10 °C/min in air. Pigment tests were carried out by the methods previously described.[7]

3.2. Preparation of 5e–5i$_{a\text{–}i}$

A mixture of one of the monoanhydride monoimides **4e–4i** (1·0 g), a 20 mole ratio of the appropriate alkylamine and 25 ml of water was heated in an autoclave at 200 °C for 10 h with stirring. Hydrochloric acid was added to the cooled reaction mixture, which was then filtered and the product washed with water. The residue was stirred in hot 1 % potassium hydroxide solution and filtered to remove unreacted **4**. The precipitate was added to water, the mixture acidified with dilute hydrochloric acid and then filtered and the product washed with water and methanol and dried to give the appropriate **5e–5i**$_{a\text{–}i}$.

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