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Synthesis and Properties of *N*-Alkyl-*N'*-aryl-3,4:9,10-Perylenebis(dicarboximide)

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SUMMARY

N'-Alkyl-N'-aryl-3,4.9,10-perylenebis(dicarboximide) (alkyl = isobutyl, pentyl, hexyl, octyl, etc., aryl = phenyl, p-tolyl, p-methoxyphenyl, etc.) were prepared by the condensation of N-alkyl-3,4 9,10-perylene-tetracarboxylic monoanhydride monoimide with arylamines (aniline, p-toluidine, p-anisidine, o-phenylenediamine, etc.). The properties of these derivatives as pigments were tested, and also the thermal stability of 3,4 9,10-perylenebis(dicarboximide) derivatives was measured

1. INTRODUCTION

In general symmetrical 3,4:9,10-perylenebis(dicarboximide)s (**2** and **3**) have excellent resistance to light, heat, and solvents. Some of them are used as dyes or pigments. Recently there have been reported several studies of their application as organic photoconductors in electro-reprography[1–4] and for colouring plastics[5–8]. One characteristic of these compounds is said to be their excellent heat resistance, but detailed measurements have not been previously reported.

Earlier papers[9,10] describe the preparation of *N*-alkyl-*N'*-aryl-3,4.9,10-perylenebis(dicarboximide) (alkyl = H, methyl, ethyl, propyl, and butyl) (**5–9**$_{(a-e)}$ and **10**$_{a,b}$) by the condensation of *N*-alkyl-3,4:9,10-perylene-tetracarboxylic monoanhydride monoimide (**4**$_{a-e}$) with aromatic amines. In this paper the preparation of similar derivatives with alkyl = isobutyl,

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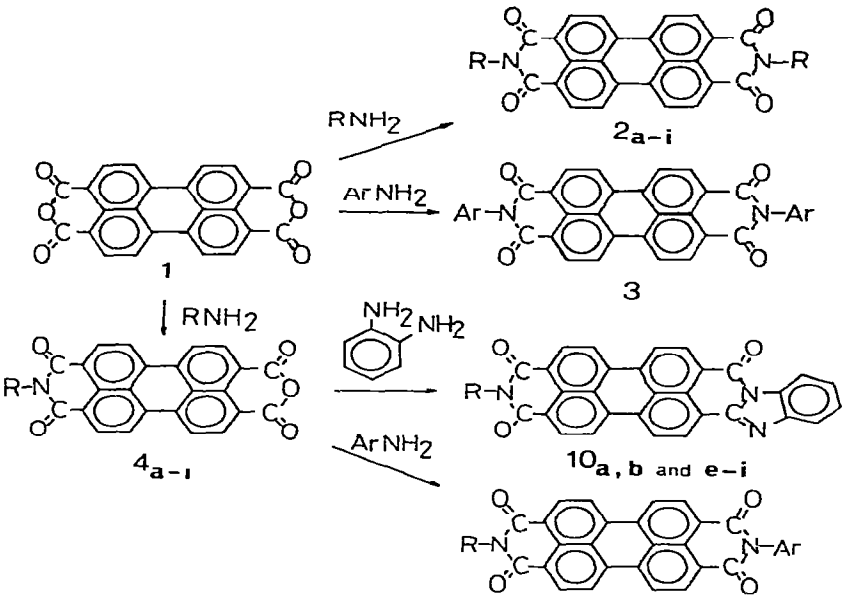
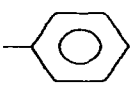
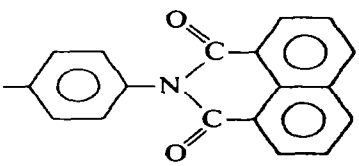
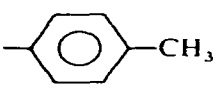
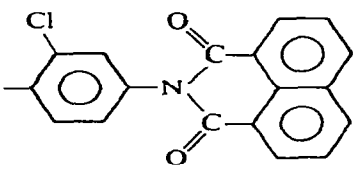
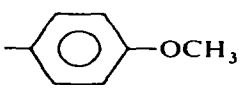
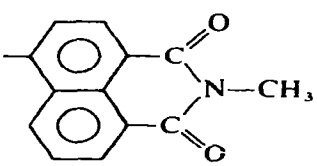
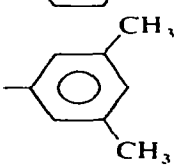
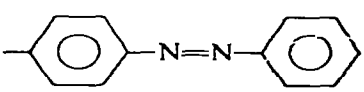


Compd	*B*	*Compd*	*B*
a	H	**f**	$CH_2CH(CH_3)_2$
b	CH_3	**g**	$(CH_2)_4CH_3$
c	CH_2CH_3	**h**	$(CH_2)_5CH_3$
d	$(CH_2)_2CH_3$	**i**	$(CH_2)_7CH_3$
e	$(CH_2)_3CH_3$		

Compd	*Ar*	*Compd*	*Ar*
5_{a-i}		$11_{b,i}$	
6_{a-i}		$12_{b,i}$	
7_{a-i}		$13_{b,i}$	
$8_{a-e,h,i}$			
9_{a-i}			

pentyl, hexyl, octyl, etc. (**5–7**$_{(f-i)}$, **8**$_{h,i}$, **9**$_{f-i}$, **10**$_{e-i}$, and **11–13**$_{(h,i)}$), is described. An extended series of aromatic amines has been used in condensation reactions. The properties of the derivatives as pigments have been tested, and also the thermal stability of 3.4:9,10-perylenebis (dicarboximide) derivatives (**2**, **3**, and **5–13**) has been examined to determine the effects of *N*-substituents on the heat resistance

2. RESULTS AND DISCUSSION

2.1. Preparation of **5–7**$_{(f-i)}$, **8**$_{h,i}$, **9**$_{f-i}$, **10**$_{e-i}$, and **11–13**$_{(h,i)}$

The *N*-alkyl-*N'*-aryl-3,4:9,10-perylenebis(dicarboximide)s (**5–7**$_{(f-i)}$, **8**$_{h,i}$, **9**$_{f,i}$, **10**$_{e,i}$, and **11–13**$_{(h,i)}$) prepared by the condensation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**4**$_{e-i}$) with arylamines are listed in Table 1 Their structures were confirmed by elemental analysis, absorption spectra, and IR or MS spectra. These data are given in Table 2. Among these compounds, **5–7**$_{(f-i)}$ and **10**$_{e-i}$ were prepared in good yield (87–99%). The reaction with *p*-toluidine and *p*-anisidine gave good yields even at lower temperatures, but a higher temperature was necessary for the reaction with *o*-phenylenediamine because it included a cyclization step, as Maki and Hashimoto[11] reported with respect to the reaction of 3.4 9,10-perylenetetracarboxylic dianhydride (**1**) with *o*-phenylenediamine. The reactivities of the arylamines were in agreement with previous results [10]

In the visible spectra in 95% conc sulphuric acid solution λ_{max} was 600–601 nm for **5–9**, 620–622 nm for **10**, and 595–600 nm for **11–13**. No difference in λ_{max} due to the alkyl group was found. The long λ_{max} of **10** was due to its benzimidazole residue All the IR spectra indicate $\nu_{C=O}$ of imide: 1690–1698 and 1650–1657 cm^{-1} for **5–9**, 1685–1687 and 1650–1651 cm^{-1} for **10**, and 1680–1688 and 1637–1644 for **11–13** No differences in $\nu_{C=O}$ due to alkyl group were found, but again **10** displayed a different value due to its benzimidazole residue. Mass spectra for **5–8** and **10**$_{e-h}$ show the corresponding molecular ion peak. But mass spectra for **9**$_{f-i}$, **10**$_{i}$, and **11–13** were not obtained because of their low volatility.

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

The properties of **5–7**$_{(f-i)}$, **8**$_{h,i}$, **9**$_{f-i}$, **10**$_{e-i}$ and **11–13**$_{(h,i)}$ as pigments were tested by methods similar to those previously described [10] Figure 1 shows

TABLE 1
Reaction Conditions for the Preparation of 3,4 9,10-Perylenebis(dicarboximide)s (**5–13**)

Starting compound	*Wt* (*g*)	*Arylamine*	*Wt* (*g*)	*Temp.* (°*C*)	*Time* (*h*)	*Product*	*Yield* (%)
4$_f$	1 0	Aniline	30	183	7	**5**$_f$	95
		p-Toluidine	30	125	7	**6**$_f$	96
		p-Anisidine	30	185	7	**7**$_f$	97
		p-Aminoazobenzene	5 0[a]	235	10	**9**$_f$	73
4$_g$	1 0	Aniline	30	183	7	**5**$_g$	99
		p-Toluidine	30	125	7	**6**$_g$	96
		p-Anisidine	30	185	7	**7**$_g$	96
		p-Aminoazobenzene	5 0[a]	235	8	**9**$_g$	75
4$_h$	1 0	Aniline	30	183	7	**5**$_h$	87
		p-Toluidine	25	105	11	**6**$_h$	97
		p-Anisidine	30	125	7	**7**$_h$	99
		3,5-Xylidine	2 0[a]	233	7	**8**$_h$	91
		p-Aminoazobenzene	5 0[a]	233	6	**9**$_h$	86
		N-(4-Aminophenyl)-1,8-naphthalenedicarboximide	2 0[a]	233	12	**11**$_h$	83
		N-(4-Amino-3-chlorophenyl)-1,8-naphthalenedicarboximide	2 0[a]	233	12	**12**$_h$	58
		N-Methyl-4-amino-1,8-naphthalenedicarboximide	2 0[a]	233	12	**13**$_h$	79
4$_i$	1 0	Aniline	30	183	7	**5**$_i$	96
		p-Toluidine	30	185	7	**6**$_i$	94
		p-Anisidine	30	125	7	**7**$_i$	92
		3,5-Xylidine	5 0[a]	233	7	**8**$_i$	88
		p-Aminoazobenzene	5 0[a]	233	7	**9**$_i$	93
		N-(4-Aminophenyl)-1,8-naphthalenedicarboximide	2 0[a]	233	12	**11**$_i$	43
		N-(4-Amino-3-chlorophenyl)-1,8-naphthalenedicarboximide	2 0[a]	233	12	**12**$_i$	66
		N-Methyl-4-amino-1 8-naphthalenedicarboximide	2 0[a]	233	12	**13**$_i$	42
4$_e$	2 0	*o*-Phenylenediamine	8 0	250	8	**10**$_e$	91
4$_f$	3 0	*o*-Phenylenediamine	12	250	8	**10**$_f$	94
4$_g$	3 0	*o*-Phenylenediamine	12	250	8	**10**$_g$	93
4$_h$	1 0	*o*-Phenylenediamine	4 0	250	8	**10**$_h$	90
4$_i$	1 0	*o*-Phenylenediamine	4 0	250	8	**10**$_i$	91

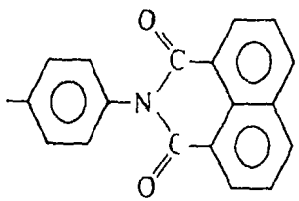
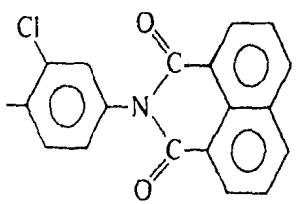
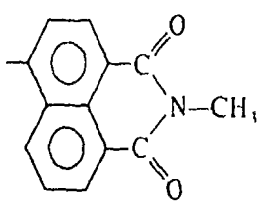
[a] Added with 50 ml of quinoline

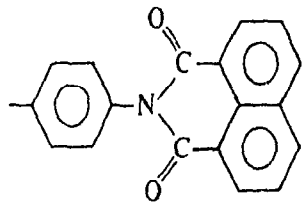
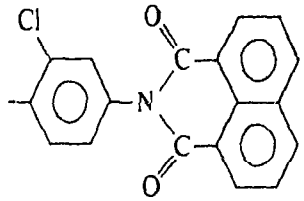
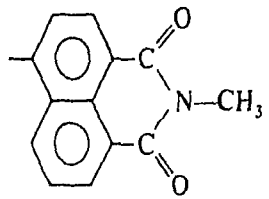
TABLE 2
Analytical and Spectral Data for 3,4·9,10-Perylenebis(dicarboximide)s (**5–13**)

Compound	*R*	*Ar*	*Analysis (%) Found (Calculated)* C H N	H_2SO λ_{max} (*nm*)	*IR(KBr)* $\nu_{C=O}$ (cm^{-1}) *Imide*	*MS(m/e)* (M^+)
5_f	$CH_2CH(CH_3)_2$	Phenyl	78 53 4 06 5 47 (78 15 4 24 5 36)	600	1 697 1 657	522
6_f	$CH_2CH(CH_3)_2$	*p*-Tolyl	78 82 4 33 5 15 (78 34 4 51 5 22)	601	1 695 1 654	536
7_f	$CH_2CH(CH_3)_2$	*p*-Methoxyphenyl	76 10 4 18 5 08 (76 08 4 38 5 07)	601	1 697 1 655	552
9_f	$CH_2CH(CH_3)_2$	*p*-Phenylazophenyl	76 02 4 09 10 37 (76 67 4 18 8 94)	601	1 690 1 652	—
5_g	$(CH_2)_4CH_3$	Phenyl	78 25 4 36 5 28 (78 38 4 51 5 22)	600	1 698 1 654	536
6_g	$(CH_2)_4CH_3$	*p*-Tolyl	78 53 4 57 5 37 (78 53 4 76 5 91)	601	1 698 1 652	550
7_g	$(CH_2)_4CH_3$	*p*-Methoxyphenyl	76 22 4 42 5 05 (76 31 4 62 4 94)	601	1 697 1 655	560
9_g	$(CH_2)_4CH_3$	*p*-Phenylazophenyl	76 50 4·49 9 13 (76 86 4 40 8 74)	601	1 690 1 652	—
5_h	$(CH_2)_5CH_3$	Phenyl	78 20 4 69 5 18 (78 53 4·76 5 09)	600	1 690 1 651	550
6_h	$(CH_2)_5CH_3$	*p*-Tolyl	78 72 4 73 5 06 (78 71 5 00 4 95)	601	1 697 1 652	564
7_h	$(CH_2)_5CH_3$	*p*-Methoxyphenyl	76 74 4 25 5 02 (76·54 4·86 4 82)	601	1 697 1 652	580
8_h	$(CH_2)_5CH_3$	3,5-Dimethylphenyl	79 06 5 10 4 91 (78 87 5 23 4 84)	603	1 689 1 651	578

(continued)

TABLE 2—*contd*

Compound	*R*	*Ar*	*Analysis (%) Found (Calculated)* C	H	N	H_2SO λ_{max} (nm)	*IR(KBr)* $\nu_{C=O}$ (cm^{-1}) *Imide*	*MS(m/e)* (M^+)
9_h	$(CH_2)_5CH_3$	*p*-Phenylazophenyl	77 62 (77 05	4 47 4 62	7 68 8 56)	600	1 688 1 650	—
11_h	$(CH_2)_5CH_3$		77 41 (77 94	4 12 3 41	5 63 5 68)	600	1 688 1 638	—
12_h	$(CH_2)_5CH_3$		73 32 (74 47	3 75 3 12	5 10 5 43)	598	1 682 1 642	—
13_h	$(CH_2)_5CH_3$		74 92 (76 21	4 15 3 42	5 75 6 20)	596	1 680 1 637	—
5_i	$(CH_2)_7CH_3$	Phenyl	78 94 (78 87	5 27 5 23	4 95 4 84)	600	1 692 1 652	578
6_i	$(CH_2)_7CH_3$	*p*-Tolyl	79 63 (79 03	5 15 5 44	4 98 4 73)	601	1 698 1 653	592
7_i	$(CH_2)_7CH_3$	*p*-Methoxyphenyl	77·44 (76 96	4 96 5 30	4 76 4 60)	601	1 697 1 653	608

8_i	$(CH_2)_7CH_3$	3,5-Dimethylphenyl	79 32 5 53 4 69 (79 12 5 65 4 62)	601	1694 1653	606
9_i	$(CH_2)_7CH_3$	*p*-Phenylazophenyl	77 69 5 02 8 21 (77 40 5 02 8 21)	600	1688 1647	—
11_i	$(CH_2)_7CH_3$		77 52 4 32 5·34 (74·86 3 52 5 24)	600	1685 1638	—
12_i	$(CH_2)_7CH_3$		74 10 4·34 5 47 (74 86 3 52 5 24)	597	1683 1644	—
13_i	$(CH_2)_7CH_3$		73 95 4 54 5 35 (76 59 3·86 5 95)	595	1680 1643	—
10_e	$(CH_2)_3CH_3$		78 49 3 82 8 06 (78 60 4 07 8 9)	620	1685 1650	519
10_f	$CH_2CH(CH_3)_2$		78 56 3 84 8 34 (78 60 4 07 8 09)	620	1687 1650	519
10_g	$(CH_2)_4CH_3$		77 12 4 51 7 21 (78 78 4 34 7·81)	620	1685 1650	533
10_h	$(CH_2)_5CH_3$		78 03 4 31 9·18 (78 96 4 60 7 67)	622	1687 1651	547
10_i	$(CH_2)_7CH_3$		78 97 4 81 7 69 (79 29 5 08 7 30)	620	1687 1651	—

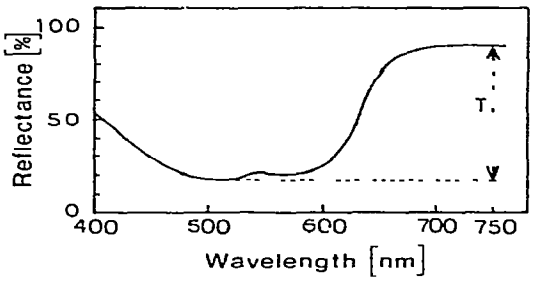
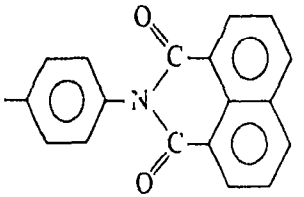


Fig. 1. Spectral reflectance curves of *N*-pentyl-*N'*(*p*-tolyl)-3,4 9,10-perylenebis (dicarboximide) ($\mathbf{6}_g$)

a typical spectral reflectance curve All compounds showed greater reflectance in the long wavelength region which indicates a reddish colour. *T* values (reflectance maximum − minimum) were calculated from reflectance curves. The differences of the *T* values of the compounds were in agreement with the observed tinting strengths, so *T* values could be used conveniently for the evaluation of tinting strength The lightfastness of the compounds was determined by light exposure in a fadeometer Table 3 shows the colour, tinting strength (expressed as *T* %) and lightfastness values obtained Compounds $\mathbf{5}$–$\mathbf{7}_{(f-i)}$ and $\mathbf{8}_{h,i}$ all gave reddish violet or reddish brown shades, $\mathbf{9}_{f-i}$ gave dark reddish violet, and $\mathbf{11}$–$\mathbf{13}_{(h,i)}$ gave a brown violet shade Compounds $\mathbf{10}_{e-i}$ gave blue violet shades The tinting strengths of $\mathbf{5}$–$\mathbf{7}_{(f,i)}$ were much the same as those of the lower alkyl compounds The lightfastness standard was excellent, as was found also with the lower alkyl compounds.[10]

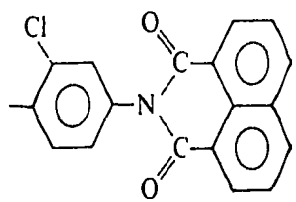
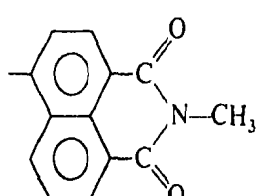
The thermal stabilities of unsubstituted ($\mathbf{2}_a$), *N*,*N'*-dibutyl- ($\mathbf{e}_e$), *N*,*N'*-diphenyl-, and *N*-butyl-*N'*-phenylperylenebis(dicarboximide) ($\mathbf{5}_e$) are shown in Fig. 2 as typical TG curves for *N*,*N'*-dialkyl-, *N*,*N'*-diaryl-, and *N*-alkyl-*N'*-arylperylenebis(dicarboximide)s. All weight losses were exothermic as shown by DTA curves. The one-step weight loss and the highest decomposition temperature are shown for $\mathbf{2}_a$ The one-step but slow initial weight loss and lower decomposition temperature is shown for *N*,*N'*-diphenylperylenebis(dicarboximide). In this case the decomposition is considered to be initiated by the degradation of *N* and *N'*-substituted phenyl groups Curves for $\mathbf{2}_e$ and $\mathbf{5}_e$ show two-step weight loss. The initial slow weight losses of 23 % (up to 480 °C) for $\mathbf{2}_e$ and 11 % (up to 460 °C) for $\mathbf{5}_e$ correspond to the degradation of each butyl group. The degradation of the butyl group in $\mathbf{5}_e$ is initiated at a higher temperature than

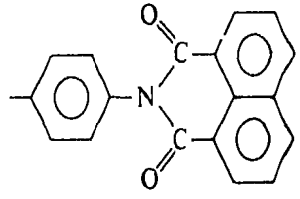
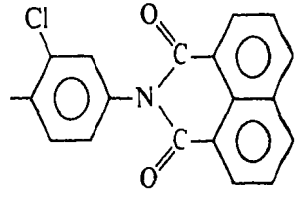
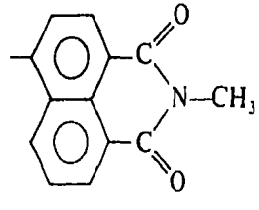
TABLE 3
Properties of 3,4 9,10-Perylenebis(dicarboximide)s (5–13)

Compound	*R*	*Ar*	*Colour*	*Tinting strength T(%)*[a]	*Lightfastness (Blue scale)*
5_f	$CH_2CH(CH_3)_2$	Phenyl	Reddish violet	66	8
6_f	$CH_2CH(CH_3)_2$	*p*-Tolyl	Reddish violet	69	8
7_f	$CH_2CH(CH_3)_2$	*p*-Methoxyphenyl	Reddish violet	59	8
9_f	$CH_2CH(CH_3)_2$	*p*-Phenylazophenyl	Dark reddish violet	29	8
5_g	$(CH_2)_4CH_3$	Phenyl	Reddish violet	64	8
6_g	$(CH_2)_4CH_3$	*p*-Tolyl	Reddish violet	73	8
7_g	$(CH_2)_4CH_3$	*p*-Methoxyphenyl	Reddish brown	56	8
9_g	$(CH_2)_4CH_3$	*p*-Phenylazophenyl	Dark reddish violet	36	8
5_h	$(CH_2)_5CH_3$	Phenyl	Reddish violet	63	8
6_h	$(CH_2)_5CH_3$	*p*-Tolyl	Reddish brown	75	8
7_h	$(CH_2)_5CH_3$	*p*-Methoxyphenyl	Reddish brown	67	8
8_h	$(CH_2)_5CH_3$	3,5-Dimethylphenyl	Reddish violet	67	8
9_h	$(CH_2)_5CH_3$	*p*-Phenylazophenyl	Dark reddish violet	33	7
11_h	$(CH_2)_5CH_3$		Brown violet	36	8

(continued)

TABLE 3 –*contd*

Compound	*R*	*Ar*	*Colour*	*Tinting strength T(%)*[a]	*Lightfastness (Blue scale)*
12_h	$(CH_2)_4CH_3$		Reddish violet	43	7
13_h	$(CH_2)_5CH_3$		Brown violet	45	8
5_i	$(CH_2)_7CH_3$	Phenyl	Reddish violet	67	8
6_i	$(CH_2)_7CH_3$	*p*-Tolyl	Reddish violet	62	8
7_i	$(CH_2)_7CH_3$	*p*-Methoxyphenyl	Reddish violet	66	8
8_i	$(CH_2)_7CH_3$	3,5-Dimethylphenyl	Reddish violet	72	8
9_i	$(CH_2)_7CH_3$	*p*-Phenylazophenyl	Dark reddish violet	37	7

11_i	$(CH_2)_7CH_3$		Brown violet	32	8
12_i	$(CH_2)_7CH_3$		Reddish violet	43	7
13_i	$(CH_2)_7CH_3$		Brown violet	41	8
10_e	$(CH_2)_3CH_3$		Bluish violet	46	8
10_f	$CH_2CH(CH_3)_2$		Bluish violet	54	8
10_g	$(CH_2)_4CH_3$		Bluish violet	48	8
10_h	$(CH_2)_5CH_3$		Dark violet	23	7
10_i	$(CH_2)_7CH_3$		Dark violet	18	7

[a] T_r Reflectance maxima (750 nm) – minima

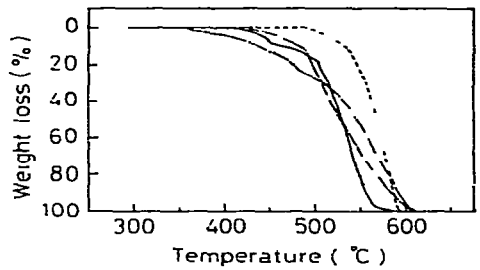


Fig. 2. Thermogravimetric curves for 3,4 9,10-perylenebis(dicarboximide) at a heating rate of 10°C min in air - - 3,4 9 10-Perylenebis(dicarboximide) (2_a). — —, *N,N'*-bisphenyl-3,4 9,10-perylenebis(dicarboximide). — —, *N,N'*-dibutyl-3,4 9,10-perylenebis(dicarboximide) (2_e). ——, *N*-butyl-*N* -phenyl-3,4 9,10-perylenebis(dicarboximide) (5_e)

that for 2_e. These phenomenon were shown for other *N,N'*-dialkyl-, *N,N'*-diaryl-, and *N*-alkyl-*N'*-arylperylenebis(dicarboximide)s. All the decompositions of *N,N'*-disubstituted perylenebis(dicarboximide)s are considered to be initiated with the degradation of *N*-substituents, and the decomposition of *N*-alkyl-*N* -arylperylenebis(dicarboximide) is considered to be initiated first with the degradation of the *N*-substituted alkyl group followed by that of the *N'*-substituted aryl group

The initiation temperatures of thermal decomposition are shown in

TABLE 4

Thermal Decomposition Temperatures of Symmetrical 3,4 9,10-perylenebis(dicarboximide)s (2 and 3)

Compound	*R or Ar*	*Decomposition temperature* (°C)
2_a	H	490
2_b	CH_3	412
2_c	CH_2CH_3	407
2_d	$(CH_2)_2CH_3$	394
2_e	$(CH_2)_3CH_3$	359
2_f	$CH_2CH(CH_3)_2$	381
2_g	$(CH_2)_4CH_3$	364
2_h	$(CH_2)_5CH_3$	314
2_i	$(CH_2)_7CH_3$	331
3	Phenyl	405
	p-Tolyl	402
	p-Methoxyphenyl	447
	3,5-Dimethylphenyl	415
	p-Phenylazophenyl	327
	Benzimidazo	467

Table 4 for symmetrical perylenebis(dicarboximide)s (**2** and **3**) and in Table 5 for *N*-alkyl-*N'*-aryl substituted compounds (**5**–**13**). The highest temperatures are shown for unsubstituted ($\mathbf{2}_a$) and bis(benzimidazo) compounds. The pressure of a higher alkyl chain in the *N*,*N'*-dialkyl and the *N*-alkyl-*N'*-aryl compounds appeared to lower the decomposition temperature, but the degradative temperature of the alkyl chain in the *N*-alkyl-*N'*-aryl substituted compounds was higher than that in *N*,*N'*-dialkyl substituted compounds. A lower temperature for the *N*-(*p*-phenylazophenyl) substituted compounds ($\mathbf{9}_{a-i}$ etc.) shows the degradation of the phenylazophenyl group at low temperature. The higher degradation temperature for the *N*-isobutyl substituted compounds ($\mathbf{2}_f$, $\mathbf{5}_f$, $\mathbf{6}_f$, $\mathbf{7}_f$), as compared with the *N*-butyl substituted compounds, shows the degradation of a branched chain to occur at a higher temperature.

3. EXPERIMENTAL

3.1. Material

Compounds $\mathbf{2}_{a-i}$, **3**, $\mathbf{5}$–$\mathbf{9}_{(a-e)}$, $\mathbf{10}_{a,b}$,[9,10] and $\mathbf{4}_{a-i}$ were prepared by the methods previously described.[12,13] Aniline, *p*-toluidine, *p*-anisidine, 3,5-xylidine, *o*-phenylenediamine, and *p*-aminoazobenzene were obtained commercially. Amines of 1,8-naphthalenedicarboximide structure were prepared as follows.

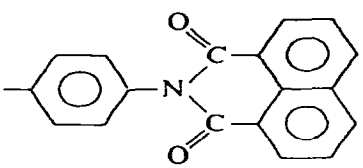
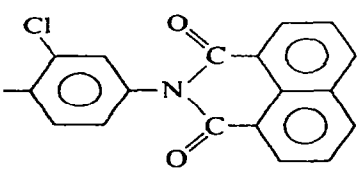
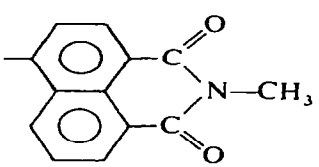
N-(*4-Aminophenyl*)-*1,8-naphthalenedicarboximide*
A mixture of 9·90 g of 1,8-naphthalenedicarboxylic anhydride, 5·40 g of *p*-phenylenediamine and 60 ml of water in a three-necked flask was stirred at 60 °C for 4 h The cooled reaction mixture was then filtered. The solid was washed with 20% methanol to remove *p*-phenylenediamine It was then added to 5% sodium carbonate solution; the mixture was boiled, and filtered. The solid was dried and recrystallized from DMF to give 9·45 g (66%) of *N*-(4-aminophenyl)-1,8-naphthalenedicarboximide, m p. 292–294 °C (289 °C[14]), MS: *m/e* 288(M^+); IR(KBr): 1648 and 1700 cm^{-1} ($\nu_{C=O}$); NMR(DMSO-d_6): δ 8·3–8·5(d,4H), 7·7–7 9(t,2H), 6 8–7·0(d,2H), 6 5–6 7(d,2H), 5·2(s,2H).

N-(*3-Chloro-4-aminophenyl*)-*1,8-naphthalenedicarboximide*
A solution of 9·60 g of *o*-chloro-*p*-phenylenediamine sulphate in 100 ml of water was neutralized with 4·24 g of sodium carbonate. To the mixture

TABLE 5
Thermal Decomposition Temperatures of *N*-Alkyl-*N'*-aryl-3,4 9,10-perylenebis(dicarboximide)s (**5–13**)

Compound	*Ar*	*R*	*Decomposition temperature* (°C)
5_{a-i}	Phenyl	H	463
		CH_3	465
		CH_2CH_3	465
		CH_2CH_3	423
		$(CH_2)_2CH_3$	422
		$(CH_2)_3CH_3$	407
		$CH_2CH(CH_3)_2$	425
		$(CH_2)_4CH_3$	373
		$(CH_2)_5CH_3$	335
		$(CH_2)_7CH_3$	305
6_{a-i}	*p*-Tolyl	H	419
		CH_3	442
		CH_2CH_3	421
		$(CH_2)_2CH_3$	417
		$(CH_2)_3CH_3$	395
		$CH_2CH(CH_3)_2$	397
		$(CH_2)_4CH_3$	353
		$(CH_2)_5CH_3$	366
		$(CH_2)_7CH_3$	317
7_{a-i}	*p*-Methoxyphenyl	H	408
		CH_3	420
		CH_2CH_3	410
		$(CH_2)_2CH_3$	396
		$(CH_2)_3CH_3$	387
		$CH_2CH(CH_3)_2$	398
		$(CH_2)_4CH_3$	364
		$(CH_2)_5CH_3$	356
		$(CH_2)_7CH_3$	317
$8_{a-c,h,i}$	3,5-Dimethylphenyl	H	388
		CH_3	411
		CH_2CH_3	432
		$(CH_2)_2CH_3$	408
		$(CH_2)_3CH_3$	378
		$(CH_2)_5CH_3$	345
		$(CH_2)_7CH_3$	315

TABLE 5—*contd*

Compound	*Ar*	*R*	*Decomposition temperature* (°C)
9_{a-i}	*p*-Phenylazophenyl	H	327
		CH_3	387
		CH_2CH_3	356
		$(CH_2)_2CH_3$	374
		$(CH_2)_3CH_3$	330
		$CH_2CH(CH_3)_2$	340
		$(CH_2)_4CH_3$	340
		$(CH_2)_5CH_3$	335
		$(CH_2)_7CH_3$	335
$10_{a\,b\,e-i}$		H	429
		CH_3	407
		$(CH_2)_2CH_3$	389
		$CH_2CH(CH_3)_2$	426
		$(CH_2)_4CH_3$	360
		$(CH_2)_5CH_3$	340
		$(CH_2)_7CH_3$	302
$11_{h,i}$		$(CH_2)_5CH_3$	305
		$(CH_2)_7CH_3$	315
$12_{h,i}$		$(CH_2)_5CH_3$	315
		$(CH_2)_7CH_3$	345
$13_{h,i}$		$(CH_2)_5CH_3$	340
		$(CH_2)_7CH_3$	350

was added 7·92 g of 1,8-naphthalenedicarboxylic anhydride and 20 ml of water. Then the mixture was stirred at 90 °C for 4 h and treated as in the previous case The solid obtained was recrystallized from DMF to give 6·70 g (47 %) of *N*-(3-chloro-4-aminophenyl)-1,8-naphthalenedicarboximide, m.p. 273–274 °C: MS: *m/e* 322(M^+), IR(KBr)· 1650 and 1698 cm^{-1} ($\nu_{C=O}$); NMR(DMSO-d_6): δ 8·35–8 5(d,4H), 7 7–7·9(t,2H), 7·2(s,1H), 6 8–7 0(m,2H), 5 4(s,2H) Found: C, 66·78; H, 3 39; N, 8·79 % Calcd for $C_{18}H_{11}O_2N_2Cl$: C. 66·99: H, 3 44: N, 8 86 %.

N-*Methyl-4-amino-1,8-naphthalenedicarboximide*
This was prepared from sodium *N*-methyl-1,8-naphthalenedicarboximide-4-sulphonate and 28 % ammonia solution,[15] and recrystallized from DMF, m p. 341–342 °C (339–340 °C[15]), MS *m/e* 226(M^+): IR(KBr)· 1630 and 1654 cm^{-1} ($\nu_{C=O}$)

3.2. Preparation of $5–7_{(f-i)}$, $8_{h\,i}$, 9_{f-i}, 10_{e-i}, and $11–13_{(h\,i)}$

Compounds $5–7_{(f-i)}$
The preparation of 5_f was as follows To a three-necked flask were added 30 g of aniline and 1 0 g of 4_f The flask was heated at 183 °C for 7 h with stirring To the cooled reaction mixture was added methanol, then the mixture was warmed, filtered and washed with methanol to remove aniline The residue was added to hot 1 % potassium hydroxide solution and filtered to remove unreacted 4_f The precipitate was washed with methanol and dried The reddish violet powder of 5_f was obtained (95 % yield) Compound 5_g was prepared by the same treatment using 4_g with aniline, 6_{f-i} and 7_{f-i} were similarly prepared by the reaction of 4_{f-i} with *p*-toluidine and *p*-anisidine, respectively

Compounds $8_{h\,i}$, 9_{f-i} *and* $11–13_{(h\,i)}$
These compounds were prepared by the reaction of $4_{h\,i}$, 4_{f-i} and $4_{h\,i}$ with 3,5-xylidine, *p*-aminoazobenzene, and the corresponding amines of 1,8-naphthalenedicarboximide structure, respectively, in boiling quinoline The treatment was similar to that for $5–7_{(f-i)}$

Compound 10_{e-i}
Compound 10_f was prepared as follows A mixture of 12 g of *o*-phenylenediamine and 3 0 g of 4_f was heated at 250 °C for 8 h with stirring. To the cooled reaction mixture was added methanol, then the mixture was

warmed, filtered and washed with methanol to remove *o*-phenylenediamine. The residue was added to hot 1% potassium hydroxide solution and filtered to remove the filtrate including unreacted $\mathbf{4}_f$. The precipitate was treated in alkaline dithionite solution (200 parts of water, 4 parts of potassium hydroxide, and 4 parts of sodium dithionite) at 45 °C for 15 min, and filtered. The filtrate included intermediate products. The residue was added to water and acidified with hydrochloric acid. The resultant precipitate was filtered, washed with water, and dried. The dark bluish violet powder of $\mathbf{10}_f$ was obtained in 94% yield Compounds $\mathbf{10}_{g-i}$ and $\mathbf{10}_e$ were prepared by the same procedures from $\mathbf{4}_{g-i}$ and $\mathbf{4}_e$ with *o*-phenylenediamine

3.3. Measurement

Mass spectra were recorded on a Hitachi RMU-7M mass spectrometer. Visible spectra were recorded on a Hitachi 124 spectrometer for solutions in conc. sulphuric acid, and IR spectra on a Nippon Bunko IR-E spectrometer Samples of **5–8** and **10** for analysis were obtained by sublimation at 300–350 °C/3–5 mmHg. Thermal decomposition was measured with a Sinku–Riko TGD-3000 RH Differential Thermal Micro Balance at a heating rate of 10 °C/min in air.

Pigment tests were carried out by the method of Japanese Industrial Standard K 5101. Prepared pigment (1·00 g) and 20 0 g of sodium sulphate were milled with a laboratory mill for 5 h. The mixture was added to water to remove sodium sulphate and filtered. The residue was dried under vacuum at room temperature The sample (100 mg), titanium dioxide (rutile) (2·0 g) and boiled oil (1·2 ml) were mixed using a muller (3 × 100 revolutions) The mixture was painted on paper over a constant area (12·5 × 8 cm) and dried in air The colour and tinting strength were estimated by measuring the reflectance with a Hitachi 124-0049 instrument Lightfastness was tested by exposure in a Suga Fadeometer FAL-3. Blue Scales were supplied by the Japanese Industrial Standards Committee.

REFERENCES

1 W Wiedemann (Kalle AG), German Offen 2 237 539 (1974).
2 T. Komiya and Y Nishigaki (Canon), Japan Kokai 59 037 (1975)
3 T Murayama (Mitsubishi Chemical Industries), Japan Kokai 20 334 (1978)

4 A Kojima, M Ohta, M Sasaki and Z Okuno (Ricoh), German Offen 2737516 (1978)
5 M Yamada (Nippon Kayaku), Japan Kokai 37918 (1976)
6 T Niwa and S. Hirako (Mitsubishi Chemical Industries), Japan Kokai 128923 (1977)
7 S Oki, I. Yamaguchi, S Ooka and Y Abe (Dainichiseika Color and Chemicals), Japan Kokai 58551, 106745 (1978)
8 M Haginoya and K Nagano (Dainippon Ink and Chemicals), Japan Kokai 10095 (1978)
9 Y Nagao, N Ishikawa, Y Tanabe and T Misono, *Chem Lett*, 151 (1979)
10 Y Nagao, N Ishikawa, Y Tanabe and T. Misono, *Nippon Kagaku Kaishi*, 1391 (1980)
11 T Maki and H Hashimoto, *Bull Chem Soc Japan*, **25**, 411 (1952)
12 Y Nagao, Y Tanabe and T Misono, *Nippon Kagaku Kaishi*, 528 (1979)
13 Y Nagao and T Misono, *Bull Chem Soc Japan*, **54**, 1191 (1981)
14 C V Sead (Imperial Chemical Industries), British Patent 901420 (1962)
15 H Okada and M Tanaka (Mitsubishi Chemicals Industries), Japan Kokai 7932 (1964)