SYNTHESIS AND PROPERTIES OF BENZIMIDAZOLE AND NAPHTHOIMIDAZOLE DERIVATIVES OF PERYLENE-DICARBOXIMIDE[≠]

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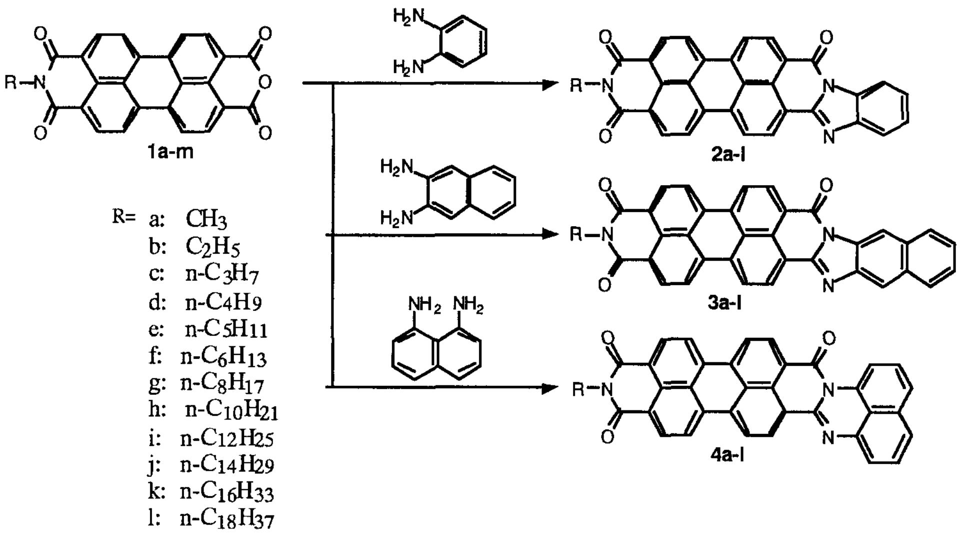
Abstract - Benzimidazole and naphthoimidazole derivatives of *N*-alkylperylenedicarboximide were prepared by the condensation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic acid monoanhydride monoimide with *o*-phenylenediamine and diaminonaphthalenes. Properties of these derivatives as pigments were tested, and the thermal stability and solubility of these derivatives were also investigated.

In general, symmetrical 3,4:9,10-perylenebis(dicarboximide)s have excellent resistance to light, heat, and solvents. Some of them are used as dyes, organic photoconductors in electrophotography[1-4] and pigments for coloring plastics.[5-8] One characteristic of these compounds is reported to be their excellent heat resistance. Recently these compounds have become of interest as conductors in organic soalar, laser dyes and fluorescent dyes. We have previously prepared benzimidazole derivatives (alkyl = H, methyl, butyl etc.) (**2a** and **2d-g**) by the condensation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic acid monoanhydride



R= a: CH_3
b: C_2H_5
c: n-C_3H_7
d: n-C_4H_9
e: n-C_5H_{11}
f: n-C_6H_{13}
g: n-C_8H_{17}
h: n-$C_{10}H_{21}$
i: n-$C_{12}H_{25}$
j: n-$C_{14}H_{29}$
k: n-$C_{16}H_{33}$
l: n-$C_{18}H_{37}$

Scheme 1

[≠] Dedicated to the memory of Professor Shô Itô.

monoimide with *o*-phenylenediamine.[9-11]

In this paper, the synthesis of benzimidazole derivatives having a long alkyl chain (**2h-l** :alkyl = decyl, lauryl, tetradecyl, cetyl, stearyl, etc.) and naphthoimidazole or perimidine derivatives (**3** or **4**) is described (Scheme 1). The absorption spectra of paint film, the thermal stability ,and the solubility of these derivatives are also reported.

Preparation of benzimidazole derivatives (2b, 2c, and 2h-l) and naphthoimidazole or perimidine derivatives (3a-l or 4a-l). Yields and spectral data of the benzimidazole derivatives (**2b,c**) and (**2h-l**) prepared by the condensation of the monoimides (**1b,c**) and (**1h-l**) with *o*-phenylenediamine are listed in Table 1. These compounds (**2b,c**) and (**2h-l**) were obtained in good yield. In the visible spectra in 95% concentrated sulfuric acid, λ max was observed at 621-623 nm for the compounds (**2b,c**) and (**2h-l**), i.e. no change in λ max was apparent with different alkyl groups. The IR spectra of **2b,c** and **2h-l** showed imide $\nu_{C=O}$ at 1685-1695 and 1650-1660 cm^{-1}, but did not show anhydride $\nu_{C=O}$.

Table 1 Yield and spectral data of **2b,c** and **2h-l**

Compound	R	Yield (%)[a]	IR [b] (cm^{-1}) $\nu_{C=O}$Imide	UV-VIS[c] λ max (nm)
2b	C_2H_5	83	1685,1650	623
2c	n-C_3H_7	65	1690,1650	620
2h	n-$C_{10}H_{21}$	70	1695,1655	621
2i	n-$C_{12}H_{25}$	82	1690,1655	622
2j	n-$C_{14}H_{29}$	88	1695,1655	621
2k	n-$C_{16}H_{33}$	81	1695,1655	621
2l	n-$C_{18}H_{37}$	66	1695,1660	621

a) Color: Black violet b) KBr disk method c)Solv.:conc.H_2SO_4(95%)

Yields and spectral data of the naphthoimidazole and perimidine derivatives (**3a,c,e,g,i,l**) and (**4a,c,e,g,i,l**) prepared by the condensation of the monoimides (**1a,c,e,g,i,l**) with 2,3-diaminonaphthalene and 1,8-diaminonaphthalene are listed in Table 2. These compounds (**3a-l**) and (**4a-l**) were obtained in good yields. In the visible spectra in 95% concentrated sulfuric acid, λ max was observed at 623-625 nm for the compounds (**3a-l**) and 605-607nm for the compounds (**4a-l**), i.e. no change in λ max was apparent with different alkyl groups, but the 2,3-naphthoimidazoles (**3a-l**) show longer λ max and 1,8-naphthoimidazoles (**4a-l**) show shorter λ max than the benzimidazoles (**2b-l**). The IR spectra of **3a-l** and **4h-l** showed imide $\nu_{C=O}$ at 1695-1700 cm^{-1} and 1650-1665 cm^{-1}, but did not show anhydride $\nu_{C=O}$.

Table 2 Yield and spectral data of **3a, c, e, g, i, l** and **4a, c, e, g, i, l**

Compound	R	Yield (%)[a]	IR [b] (cm^{-1}) $\nu_{C=O}$Imide	UV-VIS[c] λ max (nm)
3a	CH_3	88	1700,1665	623
3c	n-C_3H_7	68	1700,1660	624
3e	n-C_5H_{11}	73	1695,1660	625
3g	n-C_8H_{17}	74	1695,1655	625
3i	n-$C_{12}H_{25}$	77	1700,1660	624
3l	n-$C_{18}H_{37}$	71	1695,1655	625
4a	CH_3	74	1695,1655	605
4c	n-C_3H_7	75	1695,1655	606
4e	n-C_5H_{11}	90	1700,1650	606
4g	n-C_8H_{17}	75	1700,1655	607
4i	n-$C_{12}H_{25}$	70	1695,1655	606
4l	n-$C_{18}H_{37}$	71	1695,1660	607

a) Color: Black violet b) KBr disk method c)Solv.:conc.H_2SO_4 (95%)

Properties of benzimidadole derivatives (2b, 2c, and 2h-l) and naphthoimidazole or perimidine derivatives (3a,c,e,g,i,l or 4a,c,e,g,il). The thermogravimetry (TG) and differential thermal analysis (DTA) curves of the benzimidazole derivatives were similar to these of the *N*-alkyl-

Table 3 Thermal decomposition temperature of **2a-l**

Compound	R	Decomp. Temp.[a] (℃)
2a	CH_3	485
2b	C_2H_5	456
2c	*n*-C_3H_7	446
2d	*n*-C_4H_9	425
2e	*n*-C_5H_{11}	410
2f	*n*-C_6H_{13}	381
2g	*n*-C_8H_{17}	359
2h	*n*-$C_{10}H_{21}$	351
2i	*n*-$C_{12}H_{25}$	336
2j	*n*-$C_{14}H_{29}$	313
2k	*n*-$C_{16}H_{33}$	309
2l	*n*-$C_{18}H_{37}$	303

a) From TG-DTA , Atmosphare : Air, Rate : 10℃/min.

3,4:9,10-perylenetetracarboxylic monoanhydride monoimides.[13] The initial temperatures of thermal decomposition of **2a-l** are shown in Table 3. The longer alkyl chain in the benzimidazol derivatives appeared to lower the decomposition temperature. The lowering of decomposition temperature could be due to initial decomposition of the alkyl substituent.[13]

The solubility of benzimidazol derivatives (**2a-l**) in various solvents is shown in Table 4. The highest solubility was observed for **2l**. These results indicate that intermolecular interaction is decreased by a bulky group attached to the imide nitrogen atom. The solubility of naphthoimidazole or perimidine derivatives (**3a-l**) or (**4a-l**) showed similar solubility, and naphthoimidazole (**3l**) and perimidine (**4l**) having longest alkyl group showed the highest solubility in **3a-l** and **4a-l**, respectively.

Table 4 Solubility of **2a-l**a)b)

Compound	R	Hexane	CCl_4	Benzene	$CHCl_3$	THF	Acetone	MeOH	DMSO
2a	CH_3	−	−	−	±	±	±	±	±
2b	C_2H_5	−	−	−	±	±	±	±	±
2c	$n\text{-}C_3H_7$	−	−	−	±	±	±	±	±
2d	$n\text{-}C_4H_9$	−	−	−	±	±	±	±	±
2e	$n\text{-}C_5H_{11}$	−	−	±	±	±	±	±	±
2f	$n\text{-}C_6H_{13}$	−	±	±	±	±	±	±	±
2g	$n\text{-}C_8H_{17}$	−	±	±	±	±	±	±	±
2h	$n\text{-}C_{10}H_{21}$	−	±	±	±	±	±	±	±
2i	$n\text{-}C_{12}H_{25}$	−	±	±	±	±	±	±	±
2j	$n\text{-}C_{14}H_{29}$	−	±	±	±	±	±	±	±
2k	$n\text{-}C_{16}H_{33}$	−	±	±	±	±	±	±	±
2l	$n\text{-}C_{18}H_{37}$	−	±	±	±	±	±	±	±

a) ± : Less soluble , − : Insoluble b) At room temperature (Sample 5 mg / solv. 5 mL)

Paint film colored with the benzimidazole derivatives gave a black violet transparent color for **2a-l**. The spectra of compound (**2e**) in thin film, in chloroform, and in concentrated sulfuric acid are shown in Figure 1 and the shape of absorption curves was very similar for all derivatives. In 95% concentrated sulfuric acid, the color was bluish violet for the benzimidazole derivatives (**2a-l**), due to interaction between the solute and solvent. In chloroform, the color was yellowish orange for the benzoimidazole derivatives (**2a-l**). The difference in color of these derivatives in paint film and in solution appears to be relatable to the degree of π interaction or intermolecular overlap in the solid.[14] The λ max of benzimidazole derivatives (**2a-l**) in paint film and in chloroform is shown in Table 5. Paint film shows distant two main peaks at 502-520 nm and 632-648 nm. But chloroform solution shows near two main peaks at 532-536 nm and 571-574 nm, which are on the middle of the two peaks in paint film.

The λ max of naphthoimidazole derivatives (**3a-l**) and (**4a-l**) in paint film is shown in Table 6. Paint film of these derivatives shows two main peaks at 520-530 nm and 628-635 nm for **3a-l**, and at 513-528 and 628-637 nm for **4a-l**. The λ max 520-530 nm for **3a-l** is a little longer than the corresponding 502-520 nm for **2a-l** and 513-528 nm for **3a-l**.

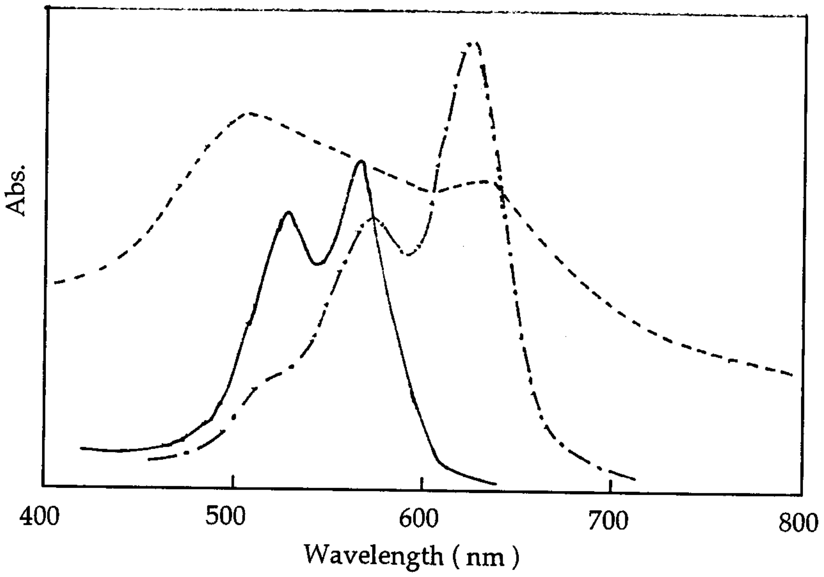


Figure 1 Visible spectra of **2e** in thin film, chloroform, and concentrated sulfuric acid

——— : Chloroform ········ : Thin film —·— : Sulfuric acid

Table 5 Absorption spectra of **2a-l**

Compound	R	λmax /nm Thin film[a)]		Solution[b)]
2a	CH_3	514	640	572
2b	C_2H_5	514	648	573
2c	n-C_3H_7	521	635	572
2d	n-C_4H_9	512	635	574
2e	n-C_5H_{11}	502	638	572
2f	n-C_6H_{13}	508	634	572
2g	n-C_8H_{17}	530	636	572
2h	n-$C_{10}H_{21}$	510	633	571
2i	n-$C_{12}H_{25}$	502	632	571
2j	n-$C_{14}H_{29}$	512	640	572
2k	n-$C_{16}H_{33}$	520	638	572
2l	n-$C_{18}H_{37}$	511	635	571

a) Thin coating film of concentrated dispersions of pigment in a poly(methylmethacrylate) binder
b) Solv. : $CHCl_3$

Table 6 Absorption spectra of **3a,c,e,g,i,l** and **4a,c,e,g,i,l** (Thin film[a])

Compd.	R	λmax / nm	
3a	CH_3	524	628
3c	n-C_3H_7	520	634
3e	n-C_5H_{11}	528	635
3g	n-C_8H_{17}	526	632
3i	n-$C_{12}H_{25}$	530	634
3l	n-$C_{18}H_{37}$	521	629
4a	CH_3	528	628
4c	n-C_3H_7	520	634
4e	n-C_5H_{11}	526	624
4g	n-C_8H_{17}	516	638
4i	n-$C_{12}H_{25}$	513	634
4l	n-$C_{18}H_{37}$	520	637

a) Thin coating film of concentrated dispersions of pigment in a poly(methylmethacrylate) binder

EXPERIMENTAL

3,4:9,10-Perylenetetracarboxylic dianhydride , all alkylamines, o-phenylenediamine , 2,3-diaminonaphthalene, and 1,8-diaminonaphthalene used were obtained commercially.

MS spectra were recorded on a Hitachi M-80A and JEOL JMS-SX102A mass spectrometer. Visible absorption spectra were recorded on a JASCO UVIDEC-610C and IR spectra on a Hitachi 260-50 spectrophotometer. Thermal decomposition was measured with a Rigaku TG-8110 differential thermal micro balance at a heating rate of 10 ℃ min^{-1} in air.

Paint film tests were carried out as follows: the prepared pigments (2.0 mg) and 2 mL of lacquer solution (contains 30 g of polymethylmethacrylate, 100 mL of tetrachloroethane and 30 mL of *o*-butylbenzylphthalate) were mixed using muller and painted on transparent plastic film over a constant area (15 mm × 50 mm). The preparation of 3,4:9,10-perylenetetracarboxylic acid monoanhydride monoimides (**3a-l**) has been previously reported.[12,13]

Benzimidazole derivatives (2a-l).

Benzoimidazole (**2a**) was prepared as follows. A mixture of 2.0 g (4.9 mmol) of **1a** and 16.5 molar ratio of *o*-phenylenediamine (8.9 g, 82 mmol) was heated at 250 ℃ for 8 h with stirring. Methanol (50 mL) was added to the cooled reaction mixture, and then the mixture was refluxed, filtered and washed with methanol to remove *o*-phenylenediamine. The residue was added to hot 5 % potassium hydroxide solution and the mixture was filtered to remove the filtrate including unreacted **1a**. The precipitate was treated in alkaline dithionite solution (100 parts of water , 2 parts of potassium hydroxide and 2 parts of sodium dithionite) at 45 ℃ for 15 min, and filtered. The residue was added to water and acidified with 10 % hydrochloric acid. The resultant precipitate was filtered, washed with water and dried. The dark bluish violet powder of **2a** was obtained in 98 % yield (2.2g).

The benzoimidazole derivatives (**2b-l**) were prepared in a similar manner by the reaction of **1b-l** with *o*-phenylenediamine. The yields of **2d-g** were 66, 87, 90, and 83 %, respectively. IR and UV-VIS spectra of **2a** and **2d-g** were in good agrement with previous data.[11]

N-Ethylbenzimidazole derivative (**2b**), Yield : 83 %, MS(m/z) : 491(M$^+$), Anal. Calcd for $C_{32}H_{17}N_3O_3$: C: 78.2,H: 3.5,N: 8.5. Found: C: 78.1,H: 3.5,N: 8.3.

N-Propylbenzimidazole derivative (**2c**), Yield : 65 %, MS(m/z) : 505(M$^+$).

N-Decylbenzimidadole derivative (**2h**), Yield : 70 %, MS(m/z) : 603(M$^+$).

N-Laurylbenzimidazole derivative (**2i**), Yield : 82 %, MS(m/z): 631(M$^+$).

N-Tetradecylbenzimidazole derivative (**2j**), Yield : 88 %, MS(m/z) : 659(M$^+$). HRMS calcd for $C_{44}H_{41}N_3O_3$ 659.3150, found 659.3145.

N-Cetylbenzimidazole derivative (**2k**), Yield : 81 %, MS(m/z) : 687(M$^+$).

N-Stearylbenzimidazole derivative (**2l**), Yield : 66 %, MS(m/z) : 715(M$^+$). HRMS calcd for $C_{48}H_{49}N_2O_3$ 715.3776, found 715.3763.

Naphthoimidazole and perimidine derivatives (3 and 4).

Naphthoimidazole (**3a**) was prepared as follows. A mixture of 0.50 g (1.0 mmol) of **1a** and 6 molar ratio of 2,3-diaminonaphthalene (1.0 g , 6.4 mmol) in 75 mL of 1-chloronaphthalene was refluxed (254℃) for 24 h. The cooled reaction mixture was filtered and the residue was washed with benzene and methanol to remove 2,3-diaminonaphthalene. The residue was treated as the preparation of **2a** to remove **1a** and intermediate product. The dark bluish violet powder of **3a** was obtained in 88 % yield. The naphthoimidazole derivatives (**3c,e,g,i,l**) were prepared in a similar manner by the reaction of **1c,e,g,i,l** with 6 molar ratio of 2,3-diaminonaphthalene.

N-Methylnaphthoimidazole derivative (**3a**), Yield : 88 %, MS(m/z) : 527(M$^+$).

N-Propylnaphthoimidadole derivative (**3c**), Yield : 68 %, MS(m/z) : 555(M$^+$).

N-Pentylnaphthoimidazole derivative (**3e**), Yield : 73 %,MS(m/z) : 583(M$^+$).

N-Octylnaphthoimidazole derivative (**3g**), Yield : 74 %, MS(m/z) : 625(M$^+$).

N-Laurylnaphthoimidazole derivative (**3i**), Yield : 77 %, MS(m/z) : 681(M$^+$).

N-Stearylnaphthoimidazole derivative (**3l**), Yield: 71 %, MS(m/z) :

765(M^+).

The perimidine derivatives (**4a,c,e,g,i,l**) were prepared in a similar manner by the reaction of **1a,c,e,g,i,l** with 10 molar ratio of 1,8-diaminonaphthalene.

N-Methylperimidine derivative (**4a**), Yield: 74 %, MS(m/z) : 527(M^+).

N-Propylperimidine derivative (**4c**), Yield: 75 %, MS(m/z) : 555(M^+).

N-Pentylperimidine derivative (**4e**), Yield: 90 %,MS(m/z) : 583(M^+).

N-Octylperimidine derivative (**4g**), Yield: 75 %, MS(m/z) : 625(M^+).

N-Laurylperimidine derivative (**4i**), Yield: 70 %, MS(m/z) : 681(M^+).

N-Stearylperimidine derivative (**4l**), Yield: 71 %, MS(m/z) : 765(M^+).

REFERENCES

1. W. Wiedemann and A. G. Kalle, *Ger. Offen.* 2237539(1974) (*Chem. Abstr.*, 1974, **80**, 126789j).
2. T. Komiya and Y. Nishigaki, Canon Inc., *Japan Kokai* 59037(1975) (*Chem. Abstr.*, 1976, **84**, 37306q).
3. T. Murayama, Mitsubishi Chemical Industries, *Japan Kokai* 20334(1978) (*Chem. Abstr.*, 1979, **90**, 31908q).
4. A. Kojima, M. Ohta, M. Sasaki, and Z. Okuno, Ricoh Inc., *Ger. Offen.* 2737516(1978) (*Chem. Abstr.*, 1978, **89**, 51417m).
5. M. Yamada. Nippon Kayaku, *Japan Kokai* 37918(1976) (*Chem. Abstr.*, 1976, **85**, 34646k).
6. T. Niwa and S. Hirano, Mitsubishi Chemical Industries, *Japan Kokai* 128923(1977) (*Chem. Abstr.*, 1978, **88**, 154417v).
7. S.Oki, I. Yamaguchi, S. Ooka,and Y. Abe, Dainichiseika Colors and Chemicals ,*Japan Kokai* 58551, 106745(1978) (*Chem. Abstr.*, 1978, **89**, 130470b, 1979, **90**, 104937k).
8. M. Hagonoya and O. Nagano, Dainippon Ink and Chemicals, *Japan Kokai* 10095(1978) (*Chem. Abstr.*, 1978, **89**, 111388q).
9. Y. Nagao, Y. Tanabe, and T. Mosono, *Nippon Kagaku Kaishi*, 1979, 528.
10. Y. Nagao and T. Misono, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1190.
11. Y. Nagao and T. Misono, *Dyes and Pigments*, 1984, **5**, 171.
12. H. Troster, *Dyes and Pigments*, 1983, **4**, 171.
13. J. M. Duff, A. M. Hor , R. O. Loutfy, and A. R. Melnyk, '*Chemistry of Functional Dyes*', Vol. 2, Mita Press, Tokyo, 1993, p. 564.
14. Y. Nagao, T. Naito, Y. Abe, and T. Misono, *Dyes and Pigments*, 1996, **32**, 71.

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