Synthesis and Reactions of Perylenecarboxylic Acid Derivatives. X. Synthesis of *N*-Alkyl-3,4-perylenedicarboximide

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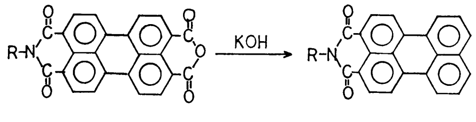
Synopsis. *N*-Alkyl-3,4-perylenedicarboximides (alkyl=methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, and octyl) were prepared by the decarboxylation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides (same alkyls) in potassium hydroxide solution.

In a previous publication we reported that the 3,4-perylenedicarboximide was sulfonated, and that the *N*-substituted perylene-3,4-dicarboximides could be prepared from the sulfonic acid *via* sulfoperylene-3,4-dicarboxylic anhydride and *N*-substituted sulfoperylene-3,4-dicarboximide.[1)] This method may be applicable to many kinds of *N*-substituted perylene-3,4-dicarboximide preparations, but it includes too many reaction steps. 3,4-Perylenedicarboximide was prepared by decarboxylation of 3,4:9,10-perylenetetracarboxylic monoanhydride monoimide in potassium hydroxide solution.[2)] The present work was undertaken to apply the decarboxylation to *N*-substituted 3,4:9,10-perylenetetracarboxylic monoanhydride monoimides to prepare *N*-alkyl-3,4-perylenedicarboximide(**2a**—**h**) (alkyl=**a**, methyl; **b**, ethyl; **c**, propyl; **d**, butyl; **e**, isobutyl; **f**, pentyl; **g**, hexyl; **h**, octyl) from *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide[3),4)] (**1a**—**h**) (same alkyls).



1a—**h** **2a**—**h**

R=**a**, methyl; **b**, ethyl; **c**, propyl; **d**, butyl; **e**, isobutyl; **f**, pentyl; **g**, hexyl; **h**, octyl.

Results and Discussion

The *N*-alkyl-3,4-perylenedicarboximides(**2a**—**h**) prepared by the decarboxylation of *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides (**1a**—**h**) in potassium hydroxide solution are listed in Table 1. Their structures were confirmed by elemental analyses, absorption spectra, and IR and MS spectra. These are given in Table 2. All compounds could be prepared in 60—80% yield. The raw products of **2a**—**h** were given in good yields. The differences of yield are due to the difficulties of recrystallization from solvent.

All λ_{max} in the visible spectra of sulfuric acid solutions are 612—614 nm, and no different λ_{max} values due to alkyl group were found. All IR spectra indicate $\nu_{C=O}$ of imide on 1637—1647 cm^{-1} and 1680—1687 cm^{-1}, and no different $\nu_{C=O}$ due to alkyl group were found either. Mass spectra show the corresponding molecular ion peak. Table 3 shows the color, tinting strength, and light-fastness obtained by a similar method in previous work.[4)] Colors were all reddish, and the colors of **2b**,**2c**,**2e**, and **2f** were very clear. Tinting strengths of **2b**,**2e**, and **2f** were high, and that of **2a** was the lowest. Light-fastness of *N*-butyl compound (**2d**) was the highest and *N*-pentyl compound(**2f**) was the lowest.

Table 1. Reaction conditions for the preparation of 3,4-perylenedicarboximide(**2a**—**h**)
Reaction temp: 220—230 °C; Time: 18 h.

1a—**h**(g)		12% KOH(ml)	Yield of **2a**—**h**/%	
1a	5.0	100	**2a**	74
1b	6.0	120	**2b**	62
1c	6.1	123	**2c**	64
1d	10.0	200	**2d**	67
1e	5.0	100	**2e**	71
1f	5.0	100	**2f**	81
1g	5.0	100	**2g**	70
1h	5.0	100	**2h**	76

Experimental

Material. **1a**—**h** were prepared by the previous methods.[3),4)]

Preparation of 2a—h. For example, **2a** was prepared as follows. **1a** (5.0 g) and 12% potassium hydroxide solution (100 ml) were heated in an autoclave at 220—230 °C for 18 h with stirring. The cooled reaction mixture was filtered, and the precipitate was washed with water and dried to yield 3.7 g (89%) of crude reddish brown powder of **2a**. The crude **2a** was recrystallized from nitrobenzene-methanol to obtain 3.0 g (74%) of **2a** (mp>300 °C). **2b**—**h** were prepared with the same treatment under the conditions given in Table 1. The obtained crude yield of **2b**—**h** was: **2b**, 89%; **2c**, 81%; **2d**, 88%; **2e**, 77%; **2f**, 85%; **2g**, 90%; **2h**, 90%. The crude **2b**—**h** were recrystallized from benzene–methanol: **2b**, **2c**, **2d**, and acetic anhydride–methanol: **2e**, **2f**, **2g**, **2h**, respectively. The yields of **2b**—**h** were: **2b**, 62% (mp 292 °C); **2c**, 64% (mp 250 °C); **2d**, 67% (mp 267 °C); **2e**, 71% (mp 293 °C); **2f**, 81% (mp 249 °C); **2g**, 70% (mp 206 °C); **2h**, 76% (mp 190 °C).

Measurement. Mass spectra were recorded on a Hitachi RMU-7M mass spectrometer. Visible spectra were measured using a Hitachi 124 spectrometer for solutions in concd sulfuric acid (95.0%), and IR spectra on a Nippon Bunko IR-E spectrometer.

The prepared pigment (1.00 g) and 20.0 g of sodium sulfate were milled with a lab mill for 5 h. The mixture was added to water to remove sodium sulfate and then filtered. The residue was dried under vacuum at room temperature. The sample (100 mg), titanium dioxide (2.0 g), and boiled oil (1.2 ml) were mixed by a muller for three hundred revolutions. The mixture was painted on paper, then the tests were carried by the previous methods.[5)]

TABLE 2. ANALYTICAL AND SPECTRAL DATA FOR 3,4-PERYLENEDICARBOXIMIDE(**2a**—**h**)

2a—**h**	R	Found (Calcd)%			$\lambda_{max}^{H_2SO_4}$/nm	IR(KBr) $\nu_{C=O}$/cm^{-1} Imide	MS(*m*/*e*) (M^+)
		C	H	N			
2a	CH_3	81.18	3.68	4.36	612	1647 1687	335
		(82.37	3.87	4.18)			
2b	CH_2CH_3	81.97	4.06	4.17	613	1639 1680	349
		(82.54	4.30	4.01)			
2c	$(CH_2)_2CH_3$	81.17	4.45	4.01	613	1642 1682	363
		(82.64	4.68	3.86)			
2d	$(CH_2)_3CH_3$	82.87	4.98	4.04	614	1641 1680	377
		(82.74	5.07	3.71)			
2e	$CH_2CH(CH_3)_2$	83.12	5.06	3.81	614	1637 1684	377
		(82.74	5.07	3.71)			
2f	$(CH_2)_4CH_3$	82.76	5.30	3.64	612	1642 1683	391
		(82.84	5.41	3.58)			
2g	$(CH_2)_5CH_3$	82.65	5.57	3.48	615	1645 1680	405
		(82.94	5.72	3.45)			
2h	$(CH_2)_7CH_3$	83.31	6.29	3.25	615	1645 1680	433
		(83.11	6.28	3.23)			

TABLE 3. PROPERTIES OF 3,4-PERYLENEDICARBOXIMIDE(**2a**—**f**)

2a—**f** R	Color	Tinting strength[a)] *T*/%	Light-fastness[b)] h
2a CH_3	Reddish violet	29	80
2b CH_2CH_3	Orange	62	100
2c $(CH_2)_2CH_3$	Reddish violet	58	100
2d $(CH_2)_3CH_3$	Reddish violet	37	140
2e $CH_2CH(CH_3)_2$	Orange	60	40
2f $(CH_2)_4CH_3$	Orange	63	30

a) *T*: Reflactance maxima(750 nm)—minima.
b) Exposure time before beginning to fade.

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