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Synthesis and Reactions of Perylenecarboxylic Acid Derivatives. VIII. Synthesis of *N*-Alkyl-3,4:9,10-Perylenetetracarboxylic Monoanhydride Monoimide

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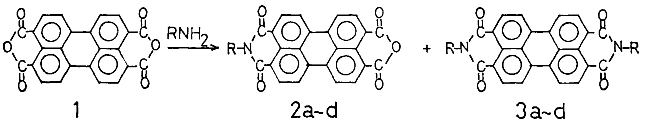
The condensations of 3,4 : 9,10-perylenetetracarboxylic dianhydride with alkylamines (isobutyl-, pentyl-, hexyl-, and octylamines) were spectroscopically determined. Under all of the reaction conditions employed, *N*-alkyl-3,4 : 9,10-perylenetetracarboxylic monoanhydride monoimide (**2a**—**d**) (alkyl=a; isobutyl, b; pentyl, c; hexyl, d; octyl) were obtained. As the reaction proceeded, the yield of **2a**—**d** increased at an initial stage but decreased gradually after reaching a maximum. This maximum yield of **2a**—**d** was: **2a**; 85—88%, **2b**; 85—89%, **2c**; 78—84%, **2d**; 79—85%. The kinetics of the reaction were also examined.

In general, 3,4 : 9,10-perylenebis(dicarboximide) derivatives are synthesized by the condensation of 3,4 : 9,10-perylenetetracarboxylic dianhydride (**1**) with amines,[1-4] and have excellent resistance to light, heat, and solvents. Some of them are used as dyes or pigments. In previous papers[5,6] we described the preparation of unsymmetrical 3,4 : 9,10-perylenebis(dicarboximide)s having different substituents on N and N′ atoms by the reaction of 3,4 : 9,10-perylenetetracarboxylic monoanhydride monoimide (**2**), which was prepared by the condensation of **1** with an alkylamine, with arylamines. In the condensation of **1** with alkylamines, higher alkylamines appeared to be favorable for the formation of **2**. This suggests a possibility of selective formation of **2** in the condensation of **1** with amines by using higher or branched alkylamines. In this paper, we report the formation of **2** from isobutyl-, pentyl-, hexyl-, and octylamines and the kinetical study of the reaction by spectroscopic techniques.



R = a; $CH_2CH(CH_3)_2$, b; $(CH_2)_4CH_3$, c; $(CH_2)_5CH_3$, d; $(CH_2)_7CH_3$

Experimental

Materials. **1** was supplied by BASF. Isobutyl-, pentyl-, hexyl-, and octylamines were obtained commercially.

Preparation of N*-Alkyl-3,4 : 9,10-perylenetetracarboxylic Monoanhydride Monoimide (2a—d) and* N,N′*-Dialkyl-3,4 : 9,10-perylenebis(dicarboximide) (3a—d).* *2a—d*: Into a solution of an amine in an appropriate solvent was added **1** with stirring at a definite temperature. The mixture was stirred vigorously for an appropriate reaction time. The reaction conditions for each reaction are given in Table 1. The reaction mixture was acidified with 10% hydrochloric acid, and the precipitate formed was filtered, washed with water to remove amine, dissolved in 1% hot potassium hydroxide, and filtered to remove insoluble precipitates of **3a**—**d**. The soluble material which remained in the precipitate was again dissolved in 1% hot potassium hydroxide. The combined filtrate was heated again to dissolved the precipitate which had formed in cooling, and filtered to remove the small amount of the floating precipitate of **3a**—**d** which had passed through the filter. To the filtrate was added potassium chloride until 10% concentration, and the precipitated potassium salt of **2a**—**d** was filtered. The solid was dissolved in water and acidified with 10% hydrochloric acid, and the precipitate formed was filtered, washed with water, and dried to yield **2a**—**d**.

3a—d: **3a**—**d** was prepared by the treatment of **1** with a corresponding amine solution at 200 °C for 10 h in an autoclave. Unreacted **1** and **2a**—**d** were dissolved in hot 1% potassium hydroxide solution and removed from the precipitate of **3a**—**d**.

IR, visible spectra, mass spectra, and analysis data are given in Table 2. Samples for elementary analysis were obtained by a sublimation at 300—350 °C/3—5 mmHg.

Condensation of 1 with Amines. To a flask containing **1** 0.50 g (1.27×10^{-3} mol) and 30 ml solvent (isobutyl- and pentylamines; water, hexyl- and octylamines; water : 1-propanol=2 : 1 and 1 : 1), and maintained at the optimum temperature in a thermostat was added an amine solution 20 ml (optimum amine was dissolved in the same solvent) maintained at the same temperature with stirring. The reaction mixture showed a complicated suspension and not a homogeneous solution. This was stirred vigorously to maintain a homogeneous solution. Samples were collected at regular intervals and acidified with 10% hydrochloric acid. The precipitate was centrifuged, dried, and dissolved in 95% sulfuric acid, and the absorbances were measured. The composition of the reaction mixture were calculated from the absorbances. The optimum wavelengths (510 nm and λ_{max} of **2a**—**d** and **3a**—**d**) for the determination were decided from the standard 95% sulfuric acid solution of **1**, **2a**—**d**, and **3a**—**d**.

Measurements and Calculations. *Paper Chromatography*: Samples were dissolved in 1% potassium hydroxide or DMSO, placed on the paper, and developed by a mixture of equal volumes of 1-butanol, pyridine, 28% ammonia, and water.

The composition and rate ratio (*K*) were calculated using an IBM 370 computer. Mass spectra were recorded on a Hitachi RMU-7M mass spectrometer. Visible spectra were recorded on a Hitachi 124 spectrometer for solutions in concd sulfuric acid, and IR spectra on a Nippon Bunko IR-E spectrometer.

Results and Discussion

Preparation of 2a—d and 3a—d. Table 1 gives the reaction conditions, and the yields of **2a**—**d** and the by-product **3a**—**d**. The analytical and spectral data for **2a**—**d** and **3a**—**d** are given in Table 2. λ_{max}

TABLE 1. REACTION CONDITIONS FOR THE PREPARATION OF 3,4 : 9, 10-PERYLENETETRACARBOXYLIC MONOANHYDRIDE MONOIMIDE (**2a**—**d**)

R	Amine (RNH_2) concn mol/l	Amine (RNH_2) ml	**1** g	Temp °C	Time min	Yield/% **2a**—**d**		Yield/% **3a**—**d**	
$CH_2CH(CH_3)_2$	(0.204)	50[a]	0.500	60	220	80	**2a**	9	**3a**
	(0.304)	50[a]	0.500	60	210	80		9	
	(0.204)	100[a]	1.00	60	220	80		10	
	(0.306)	100[a]	1.00	60	210	80		10	
$(CH_2)_4CH_3$	(0.204)	50[a]	0.500	60	210	85	**2b**	11	**3b**
	(0.306)	50[a]	0.500	60	180	84		13	
	(0.204)	100[a]	1.00	60	210	85		9	
	(0.306)	100[a]	1.00	60	180	84		12	
$(CH_2)_5CH_3$	(0.306)	100[b]	1.00	60	420	73	**2c**	15	**3c**
$(CH_2)_7CH_3$	(0.306)	100[c]	1.00	60	420	75	**2d**	15	**3d**

a) Solvent; H_2O. b) Solvent; H_2O : *n*-PrOH=2 : 1. c) Solvent; H_2O : *n*-PrOH=1 : 1.

TABLE 2. ANALYTICAL AND SPECTRAL DATA FOR 3,4 : 9,10-PERYLENETETRACARBOXYLIC MONOANHYDRIDE MONOIMIDE (**2a**—**d**) AND 3,4 : 9,10-PERYLENEBIS(DICARBOXIMIDE) (**3a**—**d**)

2a—**d** and **3a**—**d**	R	Found (Calcd) % C	H	N	$\lambda_{max}^{H_2SO_4}$/nm	IR(KBr)$\nu_{C=O}$/cm^{-1} Anhydride	Imide	MS/(*m*/*e*) (M+)
2a	$CH_2CH(CH_3)_2$	74.77 (75.16	3.65 3.83	3.09 3.13)	581	1767 1725	1693 1650	447
2b	$(CH_2)_4CH_3$	75.41 (75.48	3.84 4.12	3.81 3.04)	580	1768 1727	1695 1654	461
2c	$(CH_2)_5CH_3$	75.26 (75.78	4.19 4.45	3.06 2.98)	580	1765 1725	1690 1650	475
2d	$(CH_2)_7CH_3$	76.32 (76.33	4.99 5.00	2.98 2.78)	580	1765 1725	1690 1650	503
3a	$CH_2CH(CH_3)_2$	76.41 (76.48	5.02 5.21	5.51 5.57)	599		1691 1652	502
3b	$(CH_2)_4CH_3$	77.45 (76.96	5.60 5.70	5.11 5.18)	598		1693 1651	530
3c	$(CH_2)_5CH_3$	77.31 (77.40	5.98 6.13	4.96 5.01)	598		1695 1655	558
3d	$(CH_2)_7CH_3$	77.51 (78.15	6.50 6.89	4.70 4.56)	598		1690 1650	614

TABLE 3. THE MAXIMUM YIELDS OF 3,4 : 9,10-PERYLENETETRACARBOXYLIC MONOANHYDRIDE MONOIMIDE (**2a**—**d**)

Amine (RNH_2) R	Temp °C	Mole ratio of amine; Amine/**1** The maximum yields of **2a**—**d**/% (The reaction time/min) 4	6	8	10	12	14	24
$CH_2CH(CH_3)_2$	40	83	86	85	88	82[a]	87	88
		(3600)	(1800)	(1380)	(1140)	(690)	(720)	(320)
$(CH_2)_4CH_3$	60	82	85	84	88	87	89	69
		(420)	(260)	(180)	(180)	(180)	(120)	(75)
$(CH_2)_5CH_3$	60	84	84	81	78	78	77	71
		(630)	(660)	(480)	(340)	(340)	(320)	(190)
$(CH_2)_7CH_3$	60	85	85	84	84	83	82	79
		(480)	(540)	(480)	(350)	(300)	(300)	(210)

1; 1.27×10^{-3} mol/50 ml. a) The maximum yields have not been reached.

in visible spectra of 95% concd sulfuric acid solution is 580—581 nm for **2a**—**d** and 598—599 nm for **3a**—**d**. *N*-Alkyl substituents in **2a**—**d** or **3a**—**d** caused no significant difference in the λ_{max}. IR spectra indicate that $\nu_{C=O}$ of anhydride and imide both exist in **2a**—**d**, and only $\nu_{C=O}$ of imide exists in **3a**—**d**. Mass spectra showed the corresponding molecular ion peak.

*Condensation of **1** with Amine.* In the reactions at 40—80 °C, the reaction mixture, after the amine was removed, has been proved to give no other products than the **2a**—**d** and **3a**—**d** by paper chromatography. The molar ratios, $C_A/(C_A+C_M+C_I)$, $C_M/(C_A+C_M+C_I)$,

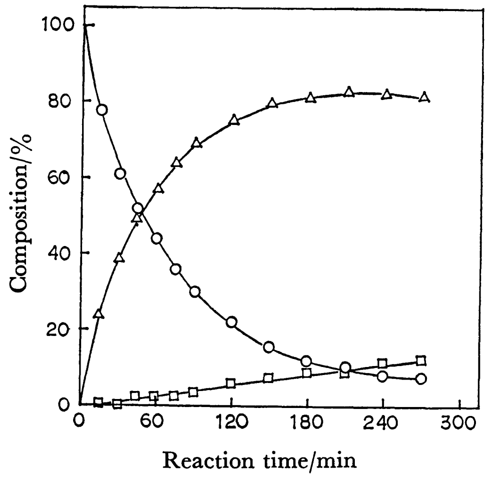


Fig. 1. Reaction of 3,4: 9,10-perylenetetracarboxylic dianhydride (**1**) with isobutylamine.
1; 1.27×10^{-3} mol/50 ml H_2O, temp; 60 °C, mole ratio (amine/**1**); 10. ○; 3,4: 9,10-Peryleneteracarboxylic dianhydride (**1**), △; *N*-Isobutyl-3,4: 9,10-perylenetetracarboxylic monoanhydride monoimide (**2a**), □; *N,N'*-Diisobutyl-3,4: 9,10-perylenebis(dicarboximide)(**3a**).

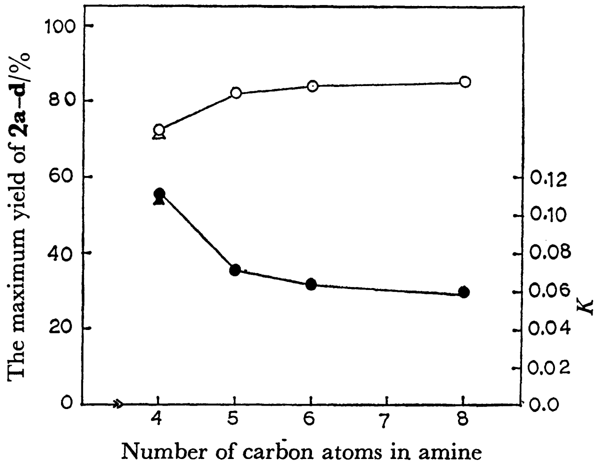


Fig. 2. Variation of the maximum yields of 3,4: 9,10-perylenetetracarboxylic monoanhydride monoimide (**2a**—**d**) and *K* with the number of carbon atoms in amine.
1; 1.27×10^{-3} mol/50 ml solvent, temp; 60 °C, mole ratio (amine/**1**); 4. The maximum yields of **2a**—**d**: ○; butyl-, pentyl-, hexyl-, and octylamines, △; isobutylamine. *K*: ●; butyl-, pentyl-, hexyl-, and octylamines, ▲; isobutylamine.

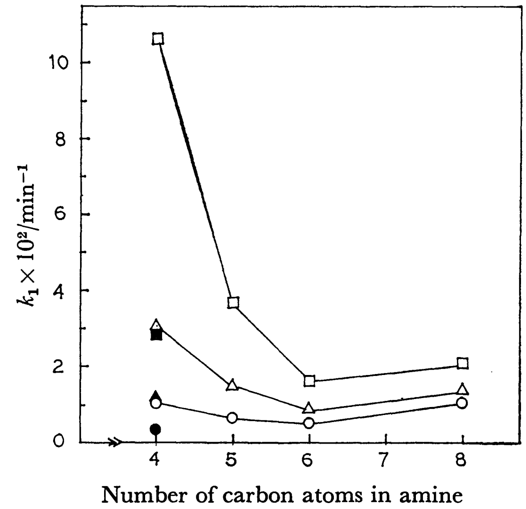


Fig. 3. Variation of k_1 with the number of carbon atoms in amine.
1; 1.27×10^{-3} mol/50 ml solvent, temp; 60 °C. Mole ratio (amine/**1**): 4: ○; butyl-, pentyl-, hexyl-, octylamines, ●; isobutylamine. 10: △; butyl-, pentyl-, hexyl-, octylamines, ▲; isobutylamine. 24: □; butyl-, dentyl-, hexyl-, octylamines, ■; isobutylamine.

$C_I/(C_A+C_M+C_I)$, were determined by spectrometry, where C_A, C_M, and C_I are the concentrations of **1**, **2a**—**d**, and **3a**—**d**, respectively. Figure 1 shows a typical time-conversion curve showing that the reaction proceeded in successive manner. The maximum yields of **2a**—**d** on the time-conversion cuves, at the best temperature, are given in Table 3 for the reactions at 40—80 °C. Lower temperatures were favorable for selective preparation of **2c** and **2d**.

Plots of $\ln(C_A/C_{A0})$, where C_{A0} is the initial concentration of **1**, *vs.* time were linear, and the rate constants k_1 for the reaction of **1** to **2a**—**d**, were calculated from the slopes. Then the rate ratios $K(=k_2/k_1)$, where k_2 is the rate constant of **2a**—**d** to **3a**—**d** were calculated from Eq. 1.[5] Most of the *K* values in each reaction were constant. These results indicated that the reaction followed a pseudo first order process of **1**→**2a**—**d**→**3a**—**d**.

$$C_M/C_{A0} = \{1/(1-K)\}\{(C_A/C_{A0})^K - (C_A/C_{A0})\} \qquad (1)$$

Figure 2 shows the variation of the maximum yield of **2a**—**d** and *K* with the number of carbon atoms in amine. As the number of carbon atoms in amine increases, the maximum yields of **2** increase in the reaction of **1** with methyl-, ethyl-, propyl-, and butylamines.[5] Though there is an increasing of the maximum yields of **2a**—**b** in isobutyl- and pentylamines, it is followed by an approximately constant in hexyl- and octylamines. It also indicate the pseudo first order reaction that the small *K* value increase the maximum yields of **2a**—**d**.

Figure 3 shows the variation of k_1 with the number of carbon atoms. This result shows that k_1 decreases with an increasing of the number of carbon atoms in all amines except octylamine. The reactions with methyl-, ethyl-, propyl-, and butylamines gave a similar results.[5] Lower k_1 in isobutylamine shows that the steric hindrance of alkyl group affects this reaction. The mixture of water and propanol was used for the solvent in the reaction with hexyl- and octylamines because of their poor solubility in water. Then the solvent effects have to be considered in these amines: the increasing k_1 in octylamine is explained as the effect of the solvent.

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