

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

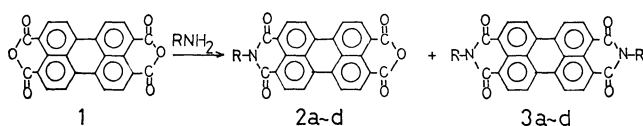
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The condensations of 3,4:9,10-perylenetetracarboxylic dianhydride with alkylamines (isobutyl-, pentyl-, hexyl-, and octylamines) were spectroscopically determined. Under all of the reaction conditions employed, *N*-alkyl-3,4:9,10-perylenetetracarboxylic 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 kinetic study of the reaction by spectroscopic techniques.



R = a; $\text{CH}_2\text{CH}(\text{CH}_3)_2$, b; $(\text{CH}_2)_4\text{CH}_3$, c; $(\text{CH}_2)_5\text{CH}_3$,
d; $(\text{CH}_2)_7\text{CH}_3$

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 dissolve 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-PERYLENETETACARBOXYLIC MONOANHYDRIDE MONOIMIDE (**2a—d**)

R	Amine (RNH ₂)		1 g	Temp °C	Time min	Yield/%		
	concn mol/l	ml				2a—d	3a—d	
CH ₂ CH(CH ₃) ₂	(0.204)	50 ^{a)}	0.500	60	220	80	9	2a 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) ₄ CH ₃	(0.204)	50 ^{a)}	0.500	60	210	85	11	2b 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) ₅ CH ₃	(0.306)	100 ^{b)}	1.00	60	420	73	15	2c 3c
(CH ₂) ₇ CH ₃	(0.306)	100 ^{c)}	1.00	60	420	75	15	2d 3d

a) Solvent; H₂O. b) Solvent; H₂O : *n*-PrOH = 2 : 1. c) Solvent; H₂O : *n*-PrOH = 1 : 1.TABLE 2. ANALYTICAL AND SPECTRAL DATA FOR 3,4 : 9,10-PERYLENETETACARBOXYLIC MONOANHYDRIDE MONOIMIDE (**2a—d**) AND 3,4 : 9,10-PERYLENEBIS(DICARBOXIMIDE) (**3a—d**)

2a—d and 3a—d R	Found (Calcd) %			$\lambda_{\text{H}_2\text{SO}_4}^{\text{max}}$ /nm	IR (KBr) $\nu_{\text{C=O}}$ /cm ⁻¹		MS/(<i>m/e</i>) (M ⁺)
	C	H	N		Anhydride	Imide	
2a CH ₂ CH(CH ₃) ₂	74.77 (75.16)	3.65 (3.83)	3.09 (3.13)	581	1767 1725	1693 1650	447
2b (CH ₂) ₄ CH ₃	75.41 (75.48)	3.84 (4.12)	3.81 (3.04)	580	1768 1727	1695 1654	461
2c (CH ₂) ₅ CH ₃	75.26 (75.78)	4.19 (4.45)	3.06 (2.98)	580	1765 1725	1690 1650	475
2d (CH ₂) ₇ CH ₃	76.32 (76.33)	4.99 (5.00)	2.98 (2.78)	580	1765 1725	1690 1650	503
3a CH ₂ CH(CH ₃) ₂	76.41 (76.48)	5.02 (5.21)	5.51 (5.57)	599		1691 1652	502
3b (CH ₂) ₄ CH ₃	77.45 (76.96)	5.60 (5.70)	5.11 (5.18)	598		1693 1651	530
3c (CH ₂) ₅ CH ₃	77.31 (77.40)	5.98 (6.13)	4.96 (5.01)	598		1695 1655	558
3d (CH ₂) ₇ CH 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-PERYLENETETACARBOXYLIC 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)						
CH ₂ CH(CH ₃) ₂	40	83 (3600)	86 (1800)	85 (1380)	88 (1140)	82 ^{a)} (690)	87 (720)	88 (320)
(CH ₂) ₄ CH ₃	60	82 (420)	85 (260)	84 (180)	88 (180)	87 (180)	89 (120)	69 (75)
(CH ₂) ₅ CH ₃	60	84 (630)	84 (660)	81 (480)	78 (340)	78 (340)	77 (320)	71 (190)
(CH ₂) ₇ CH ₃	60	85 (480)	85 (540)	84 (480)	84 (350)	83 (300)	82 (300)	79 (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 $\nu_{\text{C=O}}$ of anhydride and imide both exist in **2a—d**, and only $\nu_{\text{C=O}}$ 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, $C_A/(C_A + C_M + C_I)$, $C_M/(C_A + C_M + C_I)$,

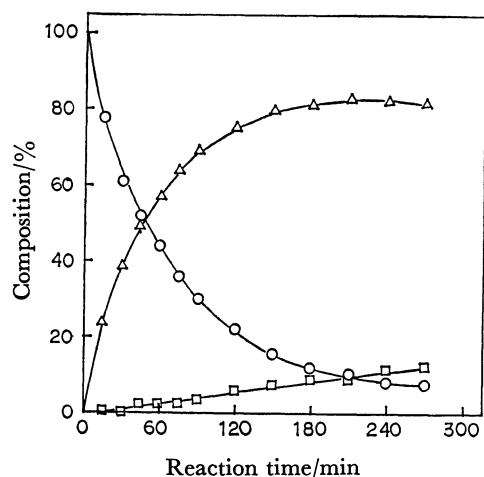


Fig. 1. Reaction of 3,4:9,10-perylenetetracarboxylic dianhydride (**1**) with isobutylamine.

1; 1.27×10^{-3} mol/50 ml H_2O , temp; $60^\circ C$, mole ratio (amine/**1**); 10. ○; 3,4:9,10-Perylenetetracarboxylic dianhydride (**1**), △; *N*-isobutyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**2a**), □; *N,N'*-Diisobutyl-3,4:9,10-perylenebis(dicarboximide) (**3a**).

$C_I/(C_A + C_M + C_I)$, 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 curves, at the best temperature, are given in Table 3 for the reactions at 40 – $80^\circ C$. 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**.

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

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

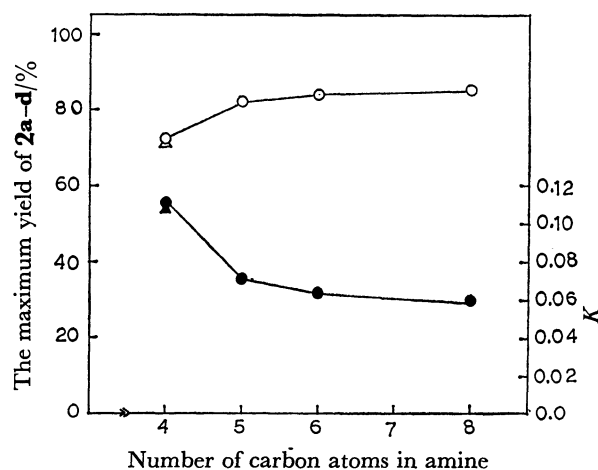


Fig. 2. Variation of the maximum yields of 3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**2a–d**) and K with the number of carbon atoms in amine. **1**; 1.27×10^{-3} mol/50 ml solvent, temp; $60^\circ C$, mole ratio (amine/**1**); 4. The maximum yields of **2a–d**: ○; butyl-, pentyl-, hexyl-,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

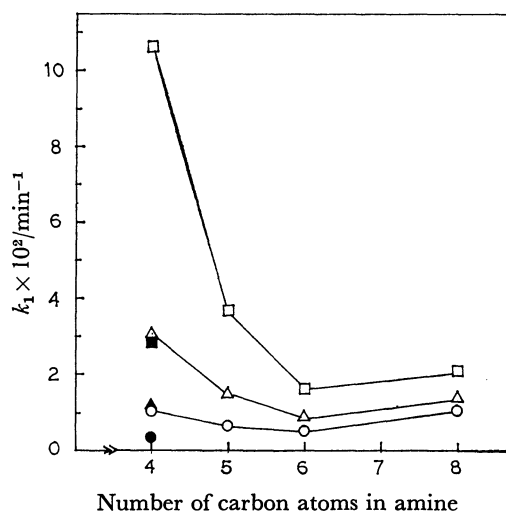


Fig. 3. Variation of k_1 with the number of carbon atoms in amine.

1; 1.27×10^{-3} mol/50 ml solvent, temp; $60^\circ C$. Mole ratio (amine/**1**): 4: ○; butyl-, pentyl-, hexyl-, octylamines, ●; isobutylamine. 10: △; butyl-, pentyl-, hexyl-, octylamines, ▲; isobutylamine. 24: □; butyl-, pentyl-, hexyl-, octylamines, ■; isobutylamine.

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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