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SYNTHESIS OF UNSYMMETRICAL PERYLENEBIS(DICARBOXIMIDE) DERIVATIVES

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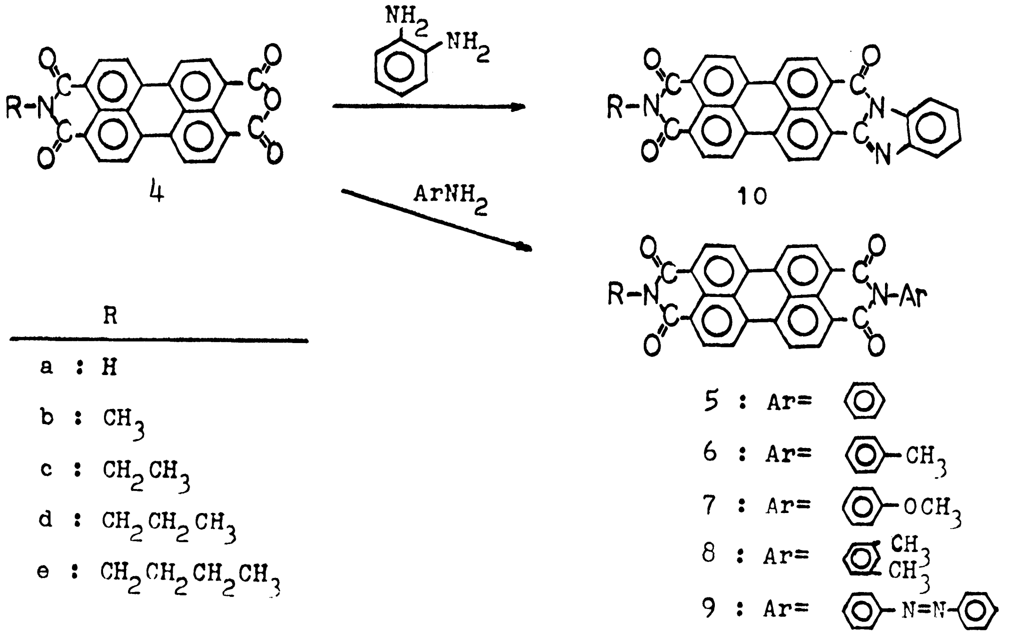
Unsymmetrical perylenebis(dicarboximide) derivatives——N-alkyl-N'-aryl-3,4:9,10-perylenebis(dicarboximide) (5a-e, 6a-e, 7a-e, 8a-e, and 9a-e)——were prepared by the condensation of N-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide(4a-e) with arylamines (aniline, p-toluidine, p-anisidine, and 3,5-xylidine etc.).

In general, 3,4:9,10-perylenebis(dicarboximide) derivatives(PTCI) are synthesized by the condensation of 3,4:9,10-perylenetetracarboxylic dianhydride(PTCA)(1) with amines. PTCI have excellent fastness to light, heat, and solvent etc. Some of them are used as dyes or pigments. Since the working by M. Kordos$^{1)}$,Maki et al.$^{2,3)}$,and Bradley et al.$^{4)}$,many kinds of N,N'-diaryl-PTCI(2) and some kinds of N,N'-dialkyl-PTCI(3) were obtained.

On the other hand, an unsymmetrical PTCI including different substituents on N and N' atoms have not been obtained. The preparation of the unsymmetrical PTCI was attempted by the formation of 3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (PTCMI)(4) by the condensation of 1 with an alkylamine, followed by the condensation of 4 with an arylamine. However 4 obtained already was only 4a.$^{5-9)}$ So in our



R	
a :	H
b :	CH_3
c :	CH_2CH_3
d :	$CH_2CH_2CH_3$
e :	$CH_2CH_2CH_2CH_3$

previous work the condensation of 1 with alkylamines had been studied and their corresponding N-alkyl-PTCMI(4a-e) were obtained.10) In this work the condensation of 4 with arylamines($ArNH_2$) were attempted and unsymmetrical PTCI(5-10) were prepared successfully.

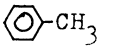
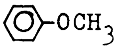
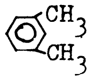
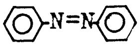
The unsymmetrical PTCI(5-10) prepared by the condensation of PTCMI(4) with arylamines are listed in Table 1. Their structures were confirmed by elemental analyses, absorption spectra, and IR and MS spectra. These are given in Table 2.

Table 1 Reaction conditions for The Condensation of N-Alkyl-PTCMI(4) with Arylamines($ArNH_2$)

N-Alkyl-PTCMI(4)			Arylamine		Temp.	Time	Product	Yield
	P	(g)		(g)	(°C)	(h)		(%)
4a	H	1.0	Aniline	39.6	181	6.5	5a	32
4b	CH_3	1.0	"	39.5	"	5.0	5b	63
4c	C_2H_5	1.0	"	81.5	183	5.0	5c	91
4d	n-C_3H_7	0.5	"	81.5	"	6.0	5d	55
4e	n-C_4H_9	1.0	"	81.5	"	7.0	5e	94
4a	H	1.0	p-Toluidine	20.6a)	125	4.0	6a	85
4b	CH_3	1.0	"	21.1a)	"	5.0	6b	84
4c	C_2H_5	0.5	"	8.2	"	5.0	6c	83
4d	n-C_3H_7	0.5	"	8.2	"	5.0	6d	94
4e	n-C_4H_9	1.0	"	15.4	"	3.0	6e	95
4a	H	1.0	p-Anisidine	15.0	187	5.0	7a	39
4b	CH_3	1.0	"	15.2b)	"	5.0	7b	83
4c	C_2H_5	1.0	"	13.5	185	5.0	7c	94
4d	n-C_3H_7	0.5	"	6.4	"	7.0	7d	77
4e	n-C_4H_9	1.0	"	13.8	"	6.0	7e	95
4a	H	1.0	3,5-Xylidine	9.8b)	190	7.0	8a	40
4b	CH_3	1.0	"	9.8b)	"	6.0	8b	99
4c	C_2H_5	0.5	"	9.8b)	"	7.0	8c	86
4d	n-C_3H_7	0.5	"	9.8b)	"	7.0	8d	55
4e	n-C_4H_9	1.0	"	9.8b)	"	7.0	8e	87
4a	H	1.0	p-Aminoazo-benzene	5.0c)	233	6.0	9a	46
4b	CH_3	1.0	"	5.0c)	"	6.0	9b	63
4c	C_2H_5	1.0	"	5.0d)	283	5.0	9c	43
4d	n-C_3H_7	1.0	"	5.0c)	233	6.0	9d	47
4e	n-C_4H_9	1.0	"	5.0d)	288	6.0	9e	51
4a	H	1.0	o-Phenylene-diamine	3.7	180	4.0	10a	61
4b	CH_3	1.0	"	3.5	"	4.0	10b	81

a) Added with 3.8 g of Acetic anhydride. b) Added with 16.4 g of DMF.
c) Added with 50 ml of Quinoline. d) Added with 15 g of Diphenylene oxide.

Table 2 Properties of Unsymmetrical PTCI

Unsymmetrical PTCI			λmax[b] (nm)	IR(KBr, cm^{-1})		MS Spectra (M^+, m/e)	Color[c]
	R	Ar		C=O (Imide)	C-H (Phenyl)		
5a	H		599	1701 1652	694	466	Red
5b	CH_3	"	598	1692 1652	699	480	Dark reddish violet
5c	C_2H_5	"	600	1698 1665	695	494	Red
5d	n-C_3H_7	"	600	1701 1660	697	508	Red
5e	n-C_4H_9	"	600	1703 1656	695	522	Red
6a	H		599	1700 1672	801 779	480	Dark violet
6b	CH_3	"	599	1696 1655	792 771	494	Dark red
6c	C_2H_5	"	601	1702 1656	804 770	508	Reddish violet
6d	n-C_3H_7	"	602	1701 1660	789 767	522	Reddish violet
6e	n-C_4H_9	"	602	1703 1659	798 785	536	Reddish violet
7a	H		598	1690 1660 1256[a]	800 779	496	Dark violet
7b	CH_3	"	599	1694 1658 1256[a]	795 771	510	Dark red
7c	C_2H_5	"	602	1699 1658 1247[a]	795 768	524	Dark violet
7d	n-C_3H_7	"	602	1698 1657 1243[a]	794	538	Dark violet
7e	n-C_4H_9	"	602	1698 1656 1242[a]	796 778	552	Dark violet
8a	H		600	1700 1661	799 682	494	Red
8b	CH_3	"	600	1702 1661	798 680	508	Dark red
8c	C_2H_5	"	602	1705 1666	805 686	522	Dark red
8d	n-C_3H_7	"	602	1701 1666	799 681	536	Dark red
8e	n-C_4H_9	"	602	1700 1664	796 680	550	Dark red
9a	H		602	1691 1653	768 687	570	Gray
9b	CH_3	"	598	1703 1661	770 689	584	Dark reddish violet
9c	C_2H_5	"	600	1700 1658	770 689	598	Dark violet
9d	n-C_3H_7	"	599	1697 1657	768 685	612	Dark red
9e	n-C_4H_9	"	600	1702 1660	770 688	625	Dark violet
10a	H		621	1705 1670	750	463	Dark violet
10b	CH_3		626	1710 1670	755	477	Gray

a) C-O(Ether). b) Solvent: Conc. H_2SO_4. c) One g of finely powdered pigment, 2 g of Titanium dioxide, and 2 ml of Boiled Oil were mixed by a maller. The mixture was painted on a paper, then the Color was observed.

For example, 5a was prepared as follows. To a three necked flask were added 39.6 g of aniline and 1.0 g of 4a. The flask was heated at 181 °C for 6.5 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 into 1% hot potassium hydroxide solution and filtered to remove unchanged 4a. The precipitate was washed with methanol and dried. Reddish violet powder of 5a was obtained(32% of yield). 5b-e were prepared by the same treatment of 4b-e with aniline. 6a-e, 7a-e, 8a-e, and 9a-e were similarly prepared by the reaction of 4a-e with p-toluidine, p-anisidine, 3,5-xylidine, p-aminoazobenzene, respectively. These reaction conditions are listed in Table 1 .

In comparison with the reaction with alkylamines, more drastic conditions were necessary for the reaction with arylamines. The basicities of arylamines (pka, aniline;4.58¹¹⁾, p-toluidine;5.08¹²⁾, p-anisidine;5.34¹²⁾, o-phenylenediamine;4.47¹³⁾) are lower than those of alkylamines, and the reaction with aniline under drastic conditions gave low yield of PTCI than with p-toluidine. Then effect in reactivity due to basicity of amine wouldbe expected.

The properties of unsymmetrical PTCI and symmetrical PTCI were compared. IR spectra of unsymmetrical PTCI(5-9) showed the bands at 1690-1705 and 1650-1670 cm^{-1} (C=O of imide). Symmetrical PTCI (2 and 3) showed the bands at 1695-1710 and 1655-1690 cm^{-1}(C=O of imide). Absorption spectra of unsymmetrical PTCI(5-9) showed the λmax at 598-602 nm. In symmetrical PTCI, 3a-e showed the λmax at 596-597 nm and 2 showed λmax at 600-606 nm. N-substituted alkyl or aryl group gave only a small influence on bands of C=O or λmax. The colors of many unsymmetrical PTCI were reddish like those of symmetrical PTCI. Most of the unsymmetrical PTCI were not melted or decomposed by heating until 400 °C in air, and some of Unsymmetrical PTCI showed a very clear color, then the detailed test for pigments are now in progress.

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