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Synthesis and Properties of *N*-Alkylbromoperylene-3,4-dicarboximides

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ABSTRACT

N-*Alkyl-9-bromoperylene-3,4-dicarboximides (alkyl = methyl, ethyl, propyl, butyl, hexyl and octyl) were prepared by the bromination of the corresponding* N-*alkyl-3,4-perylenedicarboximides with bromine; the properties of these pigments are described. Ullmann reaction of the bromoperylenedicarboximides (alkyl = ethyl, propyl and butyl) with copper bronze gave the corresponding biperylene derivatives.*

INTRODUCTION

Derivatives of 3,4:9,10-perylenetetracarboxylic dianhydride and di-imide have important semiconductive and photoconductive properties,[1] in addition to their utilization as colorants. In previous papers, the syntheses and properties of some di-imide derivatives have been reported.[2,3] Recently, some applications of these compounds in Langmuir–Blodgett films have been reported.[4,5]

In this present paper, the bromination of *N*-alkyl-3,4-perylenedicarboximides (**1a**–**1g**) was carried out, and the properties as pigments of the resulting monobromo derivatives evaluated. Ullmann reaction of the monobromo derivatives was then carried out to prepare the biperylene derivatives.

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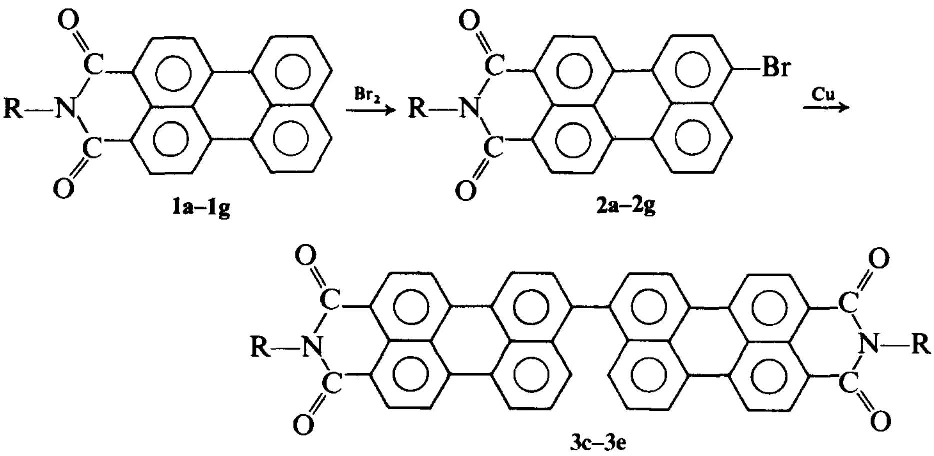


a: $R = H$
b: $R = CH_3$
c: $R = CH_2CH_3$
d: $R = (CH_2)_2CH_3$
e: $R = (CH_2)_3CH_3$
f: $R = (CH_2)_5CH_3$
g: $R = (CH_2)_7CH_3$

Scheme 1

RESULTS AND DISCUSSION

Bromination of *N*-Alkyl-3,4-perylenedicarboximides (1a–1g)

Bromination of perylene gives 3,9- and 3,10-dibromoperylene.[6,7] 3,4-Perylenedicarboximide undergoes sulfonation at the 9-position with sulfuric acid.[8]

The bromination of *N*-alkyl-3,4-perylenedicarboximides (**1a–1g**) with bromine in chlorobenzene gave the corresponding monobromo-*N*-alkyl-3,4-perylenedicarboximides (**2a–2g**) (Scheme 1). The reaction conditions and

TABLE 1
Bromination of *N*-Alkyl-3,4-perylenedicarboximide (**1a–1g**)

Compound			Mole ratio Br_2/**1a–1g**	Solvent chlorobenzene (*ml*)	Temp. (°*C*)	Time (*h*)	Yield of **2a–2g** (%)
	R	(*g*)					
1a	H	0·50	8	200	55	3·5	29
1b	CH_3	0·25	20	600	55	3·5	85
1c	CH_2CH_3	0·50	4	150	55	2·7	77
1d	$(CH_2)_2CH_3$	1·00	4	500	55	4·5	83
1e	$(CH_2)_3CH_3$	1·00	4	500	55	5·5	75
1f	$(CH_2)_5CH_3$	1·00	4	500	55	6·5	81
1g	$(CH_2)_7CH_3$	0·50	4	250	55	7·5	87

the yields of the monobromo-substituted products (**2a**–**2g**) are shown in Table 1. Under the reaction conditions shown in the table, the 3,4-perylene-dicarboximides gave the monobromo compounds. Using a higher mole ratio of bromine and a longer reaction time, polybromo-substituted compounds were obtained. The unsubstituted 3,4-perylene-dicarboximide (**1a**) gave the monobromo derivative (**2a**) only in a low yield, probably in view of its low solubility in chlorobenzene. Bromination of *N*-methyl-3,4-perylene-dicarboximide (**1b**), despite of its low solubility, gave the monobromo derivative (**2b**) in high yield when a large soluent volume was used. The other *N*-alkyl-3,4-perylenedicarboximides (**1c**–**1g**) gave the monobromo derivatives (**2c**–**2g**) in good yields.

Properties of bromoperylene-3,4-dicarboximide

Table 2 gives analytical and spectral data for the *N*-alkylbromoperylene-3,4-dicarboximides (**2a**–**2g**). The mass spectra data of the bromo derivatives confirm the molecular ion peak corresponding to a monobromo derivative and elemental analysis data are consistent with this. The visible spectra of the compounds in conc. sulfuric acid show λ_{max} at 630 nm.

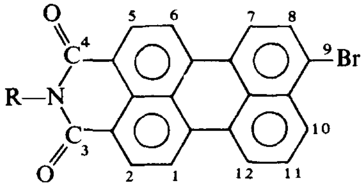
The substitution position of the bromine atom in the monobromo derivatives was assigned from ^{1}H-NMR spectra data of bromoperylene-3,4-dicarboximide and related compounds. The spectra were measured in

TABLE 2
Analytical and Spectral Data for Bromoperylene-3,4-dicarboximides (**2a**–**2g**)

	Compound R	λ_{max} *(in H_2SO_4) (nm)*	*IR (KBr)* $\nu_{C\ O}$ *(cm^{-1})*	*MS (m/e) (M^+)*	*Analysis (%): found (Calcd)* C	H	N	*M.p. (°C)*
2a	H	629	1 640	399 401	66·09	2·52	3·47	>300
			1 680		(66·02	2·52	3·56)	
2b	CH_3	630	1 642	413 415	65·46	2·73	3·19	>300
			1 684		(66·69	2·92	3·38)	
2c	CH_2CH_3	630	1 642	427 429	67·19	3·26	3·03	309–311
			1 682		(67·31	3·29	3·27)	
2d	$(CH_2)_2CH_3$	630	1 642	441 443	67·91	3·50	3·07	297–298
			1 682		(67·89	3·65	3·17)	
2e	$(CH_2)_3CH_3$	630	1 640	455 457	68·11	3·87	3·07	287–289
			1 682		(68·43	3·98	3·07)	
2f	$(CH_2)_5CH_3$	630	1 640	483 485	69·43	4·58	2·89	254·5–256
			1 680		(69·05	4·38	2·86)	
2g	$(CH_2)_7CH_3$	630	1 640	511 513	70·34	5·16	2·71	220–223
			1 680		(70·32	5·11	2·73)	

TABLE 3

^{1}H NMR Spectra Data for Bromoperylene-3,4-dicarboximide and Related Compounds



Compound	*Chemical shift (ppm)*	*Position assigned*
Bromoperylene-3,4-dicarboximide	7·72 (1H, t)	11
$R=(CH_2)_7CH_3$	7·92 (1H, d)	8
	8·16 (1H, d)	10
	8·32–8·60 (6H, m)	1. 2, 5, 6, 7, 12
3,4-Perylenedicarboximide	7·55 (2H, t)	8, 11
$R=(CH_2)_7CH_3$	7·88 (2H, d)	9. 10
	8·20–8·50 (6H, m)	1, 2, 5, 6, 7, 12
Perylene	7·45 (4H, t)	2, 5, 8, 11
	7·70 (4H, d)	3, 4, 9, 10
	8·22 (4H, d)	1, 6, 7, 12
3,10-Dibromoperylene	7·62 (2H, t)	5, 8
	7·78 (2H, d)	2, 11
	8·00 (2H, d)	4, 9
	8·15 (2H, d), 8·35 (2H, d)	1, 6, 7, 12
3,9-Dibromoperylene	7·65 (2H, t)	5, 11
	7·82 (2H, d)	2, 8
	8·03 (2H, d)	4, 10
	8·18 (2H, d), 8·36 (2H, d)	1, 6, 7, 12

DMSO-d_6 at 150°C. Table 3 gives the chemical shifts of the perylene ring system of N-octylbromoperylene-3,4-dicarboximide (**2f**) and related compounds such as octyl-3,4-perylenedicarboximide (**1f**), perylene, 3,9-dibromoperylene and 3,10-dibromoperylene. The chemical shifts of the protons for perylene were observed at 7·45(t) and 7·70(d) ppm for the 2,5,8,11 and 3,4,9,10 positions, respectively. 3,10-dibromoperylene and 3,9-dibromoperylene showed proton chemical shifts at similar positions, viz: at 7·62(t), 7·78(d), 8·00(d) ppm and at 7·65(t), 7·82(d), 8·03(d) ppm, respectively. The chemical shifts of the protons at the unsubstituted positions of the naphthalene moiety were at 7·55(t) and 7·88(d) for 3,4-perylenedicarboximide (**1f**), i.e. only slightly shifted with respect to perylene, and at 7·72(t), 7·92(d), 8·16(d) for bromoperylene-3,4-dicarboximide (**2f**). The differences in the shifts for those positions comparing perylene and 3,10-

TABLE 4
Some Properties of Perylenedicarboximides and Bromoperylene-dicarboximides as Pigments

	Compound R	*Color*	*Tinting strength*[a] *(%)*	*Lightfastness*[b]
1b	CH_3	Light brown	38·4	5
1d	$(CH_2)_2CH_3$	Brown	60·8	4
1e	$(CH_2)_3CH_3$	Orange	55·6	5
1f	$(CH_2)_5CH_3$	Brown	34·5	5
1g	$(CH_2)_7CH_3$	Brown	56·3	4
2d	$(CH_2)_2CH_3$	Orange	78·3	7
2e	$(CH_2)_3CH_3$	Orange	69·9	4
2f	$(CH_2)_5CH_3$	Yellow	57·6	4
2g	$(CH_2)_7CH_3$	Yellow	59·9	3

[a] Reflectance maximum – minimum on spectral reflectance curves.
[b] Grades 1–8 of the Blue Scale.

dibromoperylene or 3,9-dibromoperylene are similar to those comparing 3,4-perylenedicarboximide and bromoperylene-3,4-dicarboximide, and on this basis, it is reasonable to assume that the substitution position is the same as in the case of 3,9-dibromoperylene or 3,10-dibromoperylene.

Table 4 shows the color, tinting strength and lightfastness of the bromoperylenedicarboximides and perylenedicarboximides. The bromoperylenedicarboximides are yellowish orange, and have higher tinting strength and similar lightfastness compared with the perylene-di-carboximides.

Ullmann reaction of bromoperylene-3,4-dicarboximide

Ullmann reaction of the *N*-alkyl-9-bromoperylene-3,4-dicarboximides (**2c**–**2e**), using copper bronze in absence of solvent gave the corresponding biperylene derivatives (**3c**–**3e**) (Scheme 1). Table 5 shows the reaction

TABLE 5
Ullmann Reaction of Bromoperylene-3,4-dicarboximide

Compound			*Cu (g)*	*Temp. (°C)*	*Time (h)*	*Yield of* **3c–3e** *(%)*
	R	(g)				
2c	CH_2CH_3	1·00	10·0	300	9·5	37
2d	$(CH_2)_2CH_3$	0·20	2·0	290	9	44
2e	$(CH_2)_3CH_3$	0·20	2·0	280	9	43

conditions used and the yields obtained. The mass spectra of the products confirmed the molecular ion peak as corresponding to the biperylene derivatives. The visible spectra of the compounds in conc. sulfuric acid showed λ_{max} at 652 nm.

Under similar conditions, the *N*-substituted bromoperylene-3,4-dicarboximide having higher alkyl groups gave the biperylene derivatives in poor yield. Neither the *N*-unsubstituted nor the *N*-methyl-9-bromoperylene-3,4-dicarboximide (**2a, 2b**) gave biperylene derivatives.

EXPERIMENTAL

3,9-Dibromoperylene, 3,10-dibromoperylene and 3,4-perlylene-dicarboximides **1a**–**1g** were prepared as previously described,[7,9] Copper bronze was prepared by the method of Kleiderer & Adams.[10]

IR and visible spectra were measured on a Hitachi 260-50 spectrometer and Jasco Uvidec-610 spectrometer, respectively. NMR spectra were recorded using a JEOL JNM-FX100 and mass spectra were determined using a JEOL VMS-V300.

The tinting strength and lightfastness of the pigments were evaluated according to previously described procedures.[2]

Bromination of 3,4-perylenedicarboximide (1a–1g)

The compound **2d** was prepared as follows: 1·0 g of **1d** was dissolved in 500 ml of chlorobenzene with slight warming. After cooling to 55°C, 1·8 g (4 mol. equiv.) of bromine was added dropwise and the mixture stirred at 55°C for 4·5 h. Chlorobenzene and residual bromine were removed *in vacuo* and the residue, after recrystallization from chlorobenzene–benzene (3:1), gave 1·0 g of **2d**. The other bromo derivatives were obtained by a similar method, using the conditions shown in Table 1. Solvents used for recrystallization were chlorobenzene for the unsubstituted and *N*-methyl derivatives, DMSO for the *N*-ethyl derivative, and acetic anhydride–benzene (2:1 and 3:1) for the *N*-hexyl and *N*-octyl derivatives.

Ullmann reaction of bromoperylene-3,4-dicarboximide

A mixture of 1·0 g of **2c** and 10·0 g of copper bronze was heated at 300°C for 9·5 h. The mixture was cooled, powdered and extracted with chloroform. The extract was evaporated to remove chloroform and the residue was sublimed at 350°C (1–2 mm Hg) to remove **1c**; 0·45 g (55%) of **3c** was obtained as the residue.

3d and **3e** were prepared by a similar method using the conditions shown in Table 5.

3c: IR(KBr) $\nu_{C=O}$ 1640, 1690 cm^{-1}; λ_{max} 652 nm; MS (*m/e*) 697 (M$^+$).
3d: IR(KBr) $\nu_{C=O}$ 1640, 1682 cm^{-1}: λ_{max} 652 nm; MS (*m/e*) 725 (M$^+$).
3e: IR(KBr) $\nu_{C=O}$ 1644, 1684 cm^{-1}; λ_{max} 652 nm; MS (*m/e*) 753 (M$^+$).

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