Carbazoledioxazines Having Long Alkyl Groups 1. Synthesis of Carbazoledioxazines with Linear Type Structure

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Carbazoledioxazines with linear type structure (5,15-dialkyl-8,18-dichloro-5,15-dihydrodiindolo[3,2-*b*:3',2'-*m*]triphenodioxazine) were selectively synthesized by demethanolation ring closure of 2,5-bis(2-methoxy-9-alkyl-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone in a high boiling solvent. The structure has been confirmed by ^{1}H-nmr and X-ray crystallography.

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Carbazoledioxazine is a representative compound of dioxazine pigments. It shows a purple color and has excellent characteristics as a high performance organic pigment [1]. Recently, it was applied to optical recording material, organic photo-conductor, *etc.* [2].

In Scheme 1, carbazoledioxazine is usually obtained by dehydrogenation ring closure of the precursor **C** in the presence of a ring closure agent, and the structure has been exhibited as a linear type structure **A**. However, it is considered that the dehydrogenation reaction of **C** forms **A** or an angular type structure **B**. The structure has never been confirmed by structure determinating procedures, because of its poor solubility in organic solvents [3,4]. We now report that soluble carbazoledioxazines having long alkyl groups were synthesized by demethanolation ring closure of the precursors (**6**) having methoxy groups (Scheme 2) in a high boiling solvent, and their structures and properties were determined.

Results and Discussion.

Carbazoledioxazines (**7**) having long alkyl groups (R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$ and $C_{18}H_{37}$) were synthesized in six steps from 2-hydroxycarbazole (**1**) as the starting material. The synthetic route is shown in Scheme 2. 2-Methoxycarbazole (**2**) was prepared according to the literature [5]. *N*-Alkylation of **2** with *n*-alkyl bromide in the presence of a phase transfer catalyst such as benzyltriethylammonium chloride (BTEAC) gave **3** in good yield [6]. Compound **4** was obtained on nitration of **3** with nitric acid [7], and reduction of **4** with iron powder and hydrochloric acid yielded 9-alkyl-2-methoxy-3-aminocarbazole (**5**). Condensation of **5** with chloranil afforded the precursor **6** [8]. The structures of intermediates **2-6** were confirmed by ^{1}H-nmr, ir spectra and elemental analysis. Especially, the ^{1}H-nmr of **4** showed the signal due to the isolated aromatic protons of positions 1 and 4 of the carbazole ring. These results are summarized in Table 1.

It is known that thermal treatment of the precursor of triphenodioxazine (TPDO) having a methoxy group in a

Scheme 1

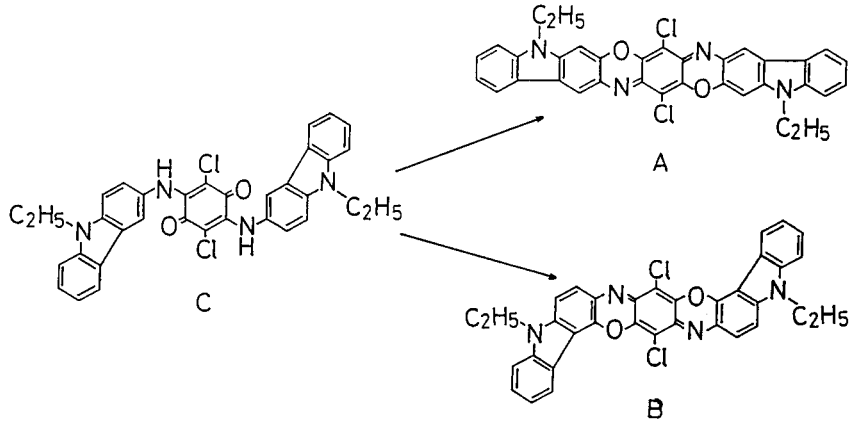


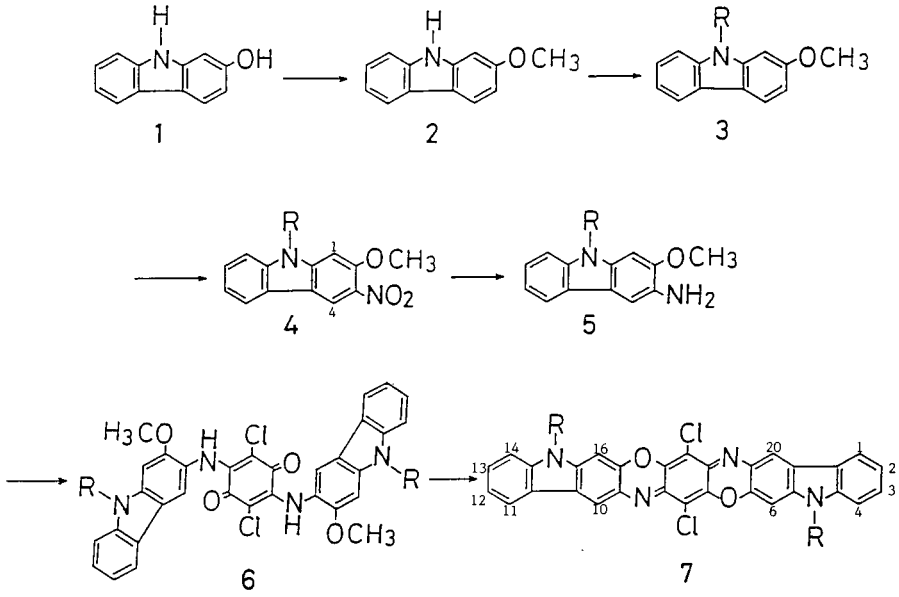
Table 1

Physical, Analytical and Spectroscopic Data for Intermediates **3-6**

Compound	R n	Yield (%)	mp (°C)	^{1}H-NMR δ(ppm)	Molecular Formula	Elemental Analysis % (C/F) C	H	N
3a	8	53	37-38	(carbon tetrachloride):0.57-2.12 (m, 15H, C_7H_{15}), 3.80 (s, 3H, CH_3), 4.09 (t, 2H, CH_2), 6.52-7.83 (m, 7H, aromatic)	$C_{21}H_{27}NO$	81.51 81.15	8.80 8.76	4.53 4.37
3b	10	43	40-41	(carbon tetrachloride): 0.65-2.10 (m, 19H, C_9H_{19}), 3.85 (s, 3H, CH_3), 4.15 (t, 2H, CH_2), 6.65-7.93 (m, 7H, aromatic)	$C_{23}H_{31}NO$	81.85 81.74	9.26 9.03	4.15 4.06
3c	12	67	36-37	(carbon tetrachloride): 0.68-2.10 (m, 23H, $C_{11}H_{23}$), 3.80 (s, 3H, CH_3), 4.13 (t, 2H, CH_2), 6.64-7.83 (m, 7H, aromatic)	$C_{25}H_{35}NO$	82.14 81.86	9.65 9.42	3.83 3.77
3d	18	82	61-62	(carbon tetrachloride): 0.68-2.10 (m, 35H, $C_{17}H_{35}$), 3.92 (s, 3H, CH_3), 4.22 (t, 2H, CH_2), 6.70-8.16 (m, 7H, aromatic)	$C_{31}H_{47}NO$	82.51 82.79	10.33 10.54	3.11 3.12
4a	8	40	73-74	(carbon tetrachloride): 0.62-2.20 (m, 15H, C_7H_{15}), 3.93 (s, 3H, CH_3), 4.10 (t, 2H, CH_2), 6.67 (s, 1H, aromatic), 6.93-7.38 (m, 3H, aromatic), 7.65-7.87 (m, 1H, aromatic), 8.31 (s, 1H, aromatic)	$C_{21}H_{26}N_2O_3$	71.16 71.04	7.39 7.34	7.91 7.75
4b	10	26	84-85	(carbon tetrachloride): 0.63-2.17 (m, 19H, C_9H_{19}), 3.91 (s, 3H, CH_3), 4.10 (t, 2H, CH_2), 6.60 (s, 1H, aromatic), 7.00-7.33 (m, 3H, aromatic), 7.63-7.87 (m, 1H, aromatic), 8.30 (s, 1H, aromatic)	$C_{23}H_{30}N_2O_3$	72.22 72.11	7.91 7.86	7.33 7.17
4c	12	56	74-75	(carbon tetrachloride): 0.71-2.08 (m, 23H, $C_{11}H_{23}$), 3.93 (s, 3H, CH_3), 4.14 (t, 2H, CH_2), 6.67 (s, 1H, aromatic), 7.08-7.40 (m, 3H, aromatic), 7.68-7.96 (m, 1H, aromatic), 8.40 (s, 1H, aromatic)	$C_{25}H_{34}N_2O_3$	73.14 73.05	8.35 8.22	6.83 6.66
4d	18	58	78-79	(deuteriochloroform): 0.68-2.14 (m, 35H, $C_{17}H_{35}$), 3.97 (s, 3H, CH_3), 4.18 (t, 2H, CH_2), 6.70 (s, 1H, aromatic), 7.06-7.38 (m, 3H, aromatic), 7.70-7.97 (m, 1H, aromatic), 8.47 (s, 1H, aromatic)	$C_{31}H_{46}N_2O_3$	75.26 75.04	9.37 9.09	5.66 5.68
5a	8	52	89-90	(carbon tetrachloride): 0.70-2.10 (m, 15H, C_7H_{15}), 3.48 (br, 2H, NH_2), 3.92 (s, 3H, CH_3), 4.08 (t, 2H, CH_2), 6.60 (s, 1H, aromatic), 6.95-7.22 (m, 4H, aromatic), 7.53-7.80 (m, 1H, aromatic)	$C_{21}H_{28}N_2O$		[b]	
5b	10	64	80-82	(carbon tetrachloride): 0.68-2.11 (m, 19H, C_9H_{19}), 3.43 (br, 2H, NH_2), 3.88 (s, 3H, CH_3), 4.07 (t, 2H, CH_2), 6.56 (s, 1H, aromatic), 6.91-7.27 (m, 4H, aromatic), 7.56-7.82 (m, 1H, aromatic)	$C_{23}H_{32}N_2O$		[b]	
5c	12	54	86-87	(carbon tetrachloride): 0.66-2.04 (m, 23H, $C_{11}H_{23}$), 3.30 (br, 2H, NH_2), 3.90 (s, 3H, CH_3), 4.17 (t, 2H, CH_2), 6.61 (s, 1H, aromatic), 6.97-7.31 (m, 4H, aromatic), 7.65-7.88 (m, 1H, aromatic)	$C_{25}H_{36}N_2O$		[b]	
5d	18	62	95-97	(deuteriochloroform): 0.61-2.08 (m, 35H, $C_{17}H_{35}$), 3.02 (br, 2H, NH_2), 3.99 (s, 3H, CH_3), 4.22 (t, 2H, CH_2), 6.80 (s, 1H, aromatic), 7.20-7.51 (m, 4H, aromatic), 7.79-8.03 (m, 1H, aromatic)	$C_{31}H_{48}N_2O$		[b]	
6a	8	74	203 [a]	(deuteriochloroform): 0.68-2.17 (m, 30H, C_7H_{15}), 4.00 (s, 6H, CH_3), 4.24 (t, 4H, CH_2), 6.82 (s, 2H, aromatic), 7.12-7.57 (m, 6H, aromatic), 7.80 (s, 2H, aromatic), 8.05 (d, 2H, aromatic), 8.62 (s, 2H, NH)	$C_{48}H_{54}N_4O_4Cl_2$	70.14 69.95	6.62 6.68	6.82 6.63
6b	10	74	84 [a]	(deuteriochloroform): 0.60-2.10 (m, 38H, C_9H_{19}), 3.98 (s, 6H, CH_3), 4.25 (t, 4H, CH_2), 6.79 (s, 2H, aromatic), 6.98-7.45 (m, 6H, aromatic), 7.72 (s, 2H, aromatic), 7.95 (d, 2H, aromatic), 8.52 (s, 2H, NH)	$C_{52}H_{62}N_4O_4Cl_2$	71.13 70.90	7.12 7.05	6.38 6.63
6c	12	84	86 [a]	(deuteriochloroform): 0.72-2.08 (m, 46H, $C_{11}H_{23}$), 3.97 (s, 6H, CH_3), 4.24 (t, 4H, CH_2), 6.76 (s, 2H, aromatic), 7.18-7.43 (m, 6H, aromatic), 7.76 (s, 2H, aromatic), 7.93 (d, 2H, aromatic), 8.53 (s, 2H, NH)	$C_{56}H_{70}N_4O_4Cl_2$	72.00 71.86	7.55 7.54	6.00 5.90
6d	18	79	98 [a]	(deuteriochloroform): 0.76-2.20 (m, $C_{17}H_{35}$, 70H), 3.96 (s, CH_3, 6H), 4.24 (t, 4H, CH_2), 6.76 (s, 2H, aromatic), 7.03-7.38 (m, 6H, aromatic), 7.70 (s, 2H, aromatic), 7.92 (d, 2H, aromatic), 8.52 (s, 2H, NH)	$C_{68}H_{94}N_4O_4Cl_2$	74.08 74.21	8.60 8.40	5.08 4.97

[a] Measured by TG-DTA under nitrogen atomosphere. [b] Compound **5** could not be dertemined by elemental analysis for their instability.

Scheme 2



high boiling solvent gave TPDO by demethanolation [9]. Compound **7** was obtained by demethanolation ring closure of **6** in 1-chloronaphthalene. Owing to introduction of the long alkyl groups, **7** became soluble in organic solvents and it made it possible to purify **7** by column chromatography and recrystallization. The carbonyl and imino stretching absorption disappeared in the ir spectra of **7**. The mass and elemental analyses were consistent with their molecular formula. The ^{1}H-nmr spectrum of **7a** indicated that the two isolated aromatic protons of the 6,16 and the 10,20 positions are singlets at δ 7.10 and 8.26 ppm, respectively. Compound **7a** formed reddish brown prisms from chloroform on evaporation. The single crystal of the pigment in this series was obtained for the first time. An ORTEP drawing of **7a** is shown in Figure 1 and the crystal data are listed in Table 2.

Table 2
Crystal Data of **7a**

Formula	$C_{48}H_{46}N_4O_2Cl_2$
Molecular weight	757.80
Space group	$P2_1/a$
a, Å	15.916(3)
b, Å	25.563(6)
c, Å	4.702(2)
β, deg.	94.12 (2)
Z	2
Dc, gcm^{-3}	1.319
μ, cm^{-1}	2.20
T, ° K	293
2Θ range, deg.	<55
Observed reflections with $F > 3\sigma(F)$	1743
R	0.13

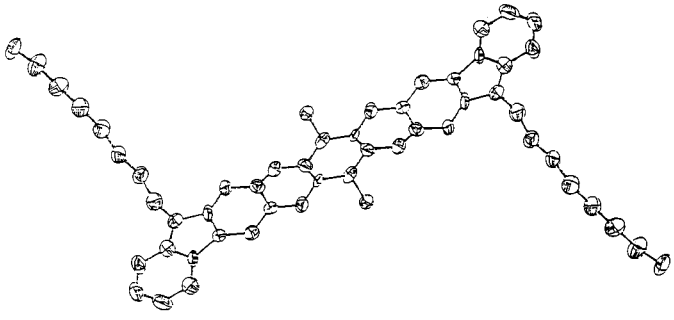


Figure 1. An ORTEP drawing of the molecule with 50% probability ellipsoids [10].

The properties of **7** are summarized in Tables 3 and 4.

Introduction of the long alkyl groups to **7** results in high solubility in haloalkane and aromatic solvents. The melting points lower in proportion to the length of the alkyl groups, while electric absorption spectra of **7a-d** are almost unchanged.

Further investigation on the synthesis of carbazoledioxazines with an angular type structure are in progress.

Table 3
Physical and Analytical Data of Carbazoledioxazines 7

Compound	R n	Yield (%)	mp (°C)	Solubility [b] (mol/l)	Molecular Formula	Molecular Weight	Elemental Analysis % (C/F) C	H	N
7a	8	12	343	2×10^{-4}	$C_{46}H_{46}N_4O_2Cl_2$	757.80	72.91 72.98	6.12 6.10	7.40 7.32
7b	10	18	306	2×10^{-3}	$C_{50}H_{54}N_4O_2Cl_2$	813.87	73.78 73.64	6.69 6.65	6.89 6.69
7c	12	13	277	1×10^{-3}	$C_{54}H_{62}N_4O_2Cl_2$	869.98	74.55 74.63	7.18 7.21	6.44 6.32
7d	18	7	236	2×10^{-4}	$C_{66}H_{86}N_4O_2Cl_2$	1038.29	76.34 76.25	8.35 8.24	5.40 5.31

[a] Measured by TG-DTA under nitrogen atmosphere. [b] Measured in chloroform at 30°.

Table 4
Spectroscopic Data of Carbazoledioxazines 7

Compound	MS (Mz/M⁺)	UV-VIS (chloroform) (λ max/log ε)				^{1}H-NHR (deuteriochloroform) δ (ppm)
7a	756	602 5.01	557 4.80	317 4.60	272 4.68	0.87 (t, CH_3), 1.11-1.60 (m, C_5H_{10}), 1.86 (m, CH_2), 4.19 (t, CH_2), 7.10 (s, CH-6 and 16), 7.19-7.52 (m, aromatic), 8.02 (d, CH-1 and 11), 8.26 (s, CH-10 and 20)
7b	812	602 5.05	557 4.85	317 4.64	272 4.71	0.87 (t, CH_3), 1.18-1.43 (m, C_7H_{14}), 1.82 (m, CH_2), 4.10 (t, CH_2), 7.00 (s, CH-6 and 16), 7.18-7.39 (m, aromatic), 7.98 (d, CH-1 and 11), 8.20 (s, CH-10 and 20)
7c	868	602 5.04	557 4.84	317 4.64	272 4.72	0.87 (t, CH_3), 1.08-1.54 (m, C_9H_{18}), 1.82 (m, CH_2), 4.10 (t, CH_2), 7.02 (s, CH-6 and 16), 7.08-7.55 (m, aromatic), 7.99 (d, CH-1 and 11), 8.20 (s, CH-10 and 20)
7d	—	602 5.01	558 4.81	317 4.63	272 4.70	0.87 (t, CH_3), 1.10-1.45 (m, $C_{15}H_{30}$), 1.80-1.90 (m, CH_2), 4.06-4.18 (m, CH_2), 7.07 (s, CH-6 and 16), 7.20-7.43 (m, aromatic), 8.01 (d, CH-1 and 11), 8,23 (s, CH-10 and 20)

EXPERIMENTAL

Melting points were determined on a Rigaku TG-DTA. The ir, mass, electronic absorption spectra were measured with a JASCO IR-A2, a Shimazu QP-1000, and a Shimazu UV-2100 spectrometers, respectively. The ^{1}H-nmr spectra were recorded with a JEOL PMX60Si, a JEOL FX90Q and a BRUKER AM400 with TMS as the internal standard.

X-Ray Structure Determination of **7a**.

A crystal of dimensions 0.6 x 0.15 x 0.15 mm was mounted on a Rigaku AFC-5 diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). Intensity was measured by the θ-2θ scan technique. The structure was solved by the direct method (MULTAN84). Block-diagonal least-squares refinement with anisotropic thermal parameters for non-H atoms was converged to R = 0.13 because of rather poor crystallinity for accurate analysis. Scattering factors from International Tables for X-Ray Crystallography [11]. Computations were performed using a Panafacom U-1200 II A with the Rigaku RASA-P5 program package system.

2-Methoxycarbazole **2**.

Compound **2** was prepared according to literature [6], colorless plates, mp 238-239° (lit mp 236°).

2-Methoxy-9-octadecylcarbazole **3d**.

1-Bromo octadecane (15 g, 45 mmoles) was added dropwise to a mixture of **2** (5.9 g, 30 mmoles) and BTEAC (0.40 g, 1.1 mmoles) as a phase transfer catalyst in benzene (20 ml) and 50% aqueous sodium hydroxide (95 ml), then the mixture was vigorously stirred for 5 hours at 40-50°. The product was extracted with benzene, the organic layer was washed with dilute hydrochloric acid and water, dried over magnesium sulfate and concentrated *in vacuo* to give a viscous oil. It was recrystallized from *n*-hexane at −78° to give **3d** (12 g, 82%) as colorless needles, mp 57-58°; ir (potassium bromide): 2920, 2847, (ν CH_2).

2-Methoxy-3-nitro-9-octadecylcarbazole **4d**.

Nitric acid (1.2 ml, d = 1.42) in acetic acid (90 ml) was added dropwise to a solution of **3d** (8.0 g, 17 mmoles) in acetic acid (90 ml) at 15° with stirring for 1 hour. Dichloromethane (200 ml) was added to the reaction mixture, and organic layer was washed with water. The solution was dried over magnesium sulfate and concentrated *in vacuo* to give a green oil, which was chromatographed on silica gel using benzene. The fraction was recrystallized from *n*-hexane to give yellow powder (5.1 g, 58%), mp 78-79°; ir (potassium bromide): 1522, 1347 (ν NO_2).

3-Amino-2-methoxy-9-octadecylcarbazole **5d**.

Iron powder (11 g atom), water (15 ml) and concentrated hydrochloric acid (3.0 ml) was stirred at 40° under nitrogen atmosphere for 30 minutes. A solution of **4d** (4.8 g, 9.7 mmoles) in ethanol (92 ml) was added and refluxed for 3 hours. The mixture was neutralized by sodium carbonate and filtered while still hot, the

filtrate was diluted with water. The precipitate was filtered, washed with water and recrystallized from *n*-hexane to give a colorless powder (2.8 g, 62%), mp 95-97°; ir (potassium bromide): 3440, 3350 (ν NH_2).

2,5-Bis(2-methoxy-9-octadecyl-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone **6d**.

A mixture of **5d** (2.6 g, 5.6 mmoles), chloranil (0.69 g, 2.8 mmoles) and sodium acetate (4.6 g, 56 mmoles) in ethanol (50 ml) was refluxed for 6 hours. The precipitate was filtered and washed with dilute hydrochloric acid, water and ethanol. The residue was chromatographed on silica gel eluting with benzene and the fraction was recrystallized from *n*-hexane:benzene (15:2) to give a dark brown powder (2.4 g, 79%); mp 74°; ir (potassium bromide): 3260 (ν NH), 1655 (ν C=O).

8,18-Dichloro-5,15-dihydro-5,15-dioctadecyldiindolo[3,2-*b*:3',2'-*m*]triphenodioxazine **7d**.

A solution of **6d** (0.70 g, 0.64 mmoles) in 1-chloronaphthalene (10 ml) was heated at 220° for 7 hours under nitrogen atmosphere. After reaction, methanol (50 ml) was added to the solution and the reaction mixture was filtered and washed with methanol and hexane. The residue was chromatographed on silica gel eluting with chloroform and recrystallized from chloroform to give a reddish brown powder (46 mg, 7%), mp 236°.

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