Carbazoledioxazines Having Long Alkyl Groups. 3. Syntheses and Properties of Halogen Free Carbazoledioxazines

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Long chain derivatives of halogen free carbazoledioxazine which is a typical organic pigment with a linear type structure (5,15-dialkyl-5,15-dihydrodiindolo[3,2-*b*:3',2'-*m*]triphenodioxazines) and an angular type structure (5,15-dialkyl-7,17-dialkoxy-5,15-dihydrodiindolo[2,3-*c*:2',3'-*n*]triphenodioxazines) were newly synthesized. Their structures were confirmed by ^{1}H-nmr, ms and elemental analysis. The thermal, spectroscopical and electrochemical properties were investigated by means of DSC, uv-vis and cyclic voltammetry.

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There has been much attention paid to organic dyes and pigments as functional materials for optic and electronic devices. Carbazoledioxazine is an important violet pigment and is used in printing inks [1]. Recently, the derivatives have been studied with regard to electronic properties [2]. We reported the compounds exist in two different structures, a linear **2** and an angular **3** type structure [3,4]. Compound **2II** was synthesized by demethanolative ring closure of the precursor **1IIIb** in a high boiling solvent [5] while **3II** was obtained by dehydrogenative ring closure of **1II** using electrochemical oxidation [6,7] as shown in Scheme 1. Langmuir-Blodgett films of these derivatives having long alkyl groups were prepared and their molecular orientation of the films were studied [8].

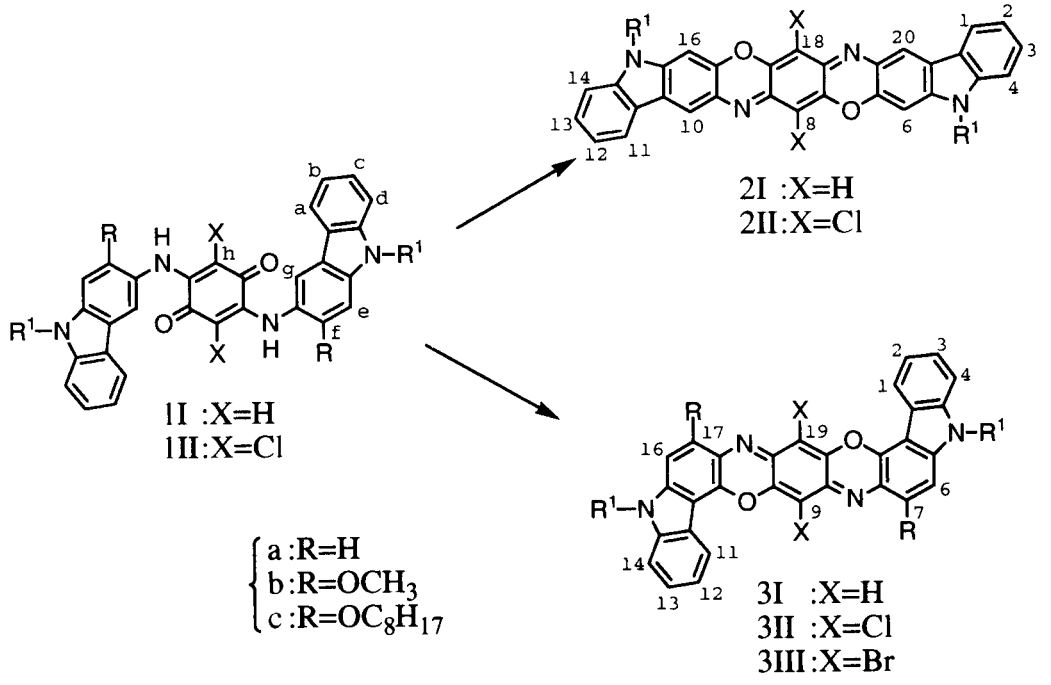
In this paper, we have synthesized chlorine-free carbazoledioxazines with a linear type structure **2I** and an angular type structure **3I**. In addition, the angular type compound containing bromine atoms, **3IIIc** and an alkoxy free derivative having chlorine atoms, **3IIa**, which is a structural isomer of **2II** were synthesized. In order to investigate the dependence of properties on their structures and substituents such as halogen atoms and alkoxy groups, we studied the thermal, spectroscopical and electrochemical properties.

Results and Discussion.

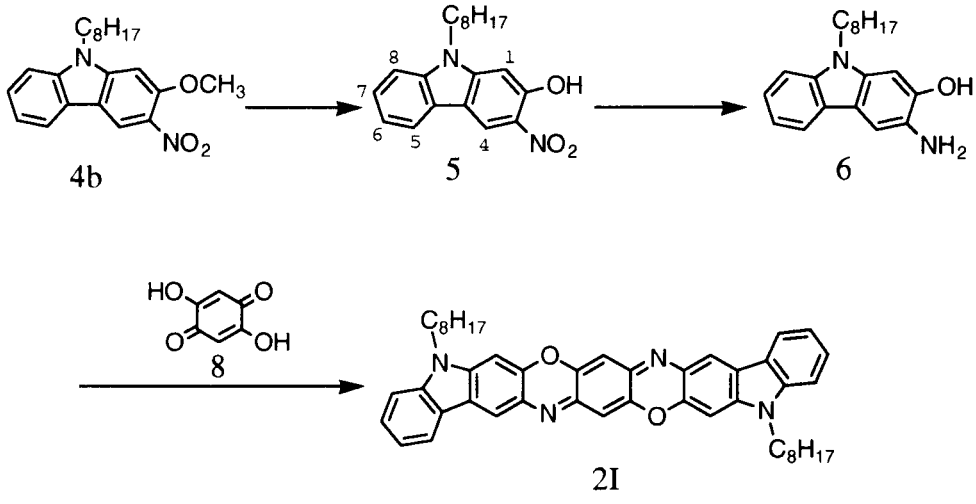
Carbazoledioxazines having octyl groups as R^1 and hydrogen (a), methoxy (b) and octyloxy (c) groups as R were synthesized. Intermediates **4a**, **4b** and **4c** were prepared in two or three steps starting from carbazole or 2-hydroxycarbazole by methods that have been described in the previous papers [4,5].

The synthetic route to the linear type of carbazoledioxazine without halogen atoms is presented in Scheme 2.

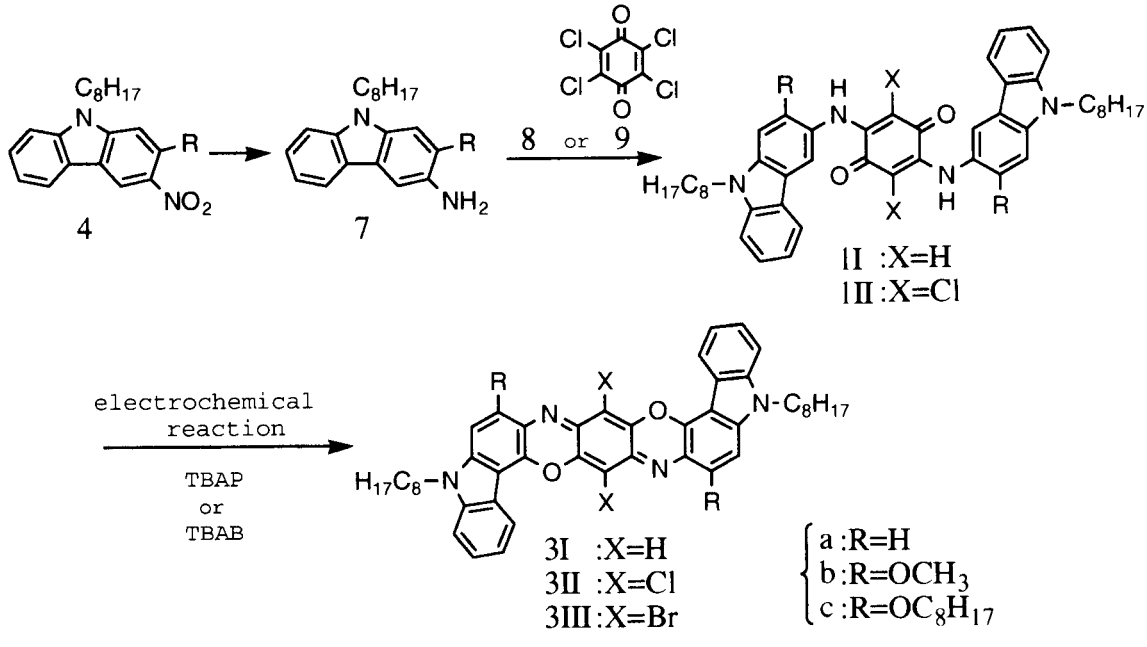
Scheme 1



Scheme 2



Scheme 3



2-Hydroxy-3-nitro-9-octylcarbazole (**5**) was obtained by cleavage of the ether linkage of **4b** using hydrobromic acid [9]. Reduction of **5** using palladium-carbon and hydrazine monohydrate gave 2-amino-3-hydroxy-9-octylcar bazole (**6**). Condensation of **6** with 2,5-dihydroxy-1,4-benzoquinone (**8**) in acetic acid afforded **2I**.

Scheme 3 shows the synthetic route to the angular type derivatives. The precursor **II** was obtained by condensation of 2-alkoxy-3-amino-9-octylcarbazole (**7**) with **8** in acetic acid. Electrochemical synthesis was adapted to the ring closure of **II** similar to that described in the previous paper [7]. Compound **3I** without a halogen atom was obtained by electrochemical oxidation which was carried out under a constant current passing 8 F/mole of electricity in the presence of tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte using platinum electrodes. In contrast, the reaction of **II** using tetra-*n*-butylammonium bromide (TBAB) as a supporting electrolyte afforded compound **3III** containing bromine atoms at X and they were identified by mass and ^{1}H-nmr spectra. These results suggest that indirect oxidation due to the electrogenerated bromonium ion is involved in the elec-

Table 1
Synthetic Results **1**, **2**, and **3**

Compound	Yield (%)	mp (°C)	Molecular Formula MS (Mz/M+)	^{1}H-NMR (deuteriochloroform) δ (ppm)	Elemental Analysis (%) (C/F) C	H	N
IIa	60	203 [a]	$C_{46}H_{52}N_4O_2$ 692	0.87 (t, CH_3, 6H), 1.16-1.98 (m, C_6H_{12}, 24H), 4.31 (t, N-CH_2, 4H), 6.10 (s, CH-h, 2H), 7.26 (dd, CH-b, 2H), 7.36 (dd, CH-f, 2H), 7.43 (d, CH-d and e, 4H), 7.51 (dd, CH-c, 2H), 8.01 (d, CH-g, 2H), 8.08 (d, CH-a, 2H) 8.38 (s, NH, 2H)	79.73 79.84	7.56 7.59	8.09 7.97
IIb	77	213 [a]	$C_{48}H_{56}N_4O_4$ 752	0.87 (t, CH_3, 6H), 1.16-1.96 (m, C_6H_{12}, 24H), 4.01 (s, O-CH_3, 6H), 4.28 (t, N-CH_2, 4H), 6.29 (s, CH-h, 2H), 6.90 (s, CH-e, 2H), 7.26 (dd, CH-b, 2H), 7.38 (d, CH-d, 2H), 7.43 (dd, CH-c, 2H), 8.03 (d, CH-a, 2H), 8.09 (s, CH-g, 2H), 8.71 (s, NH, 2H)	76.56 76.56	7.50 7.51	7.44 7.39
IIc	41	142 [a]	$C_{62}H_{84}N_4O_4$ 948	0.80-2.15 (m, C_7H_{15}, 60H), 4.16 (t, O-CH_2, 4H), 4.26 (t, N-CH_2, 4H), 6.32 (s, CH-h, 2H), 6.89 (s, CH-e, 2H), 7.25 (dd, CH-b, 2H), 7.37 (d, CH-d, 2H), 7.42 (dd, CH-c, 2H), 8.02 (d, CH-a, 2H), 8.09 (s, CH-g, 2H), 8.87 (s, NH, 2H)	78.44 78.31	8.92 8.69	5.90 5.78
IIIa	93	217 [a]	$C_{46}H_{50}N_4O_2Cl_2$ 760	0.87 (t, CH_3, 6H), 1.16-2.00 (m, C_6H_{12}, 24H), 4.31 (t, N-CH_2, 4H), 7.26 (dd, CH-b, 2H), 7.28 (dd, CH-f, 2H), 7.37 (d, CH-e, 2H), 7.43 (d, CH-d, 2H), 7.50 (dd, CH-c, 2H), 7.88 (d, CH-g, 2H), 8.07 (d, CH-a, 2H), 8.70 (s, NH, 2H)	72.52 72.61	6.62 6.59	7.35 7.34
2I	47	[b]	$C_{46}H_{48}N_4O_2$ 688	0.87 (t, CH_3, 6H), 1.18-1.82 (m, C_6H_{12}, 24H), 3.99 (t, N-CH_2, 4H), 6.49 (s, CH-8 and 18, 2H), 6.84 (s, CH-6 and 16, 2H), 7.19 (d, CH-4 and 14, 2H), 7.21 (dd, CH-2 and 12, 2H), 7.38 (dd, CH-3 and 13, 2H), 7.97 (d, CH-1 and 11, 2H), 7.98 (s, CH-10 and 20, 2H)	80.20 80.41	7.02 7.00	8.13 7.74
3Ia	21	[b]	$C_{46}H_{48}N_4O_2$ 688	0.87 (t, CH_3, 6H), 1.15-1.92 (m, C_6H_{12}, 24H), 4.25 (t, N-CH_2, 4H), 6.65 (s, CH-9 and 19, 2H), 7.14 (d, CH-6 and 16, 2H), 7.33 (dd, CH-2 and 12, 2H), 7.39 (d, CH-4 and 14, 2H), 7.49 (d, CH-7 and 17, and dd, CH-3 and 13, 4H), 832 (d, CH-1 and 11, 2H)	80.20 80.40	7.02 7.09	8.13 7.84
3Ib	15	[b]	$C_{48}H_{52}N_4O_4$ 748	0.87 (t, CH_3, 6H), 1.20-1.96 (m, C_6H_{12}, 24H), 4.11 (s, O-CH_3, 6H), 4.23 (t, N-CH_2, 4H), 6.57 (s, CH-6 and 16, 2H), 6.84 (s, CH-9 and 19, 2H), 7.30 (dd, CH-2 and 12, 2H), 7.34 (d, CH-4 and 14, 2H), 7.41 (dd, CH-3 and 13, 2H), 8.18 (d, CH-1 and 11, 2H)	76.97 76.57	7.00 7.00	7.48 7.11
3Ic	22	[b]	$C_{62}H_{80}N_4O_4$ 944	0.87 (t, CH_3, 6H), 0.92 (t, CH_3, 6H), 1.15-2.10 (m, C_6H_{12}, 48H), 4.18 (t, O-CH_2, 4H), 4.23 (t, N-CH_2, 4H), 6.56 (s, CH-6 and 16, 2H), 6.73 (s, CH-9 and 19, 2H), 7.26 (dd, CH-2 and 12, 2H), 7.31 (d, CH-4 and 14, 2H), 7.39 (dd, CH-3 and 13, 2H), 8.19 (d, CH-1 and 11, 2H)	78.77 78.68	8.53 8.48	5.93 5.75
3IIa	43	[b]	$C_{46}H_{46}N_4O_2Cl_2$ 756	0.87 (t, CH_3, 6H), 1.20-1.98 (m, C_6H_{12}, 24H), 4.33 (t, N-CH_2, 4H), 7.18-7.73 (m, aromatic, 10H), 8.56 (d, CH-1 and 11, 2H)	72.91 72.65	6.12 6.12	7.39 7.40

[a] Measured by TG-DTA under atmosphere. [b] These data are presented in Table 2.

trolysis using TBAB as described previously [7]. Compound **3IIa** which is the structural isomer of **2II** was prepared by the same method [7].

Their structures were confirmed by ^{1}H-nmr, ir, mass spectra and elemental analysis. The synthetic results are summarized in Table 1. The analysis of the ^{1}H-nmr data of **2I** indicated the isolated aromatic protons of the 8 and 18 positions were singlets at δ 6.49 ppm and that of **3Ia** exhibited a singlet signal at δ 6.65 ppm due to the 9 and 19 positions. The downfield shifts of about 0.25 ppm caused by deshielding of the chlorine atoms were observed on isolated protons of the 6, 16 and 10, 20 positions for **2II** and the 1, 11 positions for **3II**. In the ir spectra, an antisymmetric stretching vibration band due to the ether

Table 2
Spectroscopic Data of Carbazoledioxazines

Compound	R	X	Solubility (mol/l)	Transition temperature [c] (°C)	UV-VIS (chloroform) (λ max [log ε])
2I	–	H	$1x10^{-3}$ [a]	271	266 [4.80], 316 [4.54], 546 [4.86] , 589 [5.03]
2II	–	Cl	$2x10^{-4}$ [a]	342	272 [4.68], 317 [4.60], 557 [4.80], 602 [5.01]
3Ia	H	H	$2x10^{-3}$ [a]	118, 278	289 [4.63], 366 [3.88], 554 [4.69], 597 [4.88]
3IIa	H	Cl	$4x10^{-5}$ [a]	144, 361	294 [4.58], 366 [3.88], 567 [4.68], 614 [4.91]
3Ib	OCH_3	H	$2x10^{-3}$ [a]	178, 295	265 [4.72], 310 [4.53], 359 [3.84], 560 [4.67], 606 [4.86]
3IIb	OCH_3	Cl	$1x10^{-3}$ [a]	75, 290	269 [4.79], 314 [4.56], 358 [3.95], 576 [4.73], 623 [4.94]
3Ic	OC_8H_{17}	H	$1x10^{-3}$ [b]	123, 162, 222	264 [4.74], 311 [4.52], 361 [3.82], 558 [4.65], 603 [4.85]
3IIc	OC_8H_{17}	Cl	$9x10^{-4}$ [b]	125, 182, 208	269 [4.80], 314 [4.56], 360 [3.94], 572 [4.72], 619 [4.93]

[a] Measured in chloroform at 30°. [b] Measured in carbon tetrachloride at 30°. [c] Measured by DSC under atmospheric conditions.

bonds of **3IIb**, **3IIc** and **3IIIc** having halogen atoms gave absorption at about 1266 cm^{-1}, however, those bands of **3Ib** and **3Ic** with no halogen atom were observed at about 1250 cm^{-1}. These data indicate that an electron-withdrawing inductive effect of halogen atoms may contribute.

The thermal, spectroscopic and electrochemical properties of carbazoledioxazines have been studied to understand the influence of the structures and substituents. Thermal analysis, solubility and uv-vis spectral data of the carbazoledioxazines are shown in Table 2.

Thermal analyses were carried out by differential scanning calorimetry. Compound **2I** showed one endothermic peak and **3I** exhibited two or three peaks as well as the compounds **2II** and **3II** with chlorine atoms [5,7]. Owing to the introduction of chlorine atoms, the highest endothermic peaks (T) of **2II** and **3IIa** rose remarkably in comparison with those of chlorine-free derivatives **2I** and **3Ia**, respectively. However, the T of **3IIb** and **3IIc** with alkoxy groups at the 7 and 17 positions was influenced little by the chlorine atoms.

Solubility was measured in chloroform or carbon tetrachloride at 30° [7]. The solubility of **2II** and **3IIa** became lower with the introduction of chlorine atoms while that of **3IIb** and **3IIc** showed little influence. These results suggest the following: The intermolecular force was increased by the chlorine atoms, therefore, **2II** and **3IIa** exhibited the higher T and lower solubility compared with **2I** and **3Ia**. On the other hand, in case of the **3Ib** and **3Ic**, it seems to cancel the influence of the chlorine atoms by the bulky alkoxy groups.

In the visible absorption spectra, the influence of the halogen atoms was a shift of the absorption maxima to a longer wavelength of about 13-17 nm for their electron-donating resonance effect. And introduction of alkoxy groups into angular type compounds caused a bathochromic shift about 6-9 nm. Between the structural isomers, the angular type compounds **3** absorbed at longer wavelengths than the linear type compounds **2** whereas a molecular extinction coefficient of **3** was lower than that of **2**.

Electrochemical studies were carried out by means of cyclic voltammetry (CV) and constant-potential electrolysis in dichloromethane or acetonitrile. Table 3 summarizes the oxidation peak potentials for carbazoledioxazines and intermediates together with ferrocene as a standard. The electrochemical properties of the carbazole derivatives were described in detailed by Ambrose, *et al.* [10, 11] and Fujita, *et al.* [12]. Intermediates **4** and **7** showed similar behavior to that described in the literature [10,11].

The CVs of the precursors **1Ia** and **1Ic** which have no halogen atoms showed two peaks attributable to oxidation of the neutral molecule to a cation radical and subsequently to oxidation in dichloromethane as shown in Figure 1a. Whereas those of **1IIa** and **1IIc** with chlorine atoms showed only one oxidation peak with a corresponding reduction peak (Figure 1b), the constant-potential electrolysis of **1IIc** at Ep1 (1.0V *vs.* SCE) gave **3IIc** in better yield than the constant-current electrolysis. The constant-potential electrolysis of **1Ia** at Ep1 (first oxidation peak, 1.0V *vs.* SCE) did not give compound **3Ia** but that at Ep2 gave **3Ia**.

These results suggest that the CVs of **1IIa** and **1IIc** give an overlap peak of Ep1 and Ep2. The Ep1 was shifted in a positive direction with the introduction of chlorine atoms, whereas the Ep2 showed a negative shift. In the ^1H-nmr spectra, the aromatic proton of position-*g* which is the position of ring closure exhibited an upfield shift with the introduction of chlorine atoms. These data imply that the electron density of the carbazole rings increases and the Ep2 may be attributed to the oxidation of the carbazole rings. It seems that the irreversibility of chlorine-free derivatives **1Ia** and **1Ic** is due to the elimination of the protons of the secondary amine from an unstable cation radical.

The CVs of carbazoledioxazines revealed two redox peaks irrespective of the presence of the chlorine atoms

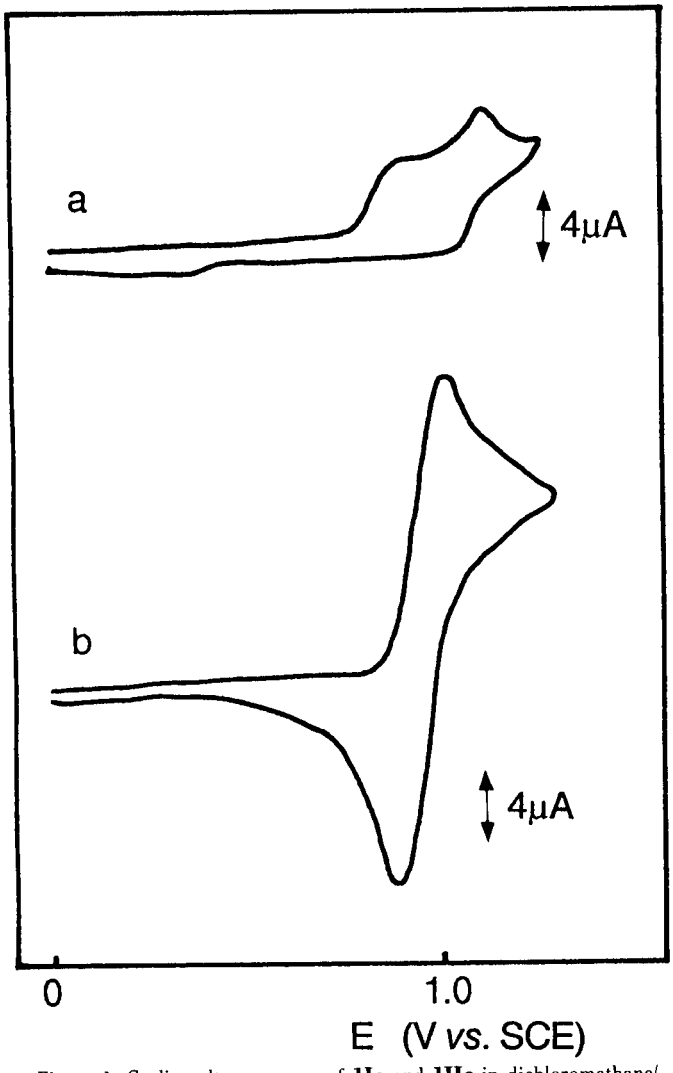


Figure 1. Cyclic voltammogram of **1Ic** and **1IIc** in dichloromethane/-TBAP. Curve a: **1Ic** (7.2 x 10^{-4} mol/l), Curve b: **1IIc** (1.2 x 10^{-3} mol/l).

and the structures except for **2II** and **3IIa** because of their low solubility in dichloromethane. The peak potentials of the angular type compounds **3** were independent of the sweep rate (50-200mV/sec) and these peak potential separation values (ΔEp) were approximately 0.06V (Figure 2a). These data suggest that compounds **3** are electrochemically reversible and each peak may be attributed to a cation radical and a dication. The redox peak potentials were shifted in a positive direction with the introduction of chlorine atoms and to a negative direction with the introduction of alkoxy groups. The observed ΔEp at Ep2 of the linear type compounds **2II** was about 0.1V for a quasi-reversible process (Figure 2b). The angular type compound **3Ia** is easily oxidized compared with **2I**.

In conclusion, long chain derivatives of halogen-free carbazoledioxazines with linear and angular type structures and a structural isomer of **2IIa** were synthesized and their structures were confirmed by ^{1}H-nmr and elemental analysis. The results of the thermal measurements,

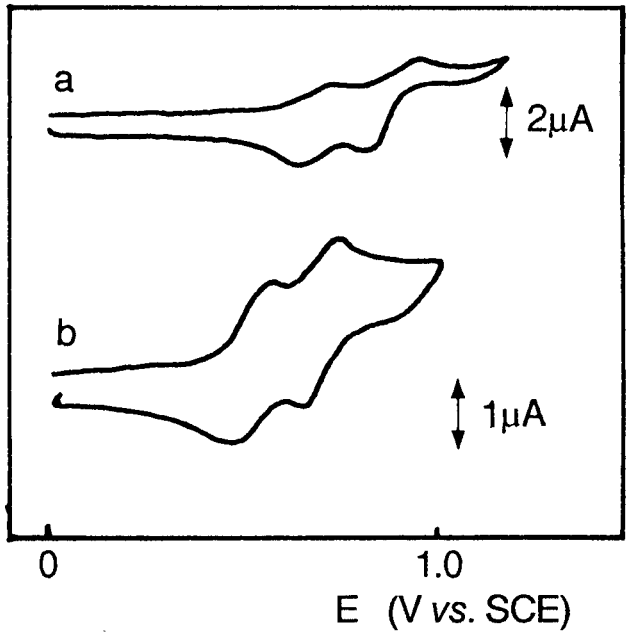


Figure 2. Cyclic voltammogram of **2I** and **3Ic** in dichloromethane/TBAP. Curve a: **2I** (3.6 x 10^{-4} mol/l), Curve b: **3Ic** (3.1 x 10^{-4} mol/l).

solubilities, spectroscopic and electrochemical properties indicated that these data were the influenced by the structures and substituents.

Table 3

Oxidation Peak Potentials (*vs.* SCE) of Carbazoledioxazines and Intermediates in *n*-Bu_4NClO_4 (0.1 mole/l) with a Sweep Rate of 100 mV/sec

Compound	Concentration (mmole/l)	Ep1	Ep2
4a	3.6x10^{-3} [a]	1.46	
4c	3.3x10^{-3} [a]	1.36	
7a	3.9x10^{-4} [a]	0.48	1.08
7c	3.2x10^{-3} [a]	0.39	1.06
1Ia	4.9x10^{-4} [b]	1.01 (sh)	1.18
1IIa	8.9x10^{-4} [b]	1.12	
1Ic	7.2x10^{-4} [b]	0.91 (sh)	1.12
1IIc	1.2x10^{-3} [b]	1.00	
2I	3.6x10^{-4} [b]	0.71	0.93
3Ia	2.0x10^{-4} [b]	0.65	0.83
3Ic	3.1x10^{-4} [b]	0.55	0.72
3IIc	7.0x10^{-4} [b]	0.68 (sh)	0.83
ferrocene	6.7x10^{-3} [a]	0.44	
	9.3x10^{-3} [b]	0.67	

[a] Acetonitrile. [b] Dichloromethane.

EXPERIMENTAL

Thermal properties were determined by a Seiko Denshi DSC and melting points were taken on a Mel-Temp apparatus (capillary method) and were uncorrected. The ir, mass and electric absorption spectra were measured with a Perkin Elmer FT-

IR 1640, a Shimadzu QP-1000 and a Shimadzu UV-2100 spectrometer, respectively. The ^{1}H-nmr spectra were obtained with a JEOL PMX60Si and a Bruker AM-400 with TMS as the internal standard. Electrochemical studies were carried out with a Nichiakeisoku Potentiogalvanostat NP-G1002E using Rikadenki X-Y recorder SS-250F in dichloromethane or acetonitrile using 0.1 mole/l TBAP as the supporting electrolyte. They were extremely sensitive to impurities, therefore, the solvent and TBAP were purified by known procedures. The reference electrode was a SCE and the working electrode was a platinum electrode.

2-Hydroxy-3-nitro-9-octylcarbazole **5**.

A mixture of 2-methoxy-3-nitro-9-octylcarbazole **4b** (0.36 g, 1.0 mmole) and hydrobromic acid (50 ml, 47%) in acetic acid (31 ml) was refluxed for 7 hours. The reaction mixture was extracted with dichloromethane, washed with water, concentrated *in vacuo* and recrystallized from ethanol to give yellow needles (0.28 g, 82%), mp 117-118°; ir (potassium bromide): 1500, 1356 (ν NO_2); ^{1}H-nmr (carbon tetrachloride): δ 0.83-2.37 (m, C_7H_{15}, 15H), 4.20 (t, N-CH_2, 2H), 6.76 (s, CH-1, 1H), 7.03-7.33 (m, aromatic, 3H), 7.86 (d, CH-5, 1H), 8.62 (s, CH-4, 1H), 11.01 (s, OH, 1H).

Anal. Calcd. for $C_{20}H_{24}N_2O_3$ (340.42): C, 70.57; H, 7.11; N, 8.23. Found: C, 70.55; H, 7.17; N, 8.08.

3-Amino-2-hydroxy-9-octylcarbazole **6**.

Hydrazine monohydrate (0.19 g, 3.8 mmoles) was added dropwise to a mixture of **5** (0.27 g, 0.78 mmole) and 5% palladium-carbon (0.30 g) in ethanol (17 ml) at reflux temperature and was stirred for 2 hours under a nitrogen atmosphere. The mixture was filtered while still hot and the filtrate was cooled with ice. The precipitate was filtered to give colorless needles (0.23 g, 90%), mp 137-138°; ir (potassium bromide): 3371, 3300 (ν NH_2); ^{1}H-nmr (deuterioacetone): δ 0.70-1.66 (m, C_7H_{15}, 15H), 2.62-2.82 (br, NH_2, 2H), 4.26 (t, N-CH_2, 2H), 6.67-7.60 (m, aromatic and OH, 7H). This compound could not be subjected to elemental analysis because of instability.

5,15-Dihydro-5,15-dioctyldiindolo[3,2-*b*:3′,2′-*m*]triphenodioxazine (Linear Type Compound) **2I**.

A mixture of **6** (170 mg, 0.51 mmole) and 2,5-dihydroxy-1,4-benzoquinone **8** (36 mg, 0.26 mmole) and nitrosobenzene (54 mg, 0.51 mmole) in acetic acid (15 ml) was refluxed for 5 hours. The precipitate was filtered and washed with ethanol, hexane and water. The residue was chromatographed on silica gel eluting with chloroform to give a reddish-brown powder (82 mg, 47%).

2,5-Bis(9-octyl-3-carbazolylamino)-1,4-benzoquinone **11a**.

A solution of 2-amino-9-octylcarbazole **7a** (1.5 g, 5.1 mmoles) and **8** (0.36 g, 2.6 mmoles) in acetic acid (50 ml) was refluxed for 3 hours under a nitrogen atmosphere. After cooling, the reaction mixture was filtered and washed with ethanol, hexane and water. The residue was chromatographed on silica gel eluting with chloroform and recrystallized from toluene to give brown needles (1.1 g, 60%); ir (potassium bromide): 3246 (ν NH), 1635 (ν C=O).

5,15-Dihydro-5,15-dioctyldiindolo[2,3-*c*:2′,3′-*n*]triphenodioxazine (Angular Type Compound) **3Ia**.

A mixture of **11a** (0.14 g, 0.18 mmole) and TBAP (0.30 g, 0.95 mmole) in acetonitrile: *N*,*N*-dimethylformamide (1:2, 33ml) was dissolved at 60° under a nitrogen atmosphere. Through the reaction mixture was passed 8F/mole of electricity under a constant current (0.02A/cm^2) using platinum electrodes. The precipitate was filtered and washed with hexane, methanol and water. The resulting residue was chromatographed on silica gel eluting with chloroform and recrystallized from toluene to give a purple powder (29 mg, 21%).

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