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Carbazoledioxazines with an angular type structure (5,15-dialkyl-7,17-dialkyloxy-9,19-dichloro-5,15-dihydroindolo[2,3-c:2',3'-n]triphenodioxazines) were selectively synthesized by electrochemical oxidative ring closure of precursors (2,5-bis(9-alkyl-2-alkyloxy-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinones). The structure was confirmed by <sup>1</sup>H-nmr and other instrumental analyses. Their thermal properties and solubilities were investigated and were compared with those of carbazoledioxazines with a linear type structure.

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Recently, organic dyes and pigments are noted for the optical and electrical properties. Especially, many chemists have given much attention to thin films of synthetic dyes. We have been investigating the synthesis of soluble organic pigments and their application to the Langmuir-Blodgett (LB) films of these compounds [1]. Carbazoledioxazine is the most important derivative of dioxazine pigments and have been used as coloring matters for plastics and printing inks [2]. Furthermore, it has been studied as an organic photoconductor [3] and can be expected to

serve as functional materials.

In a previous paper [4], we suggested that dehydrogenative ring closure of the carbazoledioxazine's precursor **6** in the presence of a ring closure agent forms a linear type compound **8** or an angular type compound **7**. But their structures had never been confirmed by instrumental analyses because of their poor solubility in organic solvents. We have already reported that soluble carbazoledioxazines with a linear type structure were synthesized by demethanolative ring closure of the precursor having methoxy groups in an high boiling solvent [5]. In this paper, we describe the synthesis of carbazoledioxazines having long alkyl groups using electrochemical oxidation for dehydrogenative ring closure. The structure, thermal properties and solubilities of **7** were studied and they were compared with those of **8**.

### Results and Discussion.

Carbazoledioxazines with an angular type structure were synthesized by the synthetic route in Scheme 1. Intermediates **2-6** were obtained by the methods as previously described [5]. That is to say, *O*-alkylation of 2-hydroxycarbazole (**1**) with haloalkane [ $R^1 = \text{CH}_3$  (I),  $\text{C}_8\text{H}_{17}$  (II),  $\text{C}_{12}\text{H}_{25}$  (III)] gave **2**. Compound **3** was obtained on *N*-alkylation of **2** with *n*-alkyl bromide [ $R^2 = \text{C}_8\text{H}_{17}$  (a),  $\text{C}_{10}\text{H}_{21}$  (b),  $\text{C}_{12}\text{H}_{25}$  (c),  $\text{C}_{16}\text{H}_{37}$  (d)] in the presence of a phase transfer catalyst such as benzyltriethylammonium chloride (BTEAC). Nitration of **3** with nitric acid in glacial acetic acid yielded **4**. Compound **5** was prepared by reduction of **4** with an iron powder and hydrochloric acid. Condensation of **5** with chloranil afforded the precursor **6**. Intermediates **2-6** were identified by <sup>1</sup>H-nmr, ir spectra and elemental analysis. These results are summarized in Table 1.

Carbazoledioxazine is conventionally obtained by dehydrogenative cyclization of the precursor containing a ring closure agent such as benzenesulfonyl chloride, *p*-toluenesulfonyl chloride or benzoyl chloride. However, it is difficult to obtain pure product because of the elimination of chlorine, substitution of a ring closure agent and so

Scheme 1

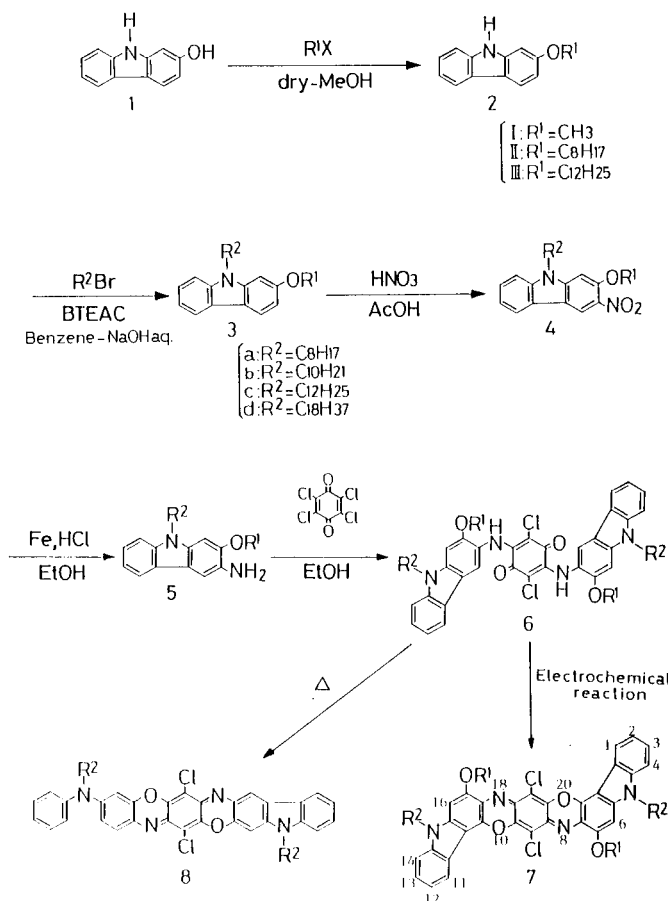


Table 1  
Physical, Analytical and Spectroscopic Data for Intermediates 2-6

Compound	R <sup>1</sup> <sub>n</sub>	R <sup>2</sup> <sub>n</sub>	Yield (%)	mp (°C)	<sup>1</sup> H-NMR δ (ppm)	Molecular Formula	Elemental Analysis % (C/F/N)		
							C	H	N
2II	8	—	73	208-209	0.65-2.05 (m, 15H, C <sub>7</sub> H <sub>15</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 6.67-8.05 (m, 8H, aromatic and NH) [b]	C <sub>20</sub> H <sub>25</sub> NO	81.31 81.25	8.53 8.55	4.74 4.64
2III	12	—	56	189-191	0.50-2.17 (m, 23H, C <sub>11</sub> H <sub>23</sub> ), 3.93 (t, 2H, CH <sub>2</sub> ), 6.66-8.07 (m, 8H, aromatic and NH) [b]	C <sub>24</sub> H <sub>33</sub> NO	82.00 81.72	9.46 9.45	3.99 3.82
3IIa	8	8	68	27-28	0.66-2.14 (m, 30H, C <sub>7</sub> H <sub>15</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.97 (t, 2H, CH <sub>2</sub> ), 4.12 (t, 2H, CH <sub>2</sub> ), 6.53-8.00 (m, 7H, aromatic) [c]	C <sub>28</sub> H <sub>41</sub> NO	82.50 82.79	10.14 10.27	3.44 3.45
3IIb	8	10	41	33-34	0.62-2.11 (m, 34H, C <sub>9</sub> H <sub>19</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.93 (t, 2H, CH <sub>2</sub> ), 4.04 (t, 2H, CH <sub>2</sub> ), 6.38-7.93 (m, 7H, aromatic) [c]	C <sub>30</sub> H <sub>45</sub> NO	82.70 82.40	10.41 10.46	3.22 3.04
3IIc	8	12	82	liquid	0.66-2.13 (m, 38H, C <sub>11</sub> H <sub>23</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.94 (t, 2H, CH <sub>2</sub> ), 4.05 (t, 2H, CH <sub>2</sub> ), 6.53-8.01 (m, 7H, aromatic) [c]	C <sub>32</sub> H <sub>49</sub> NO	82.88 83.24	10.65 10.58	3.02 2.64
3IIId	8	18	76	49-50	0.67-2.18 (m, 50H, C <sub>17</sub> H <sub>35</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.97 (t, 2H, CH <sub>2</sub> ), 4.15 (t, 2H, CH <sub>2</sub> ), 6.50-7.97 (m, 7H, aromatic) [c]	C <sub>38</sub> H <sub>61</sub> NO	83.30 83.23	11.22 11.34	2.56 2.32
3IIIa	12	8	44	25-26	0.60-2.17 (m, 38H, C <sub>7</sub> H <sub>15</sub> and C <sub>11</sub> H <sub>23</sub> ), 3.95 (t, 2H, CH <sub>2</sub> ), 4.05 (t, 2H, CH <sub>2</sub> ), 6.50-8.00 (m, 7H, aromatic) [c]	C <sub>32</sub> H <sub>49</sub> NO	82.88 82.68	10.65 10.75	3.02 2.73
3IIIb	12	10	70	35-37	0.60-2.17 (m, 42H, C <sub>9</sub> H <sub>19</sub> and C <sub>11</sub> H <sub>23</sub> ), 3.90 (t, 2H, CH <sub>2</sub> ), 4.03 (t, 2H, CH <sub>2</sub> ), 6.50-8.00 (m, 7H, aromatic) [c]	C <sub>34</sub> H <sub>53</sub> NO	83.03 82.70	10.86 10.92	2.85 2.70
3IIIc	12	12	87	47-48	0.66-2.17 (m, 46H, C <sub>11</sub> H <sub>23</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.13 (t, 2H, CH <sub>2</sub> ), 6.50-8.00 (m, 7H, aromatic) [c]	C <sub>36</sub> H <sub>57</sub> NO	83.17 83.14	11.05 11.20	2.70 2.56
3IIId	12	18	91	53-54	0.60-2.45 (m, 58H, C <sub>17</sub> H <sub>35</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.17 (t, 2H, CH <sub>2</sub> ), 6.50-8.05 (m, 7H, aromatic) [c]	C <sub>42</sub> H <sub>69</sub> NO	83.52 83.22	11.52 11.69	2.32 2.35
4IIa	8	8	67	58-59	0.67-2.18 (m, 30H, C <sub>7</sub> H <sub>15</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.01 (t, 2H, CH <sub>2</sub> ), 4.10 (t, 2H, CH <sub>2</sub> ), 6.61 (s, 1H, aromatic), 7.00-7.42 (m, 3H, aromatic), 7.67-7.94 (m, 1H, aromatic), 8.38 (s, 1H, aromatic) [c]	C <sub>28</sub> H <sub>40</sub> N <sub>2</sub> O <sub>3</sub>	74.30 74.04	8.91 8.65	6.19 6.13
4IIb	8	10	59	54-55	0.67-2.32 (m, 30H, C <sub>9</sub> H <sub>19</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.99 (t, 2H, CH <sub>2</sub> ), 4.09 (t, 2H, CH <sub>2</sub> ), 6.58 (s, 1H, aromatic), 6.90-7.45 (m, 3H, aromatic), 7.65-7.97 (m, 1H, aromatic), 8.32 (s, 1H, aromatic) [c]	C <sub>30</sub> H <sub>44</sub> N <sub>2</sub> O <sub>3</sub>	74.96 74.80	9.23 9.21	5.83 5.69
4IIc	8	12	53	64-66	0.58-2.04 (m, 38H, C <sub>11</sub> H <sub>23</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.09 (t, 2H, CH <sub>2</sub> ), 6.56 (s, 1H, aromatic), 6.97-7.36 (m, 3H, aromatic), 7.70-7.87 (m, 1H, aromatic), 8.33 (s, 1H, aromatic) [c]	C <sub>32</sub> H <sub>48</sub> N <sub>2</sub> O <sub>3</sub>	75.55 75.30	9.51 9.51	5.51 5.46
4IIId	8	18	56	62-63	0.65-2.14 (m, 50H, C <sub>17</sub> H <sub>35</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.06 (t, 2H, CH <sub>2</sub> ), 4.15 (t, 2H, CH <sub>2</sub> ), 6.65 (s, 1H, aromatic), 7.00-7.39 (m, 3H, aromatic), 7.75-8.00 (m, 1H, aromatic), 8.43 (s, 1H, aromatic) [c]	C <sub>38</sub> H <sub>60</sub> N <sub>2</sub> O <sub>3</sub>	76.98 76.89	10.20 10.33	4.73 4.50
4IIIa	12	8	36	49-50	0.70-2.33 (m, 38H, C <sub>7</sub> H <sub>15</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.12 (t, 2H, CH <sub>2</sub> ), 4.20 (t, 2H, CH <sub>2</sub> ), 6.71 (s, 1H, aromatic), 7.10-7.45 (m, 3H, aromatic), 7.80-8.10 (m, 1H, aromatic), 8.50 (s, 1H, aromatic) [c]	C <sub>32</sub> H <sub>48</sub> N <sub>2</sub> O <sub>3</sub>	75.55 75.48	9.51 9.56	5.51 5.48
4IIIb	12	10	47	54-55	0.60-2.33 (m, 42H, C <sub>9</sub> H <sub>19</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.10 (t, 2H, CH <sub>2</sub> ), 4.20 (t, 2H, CH <sub>2</sub> ), 6.75 (s, 1H, aromatic), 7.10-7.40 (m, 3H, aromatic), 7.80-8.10 (m, 1H, aromatic), 8.50 (s, 1H, aromatic) [c]	C <sub>34</sub> H <sub>52</sub> N <sub>2</sub> O <sub>3</sub>	76.07 75.80	9.76 9.82	5.22 5.04
4IIIc	12	12	57	70-71	0.50-2.13 (m, 46H, C <sub>11</sub> H <sub>23</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.05 (t, 2H, CH <sub>2</sub> ), 4.15 (t, 2H, CH <sub>2</sub> ), 6.67 (s, 1H, aromatic), 7.10-7.40 (m, 3H, aromatic), 7.75-8.00 (m, 1H, aromatic), 8.50 (s, 1H, aromatic) [c]	C <sub>36</sub> H <sub>56</sub> N <sub>2</sub> O <sub>3</sub>	76.55 76.32	9.99 10.05	4.96 4.63
4IIId	12	18	61	77-78	0.60-2.33 (m, 58H, C <sub>17</sub> H <sub>35</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.03 (t, 2H, CH <sub>2</sub> ), 4.10 (t, 2H, CH <sub>2</sub> ), 6.63 (s, 1H, aromatic), 7.08-7.40 (m, 3H, aromatic), 7.70-7.95 (m, 1H, aromatic), 8.45 (s, 1H, aromatic) [c]	C <sub>42</sub> H <sub>68</sub> N <sub>2</sub> O <sub>3</sub>	77.72 77.71	10.56 10.59	4.32 4.11

Table 1 (continued)

Compound	R <sup>1</sup> <sub>n</sub>	R <sup>2</sup> <sub>n</sub>	Yield (%)	mp (°C)	<sup>1</sup> H-NMR δ (ppm)	Molecular Formula	Elemental Analysis % (C/F)		
							C	H	N
5IIa	8	8	60	58-59	0.61-2.10 (m, 30H, C <sub>7</sub> H <sub>15</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.26 (br, 2H, NH <sub>2</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.10 (t, 2H, CH <sub>2</sub> ), 6.53 (s, 1H, aromatic), 6.75-7.21 (m, 4H, aromatic), 7.50-7.80 (m, 1H, aromatic) [c]	C <sub>28</sub> H <sub>42</sub> N <sub>2</sub> O			[d]
5IIb	8	10	49	45-46	0.63-2.08 (m, 34H, C <sub>9</sub> H <sub>19</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.38 (br, 2H, NH <sub>2</sub> ), 4.01 (t, 2H, CH <sub>2</sub> ), 4.10 (t, 2H, CH <sub>2</sub> ), 6.57 (s, 1H, aromatic), 6.84-7.25 (m, 4H, aromatic), 7.54-7.80 (m, 1H, aromatic) [c]	C <sub>30</sub> H <sub>46</sub> N <sub>2</sub> O			[d]
5IIc	8	12	24	50-51	0.66-2.21 (m, 38H, C <sub>11</sub> H <sub>23</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.42 (br, 2H, NH <sub>2</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.10 (t, 2H, CH <sub>2</sub> ), 6.57 (s, 1H, aromatic), 6.86-7.22 (m, 4H, aromatic), 7.57-7.80 (m, 1H, aromatic) [c]	C <sub>32</sub> H <sub>50</sub> N <sub>2</sub> O			[d]
5IId	8	18	51	52-53	0.71-2.18 (m, 50H, C <sub>17</sub> H <sub>35</sub> and C <sub>7</sub> H <sub>15</sub> ), 3.44 (br, 2H, NH <sub>2</sub> ), 4.02 (t, 2H, CH <sub>2</sub> ), 4.12 (t, 2H, CH <sub>2</sub> ), 6.58 (s, 1H, aromatic), 6.89-7.26 (m, 4H, aromatic), 7.59-7.82 (m, 1H, aromatic) [c]	C <sub>38</sub> H <sub>62</sub> N <sub>2</sub> O			[d]
5IIIa	12	8	40	44-45	0.60-2.15 (m, 38H, C <sub>7</sub> H <sub>15</sub> and C <sub>11</sub> H <sub>23</sub> ), 3.76 (br, 2H, NH <sub>2</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.16 (t, 2H, CH <sub>2</sub> ), 6.65 (s, 1H, aromatic), 6.95-7.32 (m, 4H, aromatic), 7.67-7.87 (m, 1H, aromatic) [c]	C <sub>32</sub> H <sub>50</sub> N <sub>2</sub> O			[d]
5IIIb	12	10	47	53-54	0.50-2.33 (m, 42H, C <sub>9</sub> H <sub>19</sub> and C <sub>11</sub> H <sub>23</sub> ), 3.50 (br, 2H, NH <sub>2</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.16 (t, 2H, CH <sub>2</sub> ), 6.60 (s, 1H, aromatic), 6.92-7.40 (m, 4H, aromatic), 7.60-7.93 (m, 1H, aromatic) [c]	C <sub>34</sub> H <sub>54</sub> N <sub>2</sub> O			[d]
5IIIc	12	12	49	48-51	0.50-2.13 (m, 46H, C <sub>11</sub> H <sub>23</sub> and C <sub>11</sub> H <sub>23</sub> ), 3.50 (br, 2H, NH <sub>2</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.09 (t, 2H, CH <sub>2</sub> ), 6.56 (s, 1H, aromatic), 6.90-7.21 (m, 4H, aromatic), 7.56-7.80 (m, 1H, aromatic) [c]	C <sub>36</sub> H <sub>58</sub> N <sub>2</sub> O			[d]
5IIId	12	18	50	59-60	0.63-2.20 (m, 58H, C <sub>17</sub> H <sub>35</sub> and C <sub>11</sub> H <sub>23</sub> ), 3.48 (br, 2H, NH <sub>2</sub> ), 4.00 (t, 2H, CH <sub>2</sub> ), 4.17 (t, 2H, CH <sub>2</sub> ), 6.55 (s, 1H, aromatic), 6.92-7.20 (m, 4H, aromatic), 7.54-7.77 (m, 1H, aromatic) [c]	C <sub>42</sub> H <sub>70</sub> N <sub>2</sub> O			[d]
6IIa	8	8	50	124 [a]	0.60-2.12 (m, 60H, C <sub>7</sub> H <sub>15</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.08 (t, 4H, CH <sub>2</sub> ), 4.21 (t, 4H, CH <sub>2</sub> ), 6.78 (s, 2H, aromatic), 7.02-7.46 (m, 6H, aromatic), 7.75 (s, 2H, aromatic), 7.98 (d, 2H, aromatic), 8.67 (s, 2H, NH) [b]	C <sub>62</sub> H <sub>82</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	73.13 73.15	8.12 8.10	5.50 5.44
6IIb	8	10	51	117 [a]	0.72-2.09 (m, 68H, C <sub>9</sub> H <sub>19</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.08 (t, 4H, CH <sub>2</sub> ), 4.21 (t, 4H, CH <sub>2</sub> ), 6.76 (s, 2H, aromatic), 7.10-7.40 (m, 6H, aromatic), 7.72 (s, 2H, aromatic), 7.93 (d, 2H, aromatic), 8.60 (s, 2H, NH) [b]	C <sub>66</sub> H <sub>90</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	73.78 73.52	8.44 8.33	5.22 5.36
6IIc	8	12	67	113 [a]	0.70-2.07 (m, 76H, C <sub>11</sub> H <sub>23</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.09 (t, 4H, CH <sub>2</sub> ), 4.23 (t, 4H, CH <sub>2</sub> ), 6.75 (s, 2H, aromatic), 7.08-7.40 (m, 6H, aromatic), 7.69 (s, 2H, aromatic), 7.92 (d, 2H, aromatic), 8.57 (s, 2H, NH) [b]	C <sub>70</sub> H <sub>98</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	74.37 74.27	8.74 8.59	4.96 4.99
6IId	8	18	71	98 [a]	0.71-2.08 (m, 100H, C <sub>17</sub> H <sub>35</sub> and C <sub>7</sub> H <sub>15</sub> ), 4.09 (t, 4H, CH <sub>2</sub> ), 4.22 (t, 4H, CH <sub>2</sub> ), 6.73 (s, 2H, aromatic), 7.03-7.42 (m, 6H, aromatic), 7.68 (s, 2H, aromatic), 7.90 (d, 2H, aromatic), 8.58 (s, 2H, NH) [b]	C <sub>82</sub> H <sub>122</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	75.83 75.74	9.47 9.40	4.28 4.28
6IIIa	12	8	36	116 [a]	0.50-2.33 (m, 76H, C <sub>7</sub> H <sub>15</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.00 (t, 4H, CH <sub>2</sub> ), 4.12 (t, 4H, CH <sub>2</sub> ), 6.66 (s, 2H, aromatic), 7.00-7.33 (m, 6H, aromatic), 7.66 (s, 2H, aromatic), 7.85 (d, 2H, aromatic), 8.30 (s, 2H, NH) [b]	C <sub>70</sub> H <sub>98</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	74.37 74.23	8.74 8.61	4.96 4.96
6IIIb	12	10	77	102 [a]	0.50-2.17 (m, 84H, C <sub>9</sub> H <sub>19</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.03 (t, 4H, CH <sub>2</sub> ), 4.20 (t, 4H, CH <sub>2</sub> ), 6.70 (s, 2H, aromatic), 7.00-7.55 (m, 6H, aromatic), 7.66 (s, 2H, aromatic), 7.95 (d, 2H, aromatic), 8.55 (s, 2H, NH) [b]	C <sub>74</sub> H <sub>106</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	74.91 75.09	9.00 8.95	4.72 4.72

Table 1 (continued)

Compound	R <sup>1</sup> <sub>n</sub>	R <sup>2</sup> <sub>n</sub>	Yield (%)	mp (°C)	<sup>1</sup> H-NMR δ (ppm)	Molecular Formula	Elemental Analysis % (C/F/N)		
							C	H	N
6IIIc	12	12	77	105 [a]	0.50-2.20 (m, 92H, C <sub>11</sub> H <sub>23</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.03 (t, 4H, CH <sub>2</sub> ), 4.22 (t, 4H, CH <sub>2</sub> ), 6.80 (s, 2H, aromatic), 7.05-7.50 (m, 6H, aromatic), 7.77 (s, 2H, aromatic), 8.05 (d, 2H, aromatic), 8.67 (s, 2H, NH) [b]	C <sub>78</sub> H <sub>114</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	75.39 75.25	9.25 9.24	4.51 4.49
6IIId	12	18	76	99 [a]	0.55-2.20 (m, 116H, C <sub>17</sub> H <sub>35</sub> and C <sub>11</sub> H <sub>23</sub> ), 4.00 (t, 4H, CH <sub>2</sub> ), 4.20 (t, 4H, CH <sub>2</sub> ), 6.75 (s, 2H, aromatic), 7.05-7.45 (m, 6H, aromatic), 7.68 (s, 2H, aromatic), 7.90 (d, 2H, aromatic), 8.56 (s, 2H, NH) [b]	C <sub>90</sub> H <sub>138</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	76.61 76.46	9.86 9.89	3.97 4.06

[a] Measured by TG-DTA under nitrogen atmosphere. [b] Deuteriochloroform. [c] Carbon tetrachloride. [d] Compounds 5 could not be determined by elemental analysis for their instability.

on [6]. We reported the synthesis of triphenodioxazines using electrochemical reaction which was clean and gave few by-products [7]. Therefore, this method was employed to obtain carbazodioxazines. The electrochemical oxidation was carried out using platinum electrodes and tetra-*n*-butylammonium bromide (TBAB) as a supporting electrolyte under a constant current. It was considered that the formation of 1,4-dioxazine ring occurred by indirect oxidation due to the bromonium ion generated by elec-

trolysis of TBAB.

Carbazodioxazines having long alkyl groups became soluble in organic solvents. The structures were established on the basis of elemental and spectroscopic analyses in Table 2 and 3. In particular, the <sup>1</sup>H-nmr spectra of 7 indicated the signal due to the isolated aromatic protons of the 6 and 16 positions as a singlet at δ 6.61-6.64 ppm. It suggests that electrochemical oxidation of 6 selectively proceeded to give the angular type compound 7.

Table 2  
Physical and Analytical Data of Carbazodioxazines 7

Compound	R <sup>1</sup> <sub>n</sub>	R <sup>2</sup> <sub>n</sub>	Yield (%)	Solubility (mol/l)	Molecular Formula	Molecular Weight	Elemental Analysis % (C/F/N)		
							C	H	N
7Ia	1	8	27	1 x 10 <sup>-3</sup> [a]	C <sub>48</sub> H <sub>50</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	817.82	70.49 70.24	6.16 6.21	6.85 6.77
7Ib	1	10	37	6 x 10 <sup>-4</sup> [a]	C <sub>52</sub> H <sub>58</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	873.92	71.46 71.21	6.69 6.92	6.41 6.33
7Ic	1	12	24	2 x 10 <sup>-4</sup> [a]	C <sub>56</sub> H <sub>66</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	930.03	72.32 71.94	7.15 7.22	6.03 5.69
7Id	1	18	20	5 x 10 <sup>-5</sup> [a]	C <sub>68</sub> H <sub>90</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1098.34	74.36 73.97	8.26 8.20	5.10 4.95
7IIa	8	8	34	9 x 10 <sup>-4</sup> [b]	C <sub>62</sub> H <sub>78</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1014.18	73.42 73.33	7.75 7.62	5.53 5.61
7IIb	8	10	20	1 x 10 <sup>-4</sup> [b]	C <sub>66</sub> H <sub>86</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1070.29	74.06 73.93	8.10 8.04	5.24 5.28
7IIc	8	12	29	2 x 10 <sup>-5</sup> [b]	C <sub>70</sub> H <sub>94</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1126.39	74.64 74.65	8.41 8.33	4.98 4.86
7IId	8	18	16	3 x 10 <sup>-4</sup> [b]	C <sub>82</sub> H <sub>118</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1294.70	76.07 75.78	9.19 9.11	4.33 4.35
7IIIa	12	8	35	8 x 10 <sup>-4</sup> [b]	C <sub>70</sub> H <sub>94</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1126.39	74.64 74.53	8.41 8.25	4.96 4.83
7IIIb	12	10	31	8 x 10 <sup>-4</sup> [b]	C <sub>74</sub> H <sub>102</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1182.50	75.16 75.13	8.69 8.72	4.74 4.66
7IIIc	12	12	27	1 x 10 <sup>-3</sup> [b]	C <sub>78</sub> H <sub>110</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1238.60	75.63 75.49	8.95 8.93	4.52 4.64
7IIId	12	18	38	1 x 10 <sup>-4</sup> [b]	C <sub>90</sub> H <sub>134</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub>	1406.91	76.83 76.56	9.60 9.53	3.98 3.86

[a] Measured in chloroform at 30°. [b] Measured in carbon tetrachloride at 30°.

Table 3  
Spectroscopic Data of Carbazoledioxazines 7

Compound	MS (Mz/M <sup>+</sup> )	UV-VIS (chloroform) (λ max/log ε)	<sup>1</sup> H-NMR (deuteriochloroform) δ (ppm)
7Ia	816	623, 576, 358, 314, 269 4.94, 4.73, 3.95, 4.56, 4.79	0.87 (t, CH <sub>3</sub> ), 1.15-1.90 (m, C <sub>6</sub> H <sub>12</sub> ), 4.12 (s, CH <sub>3</sub> ), 4.26 (t, CH <sub>2</sub> ), 6.62 (s, CH-6 and 16), 7.30-7.45 (m, aromatic), 8.44 (d, CH-1 and 11)
7Ib	872	622, 575, 357, 314, 269 4.94, 4.73, 3.94, 4.56, 4.79	0.87 (t, CH <sub>3</sub> ), 1.13-1.89 (m, C <sub>8</sub> H <sub>16</sub> ), 4.12 (s, CH <sub>3</sub> ), 4.25 (t, CH <sub>2</sub> ), 6.61 (s, CH-6 and 16), 7.30-7.50 (m, aromatic), 8.43 (d, CH-1 and 11)
7Ic	928	623, 576, 358, 314, 269 4.94, 4.73, 3.96, 4.58, 4.83	0.87 (t, CH <sub>3</sub> ), 1.20-1.90 (m, C <sub>10</sub> H <sub>20</sub> ), 4.12 (s, CH <sub>3</sub> ), 4.25 (t, CH <sub>2</sub> ), 6.61 (s, CH-6 and 16), 7.30-7.46 (m, aromatic), 8.42 (d, CH-1 and 11)
7Id	[a]	623, 576, 354, 315, 269 4.89, 4.67, 3.92, 4.53, 4.77	0.87 (t, CH <sub>3</sub> ), 1.20-1.95 (m, C <sub>16</sub> H <sub>32</sub> ), 4.12 (s, CH <sub>3</sub> ), 4.26 (t, CH <sub>2</sub> ), 6.62 (s, CH-6 and 16), 7.33-7.48 (m, aromatic), 8.44 (d, CH-1 and 11)
7IIa	1012	619, 572, 360, 314, 269 4.93, 4.72, 3.94, 4.56, 4.80	0.87 (t, CH <sub>3</sub> ), 0.93 (t, CH <sub>3</sub> ), 1.20-2.10 (m, C <sub>6</sub> H <sub>12</sub> and C <sub>6</sub> H <sub>12</sub> ), 4.11-4.34 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.61 (s, CH-6 and 16), 7.25-7.44 (m, aromatic), 8.41 (d, CH-1 and 11)
7IIb	[a]	619, 573, 360, 314, 269 4.92, 4.71, 3.94, 4.54, 4.79	0.87 (t, CH <sub>3</sub> ), 0.93 (t, CH <sub>3</sub> ), 1.13-2.10 (m, C <sub>8</sub> H <sub>16</sub> and C <sub>6</sub> H <sub>12</sub> ), 4.16-4.32 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.63 (s, CH-6 and 16), 7.23-7.47 (m, aromatic), 8.43 (d, CH-1 and 11)
7IIc	[a]	619, 572, 358, 314, 269 4.94, 4.73, 3.96, 4.56, 4.80	0.86 (t, CH <sub>3</sub> ), 0.92 (t, CH <sub>3</sub> ), 1.09-2.06 (m, C <sub>10</sub> H <sub>20</sub> and C <sub>6</sub> H <sub>12</sub> ), 4.13-4.30 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.61 (s, CH-6 and 16), 7.16-7.47 (m, aromatic), 8.42 (d, CH-1 and 11)
7IId	[a]	618, 572, 361, 314, 270 4.96, 4.75, 3.98, 4.57, 4.82	0.87 (t, CH <sub>3</sub> ), 0.93 (t, CH <sub>3</sub> ), 1.13-2.09 (m, C <sub>16</sub> H <sub>32</sub> and C <sub>6</sub> H <sub>12</sub> ), 4.20-4.31 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.63 (s, CH-6 and 16), 7.29-7.47 (m, aromatic), 8.43 (d, CH-1 and 11)
7IIIa	[a]	620, 573, 358, 314, 270 4.88, 4.67, 3.97, 4.52, 4.77	0.83-0.99 (m, CH <sub>3</sub> and CH <sub>3</sub> ), 1.30-2.10 (m, C <sub>6</sub> H <sub>12</sub> and C <sub>10</sub> H <sub>20</sub> ), 4.12-4.34 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.63 (s, CH-6 and 16), 7.26-7.45 (m, aromatic), 8.43 (d, CH-1 and 11)
7IIIb	[a]	620, 573, 352, 314, 270 4.87, 4.66, 3.93, 4.51, 4.76	0.83-0.92 (m, CH <sub>3</sub> and CH <sub>3</sub> ), 1.21-2.09 (m, C <sub>8</sub> H <sub>16</sub> and C <sub>10</sub> H <sub>20</sub> ), 4.20-4.28 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.64 (s, CH-6 and 16), 7.28-7.44 (m, aromatic), 8.44 (d, CH-1 and 11)
7IIIc	[a]	620, 584, 357, 314, 270 4.85, 4.64, 3.90, 4.48, 4.73	0.83-0.95 (m, CH <sub>3</sub> and CH <sub>3</sub> ), 1.20-2.10 (m, C <sub>10</sub> H <sub>20</sub> and C <sub>10</sub> H <sub>20</sub> ), 4.21-4.32 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.63 (s, CH-6 and 16), 7.26-7.46 (m, aromatic), 8.44 (d, CH-1 and 11)
7IIId	[a]	619, 572, 361, 314, 270 4.95, 4.74, 3.99, 4.57, 4.82	0.83-0.91 (m, CH <sub>3</sub> and CH <sub>3</sub> ), 1.20-2.09 (m, C <sub>16</sub> H <sub>32</sub> and C <sub>10</sub> H <sub>20</sub> ), 4.20-4.30 (m, CH <sub>2</sub> and CH <sub>2</sub> ), 6.64 (s, CH-6 and 16), 7.30-7.48 (m, aromatic), 8.44 (d, CH-1 and 11)

[a] Molecular weights of these compounds were too large to measure the mass spectrum.

Introduction of four long alkyl groups into carbazoledioxazines results in increasing solubility in organic solvents such as haloalkanes and aromatic hydrocarbons. The solubility was measured in chloroform or carbon tetrachloride. The solubility of **7Id** and **7IIId** which have too long alkyl groups was lower than that of the others. These results suggested that the solubility was concerned with chromophore-chromophore interaction, cohesive force of long alkyl groups, and affinity for solvent. Compounds **7** were less soluble than compounds **8**. In order to prepare the LB film, it is usually required that the compounds are soluble over 10<sup>-5</sup> mole/l range and carbazoledioxazines having long alkyl groups were applicable to the LB film.

In the visible spectra, **7** showed a bathochromic shift about 20 nm in comparison with **8** because of electron donation of the alkyloxy groups.

Thermal behavior of **7** was investigated by TG-DTA and DSC under a nitrogen atmosphere and the decomposition temperature (*T<sub>dec</sub>*) and the transition temperature (*T<sub>i</sub>*) are shown in Figure 1. No endothermic peaks of **8** were observed before the melting point but some endothermic peaks were observed for **7**. Several endothermic peaks (*T<sub>i</sub>*) were based on the phase transitions as they were not accompanied by weight loss. The *T<sub>1</sub>* and *T<sub>2</sub>* were lower and the *T<sub>3</sub>* was higher in proportion to the length of the alkyl groups. In particular, the *T<sub>1</sub>* was the transition points into a viscous liquid; it may be a type of a mesophase.

In conclusion, carbazoledioxazines with an angular type structure were synthesized by electrochemical oxidation. The introduction of long alkyl groups results in increasing their solubility in organic solvents; the structure can be confirmed by <sup>1</sup>H-nmr. The phase transitions are observed on thermal analyses. In the visible spectra **7** shows a little bathochromic shift in comparison with **8**.

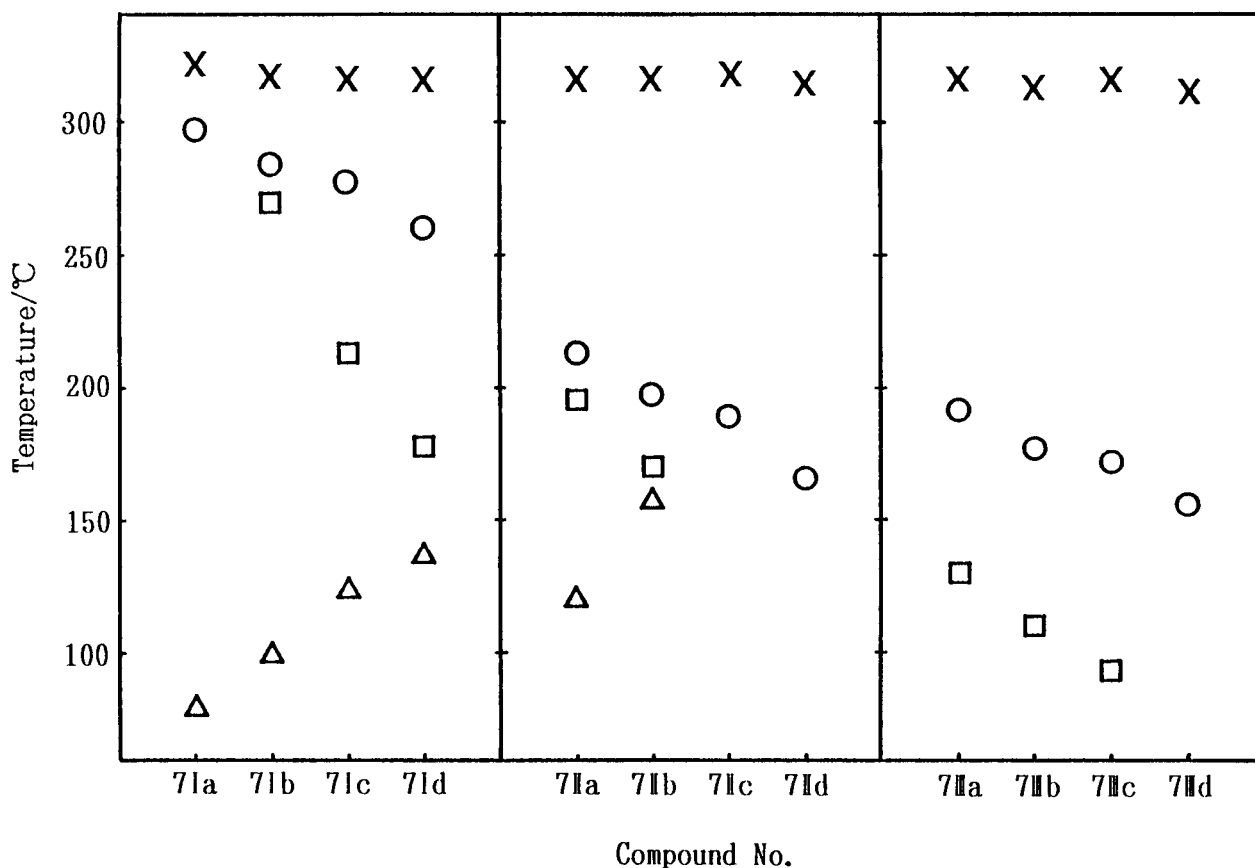


Figure 1. Transition and decomposition temperatures of **7**.

× : T<sub>dec</sub>, ○ : T<sub>1</sub>, □ : T<sub>2</sub>, △ : T<sub>3</sub>

## EXPERIMENTAL

Thermal behavior was measured on a Rigaku TG-DTA and a Seiko Denshi DSC. Infrared spectra were obtained on a Jasco IR-A2 and a Perkin-Elmer FT-IR1640. The mass and electronic absorption spectra were measured with a Shimadzu QP-1000 and a Shimadzu UV-2100, respectively. The <sup>1</sup>H-nmr spectra were recorded with a JEOL PMX60Si, a JEOL FX90Q and a Bruker AM400 with TMS as the internal standard.

### Solubility Measurements.

The solution of the sample was saturated by heating, and kept at 30° for 3 days to attain equilibrium. The equilibrium solution (1 ml) was filtered with a glass filter and the filtrate was evaporated. A certain quantity of chloroform was added to the residue and the uv spectra of the solution was measured in order to determine the solubility by their absorbance and a known molecular extinction coefficient.

The intermediate **2-6** were prepared according to the previous procedure [4].

### 2-Octyloxycarbazole **2II**.

Metallic sodium (130 mg-atom) dissolved in methanol (50 ml)

was added to a solution of 2-hydroxycarbazole **1** (20 g, 110 mmoles) in dry methanol (310 ml). 1-Bromooctane (27 g, 140 mmoles) was added to the solution and refluxed for 7 hours. The reaction mixture was filtered, washed with cool methanol and water and recrystallized from ethanol to give colorless plates, (24 g, 73%), mp 208-209°; ir (potassium bromide): 3400 (ν NH), 1228, 1023 (ν OCH<sub>2</sub>).

### 2-Octyloxy-9-octadecylcarbazole **3IIId**.

1-Bromooctadecane (8.6 g, 36 mmoles) was added dropwise to a mixture of **2II** (7.0 g, 24 mmoles) and BTEAC (0.14 g, 0.61 mmole) as a phase transfer catalyst in benzene (6 ml) and 50% aqueous sodium hydroxide (50 ml), then the mixture was vigorously stirred for 6 hours at 50°. The reaction mixture was added to hot water (500 ml) and stirred for 2 hours. After cooling, the precipitate was filtered, washed with dilute aqueous sodium hydroxide and water and recrystallized from *n*-hexane at -78° to give a colorless powder (10 g, 76%), mp 49-50°; ir (potassium bromide): 2920, 2850 (ν CH<sub>2</sub>).

### 3-Nitro-9-octadecyl-2-octyloxycarbazole **4IIId**.

Nitric acid (1.2 ml, d = 1.42) in acetic acid (90 ml) was added dropwise to a solution of **3IIId** (11 g, 19 mmoles) in acetic acid

(130 ml) at 17° with stirring for 2 hours. 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:*n*-hexane (5:3). The fraction was recrystallized from *n*-hexane to give a yellow powder (6.5 g, 56%), mp 62-63°; ir (potassium bromide): 1518, 1340 ( $\nu$  NO<sub>2</sub>).

#### 3-Amino-9-octadecyl-2-octyloxycarbazole **5IIId**.

Iron powder (10 g-atoms), water (16 ml) and concentrated hydrochloric acid (2.5 ml) was stirred at 40° under a nitrogen atmosphere for 30 minutes. A solution of **4IIId** (5.4 g, 9.1 mmoles) in ethanol (100 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 (2.6 g, 51%), mp 52-53°; ir (potassium bromide): 3420, 3350 ( $\nu$  NH<sub>2</sub>).

#### 2,5-Bis(9-octadecyl-2-octyloxy-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone **6IIId**.

A mixture of **5IIId** (1.1 g, 2.0 mmoles), chloranil (0.24 g, 0.98 mmole) and sodium acetate (1.6 g, 20 mmoles) in ethanol (17 ml) was refluxed for 6 hours. The precipitate was filtered and washed with dilute hydrochloric acid, water and ethanol. The residue was recrystallized from *n*-hexane to give a brown powder (1.2 g, 71%), mp 98°; ir (potassium bromide): 3240 ( $\nu$  NH), 1655 ( $\nu$  C=O).

9,19-Dichloro-5,15-dihydro-5,15-dioctadecyl-7,17-dioctyloxydiindolo[2,3-*c*:2',3'-*n*]triphenodioxazine (Carbazoledioxazine with an Angular Type Structure) **7IIId**.

A mixture of **6IIId** (0.65 g, 0.50 mmole) and TBAB (1.1 g, 3.4 mmoles) in acetonitrile:*N,N*-dimethylformamide (1:2, 83 ml) was dissolved at 60° under a nitrogen atmosphere. The reaction mixture was passed 8F/mole of electricity under a constant current (0.02A/cm<sup>2</sup>) using platinum electrodes. The precipitate was filtered and washed with *n*-hexane, methanol and water. The resulting residue was chromatographed on silica gel eluting with toluene and recrystallized from chloroform:*n*-hexane (1:1) to give a purple powder (105 mg, 16%); ir (potassium bromide): 1638, 1550 ( $\nu$  C=N), 1605 ( $\nu$  C=C).

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