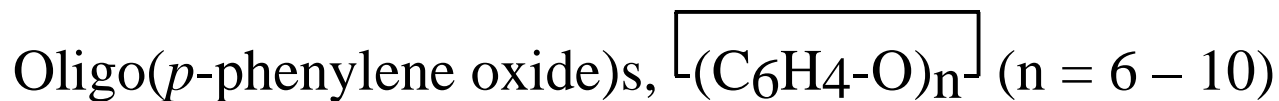


## Synthesis and Structure of Cyclic



*Daisuke Takeuchi, Itaru Asano, and Kohtaro Osakada\**

**Crystal Structure Determination.** Crystals were mounted in glass capillary. The data were collected at a temperature of  $-160 \pm 1$  °C to a maximum  $2\theta$  value of  $55.0^\circ$  on Rigaku Saturn CCD area detector. Calculations were carried out by using the program package Crystal Structure for Windows. The structure was solved by direct methods and expanded using Fourier techniques. A full matrix least squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Atomic scattering factors were obtained from the literature.<sup>9</sup> Crystallographic data and details of refinement of the cyclic oligo(*p*-phenylene oxide)s are summarized in Table S-1.

TABLE S-1. Crystallographic Parameters of Cyclic Oligo(*p*-phenylene oxide)s

	(C-6) <sub>2</sub> (CH <sub>2</sub> Cl <sub>2</sub> ) <sub>3</sub>	C-7·(CHCl <sub>3</sub> ) <sub>2</sub>	C-8·(CHCl <sub>3</sub> ) <sub>2</sub>	C-9·(CHCl <sub>3</sub> )(C <sub>6</sub> H <sub>14</sub> )
Empirical Formula	C <sub>75</sub> H <sub>54</sub> Cl <sub>6</sub> O <sub>12</sub>	C <sub>44</sub> H <sub>30</sub> Cl <sub>6</sub> O <sub>7</sub>	C <sub>50</sub> H <sub>34</sub> Cl <sub>6</sub> O <sub>8</sub>	C <sub>61</sub> H <sub>51</sub> Cl <sub>3</sub> O <sub>9</sub>
Formula Weight	1359.96	883.43	975.53	1034.43
Crystal System	Triclinic	monoclinic	Triclinic	Triclinic
Space Group	P-1 (# 2)	P2 <sub>1</sub> /n (# 14)	P-1 (# 2)	P-1 (# 2)
<i>a</i> , Å	10.127(8)	14.61(2)	9.596(7)	10.566(9)
<i>b</i> , Å	12.462(9)	10.187(15)	14.145(10)	14.099(11)
<i>c</i> , Å	25.76(2)	26.99(4)	17.077(13)	19.13(1)
<i>α</i> , deg	84.40(4)		83.87(4)	77.94(4)
<i>β</i> , deg	84.69(3)	101.36(3)	81.88(3)	74.87(3)
<i>γ</i> , deg	78.62(3)		87.12(3)	76.71(3)
<i>V</i> , Å <sup>3</sup>	3163(4)	3938(11)	2280(3)	2642.8(35)
<i>Z</i>	2	4	2	2
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.428	1.490	1.421	1.300
No. of data	17660	28432	16649	15257
No. of obsd. data	4234	2616	5569	3439
No. of Variables	892	544	611	655
<i>R</i> ( <i>F</i> <sub>0</sub> )	0.069	0.056	0.081	0.110
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>0</sub> )	0.104	0.050	0.133	0.159
GOF	0.997	0.907	0.954	0.784

## Thermogravimetric Analysis and Differential Scanning Carolimetry

Results of thermogravimetric analysis and differential scanning carolimetry of the obtained cyclic oligo(*p*-phenylene oxide)s are summarized in Table S-2. Temperature of 5% weight loss,  $T_d^5$ , is raised with increment of the ring size . DSC of **C-6** showed no melting point of **C-6**, presumably due to its higher melting point than decomposition temperature. Melting points of **C-8** and **C-10** are 350 and 148 °C, respectively. First scan of **C-9** shows a single endothermic peak at 280 °C, whereas second scan of **C-9** shows two endothermic peaks at 210 and 273 °C. These results indicate some phase transition takes place at the temperature. The melting points of **C-6**, **C-8**, **C-9**, and **C-10** decrease in this order. On the other hand, melting point of **C-7** is 190 °C, which is exceptionally lower than other cyclic oligo(*p*-phenylene oxide)s. This is probably due to the more flexible structure of **C-7** as revealed by X-ray crystal structure analysis. The melting points of poly(*p*-phenylene oxide) and linear hexamer are 171 °C, which is lower than the cyclic oligo(*p*-phenylene oxide)s.

TABLE S-2. Thermogravimetric Analysis and Differential Scanning Carolimetry of Cyclic Oligo(*p*-phenylene oxide)s

	$T_d^5/^\circ\text{C}$	$T_m/^\circ\text{C}$
C-6	340	-
C-7	380	190
C-8	408	350
C-9	450	210 and 280
C-10		148