The Molecular and Crystal Structure of the Cyclic Pentamer of Formaldehyde, 1,3,5,7,9-Pentoxecane

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The crystal structure of the cyclic pentamer of formaldehyde, 1,3,5,7,9-pentoxecane, has been determined by the X-ray diffraction method. The unit cell is orthorhombic, with $a=8.154$ Å, $b=10.673$ Å, $c=7.666$ Å. The space group is Pbcn, and there are four molecules per unit cell. The structure was refined by the block-diagonal least-squares method to a final discrepancy factor, R, of 0.049, using 712 reflections observed with an automatic four-circle single-crystal diffractometer. The molecules in the crystals are ten-membered rings with an exact C_2–2 symmetry; the torsion angles of the five independent C–O bonds are 72.9°, −118.7°, 84.2°, −123.4°, and 69.8°, and the two halves of the molecule are related by a twofold rotation axis. The averaged C–O bond length is 1.410 Å, and the averaged C–O–C and O–C–O bond angles are 115.6° and 111.8° respectively. The close intramolecular H···H distances are 2.17 Å and 2.20 Å.

In a previous paper,[1] the molecular and crystal structure of the cyclic hexamer of formaldehyde, 1,3,5,7,9,11-hexoxecane $(-CH_2-O-)_6$, was reported. The cyclic pentamer, 1,3,5,7,9-pentoxecane $(-CH_2-O-)_5$, is also of interest from the viewpoint of molecular conformation. To date, many investigations have been made with regard to the structure determination of ring compounds of the $(-X-)_m$ or $(-X-Y-)_m$ type. However, little is known of ten-membered ring compounds with such a sequence. Pentoxecane is also interesting with respect to the radiation-induced solid-state polymerization.[2,3] Pentoxecane undergoes a ring-opening polymerization in the crystalline state to form linear polyoxymethylene $(-CH_2-O-)_n$ under irradiation. The polymer resulting from the solid-state polymerization is highly crystalline, just as in the cases of trioxecane $(-CH_2-O-)_3$,[4-6] tetroxocane $(-CH_2-O-)_4$,[7] and hexoxecane $(-CH_2-O-)_6$.[1] The preferred orientations of the resultant polymer crystals are, however, characteristic for each cyclic oligomer. In the present paper, the molecular and crystal structure of pentoxecane will be reported, and the relationship between the crystal structure and the solid-state polymerization will be discussed briefly.

Experimental

The pentoxecane was obtained through the courtesy of Drs. Miyaka and Yamauchi of Mitsui-Toatsu Chemicals, Inc. The melting point of pentoxecane is 61.3 °C. Crystals were grown as rhombohedrons by the slow evaporation of a methanol solution. The crystals were found to sublime slowly when exposed to the atmosphere. To prevent the sublimation of the samples, single crystals were sealed in thin-walled Lindemann glass capillary tubes. The cell constants were determined from Weissenberg photographs and θ values measured with a single-crystal diffractometer.

Crystal data:

1,3,5,7,9-pentoxecane, $(-CH_2-O-)_5$

Molecular weight 150.1

Orthorhombic $a=8.154\pm0.005$ Å

$b=10.673\pm0.009$

$c=7.666\pm0.005$

Volume of the unit cell: $V=661.8$ Å^3

Density, calculated with $Z=4$: $D_x=1.494$ g/cm^3; measured: $D_m=1.49$ g/cm^3

Number of electrons per unit cell: $F(000)=320$

Absorption coefficient for $\lambda_{MoK\alpha}$ (=0.7107 Å): $\mu=1.62$ cm^{-1}.

The systematic absences of $0kl$ for k odd, of $h0l$ for l odd, and of $hk0$ for $h+k$ odd indicate that the space group is Pbcn.

Intensity measurements were performed using a Rigaku-Denki automatic four-circle single-crystal diffractometer with MoKα radiation. The crystal used for intensity measurements was $0.2\times0.2\times0.3$ mm^3 in size. The integrated intensities were measured for all reflections in the sphere of the radius $\sin\theta/\lambda<0.65$ Å^{-1}, using the θ—2θ (moving crystal, moving counter) technique. The procedures used in getting the observed structure factors were similar to those used in the case of hexoxecane.[1] A total of 749 independent reflections were examined, and 712 reflections were observed. No correction was made for absorption. In a previous paper,[2] the solid-state polymerization of pentoxecane by X- or γ-irradiation was reportod. The polymer yield depends upon the irradiation temperature. The present intensity measurements were performed at 16 °C, and, judging from the constancy of the intensities of three reference reflections measured every 25 reflections, such a polymerization was found to be suppressed during the measurements. Therefore, it was unnecessary to correct the observed structure factors for any decrease caused by polymerization.

Structure Determination

The space group Pbcn possesses eight general equivalent points. Since there are four molecules in the unit cell, the molecules themselves have one kind of twofold symmetry. The possible symmetry of the molecule which can possess in the space group Pbcn is either a center of symmetry or a twofold rotation

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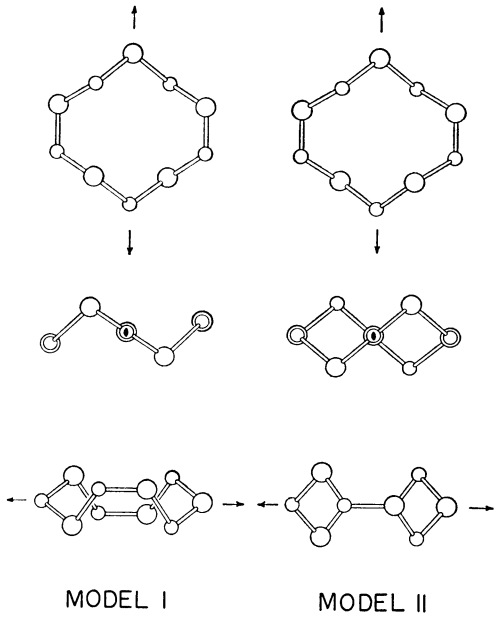

Fig. 1. Two models of a pentoxecane molecule.

axis. Since the ten-membered cyclic molecules of pentoxecane cannot have a center of symmetry, they must possess a twofold rotation axis. In the pentoxecane ring, the twofold rotation axis can pass through a carbon atom and an oxygen atom lying across the ring from each other. Two typical possible models which can satisfy the twofold rotation symmetry are shown in Fig. 1. The conformation of Model I is denoted by the sequence of $G\bar{S}CS\bar{G}\bar{G}GSC\bar{S}G$, and Model II, by $\bar{G}S\bar{G}S\bar{G}\bar{G}GS\bar{G}SG$, or their enantiomers, C is a *cis*-form (the torsion angle is defined as 0°), G and S are a clockwise *gauche*-form and a *skew*-form respectively, and $\bar{G}$ and $\bar{S}$ are a counter-clockwise *gauche*-form and a *skew*-form respectively. Since the twofold rotation axis in the molecule coincides with the twofold rotation axis parallel to the *b* axis, the two models were selected by a comparison of the F_o and F_c of (*h*0*l*) reflections, varying the rotation angle of the molecule about the twofold rotation axis. Model I was easily excluded. Therefore Model II was refined three-dimensionally by a block-diagonal least-squares program of Dr. Ashida using a NEAC 2200 electronic computer at Osaka University. The five independent hydrogen atoms were revealed unambigously by a difference Fourier synthesis, as is shown in Fig. 2, the maxima being between 0.6 and 0.7 e/Å^3. The coordinates of these peaks were introduced into the refinement as hydrogen atoms and were given isotropic thermal factors. The weighting scheme used in the least-squares calculation was:

$$w = 0 \text{ for } F_o = 0$$
$$w = 0.4 \text{ for } 0 < |F_o| \leq F_{min}$$
$$w = 1.0 \text{ for } F_{min} < |F_o| \leq 4F_{min}$$
$$w = (4F_{min}/|F_o|)^2 \text{ for } |F_o| > 4F_{min}$$
$$F_{min} = 30 \text{ in the scale of Table 2.}$$

The atomic scattering factors used for carbon and

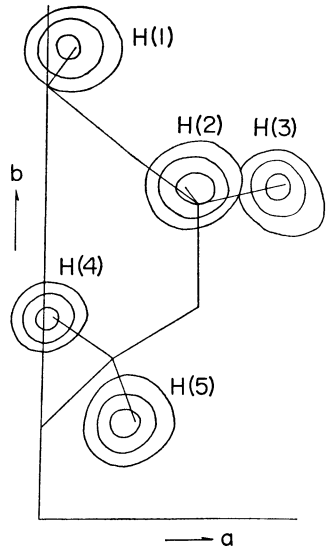

Fig. 2. Composite difference Fourier map. Contours are at intervals of 0.2 e/Å^3, begining at 0.2 e/Å^3.

oxygen were those[8] in the International Tables for X-ray Crystallography, Vol. III, while for hydrogen the bonded values of Stewart *et al.*[9] were used. A set of final structure factors for all the observed reflections shown in Table 2 was calculated on the basis of the final positional and thermal parameters shown in Table 1. The discrepancy factor, $R(= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$, for the observed reflections was 0.049.

Results and Discussion

Molecular Structure and Thermal Motion. Figure 3 shows the molecular structure of pentoxecane. The ten-membered ring molecule has a C_2–2 symmetry; the twofold rotation axis passes through C(1) and O(3). The bond lengths, bond angles, and torsion

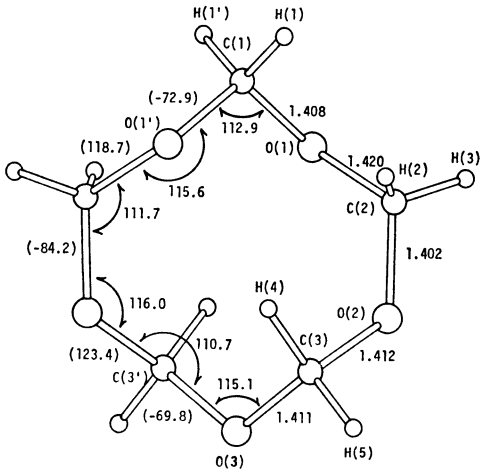

Fig. 3. Bond lengths (Å), bond angles (°), and torsion angles in parentheses (°) of pentoxecane molecule.

8) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.
9) R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

TABLE 1. THE FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

	x	y	z	$B_{ij}\times 10^5$					
				$B_{11}(B)$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.5000	0.4968(2)	0.2500	1257(34)	671(18)	1481(41)	0	468(65)	0
O(1)	0.6290(1)	0.4239(1)	0.1820(2)	1139(18)	882(11)	1310(19)	99(23)	428(31)	14(24)
C(2)	0.7290(2)	0.3626(2)	0.3075(2)	1011(24)	892(17)	1719(33)	−166(33)	−180(48)	−238(38)
O(2)	0.7234(2)	0.2321(1)	0.2888(2)	1207(21)	874(12)	2063(27)	347(25)	−104(37)	−280(29)
C(3)	0.5910(2)	0.1710(2)	0.3716(2)	1529(29)	784(16)	1823(35)	59(38)	−865(57)	286(38)
O(3)	0.5000	0.1000(2)	0.2500	2019(38)	666(16)	2695(47)	0	−1814(72)	0
H(1)	0.543(2)	0.548(2)	0.346(2)	3.3(4)					
H(2)	0.695(2)	0.388(2)	0.428(2)	3.2(4)					
H(3)	0.843(3)	0.394(2)	0.278(3)	5.8(6)					
H(4)	0.516(2)	0.238(2)	0.434(2)	3.8(4)					
H(5)	0.637(2)	0.113(2)	0.456(3)	3.8(4)					

The anisotropic temperature factors are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$. The isotropic temperature factors for hydrogen atoms are of the form $\exp(-B\sin^2\theta/\lambda^2)$ and are given in Å^2.

TABLE 2. THE OBSERVED AND THE FINAL CALCULATED STRUCTURE FACTORS ($\times 10$)

H	K	F_o	F_c
		(L = 0)	
0	2	183	-191
0	4	204	-224
0	6	279	-304
0	8	86	88
0	10	7	2
0	12	94	100
1	1	207	203
1	3	574	603
1	5	27	-26
1	7	32	-27
1	9	4	-7
1	11	7	-8
1	13	32	38
2	0	270	-261
2	2	606	606
2	4	94	-79
2	6	148	150
2	8	99	-104
2	10	123	138
2	12	47	54
3	1	290	-279
3	3	104	108
3	5	412	427
3	7	99	103
3	9	42	50
3	11	22	-28
3	13	11	13
4	0	227	229
4	2	258	-254
4	4	194	191
4	6	18	19
4	8	254	269
4	10	4	3
4	12	31	-28
5	1	17	-18
5	3	53	-53
5	5	137	135
5	7	242	247
5	9	70	-69
5	11	24	22
6	0	94	-101
6	2	229	234
6	4	19	15
6	6	54	-53
6	10	85	83
7	1	77	77
7	3	43	44
7	5	101	107
7	7	91	-96
7	9	4	-1
8	0	196	202
8	2	60	61
8	4	20	-21
8	6	56	-57
8	8	20	17
9	1	58	60
9	3	16	22
9	5	38	-41
9	7	55	54
10	0	34	31
10	4	10	11
		(L = 1)	
0	2	194	190
0	4	485	484
0	6	189	-182
0	8	99	101
0	10	59	-62
0	12	33	-33
1	1	658	664
1	2	136	-127
1	3	404	386
1	5	56	51
1	6	128	-124
1	7	86	-81
1	8	45	46
1	9	84	-88
1	10	41	41
1	11	21	-25
1	13	47	42
2	1	191	195
2	2	518	-521
2	3	181	-171
2	4	159	-148
2	5	174	-177
2	6	297	294
2	7	49	52
2	8	75	-78
2	9	38	38
2	10	51	53
2	11	9	3
2	12	40	-37
2	13	14	16
3	1	284	-283
3	2	319	-309
3	3	14	10
3	4	19	16
3	5	150	-136
3	6	34	33
3	7	10	-11
3	8	54	-54
3	9	6	-1
3	10	56	55
3	11	63	61
3	13	35	33
4	1	2	-3
4	2	192	-174
4	3	24	-22
4	4	287	-287
4	5	44	-43
4	6	125	-128
4	7	65	64
4	8	227	228
4	9	22	-21
4	10	26	24
4	11	20	-18
4	12	16	13
5	1	145	150
5	2	75	75
5	3	126	-119
5	4	78	75
5	5	31	35
5	6	35	-34
5	7	132	-132
5	8	13	-9
5	9	78	77
5	11	50	47
6	1	77	76
6	2	32	-35
6	3	33	37
6	4	54	-52
6	5	38	40
6	6	97	102
6	7	26	-29
6	8	5	6
6	10	22	-21
6	11	13	-11
7	1	114	-116
7	2	44	46
7	3	175	179
7	4	6	4
7	5	52	52
7	9	81	-78
7	10	23	-22
8	1	74	-70
8	2	73	73
8	4	38	41
8	5	27	20
8	6	9	8
8	7	9	-9
8	8	5	8
9	1	136	134
9	2	10	7
9	3	10	15
9	4	39	-40
9	5	13	15
9	7	42	-38
10	2	40	-43
10	3	20	-21
		(L = 2)	
0	0	1208	1418
0	2	30	-19
0	4	27	-10
0	6	258	255
0	8	126	-117
0	10	24	-18
0	12	51	-52
1	0	424	-432
1	1	187	-188
1	2	440	433
1	3	227	-220
1	4	9	8
1	5	111	-112
1	6	140	-146
1	7	22	-30
1	8	109	-107
1	10	50	46
1	11	20	-14
1	12	15	12
1	13	38	-32
2	0	257	245
2	1	378	356
2	2	556	-552
2	3	168	-163
2	4	146	133
2	5	18	-13
2	6	91	-91
2	7	125	-123
2	8	38	44
2	9	74	-75
2	10	123	-126
2	11	48	48
2	12	36	-30
2	13	39	32
3	0	254	237
3	1	175	169
3	2	44	45
3	3	88	-92
3	4	13	-7
3	5	320	-317
3	6	219	-217
3	7	64	-68
3	8	72	70
3	9	45	-43
3	10	15	-10
3	11	20	22
3	12	24	-19
4	0	304	-306
4	1	44	45
4	2	151	154
4	3	140	-134
4	4	82	-82
4	5	11	9
4	6	27	-30
4	7	81	84
4	8	177	-178
4	9	56	-54
4	10	16	-14
4	11	16	18
4	12	3	1
5	0	288	-289
5	1	59	57
5	2	14	16
5	3	69	-68
5	4	23	22
5	5	88	-84
5	6	45	45
5	7	163	-161
5	8	10	11
5	9	24	26
5	10	34	31
5	11	6	-4
6	0	11	8
6	1	168	-172
6	2	154	-158
6	3	27	25
6	4	18	13
6	5	98	103
6	6	13	-15
6	7	3	3
6	8	19	22
6	9	32	36
6	10	69	-64
6	11	25	-21
7	0	42	39
7	1	46	-45
7	2	78	-81
7	3	66	-62
7	4	15	-17
7	5	70	-72
7	6	60	61
7	7	61	65
7	8	17	18
7	9	29	-22
8	0	157	-156
8	1	6	-1
8	3	26	25
8	4	33	-31
8	5	24	25
8	6	24	-23
8	7	23	24
8	8	19	-18
9	0	64	60
9	1	41	-41
9	2	11	9
9	3	22	-18
9	4	20	-20
9	5	21	17
10	0	10	-12
10	1	6	5
10	2	10	-10
10	3	29	29
		(L = 3)	
0	2	134	-136
0	4	33	31
0	6	30	29
0	8	152	-155
0	10	68	72
0	12	6	-1
1	1	16	-12
1	2	125	119
1	3	195	-187
1	4	83	80
1	5	109	-107
1	6	218	217
1	7	110	112
1	8	117	-118
1	9	18	20
1	10	60	-57
1	11	28	-27
1	12	18	-16
2	1	35	-41
2	2	122	117
2	3	366	362
2	4	159	159
2	5	202	205
2	6	174	-170
2	7	75	-74
2	9	86	-87
2	10	19	-17
2	11	20	-17
2	12	29	26
3	1	52	57
3	2	321	318
3	3	167	-158
3	4	60	62
3	5	80	76
3	6	74	-71
3	7	12	14
3	8	82	83
3	9	21	23
3	10	75	-76
3	11	32	-34
3	12	15	-8
4	1	82	82
4	2	158	155
4	3	37	-39
4	4	36	32
4	5	46	45
4	6	32	38
4	7	66	-68
4	8	87	-88
4	9	30	34
4	10	24	-22
4	11	16	17
4	12	5	5
5	1	176	-183
5	2	155	-156
5	3	26	25
5	4	105	-110
5	5	7	8
5	6	48	50
5	7	21	24
5	8	6	1
5	9	8	-11
5	10	31	31
6	1	145	-147
6	2	87	89
6	3	73	-74
6	4	28	-26
6	5	67	-72
6	6	48	-51
6	7	53	53
6	8	22	18
6	9	7	3
6	10	26	-20
7	1	29	27
7	2	51	-52
7	3	87	-94
7	4	27	-26
7	5	21	24
7	6	36	-33
7	7	26	-31
7	8	36	29
7	9	45	42
8	1	120	120
8	2	9	-6
8	3	5	2
8	5	8	-17
8	6	7	-2
8	7	8	-8
8	8	10	-7
9	1	58	-58
9	3	16	4
9	4	56	57
9	5	11	-15
10	1	32	-21
		(L = 4)	
0	0	173	176
0	2	36	39
0	4	118	125
0	6	137	-142
0	8	154	156
0	10	50	50
0	12	9	-4
1	0	149	151
1	1	5	0
1	2	339	-336
1	3	11	-11
1	4	89	91
1	5	199	204
1	6	82	79
1	7	98	103
1	8	137	137
1	9	47	-44
1	10	52	-54
1	11	28	26
1	12	26	-29
2	0	47	-49
2	1	209	-208
2	2	244	240
2	3	16	-20
2	4	58	-57
2	5	75	77
2	6	20	25
2	7	138	143
2	8	27	26
2	9	26	23
2	10	77	74
2	11	21	-17
2	12	11	7
3	0	414	-424
3	1	6	14
3	2	78	80
3	3	73	75
3	4	37	34
3	5	107	104
3	6	126	124
3	7	20	24
3	8	36	-33
3	9	23	21
3	10	24	25
3	11	4	-7
3	12	13	-7
4	0	286	296
4	1	27	29
4	2	15	-20
4	3	11	10
4	4	15	21
4	5	33	33
4	7	80	-76
4	8	34	35
4	9	31	26
4	10	23	23
4	11	8	4
5	0	236	247
5	1	13	-17
5	2	2	0
5	3	138	141
5	4	22	-19
5	5	7	2
5	6	75	-74
5	7	29	32
5	8	6	12
5	9	19	20
5	10	26	-31
6	0	105	106
6	1	141	148
6	2	51	51
6	3	17	-11
6	4	36	-37
6	5	100	-105
6	6	58	59
6	7	10	3
6	8	19	-15
6	9	40	-37
7	0	33	-31
7	1	10	-11
7	2	63	64
7	3	54	56
7	4	9	11
7	5	47	49
7	6	34	-27
7	7	9	1
7	8	41	-39
9	4	56	57
8	1	19	-20
8	2	11	10
8	3	9	11
8	5	40	37
8	6	18	11
8	7	36	-35
9	0	34	-29
9	1	9	5
9	2	26	-28
9	3	10	13
9	4	13	10
		(L = 5)	
0	2	101	-108
0	4	144	-143
0	6	26	20
0	8	104	103
0	10	5	-10
1	1	31	-29
1	4	92	-90
1	5	34	32
1	6	135	-134
1	7	60	-64
1	8	114	115
1	9	11	18
1	11	40	41
2	1	74	-71
2	2	8	-10
2	3	179	-179
2	4	65	-64
2	5	36	-36
2	6	35	38
2	7	20	-24
2	8	44	47
2	9	70	73
2	10	10	6
2	11	36	32
3	1	70	71
3	2	70	-67
3	3	119	120
3	4	118	-122
3	5	13	13
3	6	83	82
3	7	4	-9
3	8	25	-25
3	9	28	-28
3	10	4	10
3	11	9	-2
4	1	133	-138
4	3	31	-30
4	4	91	92
4	5	18	21
4	6	28	27
4	8	18	-12
4	9	18	-19
5	1	102	107
5	2	134	138
5	3	45	47
5	4	50	57
5	5	21	20
5	6	41	-42
5	8	15	15
5	9	24	-23
5	10	31	-32
6	1	113	117
6	2	41	-42
6	3	29	26
6	4	7	11
6	5	38	46
6	6	12	10
6	7	31	-28
7	1	7	5
7	3	13	14
7	4	44	45
7	5	42	-43
7	6	17	20
7	8	63	-63
8	2	41	-40
8	3	5	-6
8	4	32	-32
8	5	20	-19
9	1	7	-8
9	2	21	-18
		(L = 6)	
0	0	67	74
0	2	20	23
0	4	93	-93
0	6	36	-41
0	8	67	-68
0	10	47	-45
1	0	87	-89
1	1	75	79
1	2	126	127
1	3	35	-40
1	4	52	-53
1	5	114	-114
1	6	19	27
1	7	88	-83
1	8	96	-94
1	10	27	24
2	0	111	-117
2	1	26	29
2	2	43	-46
2	3	67	68
2	4	24	28
2	5	48	-49
2	6	31	-33
2	7	71	-73
2	8	32	-33
2	9	33	24
2	10	23	-25
3	0	258	259
3	1	75	-77
3	2	95	-97
3	3	53	-53
3	4	24	-26
3	5	10	-9
3	6	15	-11
3	8	15	8
3	9	8	0
3	10	28	-25
4	0	149	-153
4	1	38	-38
4	2	81	-80
4	3	35	38
4	4	5	-9
4	5	39	-38
4	6	56	56
4	7	33	33
4	8	19	14
4	9	5	1
5	0	101	-101
5	1	37	-37
5	2	15	17
5	3	60	-64
5	4	14	-13
5	5	15	-16
5	6	40	41
5	7	19	21
5	8	24	-19
6	0	58	-58
6	1	56	-57
6	2	32	-28
6	3	8	-7
6	4	10	13
6	5	66	65
6	6	23	-20
6	7	19	-15
7	0	14	8
7	1	17	11
7	2	15	-12
7	3	9	1
7	4	7	-2
7	5	45	-48
7	6	27	-20
7	8	28	26
8	0	28	26
8	1	25	26
8	3	30	-29
		(L = 7)	
0	2	171	175
0	4	56	58
0	6	22	-24
0	8	12	-12
1	1	2	0
1	2	41	-38
1	3	44	46
1	4	9	8
1	5	44	45
1	6	54	54
1	7	19	-17
1	8	49	-45
1	9	15	-12
2	1	18	15
2	3	31	29
2	5	26	-28
2	6	27	20
2	7	30	28
2	8	31	-30
2	9	21	-16
3	1	65	-69
3	2	17	-19
3	3	88	-92
3	4	41	39
3	5	24	-23
3	6	40	-39
3	7	19	19
3	9	14	19
4	1	57	62
4	2	23	-22
4	3	16	-22
4	4	53	-51
4	5	12	-11
4	6	48	-54
4	7	4	-9
4	8	19	23
5	1	14	9
5	2	41	-37
5	3	52	-52
5	4	16	-21
5	5	50	-47
5	6	32	25
5	7	25	22
6	1	48	-53
6	2	17	-18
6	3	29	20
6	4	37	33
6	5	3	-8
7	2	25	20
7	3	22	15
		(L = 8)	
0	0	58	-61
0	4	42	41
0	6	79	80
1	0	66	62
1	1	46	-52
1	2	29	-31
1	3	50	55
1	4	28	25
1	5	44	48
1	6	39	-34
1	7	40	35
1	8	12	17
2	0	119	116
2	1	28	27
2	4	19	-19
2	5	19	-19
2	6	27	25
2	7	5	1
3	0	41	-37
3	1	68	66
3	2	44	42
3	3	21	19
3	4	16	-11
3	6	13	8
4	0	29	31
4	1	14	12
4	2	83	81
4	3	5	-2
4	4	14	14
4	5	5	2
4	6	47	-48
5	0	27	24
5	1	35	34
5	2	27	-26
5	3	12	10
5	4	16	15
5	5	12	14
6	1	6	-8
6	2	25	17
		(L = 9)	
0	2	92	-87
0	4	25	-21
1	2	8	8
1	3	20	-16
1	4	38	37
1	5	31	-26
2	1	32	29
2	2	11	13
2	3	17	18
2	5	15	18
3	1	29	28
3	2	20	17
3	3	34	35
3	4	24	25

Table 3. Molecular dimensions of pentoxecane

Bond lengths (Å)			
C(1)–O(1)	1.408(3)	C(1)–H(1)	0.98(2)
O(1)–C(2)	1.420(2)	C(2)–H(2)	1.00(2)
C(2)–O(2)	1.402(2)	C(2)–H(3)	1.01(2)
O(2)–C(3)	1.412(2)	C(3)–H(4)	1.05(2)
C(3)–O(3)	1.411(3)	C(3)–H(5)	0.97(2)
average	1.410		1.00
Bond angles (°)			
O(1')–C(1)–O(1)	112.9(2)	H(2)–C(2)–O(1)	110(1)
C(1)–O(1)–C(2)	115.6(2)	H(2)–C(2)–O(2)	112(1)
O(1)–C(2)–O(2)	111.7(2)	H(3)–C(2)–O(1)	103(2)
C(2)–O(2)–C(3)	116.0(2)	H(3)–C(2)–O(2)	110(2)
O(2)–C(3)–O(3)	110.7(2)	H(4)–C(3)–H(5)	110(2)
C(3)–O(3)–C(3')	115.1(2)	H(4)–C(3)–O(2)	110(1)
H(1)–C(1)–H(1')	113(2)	H(4)–C(3)–O(3)	111(1)
H(1)–C(1)–O(1)	109(1)	H(5)–C(3)–O(2)	107(1)
H(1')–C(1)–O(1)	107(1)	H(5)–C(3)–O(3)	108(1)
H(2)–C(2)–H(3)	112(2)		
Torsion angles (°)			
C(1)–O(1)	−72.9	O(2)–C(3)	123.4
O(1)–C(2)	118.7	C(3)–O(3)	−69.8
C(2)–O(2)	−84.2		
Intramolecular H···H distances (Å)			
H(2)···H(4)	2.17(3)	H(1)···H(2)	2.20(3)

Estimated standard deviations shown in parentheses refer to the last decimal positions.

angles derived from the final atomic parameters are listed in Table 3 and are also shown in Fig. 3. The rings have five independent C–O bonds, and their lengths range from 1.402 Å to 1.420 Å and are averaged to be 1.410 Å. The O–C–O bond angles range from 110.7° to 112.9° and are averaged to be 111.8°. The C–O–C bond angles range from 115.1° to 116.0° and are averaged to be 115.6°. The five independent torsion angles are −72.9°, 118.7°, −84.2°, 123.4°, and −69.8°, which indicate approximately either a *gauche*-form or a *skew*-form.

Table 4 shows the molecular dimensions of some cyclic oligomers of formaldehyde: trioxecane, pentoxecane and hexoxecane. In the trioxecane molecule, the O–C–O and C–O–C bond angles are close to the tetrahedral angle of 109.5°. The average C–O–C bond angles in both pentoxecane and hexoxecane are about 6° larger than the tetrahedral angle. In the hexoxecane molecule, the O–C–O bond angle is also 4.5° larger than the tetrahedral angle. Such large departures from the tetrahedral angle can be attributed to the effect of close H···H overlapping; the resultant close intramolecular H···H distances are 2.17 Å and 2.20 Å for pentoxecane, and 2.13 Å for hexoxecane.

Hendrickson[13] examined many possible molecular conformations of cyclodecane in terms of the strain energy: bond angle bending strain, torsional strain, and nonbonded interactions of hydrogen atoms. The conformation of the pentoxecane ring is similar to Model XXIX in his article. In the case of cyclodecane, however, he ignored Model XXIX, since the model is incapable of escaping serious nonbonded H···H interactions.

Table 5 lists the root mean square vibration amplitudes and the direction cosines of the principal axes of the thermal ellipsoids to the crystallographic *a*, *b*, and *c* axes (see Fig. 4). In the case of hexoxecane,[1] the rigid body approximation[14,15] was undertaken for the molecule of the $\bar{3}$ symmetry, but a reasonable result could not be obtained. In the cases of hexoxecane and also pentoxecane, the thermal ellipsoids suggest that there are considerable intramolecular motions, *i.e.*, torsional motions. Therefore, no corrections of the bond lengths and bond angles for thermal motions were made.

Crystal Structure. Two projections of the crystal structure of pentoxecane, viewed along the *c* and *b* axes, are shown in Fig. 5. Some close intermolecular atomic distances, less than 3.8 Å for the C···O pair and less than 4.2 Å for the C···C pair, are listed in Table 6. There are no abnormal distances between

Taele 4. Molecular dimensions[a] of cyclic oligomers of formaldehyde

	Trioxecane $(-CH_2-O-)_3$			Pentoxecane $(-CH_2-O-)_5$	Hexoxecane $(-CH_2-O-)_6$
Molecular symmetry	C_{3v}–3m			C_2–2	C_{3i}–$\bar{3}$
Method	X[b]	M[c]	ED[d]	X	X
C–O (Å)	1.421	1.411	1.411	1.410	1.411
C–H (Å)	1.07	1.09[e]	1.116	1.00	1.06
O–C–O (°)	109.6	111.2	111.0	111.8	114.0
C–O–C (°)	110.4	108.2	109.2	115.6	115.4
H–C–H (°)	114	109.5[e]	111.8	112	116
Ref.	(10)	(11)	(12)	This work	(1)

a) Average values of nonequivalent bond lengths and bond angles when there are nonequivalent values. b) X-ray diffraction. c) Microwave. d) Electron diffraction. e) Assumed value.

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Table 5. Temperature parameters (B_i in Å^2) and r.m.s. displacements (U_i in Å) along the principal axes of the thermal ellipsoids and the direction cosines of these axes with respect to the a, b, and c axes

	B_i	U_i	l	m	n	$B^{a)}$
C(1)	2.82	0.189	0.7472	0.0000	−0.6645	
	3.06	0.197	0.0000	−1.0000	0.0000	3.29
	4.00	0.225	0.6645	0.0000	0.7473	
O(1)	2.51	0.178	0.7274	−0.0733	−0.6822	
	3.55	0.212	−0.6434	0.2728	−0.7153	3.37
	4.06	0.227	0.2386	0.9593	0.1513	
C(2)	2.57	0.180	0.9490	0.2370	0.2077	
	3.78	0.219	0.3136	−0.6444	−0.6974	3.60
	4.44	0.237	−0.0315	0.7270	−0.6859	
O(2)	2.87	0.191	0.8659	−0.4967	−0.0585	
	4.05	0.226	−0.4571	−0.7383	−0.4958	4.01
	5.12	0.255	−0.2031	−0.4560	0.8665	
C(3)	2.86	0.190	−0.6032	0.4983	−0.6229	
	3.75	0.218	−0.4768	−0.8512	−0.2192	3.97
	5.30	0.259	−0.6394	0.1648	0.7510	
O(3)	3.03	0.196	0.0000	1.0000	0.0000	
	3.53	0.212	−0.7772	0.0000	−0.6291	4.91
	8.17	0.322	−0.6291	0.0000	0.7772	

a) Isotropic temperature parameter equivalent to the given anisotropic temperature parameters.

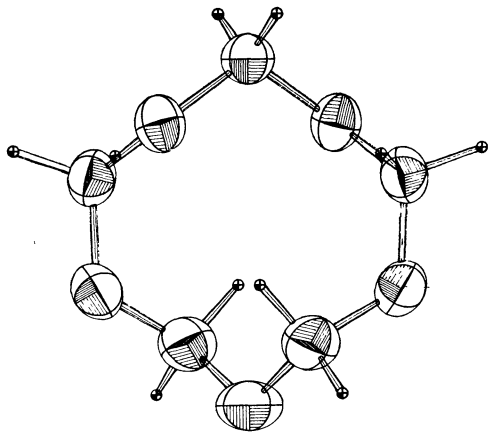

Fig. 4. Thermal ellipsoids of carbon and oxygen atoms in a pentoxecane molecule viewed along the c axis.

the molecules.

As has already been mentioned, the solid-state polymerization of pentoxecane by X- or γ-irradiation was successful. The single crystal habit of pentoxecane is retained at the completion of polymerization, and the orientation of the resultant polyoxymethylene crystallites is governed by the symmetry of the parent pentoxecane crystal. The polymer chains grow along the two face-diagonal axes, [110] and [$\bar{1}$10], which are equivalent to each other, as if the crystals were "twinned crystals." In addition to the crystals, a small amount of crystallites with another preferred orientation is formed, that is, the polymer chains are oriented along the [101] and [$\bar{1}$01] axes, which are equivalent to each other. The details of the orientation of polymer crystals have already been reported.[2)]

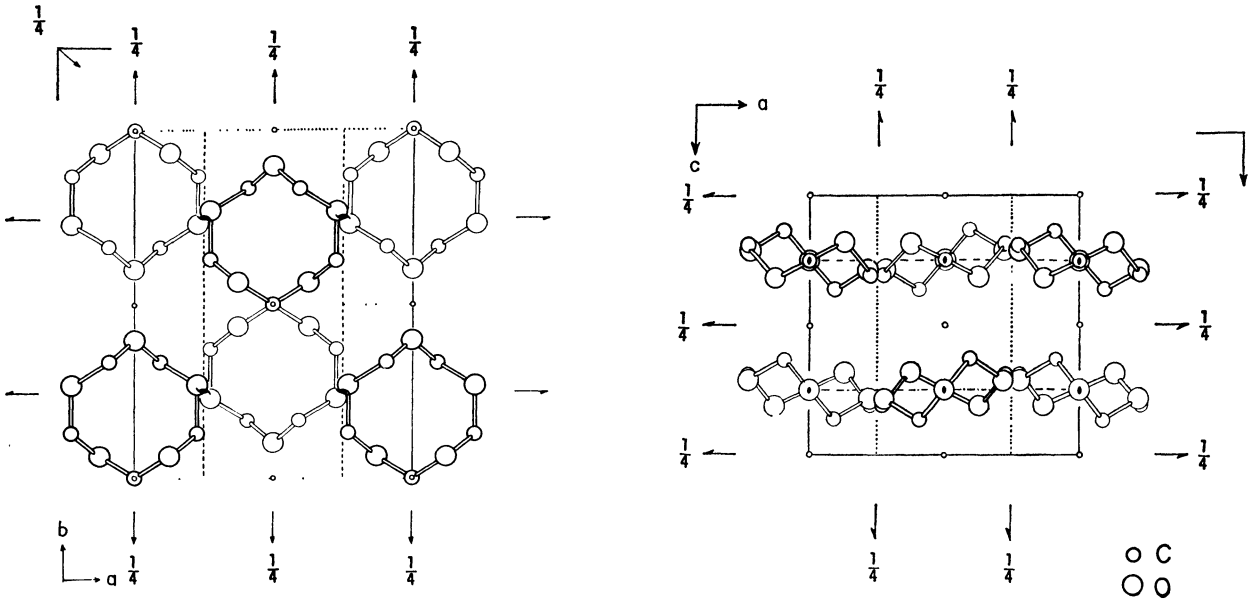

Fig. 5. Crystal structure of pentoxecane viewed along the c axis (left) and b axis (right).

Table 6. Intermolecular atomic distances less than 3.8 Å for C···O and 4.2 Å for C···C

C···O		C···C	
C(1, a)···O(2, e)	3.39 Å	C(2, a)···C(3, e)	3.64Å
C(2, a)···O(3, e)	3.39	C(3, a)···C(2, d)	3.67
C(3, a)···O(1, d)	3.45	C(1, a)···C(1, b)	3.83
C(1, a)···O(1, b)	3·58	C(3, a)···C(2, c)	3.86
C(3, a)···O(2, d)	3.69	C(1, a)···C(3, e)	3.93
C(2, a)···O(1, b)	3.75	C(2, a)···C(1, b)	4.15
O(1, a)···C(1, e)	3.78		

a: x, y, z; b: $x, 1-y, -\frac{1}{2}+z$; c: $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; d: $1\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; e: $1\frac{1}{2}-x, \frac{1}{2}+y, z$

It has also been noted that the polymer formation can be detected by irradiation at 20 °C. The polymerization rate increases with the elevation of the irradiation temperature, and the maximum rate is found at about 50 °C. No polymer is obtained by irradiation above the melting point, 61.3 °C. In order to clarify such specificities of the solid-state polymerization, many physicochemical investigations are necessary.

The authors wish to thank Professor H. Tadokoro of Osaka University for his interest in the work and his constant encouragement. The thermal ellipsoids of the pentoxecane molecule were drawn with a plotter by the use of the universal crystallographic computation program system 5020 UNICS of the University of Tokyo.