The Molecular and Crystal Structure of the Cyclic Tetramer of Formaldehyde, 1,3,5,7-Tetroxocane

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The crystal structure of the cyclic tetramer of formaldehyde, 1,3,5,7-tetroxocane, has been determined by the X-ray diffraction method. The unit cell is monoclinic, with $a=11.455$, $b=4.160$, $c=12.232$ Å, and $\beta=108.4°$. The space group is C2/c, and there are four molecules per unit cell. The structure was solved by using a molecular transform method and was refined by the block-diagonal least-squares method to a final R factor of 0.051, using 728 reflections measured with an automated four-circle diffractometer. The molecules in the crystal are of the so-called crown form, with an approximate C_{4v} symmetry but an exact C_2 symmetry. The torsion angles about the four independent C–O bonds appear in two distinguishable values: two bonds with 83.7 and −83.6°, and the other two bonds with 93.6 and −94.1°. The average C–O bond length is 1.403 Å, while the average C–O–C and O–C–O bond angles are 116.6 and 113.8° respectively. The deformation from a regular crown form by taking the two distinguishable torsion angles and the increase in bond angles is favorable to compensating for the intramolecular H···H repulsions; the close H···H distances in the deformed crown form are 2.16 and 2.20 Å.

The cyclic tetramer of formaldehyde, 1,3,5,7-tetroxocane $(\text{-}CH_2\text{-}O\text{-})_4$, presents two interesting problems which can be investigated by X-ray study. One is the molecular conformation of this eight-membered cyclic compound, and the other is the radiation-induced solid-state polymerization of tetroxocane, by which tetroxocane molecules in the crystal are converted into highly crystalline linear polyoxymethylene $(\text{-}CH_2\text{-}O\text{-})_n$.[1] Studies along similar lines have been performed on some cyclic oligomers of formaldehyde: 1,3,5-trioxane $(\text{-}CH_2\text{-}O\text{-})_3$,[2] 1,3,5,7,9-pentoxecane $(\text{-}CH_2\text{-}O\text{-})_5$,[3,4] and 1,3,5,7,9,11-hexoxecane $(\text{-}CH_2\text{-}O\text{-})_6$.[5] As for tetroxocane, a structural study of the solid-state polymerization has already been reported,[6] in which the crystal structure of this substance has been shown; also, it has been stated that the molecular conformation in the crystal is of a crown form. On the other hand, the presence of two conformations is suggested by the study of the temperature dependence of the NMR spectra of the tetroxocane in solutions:[7,8] one has a boat-chair or a distorted boat-chair conformation, and the other, preponderant at low temperatures, presumably has a crown form which was expected to be found in the crystal. The present paper will describe the crystal structure of tetroxocane in detail.

Experimental

The tetroxocane was synthesized by the method of Staudinger and Luthy.[9] The melting point of tetroxocane is 114 °C. Recrystallization from a benzene solution or sublimation yielded prismlike crystals elongated along the b axis. Because of its high vapor pressure, single crystals were sealed in thin-walled Lindemann glass capillaries. The cell dimensions were determined from Weissenberg photographs and from θ values as measured with a single-crystal diffractometer. Crystal data:

1,3,5,7-Tetroxocane, $(\text{-}CH_2\text{-}O\text{-})_4$
Molecular weight 120.1
Monoclinic $a=11.455\pm0.007$ Å
$b=4.160\pm0.006$
$c=12.232\pm0.009$
$\beta=108.4\pm0.1°$
$Z=4$
Volume of the unit cell: $V=553.0$ Å^3
Density, calculated: $D_x=1.442$ g/cm^3; measured: $D_m=1.435$ g/cm^3
Number of electrons per unit cell: $F(000)=256$
Absorption coefficient for $\lambda_{MoK\alpha}(=0.7107$ Å$)$: $\mu=1.40$ cm^{-1}

The systematic extinctions occur for hkl with $h+k$ odd, for $h0l$ with either h or l odd, and for $0k0$ with k odd. The space group is, therefore, either Cc or C2/c, of which the latter was adopted on the basis of the plot of the intensity distribution.[10,11]

The intensity measurements were performed using a Rigaku-Denki automated four-circle diffractometer. The crystal used for the intensity measurements was $0.4\times0.4\times0.5$ mm^3 in size. The integrated intensities were measured using the $\theta-2\theta$ (moving-crystal, moving-counter) technique for all the reflections in the sphere of the $\sin\theta/\lambda<0.70$ Å^{-1} radius, with MoKα radiation. The scanning speed was 2°/min, and the scan range was calculated by this formula:

$$\text{scan range}=(0.8+1.0\tan\theta)\ \text{degrees}.$$

The background counts were measured at the beginning and at the end of the scan range for a period of 20 seconds and corrected for the time factor. No correction was made for absorption. The F values of 52 out of the 780 non-equivalent reflections within the sphere were set as equal to zero, since the F values were smaller than the estimated standard deviation of the values, and were not included in the refinement. In a previous paper[6] solid-state polymerization by X- or γ-irradiation was reported. The yield of the polymer depends upon the irradiation temperature. The present measurements were performed at 19 °C; judging from the approximate constancy of the intensities of the three reference reflections measured every 25 reflections, such a polymerization was almost suppressed, the gradual decrease in the observed F values being 2% at the end of the measurements (the total exposure was 42 hours). Therefore, the correction for the time dependence was made for the observed F values. It was also noticed that the diffraction spots of tetroxocane crystal were not altered in location and remained fairly sharp in spite of the polymerization.

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Structure Determination

b-Projection. There are eight equivalent general positions in the C2/c space group, while the number of molecules in the unit cell is four. Therefore, the molecules in the unit cell must be situated at one of the twofold positions. There are, in this space group, four sets of centers of symmetry and a set of twofold rotation axes along the b axis. In the b-projection, however, these two kinds of symmetry elements are not distinguishable, and a smaller cell with one molecule can be chosen. The shortness of the b dimension (4.160 Å) indicates that there can be no superposition of atoms in the b-projection, and the eight-membered rings are oriented almost perpendicularly to the b axis. On the b-projection, we could assume a regular octagonal ring as a gross structure of the projected molecule, although the molecular conformation was still uncertain. Accordingly, as a first step, the molecular transform of a regular octagonal ring of the tetroxocane molecule was calculated, taking the polar coordinates (r, ϕ) and (R, ψ) in the real space and the reciprocal space respectively. On the regular octagonal model, there is a fourfold rotation symmetry. The molecular transform, F_m, thus can be written by analogy with the molecular transform of a helix proposed by Cochran, Crick, and Vand:[12]

$$F_m(R, \psi) = 4\sum_n\sum_j f_j J_n(2\pi R r_j) \exp\{in(\psi - \phi_j + \pi/2)\},$$

where J_n is the Bessel function of the n-th order. In the present case, only $n=0$, ± 4 and ± 8 need be considered in the range of $\sin\theta/\lambda < 0.70$ Å^{-1}, and the ϕ_j's for the reference oxygen and carbon atoms are 0 and $\pi/4$ respectively. By using this expression, the molecular transform was evaluated very fast by handwork. A satisfactory fitting of the squares of the molecular transform, $F_m{}^2$, to the weighted reciprocal lattice points, as is shown in Fig. 1a, was obtained when the oxygen atom was oriented at an angle of 27° from the c axis (Fig. 1b). The signs of all the observed $F(h0l)$'s except for a few weak ones were determined from the molecular transform. By two cycles of two-dimensional Fourier syntheses, the atomic coordinates were refined up to the discrepancy factor, $R(=\sum||F_o|-|F_c||/\sum|F_o|)$, of 0.12 without hydrogen atoms.

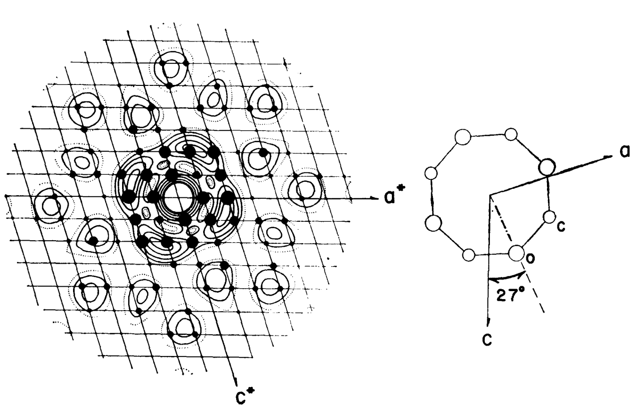

Fig. 1. (a) Contour map of $F_m{}^2\ (R, \psi)$ of the regular octagonal shape model of tetroxocane molecule and the weighted $(h0l)$ reciprocal lattice points. (b) Orientation of the model in the crystal lattice.

Three-dimensional Structure. A good agreement of F_0 and F_c was obtained when the molecular conformation was a crown form with a twofold rotation axis and when the center of gravity of the molecule was at approximate $y=0.25$. Further refinement was made using the block-diagonal least-squares method.[13] The R value was reduced to 0.14 by using isotropic thermal factors. The anisotropic thermal factors were then introduced, and the R value dropped to 0.09 after six cycles. Hydrogen atoms were located at this stage from a difference Fourier synthesis (Fig. 2) and were included in the least-squares refinement with isotropic thermal factors. In the last stage, the 002 and $\bar{1}11$ reflections were excluded from the least-squares calculation because they appeared to be seriously affected by extinction. The $\sum w(F_o-kF_c)^2$ quantity was minimized, where w is the weight function and k is the scale factor. At the final stage of the refinement, the following weighting scheme was employed: $w=(4F_{\min}/F_o)^2$ if $F_o \geq 4F_{\min}$, $w=1$ if $4F_{\min} > F_o \geq F_{\min}$, and $w=0.2$ if $F_o < F_{\min}$, where $F_{\min}=2.0$. The R value dropped to 0.048 for all the observed reflections except 002 and $\bar{1}11$, and to 0.051 including these two reflections. The atomic scattering factors used for the carbon and oxygen atoms were those in the International Tables for X-ray Crystallography, Vol. III,[14] while for hydrogen the values of Stewart *et al.*[15] were used. The final atomic coordinates and thermal parameters are listed in Table 1. A comparison of the observed and calculated structure factors is given in Table 2.

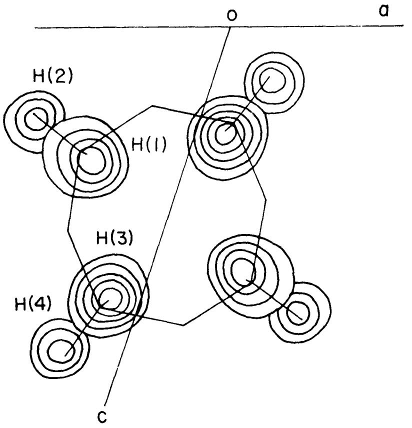

Fig. 2. Sections of three-dimensional difference Fourier synthesis through the atomic centers parallel to the (010). The contours are at intervals of 0.1 e/Å^3, starting with 0.2 e/Å^3.

Results and Discussion

The molecular dimensions derived from the final atomic coordinates are shown in Table 3 and Fig. 3. The molecular conformation of tetroxocane in the crystal was established to have a crown form, like that of methaldehyde[16] and sulphur,[17] though 1,3,5,7-tetrathiocane $(\text{-CH}_2\text{-S-})_4$[18] was found to exist not in

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)	−0.1477(2)	0.2911(5)	0.1633(2)	809(15)	7216(127)	729(13)	642(72)	328(22)	−93(67)
C(2)	−0.0476(2)	0.2907(4)	0.3672(2)	1042(17)	5981(109)	663(12)	10(70)	748(23)	−99(61)
O(1)	−0.0714(1)	0.1648(3)	0.1030(1)	1001(12)	7094(90)	683(9)	−281(53)	464(17)	−1153(46)
O(2)	−0.1309(1)	0.1446(3)	0.2702(1)	911(11)	5942(77)	827(10)	−618(49)	640(17)	72(45)
H(1)	−0.142(2)	0.538(6)	0.169(2)	5.4(5)					
H(2)	−0.235(2)	0.233(5)	0.112(2)	6.0(5)					
H(3)	−0.038(2)	0.528(5)	0.354(2)	4.2(4)					
H(4)	−0.074(2)	0.247(5)	0.434(2)	5.7(5)					

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 Å².

Table 2. The observed and the final calculated structure factors (× 10)

H	L	F_o	F_c
(K = 0)			
0	2	519	-626
0	4	501	-554
0	6	180	-180
0	8	242	247
0	10	7	-7
0	12	9	12
0	14	17	-17
0	16	20	-20
2	0	533	548
2	2	480	484
2	4	238	-236
2	6	320	-323
2	8	191	191
2	10	87	-95
2	12	55	56
2	14	21	17
-2	2	234	-223
-2	4	624	-596
-2	6	187	176
-2	8	39	51
-2	10	244	246
-2	12	188	-190
-2	14	27	-27
-2	16	30	31
4	0	619	-619
4	2	354	354
4	4	40	50
4	6	57	55
4	8	157	-179
4	10	25	28
4	12	14	17
4	14	24	22
-4	2	562	573
-4	4	577	-563
-4	6	93	83
-4	8	296	289
-4	10	39	38
-4	12	189	-180
-4	14	19	-19
-4	16	69	73
6	0	84	-97
6	2	230	-240
6	4	185	172
6	6	209	216
6	8	178	-175
6	10	29	-26
6	12	24	26
-6	2	96	-93
-6	4	162	151
-6	6	9	-11
-6	8	224	217
-6	10	205	-203
-6	12	27	31
-6	14	30	-31
-6	16	40	40
8	2	204	-197
8	4	111	110
8	6	47	45
8	8	31	29
8	10	70	-68
-8	2	155	-155
-8	4	392	385
-8	6	67	-67
-8	8	158	-158
-8	10	33	28
-8	12	37	41
-8	14	11	-11
10	0	168	-171
10	2	17	-22
10	4	39	45
10	6	15	-21
10	8	21	28
-10	2	161	172
-10	4	92	92
-10	6	45	-46
-10	8	184	-186
-10	10	122	124
-10	12	3	0
-10	14	18	18
12	0	32	-37
12	4	14	-15
-12	2	110	113
-12	4	45	-42
-12	6	18	-23
-12	8	33	-31
-12	10	4	0
-12	12	68	62
-12	14	15	-11
14	0	49	48
14	2	12	9
-14	4	18	16
-14	6	6	-10
-14	10	24	-23
-14	12	52	53
(K = 1)			
1	0	250	221
1	1	652	-691
1	2	78	-79
1	3	389	-404
1	4	255	246
1	5	38	-33
1	6	327	-317
1	7	299	296
1	8	65	61
1	9	130	-126
1	10	41	39
1	11	62	63
1	12	32	32
1	13	17	-20
1	14	35	-36
1	15	23	-22
-1	1	1072	-1116
-1	2	89	-82
-1	3	182	-172
-1	4	74	-70
-1	5	289	281
-1	6	96	-89
-1	7	118	123
-1	8	55	54
-1	9	21	25
-1	10	73	74
-1	11	113	-120
-1	12	41	-41
-1	15	24	21
-1	16	15	-13
3	0	128	-123
3	1	388	378
3	2	310	302
3	3	255	-263
3	4	6	-9
3	5	97	-98
3	6	71	-69
3	7	48	48
3	8	53	-51
3	10	17	18
3	11	34	35
3	12	44	43
3	13	10	8
3	14	21	-19
-3	1	215	214
-3	2	27	-22
-3	3	413	-408
-3	4	347	-325
-3	5	319	313
-3	6	330	311
-3	7	97	100
-3	8	62	-54
-3	9	17	17
-3	10	22	23
-3	11	235	-233
-3	12	35	-38
-3	13	69	71
-3	14	6	5
-3	15	67	63
5	0	186	-189
5	1	184	175
5	2	285	284
5	3	132	132
5	4	65	-56
5	5	9	7
5	6	36	33
5	7	217	-217
5	8	62	-62
5	9	92	93
5	10	17	16
5	11	27	24
5	12	2	-1
5	13	4	5
-5	1	243	247
-5	2	213	-205
-5	3	119	-126
-5	4	73	74
-5	5	151	142
-5	6	160	149
-5	7	154	156
-5	8	7	4
-5	9	230	-222
-5	10	87	-87
-5	11	22	-20
-5	12	22	22
-5	13	38	31
-5	14	12	-10
-5	15	56	55
-5	16	22	23
7	0	15	-20
7	1	108	-113
7	2	31	-34
7	3	222	217
7	4	76	79
7	5	36	35
7	6	9	-12
7	7	115	-110
7	8	2	-4
7	9	27	-26
7	10	2	-2
7	11	51	48
-7	1	34	-40
-7	2	163	-160
-7	3	290	291
-7	4	213	216
-7	5	160	-165
-7	6	44	-46
-7	7	31	-29
-7	8	47	43
-7	9	46	-46
-7	10	92	-92
-7	11	67	72
-7	12	12	17
-7	13	31	-32
-7	14	23	23
-7	15	22	23
-7	16	5	7
9	0	26	23
9	1	20	23
9	2	85	-83
9	3	78	81
9	4	36	37
9	5	20	-22
9	7	27	25
9	8	18	17
9	9	46	-44
9	10	16	-16
-9	1	110	115
-9	2	18	14
-9	3	111	111
-9	4	12	12
-9	5	172	-170
-9	6	26	31
-9	7	95	-100
-9	8	40	-43
-9	9	162	167
-9	10	10	-7
-9	11	30	-28
-9	12	9	-8
-9	13	8	-9
-9	14	42	43
-9	15	13	-11
-9	16	22	-19
11	0	3	-5
11	1	39	35
11	2	1	0
11	3	17	19
11	4	39	-36
11	5	7	-6
11	6	20	20
11	7	8	0
-11	1	146	149
-11	2	59	56
-11	3	85	-87
-11	4	51	-49
-11	5	43	-46
-11	6	32	33
-11	7	27	-27
-11	8	46	-47
-11	9	81	84
-11	10	23	24
-11	11	11	3
-11	12	1	3
-11	13	20	-18
-11	15	25	-25
13	0	4	3
13	1	19	-20
13	2	9	10
13	3	20	-15
13	4	24	-21
-13	1	18	-16
-13	2	14	14
-13	3	12	-15
-13	4	8	-4
-13	6	31	-31
-13	8	18	18
-13	10	11	4
-13	11	53	52
-13	12	13	8
-13	13	48	-47
(K = 2)			
0	0	513	-565
0	1	342	-337
0	2	98	70
0	3	85	79
0	4	234	227
0	5	236	-231
0	6	24	14
0	7	223	223
0	8	70	-62
0	9	33	29
0	10	11	12
0	11	52	-50
0	12	13	-12
0	13	31	-30
0	15	4	7
2	0	149	-130
2	1	58	64
2	2	155	-147
2	3	45	-44
2	4	100	101
2	5	241	-242
2	6	73	66
2	7	110	112
2	8	60	-60
2	9	58	53
2	10	44	48
2	11	29	29
2	12	9	-6
2	13	71	-71
2	14	29	-30
-2	1	155	-148
-2	2	40	44
-2	3	171	-165
-2	4	135	125
-2	5	293	297
-2	6	26	20
-2	7	51	-50
-2	8	40	-40
-2	9	31	32
-2	10	90	-96
-2	11	86	-88
-2	12	59	62
-2	13	29	31
-2	14	30	28
-2	15	5	-10
4	0	137	122
4	1	390	388
4	2	33	-9
4	3	248	-241
4	4	73	-67
4	5	2	5
4	6	18	-17
4	7	70	-72
4	8	57	55
4	9	69	68
4	11	18	18
4	12	3	0
4	13	17	-15
-4	1	12	11
-4	2	152	-153
-4	4	123	122
-4	5	323	325
-4	6	69	70
-4	7	177	-170
-4	8	146	-146
-4	9	49	-51
-4	10	39	-40
-4	11	21	16
-4	12	88	84
-4	14	17	17
-4	15	17	17
6	0	12	17
6	1	163	158
6	2	127	129
6	3	19	-10
6	4	70	-68
6	5	30	-27
6	6	99	-97
6	7	37	-41
6	8	62	60
6	9	22	22
6	10	29	27
6	11	12	-8
-6	1	52	-56
-6	2	6	-2
-6	3	286	292
-6	4	17	-13
-6	5	76	-75
-6	6	4	-7
-6	7	10	-10
-6	8	60	-62
-6	9	129	-132
-6	10	35	35
-6	11	86	90
-6	12	9	6
-6	14	14	19
-6	15	13	14
8	0	36	35
8	1	71	-72
8	2	41	40
8	3	128	129
8	4	13	-11
8	5	48	-46
8	6	32	-30
8	7	6	7
8	8	14	-15
8	9	24	-21
8	10	34	30
-8	1	22	-22
-8	2	32	28
-8	3	121	122
-8	4	135	-121
-8	5	80	-82
-8	6	6	6
-8	7	15	-14
-8	8	82	86
-8	9	46	-45
-8	10	41	-37
-8	11	43	41
-8	12	14	-15
-8	13	47	48
-8	14	21	22
-8	15	41	-40
10	0	83	84
10	1	50	-44
10	2	4	-4
10	3	19	18
10	4	22	-22
10	5	33	33
10	6	15	15
-10	1	39	43
-10	2	61	-61
-10	3	72	-72
-10	4	60	-62
-10	5	50	48
-10	6	40	40
-10	7	75	-76
-10	8	59	62
-10	9	50	51
-10	10	37	-39
-10	12	8	-9
-10	13	20	25
12	0	7	5
12	2	10	12
12	3	42	-39
12	4	10	-6
12	5	37	38
-12	1	23	25
-12	2	31	-30
-12	3	53	-50
-12	6	6	10
-12	7	8	4
-12	8	10	11
-12	9	24	24
-12	10	14	14
-12	11	8	-3
-12	12	36	-35
-12	13	21	-20
14	0	22	-21
-14	1	10	-9
-14	2	35	29
-14	3	8	-5
-14	4	15	-7
-14	5	28	-28
-14	6	6	-11
-14	7	55	55
-14	8	20	15
-14	9	19	-17
-14	10	8	7
(K = 3)			
1	0	142	-140
1	1	18	18
1	2	28	23
1	3	125	128
1	4	128	-135
1	5	122	-116
1	6	202	209
1	7	37	36
1	8	11	-15
1	9	21	24
1	10	51	-48
1	11	13	-18
1	12	35	-38
1	13	19	-20
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-1	2	63	52
-1	3	42	40
-1	4	53	54
-1	5	40	-41
-1	6	62	60
-1	7	7	4
-1	8	30	-31
-1	9	6	-2
-1	10	64	-65
-1	11	11	-6
-1	12	26	25
-1	13	12	13
3	0	59	61
3	1	47	45
3	2	184	-187
3	3	35	-32
3	4	4	-3
3	5	2	-5
3	6	48	46
3	8	62	59
3	9	20	23
3	10	17	-15
3	11	9	-1
3	12	49	-46
-3	1	11	-14
-3	2	31	32
-3	4	192	196
-3	5	106	101
-3	6	195	-198
-3	7	123	-118
-3	8	23	24
-3	9	13	20
-3	10	10	-6
-3	11	37	39
-3	12	18	19
-3	13	4	2
-3	14	8	0
5	0	107	108
5	1	97	98
5	2	177	-180
5	3	116	-112
5	4	24	27
5	5	9	10
5	6	15	-19
5	7	21	24
5	8	43	45
5	9	7	9
5	11	12	-13
-5	1	34	-30
-5	2	146	148
-5	3	80	78
-5	4	43	-43
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-5	6	113	-113
-5	7	73	-74
-5	8	10	-12
-5	9	10	14
-5	10	78	78
-5	11	43	43
-5	12	17	-17
-5	13	12	-10
-5	14	4	9
7	0	21	19
7	1	18	18
7	2	25	27
7	3	12	-11
7	4	65	-66
7	5	37	-38
7	6	17	15
7	7	19	22
7	8	9	-3
7	9	16	14
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-7	2	104	106
-7	3	39	37
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-7	6	12	13
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-7	8	38	-37
-7	9	41	-39
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-7	14	32	-32
9	0	20	-18
9	1	48	-44
9	2	70	71
9	3	23	18
9	4	21	-22
9	6	6	-8
9	7	9	-2
-9	1	38	-39
-9	2	25	-25
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-9	10	20	20
-9	11	3	9
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-9	13	18	16
11	0	7	-5
11	1	2	-4
11	3	15	-17
11	4	47	43
-11	1	17	-14
-11	2	43	-45
-11	3	16	-12
-11	4	44	42
-11	5	31	34
-11	6	23	-24
-11	7	16	-16
-11	8	35	34
-11	9	10	8
-11	10	9	-13
-11	11	17	-16
13	0	8	-6
-13	2	8	-11
-13	3	2	-10
-13	5	9	-6
-13	6	37	38
-13	7	19	20
-13	8	23	-21
(K = 4)			
0	0	41	-45
0	2	43	47
0	3	9	-9
0	4	60	-58
0	5	82	85
0	6	66	65
0	7	48	-52
0	8	22	-25
0	9	39	-38
0	10	19	-17
0	11	17	18
2	1	31	-33
2	2	11	-10
2	4	37	-37
2	5	78	80
2	6	56	55
2	8	4	-5
2	9	48	-47
2	10	10	-11
-2	1	19	18
-2	3	26	29
-2	4	54	54
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-2	6	59	-56
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-2	10	13	-11
-2	12	17	18
4	0	53	55
4	1	78	-84
4	2	101	-101
4	3	55	58
4	4	41	37
4	5	7	8
4	6	6	-2
4	7	18	18
4	8	21	21
4	9	14	-17
-4	1	50	48
-4	2	22	17
-4	3	53	-51
-4	4	33	31
-4	5	72	-76
-4	6	87	-83
-4	7	56	58
-4	8	31	32
-4	9	17	15
-4	10	15	17
-4	11	14	-17
-4	12	8	-5
6	0	24	21
6	1	56	-58
6	2	38	-40
6	3	10	14
6	4	7	-1
6	5	20	18
6	6	11	7
6	7	2	-6
6	8	14	12
-6	1	27	26
-6	2	52	50
-6	3	92	-96
-6	4	57	-54
-6	5	10	9
-6	6	8	8
-6	7	21	21
-6	8	15	-17
-6	9	30	34
-6	10	45	42
-6	11	13	-19
-6	12	12	-15
8	0	26	-24
8	1	10	13
8	2	38	34
8	3	27	-30
8	4	31	-30
8	5	11	9
-8	2	26	26
-8	3	11	-12
-8	4	19	-23
-8	7	12	12
-8	8	16	-11
-8	9	27	28
-8	10	22	24
-8	11	8	-13
10	1	26	24
10	2	11	10
-10	1	3	0
-10	2	7	-10
-10	3	31	27
-10	4	26	22
-10	5	24	-29
-10	6	19	-25
-10	7	22	23
-10	8	18	23
-10	9	9	2
(K = 5)			
1	0	36	-31
1	1	24	25
1	2	19	17
1	3	14	-13
1	4	29	30
1	5	37	38
1	6	19	-24
1	7	29	-33
-1	1	35	34
-1	2	21	17
-1	3	9	0
-1	4	8	6
-1	6	16	-18
-1	7	1	-11
-1	8	10	-3
3	0	1	5
3	1	37	-37
3	2	12	14
3	3	28	27
3	4	13	12
3	5	14	10
3	6	6	-4
-3	1	9	-2
-3	2	34	-31
-3	3	16	19
-3	4	8	0
-3	5	50	-52
-3	6	18	19
-3	7	29	26
5	0	5	0
5	1	41	-41
5	2	25	27
5	3	21	22
5	4	4	0
-5	1	4	-3
-5	2	48	-50
-5	3	21	-19
-5	4	15	20
-5	5	6	-8
-5	6	26	25
-5	7	6	7
-5	8	14	-9
7	0	14	-12
-7	1	13	12
-7	2	5	-7
-7	3	30	-32
-7	4	8	1
-7	5	19	20
-7	6	16	15

TABLE 3. MOLECULAR DIMENSIONS OF TETROXOCANE

Bond lengths (Å)			
O(1)-C(1)	1.411(3)	C(1)-H(1)	1.03(2)
C(1)-O(2)	1.399(2)	C(1)-H(2)	1.03(3)
O(2)-C(2)	1.405(3)	C(2)-H(3)	1.01(2)
C(2)-O(1′)	1.396(3)	C(2)-H(4)	0.97(3)
Bond angles (°)			
O(1)-C(1)-O(2)	113.6(2)	O(1)-C(1)-H(2)	104(1)
C(1)-O(2)-C(2)	117.2(2)	O(2)-C(1)-H(1)	113(1)
O(2)-C(2)-O(1′)	113.9(2)	O(2)-C(1)-H(2)	107(1)
C(1)-O(1)-C(2′)	116.0(2)	O(2)-C(2)-H(3)	112(1)
H(1)-C(1)-H(2)	108(2)	O(2)-C(2)-H(4)	109(2)
H(3)-C(2)-H(4)	113(2)	O(1′)-C(2)-H(3)	105(1)
O(1)-C(1)-H(1)	111(1)	O(1′)-C(2)-H(4)	105(1)
Torsion angles (°)			
C(2′)-O(1)	83.7	C(1)-O(2)	93.6
O(1)-C(1)	−83.6	O(2)-C(2)	−94.1
Intramolecular H···H distances (Å)			
H(1)···H(3)	2.20(3)	H(1)···H(3′)	2.16(3)

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

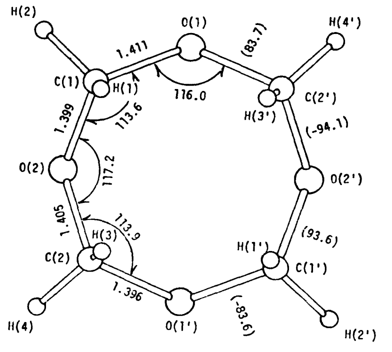

Fig. 3. Bond lengths, bond angles and torsion angles (shown in parentheses) of tetroxocane molecule.

a crown form but in a boat-chair form in the crystalline state. On a closer examination, the molecular conformation of tetroxocane in the crystal is found to depart from the regular crown form: the molecular shape has an approximate C_{4v} symmetry but an exact C_2 symmetry. That is, the crown is elongated in the direction of O(1)···O(1′) (3.448 Å) and is shrunk along the direction of O(2)···O(2′) (3.190 Å). The difference, 0.258 Å, is significant. The torsion angles about the four independent C–O bonds thus appear in two distinguishable values: two bonds with 83.7 and −83.6°, and the other two bonds with 93.6 and −94.1°. The average C–O bond length is 1.403 Å, and the average C–O–C and O–C–O bond angles are 116.6 and 113.8° respectively. This deformation from the regular crown form with the tetrahedral angle may be due to the steric effects of the hydrogen atoms. If a regular crown form is constructed from the normal bond lengths and the tetrahedral angle, the torsion angle is calculated to be 96°58′ and the H···H distances become 1.90 Å, while the actual short H···H distances in the distorted crown form were found to be 2.16 and 2.20 Å. Table 4 shows the molecular dimensions of the cyclic oligomers of formaldehyde from trimer to hexamer. The average C–O bond length in the tetroxocane is the shortest. This may be partly due to the thermal motions. Except for trioxane, the C–O–C bond angles are larger than the O–C–O bond angles, but all the C–O–C and O–C–O bond angles are evidently larger than the tetrahedral angle, 109°28′. The increase in the bond angles, especially those of the C–O–C bond angles, may compensate for the intramolecular steric hindrances. The bending force constant of C–O–C is smaller than that of O–C–O. Therefore, the larger increase in the C–O–C bond angles might be favorable in terms of the conformation energy.

Table 5 lists the root-mean-square vibration am-

TABLE 4. MOLECULAR DIMENSIONS[a)] OF CYCLIC OLIGOMERS OF FORMALDEHYDE

	$(-CH_2-O-)_3$			$(-CH_2-O-)_4$	$(-CH_2-O-)_5$	$(-CH_2-O-)_6$
Molecular symmetry	$C_{3v}-3m$			C_2-2	C_2-2	$C_{3i}-\bar{3}$
Method	X[b)]	M[c)]	ED[d)]	X	X	X
C–O (Å)	1.421	1.411	1.411	1.403	1.410	1.411
C–H (Å)	1.07	1.09[e)]	1.116	1.01	1.00	1.06
O–C–O (°)	109.6	111.2	111.0	113.8	111.8	114.0
C–O–C (°)	110.4	108.2	109.2	116.6	115.6	115.4
H–C–H (°)	114	109.5[e)]	111.8	111	112	116
Intramolecular H···H distance (Å)	2.46			2.16 2.20	2.17 2.20	2.13
C–O torsion angle (°)	58.8 −58.8			83.7 −83.6 93.6 −94.1	−72.9 118.7 −84.2 123.4 −69.8	−84.3 85.5
Ref.	19) (at −170 °C)	20)	21)	This work	22)	5)

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

TABLE 5. TEMPERATURE PARAMETERS (B_i) AND R.M.S. DISPLACEMENTS(U_i) ALONG THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS AND THE ANGLES BETWEEN THE PRINCIPAL AXES AND THE CRYSTALLOGRAPHIC a, b, AND c* AXES (ω_{ia}, ω_{ib}, and ω_{ic^*})

	i	B_i(Å^2)	U_i(Å)	ω_{ia}(°)	ω_{ib}(°)	ω_{ic^*}(°)
C(1)	1	3.48	0.210	39	107	56
	2	4.40	0.236	125	90	36
	3	5.13	0.255	103	163	99
C(2)	1	3.13	0.199	119	84	30
	2	4.14	0.229	87	6	95
	3	4.97	0.251	30	91	61
O(1)	1	3.03	0.196	93	60	30
	2	4.86	0.248	177	91	92
	3	5.59	0.266	90	30	120
O(2)	1	3.48	0.210	42	50	101
	2	4.51	0.239	99	97	169
	3	4.74	0.245	49	139	90

plitudes along the principal axes of the thermal ellipsoids and the angles between the principal axes and the crystallographic a, b, and c* axes. The thermal motion of each skeletal atom is predominant in the direction perpendicular to the plane formed by the atom and both neighboring atoms. Such a feature has previously been found in the cases of pentoxecane[22] and hexoxecane.[5] In the case of hexoxecane, a rigid body approximation[23,24] was undertaken for the molecule of the $\bar{3}$ symmetry, but no reasonable result could be obtained. These facts might imply that, besides the translational and vibrational motions, intramolecular motions, *e.g.*, torsional and bending motions, are also appreciable in these cyclic oligomers. Since we do not yet know the mode of the intramolecular motions, corrections of bond lengths and bond angles for the thermal motions were not made.

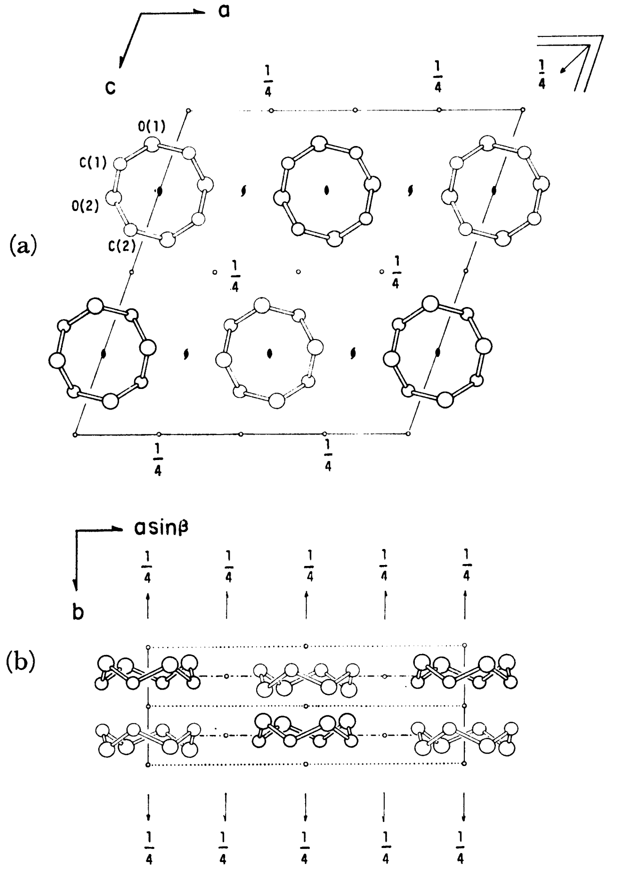

Fig. 4. (a) Crystal structure viewed along the b axis. (b) Crystal structure viewed along the c axis.

TABLE 6. INTERMOLECULAR ATOMIC DISTANCES

C···O (Å)		C···C (Å)	
C(1,a)···O(1,b)	3.86	C(2,a)···C(2,f)	3.54
C(1,a)···O(2,b)	3.77	C(2,a)···C(2,g)	3.92
C(2,a)···O(2,b)	3.77	C(1,a)···C(1,h)	4.18
C(2,a)···O(1,c)	3.86	C(1,a)···C(2,h)	3.98
C(2,a)···O(1,d)	3.75	C(2,a)···C(1,h)	3.98
C(2,a)···O(1,e)	3.53	C(1,a)···C(1,i)	3.96
C(1,a)···O(2,h)	3.25		
C(1,a)···O(1,i)	3.79		

a: x, y, z; b: $x, 1+y, z$; c: $-x, 1+y, 1/2-z$; d: $x, 1-y, 1/2+z$; e: $x, -y, 1/2+z$; f: $-x, 1-y, 1-z$; g: $-x, -y, 1-z$; h: $-1/2-x, 1/2+y, 1/2-z$; i: $-1/2-x, 1/2-y, -z$.

The molecular packing is shown in Fig. 4. The ring molecules are piled up along the b axis. The shortest intermolecular (between centers of gravity) distance of 4.16 Å is in the b direction, along which the dipole moment vectors of all the molecules in a row are parallel. Some short intermolecular atomic distances are shown in Table 6. The closest C···O distance is 3.25 Å. The C···C distances are longer than 3.92 Å except for the 3.54 Å of C(2,a)···C(2,f).

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