

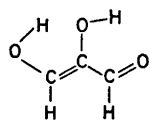
# The Crystal Structure of Triose Reductone

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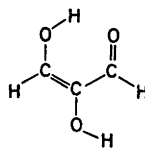
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The crystal and molecular structure of triose reductone (2-propen-2,3-diol-1-one) has been determined from three-dimensional X-ray diffraction data measured by counter methods. The space group is  $Pna2_1$ ;  $a=10.601(2)$  Å,  $b=3.647(1)$  Å,  $c=10.008(3)$  Å. The structure has been refined to  $R_w=0.04$  for 811 independent observed reflections. The estimated standard deviations in bond lengths involving non-hydrogen atoms are 0.002 Å. The compound crystallizes in a *trans*-enol form. Both hydrogen bonds are *intermolecular* and form a three-dimensional network.

Triose reductone ( $C_3H_4O_3$ ) is a labile decomposition product which is formed when monosaccharides are heated with alkali in aqueous solutions at elevated temperatures.<sup>1</sup> It is known that the compound carries an *aci*-reductone group ( $-\text{CO}-\text{COH}=\text{COH}-$ ); however, the molecule may exist in two enol forms:



I



II

In contrast to the acyclic  $\beta$ -diketones the *trans*-enol(I) may also be stabilized through *intra*-molecular hydrogen bonds. A previous X-ray investigation<sup>2</sup> of the rubidium salt of triose reductone has shown that the anion has a *trans* structure corresponding to I. Recent work based upon NMR studies has established the existence of the *cis*-isomer (II) in acetone solutions.<sup>3</sup> However, spectroscopic investigations (infrared, Raman) seem to indicate that in the

crystalline state the molecule prefers the *trans*-enol form (I) with the two available hydrogen atoms engaged in *intra*-molecular hydrogen bonds forming two five-membered rings.<sup>4</sup>

The present X-ray diffraction study was undertaken in order to establish the structure in the crystalline state and to examine the hydrogen bonding properties of this compound. A comparative study of the cyclic homologue, reductic acid (2-cyclopentene-2,3-diol-1-one) is now being carried out in this laboratory.

## EXPERIMENTAL

The compound was synthesized by the method described by von Euler and Eistert,<sup>1</sup> and purified by slow sublimation (55°C, 0.01 mmHg). Single crystals were obtained by recrystallization from a mixture of ether and hydrochloric acid. Preliminary photographic investigations implied the space group to be either  $Pnma$  or  $Pna2_1$ , thus confirming the results of Aurivillius and Lundgren.<sup>5</sup> The space group  $Pna2_1$  was tentatively assumed and proved correct by the successful outcome of the analysis. Unit cell dimensions were determined from measurements of 18 reflections using a manual Picker four-circle diffractometer (CuK radiation). For intensity measurements a crystal with approximate dimensions  $0.39 \times 0.27 \times 0.43$  mm<sup>3</sup> was used. Due to instability in air and moisture, the crystal was mounted in a sealed glass capillary. Intensity measurements were made on a SYNTAX P1 automatic four-circle diffractometer with graphite monochromated MoK $\alpha$  radiation. The crystal was mounted with the  $b$ -axis near the goniometer head spindle axis. Intensities were measured within one octant for  $2\theta < 75^\circ$  with the  $\omega-2\theta$  scanning mode and a scan range in  $2\theta$  from  $1.0^\circ$  below  $2\theta$  ( $\alpha_1$ ) to  $1.0^\circ$  above  $2\theta$  ( $\alpha_2$ ). The scan speed for each reflection was calculated from a preliminary stationary-crystal stationary-counter measurement of the intensity and varied between 1.0 and 8.0°/min so as to main-

tain satisfactory counting statistics even for reflections of moderate intensity. Above  $2\theta = 45^\circ$  a rejection level was specified to avoid measurement of reflections with intensities less than the threshold value. A total of 957 independent intensities were recorded of which 811 had in-

tensities greater than twice their standard deviations estimated from counting statistics. The intensities of three standard reflections measured for every 50 reflections showed no polarization change in intensity. Lorentz and polarization corrections were applied. Atomic

Table 1. Observed and calculated structure factors. (The five columns list values of  $h, k, l, 10F_o,$  and  $10F_c$ .)

Table with 5 columns: h, k, l, 10F\_o, 10F\_c. The table contains multiple rows of numerical data representing observed and calculated structure factors for various h, k, l indices.

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ( $\times 10^5$ ). The anisotropic temperature factor is given by  $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$ .

Atom <sup>a</sup>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub> (B)	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
O1	3467	28064	12802	516	10347	728	558	-97	-1065
	10	42	20	7	120	10	48	16	63
O2	28273	4680	12810	521	12893	469	202	-57	-279
	10	41	18	7	137	7	54	15	69
O3	37454	-13225	-12896	646	10352	580	209	66	-998
	12	41	20	8	116	10	52	15	56
C1	8747	17989	2363	603	7891	665	289	-222	-779
	13	46	22	10	119	13	60	20	79
C2	21456	6482	1426	563	6077	502	-169	-89	-245
	12	40	0	9	93	9	50	18	66
C3	25731	-2190	-10897	670	6614	536	195	-82	-413
	14	43	20	11	105	10	61	18	63
H1	4255	17975	-5913	2.93					
	205	546	226	.38					
H2	36679	7721	11513	5.88					
	288	780	369	.68					
H3	37930	-16225	19996	4.18					
	255	664	333	.55					
H4	20561	-257	-18368	2.90					
	188	504	220	.42					

<sup>a</sup> For numbering of atoms see Fig. 1.

Table 3. R.m.s. amplitudes ( $u^2$ )<sup>‡</sup> and *B*-values along the principal axes of vibration given by the components of a unit vector *e* in fractional coordinates ( $\times 10^3$ ).

Atom	( $u^2$ ) <sup>‡</sup>	<i>B</i>	<i>e</i> <sub><i>x</i></sub>	<i>e</i> <sub><i>y</i></sub>	<i>e</i> <sub><i>z</i></sub>
O1	.270	5.76	13	262	-26
	.186	2.74	-18	78	94
	.169	2.26	92	-21	23
O2	.295	6.87	4	274	-4
	.174	2.38	-92	13	20
	.152	1.83	19	8	98
O3	.267	5.63	4	268	-21
	.191	2.89	92	1	22
	.166	2.18	-21	58	95
C1	.238	4.49	22	248	-36
	.191	2.89	-72	110	51
	.166	2.18	57	43	78
C2	.204	3.29	14	-270	11
	.180	2.56	88	28	-34
	.156	1.93	31	41	93
C3	.215	3.65	27	257	-22
	.195	3.00	-90	82	10
	.161	2.05	15	52	97

Table 4. Bond distances, bond angles, and hydrogen bond lengths and angles (equivalent position numbers in parentheses as defined below). Estimated standard deviations in bond lengths between heavy atoms are 0.002 Å, in angles 0.1° (0.02 Å and 2° in bonds involving hydrogen bonds). Distances in parentheses are corrected for anisotropic thermal motion (see text).

Bond distances (Å)		Bond angles (°)	
C1 - C2	1.414 (1.423)	C1 - C2 - C3	116.7
C2 - C3	1.352 (1.356)	C1 - C2 - O2	117.9
C1 - O1	1.241 (1.244)	C2 - C3 - O3	121.7
C2 - O2	1.351 (1.360)	C2 - C1 - O1	125.0
C3 - O3	1.322 (1.327)	C3 - C2 - O2	125.4
C1 - H1	0.96	O1 - C1 - H1	120.3
C3 - H4	0.93	C2 - C1 - H1	114.7
O2 - H2	0.91	C2 - C3 - H4	121.2
O3 - H3	0.73	O3 - C3 - H4	117.1
		C2 - O2 - H2	113.5
		C3 - O3 - H3	105.2
Hydrogen bond distances (Å)		Hydrogen bond angles (°)	
O1...O2 (I)	2.744	O1...H2 - O2 (I)	164.9
O1...O3 (II)	2.635	O1...H3 - O3 (II)	156.5
O1...H2 (I)	1.86	O1...O2 - H2 (I)	10.1
O1...H3 (II)	1.96	O1...O3 - H3 (II)	17.2
I: $(x - \frac{1}{2}, \frac{1}{2} - y, z)$			
II: $(\frac{1}{2} - x, y - \frac{1}{2}, z + \frac{1}{2})$			

scattering factors were taken from Hanson *et al.*<sup>6</sup> except those for the hydrogen atoms.<sup>7</sup> All programs used are written or revised for CD-3300 by Dahl *et al.*<sup>8</sup>

#### CRYSTAL DATA

Triose reductone C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>, orthorhombic;  $a = 10.601(2)$  Å,  $b = 3.647(1)$  Å,  $c = 10.008(3)$  Å,  $\rho_{\text{obs}} = 1.50$  g/cm<sup>3</sup> (flotation).  $\rho_{\text{calc}} = 1.49$  g/cm<sup>3</sup>,  $Z = 4$ .

#### STRUCTURE DETERMINATION

The orientation of the molecule was found from a three-dimensional Patterson synthesis. The model was then translated stepwise through the unit cell and  $R$  over 50 low order reflections was determined for each step. The coordinates corresponding to the  $R$ -minimum were refined further by the "minimum residual method".<sup>9</sup> Least squares refinements assuming isotropic thermal parameters converged with  $R_w = 0.22$  and  $R = 0.17$ . Introduction of anisotropic thermal parameters yielded  $R_w = 0.052$  and  $R = 0.047$ . The hydrogen atoms were located from a difference Fourier map.

Refinement of individual isotropic temperature factors for these atoms gave reasonable values, and refinements terminated with  $R_w = 0.043$  and  $R = 0.035$ . The weight analysis based on the standard deviations from counting statistics showed only small intensity variations except for the smallest  $F$ -values. No secondary extinction effects were observed. A final difference Fourier map contained no larger density fluctuations than  $\pm 0.35$  e Å<sup>-3</sup>. Observed and calculated structure factors are listed in Table 1 and atomic parameters in Table 2. Magnitudes and directions of the principal axes of the ellipsoids of vibration are given in Table 4. The r.m.s. discrepancy between the atomic vibration tensor components obtained in the structure analysis and those calculated from the rigid-body parameters found by analysis of the librational, translational, and screw motion of the molecule<sup>10</sup> is 0.0009, indicating that the molecule may be regarded as a rigid body. However, the ratio of "observed" to calculated parameters is small (1.8). The eigen values of  $T$  are 0.21, 0.17, and 0.16 Å while the r.m.s. libration amplitudes are 7.9, 4.1, and 2.1°. The two larger axes of libration lie approximately in the molecular plane (see below), the largest being nearly

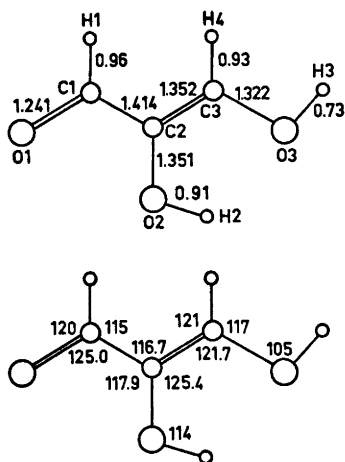


Fig. 1. Schematical drawing of the molecule showing bond distances and angles (uncorrected values).

parallel with the axis of minimum inertia. The translational vibration is largest in the direction perpendicular to the molecular plane. Corrections in bond lengths for librational motion range from 0.003 Å to 0.009 Å (Table 4).

## DISCUSSION

Bond lengths and angles are listed in Table 4 and Fig. 1. The compound is found to have the *trans* structure (I). However, both hydrogen bonds are *inter*-molecular.

The molecular dimensions of triose reductone agree fairly well with those found in dialuric acid,<sup>11,12</sup> and thus there is also considerable conjugation in the alternating bond system of triose reductone. In both ascorbic<sup>13</sup> and dialuric acids<sup>11,12</sup> a large difference between the C—O bond lengths of the central and terminal hydroxyl groups is found. A similar difference is also observed in triose reductone (0.03 Å). It therefore appears likely that the terminal hydroxyl group carries the acidic proton, as it does in ascorbic acid.<sup>14</sup>

The molecule is nearly planar (Table 5). Deviations from planarity are mostly due to a slight rotation around the C1—C2 single bond, the dihedral angle O1—C1—C2—O2 being 3.3°. The enediol group (—COH=COH—), however, is exactly planar and the atoms H3 and

Table 5. Deviations from least squares planes (Å). Plane No. 1 is through all heavy atoms, plane no. 2 is through all heavy atoms except O1. Deviations of atoms not defining the planes in parentheses.

Atom 1	2	
O1	0.019	(0.050)
O2	-0.006	-0.001
O3	0.011	-0.000
C1	-0.024	-0.001
C2	-0.006	0.003
C3	-0.002	-0.001
H1	(-0.050)	(-0.025)
H2	(0.380)	(0.377)
H3	(0.020)	(0.006)
H4	(0.003)	(0.007)

H4 also lie in this plane, while H2 deviates significantly.

The two hydroxylic protons are both involved in *inter*-molecular hydrogen bonds to the carbonyl oxygen atom at distances 2.635(2) Å, and 2.744(2) Å. The shorter bond is that involving the terminal hydroxyl group. This bond lies approximately in the plane of the molecule, while the other bond is significantly out of this plane. A similar situation is also found in dialuric<sup>11,12</sup> and ascorbic acid.<sup>13</sup>

There are two short *intra*-molecular O...O contacts (O1...O2 2.76 Å, O2...O3 2.83 Å) which may be regarded as possible hydrogen bond contacts. There were, however, no maxima in the difference Fourier map that could be interpreted in terms of hydrogen bonding between these atoms. There is therefore no evidence of a disordered or bifurcated hydrogen bond system. The distance O3...H2 is 2.56 Å and must therefore be regarded as a normal van der Waals contact. The facile sublimation of triose reductone has been attributed to the existence of a double five-membered chelate ring structure.<sup>15</sup> Attempts to verify this kind of structure in the vapour phase by electron diffraction and microwave spectroscopy at this institute have so far been unsuccessful, due to the low stability and the low volatility of this compound.

As illustrated in Fig. 2 the molecules are hydrogen bonded to each other to form a three-dimensional network. The stronger hydrogen

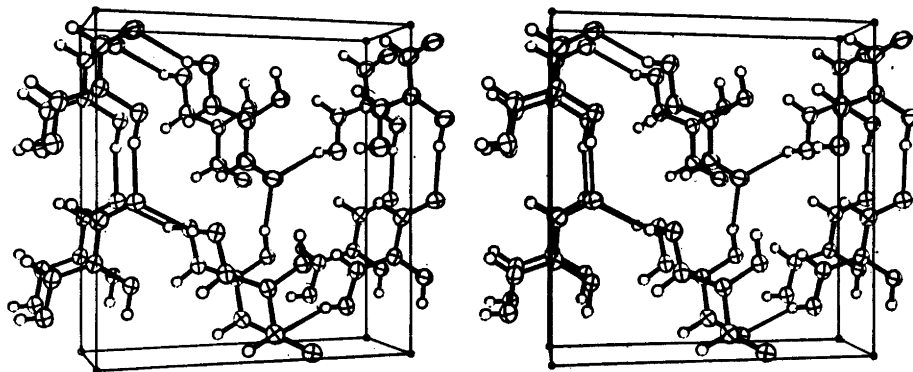


Fig. 2. Stereoscopic illustration of the structure of triose reductone. Thermal ellipsoids are scaled to include 50 % probability. Covalent bonds are filled, hydrogen bonds are open. (Johnson, C.K. (1965) *ORTEP*. ORNL-3794, Oak Ridge National Laboratory, Tennessee).

bonds between the terminal oxygen atoms form alternating zig-zag chains running parallel with the (011) and (0 $\bar{1}$ 1) planes, respectively. These chains are cross-linked by the weaker hydrogen bonds along [100].

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