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# The Structure of Trioxane at Low Temperature*

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An X-ray crystal structure analysis of trioxane, $C_3H_6O_3$, has been carried out at −170 °C. The crystals are trigonal, space group $R3c$, as at room temperature, with $a = 9{\cdot}320 \pm 0{\cdot}006$, $c = 8{\cdot}196 \pm 0{\cdot}005$ Å and with six formula units in the cell. Full-matrix least-squares refinement of three-dimensional data, photographically collected up to $|S| = 2$ Å$^{-1}$, resulted in a final $R$ index of 0·073, including the H atoms which were located. The ring molecules, which have point group symmetry 3 in the crystal, still retain their maximum molecular symmetry $3m$ (C–O, 1·421 and 1·422 Å; O–C–O, 109·6°; C–O–C, 110·4°). The packing is controlled by C–H---O contacts of 3·321, 3·454 and 3·645 Å. The most significant variations from the room-temperature structure are a reduction in the thickness of the molecule and in the distances of closest approach between adjacent molecules.

## Introduction

It is well known that trioxane, the cyclic trimer of formaldehyde, $(CH_2O)_3$, can be easily polymerized in the crystalline state either by high-energy radiation or by catalytic initiation, giving twinned crystals of polyoxymethylene (Kohlschütter & Sprenger, 1932; Okamura, Hayashi & Nakamura, 1960; Carazzolo, Leghissa & Mammi, 1963; Jamison & Noether, 1963; Okamura, Kobayashi & Higashimura, 1965).

The polymer yield depends upon the post-irradiation temperature (Okamura, Kobayashi, Takeda, Tomikawa & Higashimura, 1963), but the twinning geometry is determined by the symmetry of the trioxane crystals (Bezzi, 1962; Carazzolo, Leghissa, Mammi & Bezzi, 1963; Carazzolo & Mammi, 1967). The structure determination at room temperature (Moerman, 1937; Busetti, Mammi & Carazzolo, 1963) indicated also a rather loose molecular packing, near to the lower limit of the Kitaigorodskii coefficient, *i.e.* 0·65 (Kitaigorodskii, 1961; Valle, Carazzolo & Mammi, 1965). However, the crystal was reported to be effectively rigid below −10 °C, while near to the melting point large molecular motions like chair-chair and chair-boat interconversion and molecular rotation were postulated (Komaki & Matsumoto, 1963), which could account for the temperature-dependence of the polymerization. This was suggested by the sharp differences in the nuclear magnetic resonance spectra of crystalline trioxane at different temperatures, from −70 °C to near the melting point, 64 °C. On the other hand infrared spectra do not undergo essential changes from −130 °C to 64 °C (Kobayashi, Iwamoto & Tadokoro, 1966).

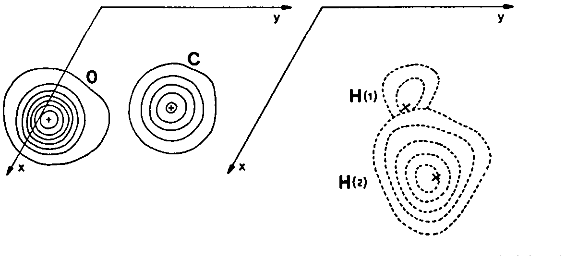

Fig. 1. Electron density sections at the $z$ levels of each individual atom. Intervals of 4 e.Å$^{-3}$ for carbon and oxygen, starting from the 2 e.Å$^{-3}$ contour (full lines). The broken lines are at intervals of 0·1 e.Å$^{-3}$, starting from 0·1 e.Å$^{-3}$ and show the electron density, at the hydrogen atom positions, from a difference-Fourier synthesis calculated with reflexions having $\sin\theta/\lambda < 0{\cdot}7$ Å$^{-1}$.

Additional information on the mechanism of the solid state process could be obtained by X-ray investigations from low temperatures to near the melting point, and the results of the three-dimensional refinement at −170 °C are now reported. The room temperature data taken for comparison in this paper are those given by Busetti *et al.* (1963).

## Experimental

Trioxane single crystals were grown from the melt in sealed and completely filled Lindemann capillaries, 0·5 mm in diameter, as described by Busetti *et al.* (1963). The crystals, elongated along **c**, were examined at −170 °C in a Weissenberg camera with an automatic low-temperature device (Del Pra, Valle & Mammi, 1967). No phase transition was observed. Cell parameters were determined using silicon powder diffraction lines as an internal standard (*International Tables for X-ray Crystallography*, 1962*a*) and by comparison of low- and room-temperature reflexions collected on the same film.

*Crystal data* (with room-temperature values in brackets).

Trioxane, $C_3H_6O_3$, *F. W.* 90·1, m.p. 64 °C
Trigonal, space group $R3c$–$C_{3v}^6$

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* Work carried out with C.N.R. aid. A report was given at the VIIth International Congress of the I.U.Cr., Moscow (1966), paper 8.20.

$a=9{\cdot}320\pm0{\cdot}006(9{\cdot}395)$, $c=8{\cdot}196\pm0{\cdot}005(8{\cdot}350)$ Å,
$V=616{\cdot}5(638{\cdot}3)$ Å$^3$
$D_m=(1{\cdot}39)$, $D_x=1{\cdot}45(1{\cdot}41)$ g.cm$^{-3}$, $Z=6$,
$F(000)=288$, $\mu_{\text{Cu } K\alpha}=12{\cdot}7$, $\mu_{\text{Mo } K\alpha}=1{\cdot}6$ cm$^{-1}$.

Fourteen *hkn* layers were recorded on equi-inclination Weissenberg photographs, with Mo $K\alpha$ radiation. Packs of four Ilford Industrial films were used for each exposure, in the order $C:G:B:C$, corresponding to intensity ratios of about 2·5:20:6:1.

Reflexions were observed up to $\theta=45°$ ($|S|=2$ Å$^{-1}$). Within that limit, 578 independent reflexions are possible (27 in uncollected layers) and the integrated intensity of 320 of them was measured by a recording microdensitometer, leaving 3·4% of the total diffracted intensity to the 227 unobserved reflexions (on an $F_c$ basis). Four low-angle reflexions, cut off by the beam stop, were given the corresponding $F_c$ values. Owing to experimental difficulties in getting crystals suitable for different alignments and on account of space group extinctions, interlayer scaling was carried out by collecting sets of three contiguous layers at the same time on oscillating photographs, with stationary or moving film.

Data for absorption correction for cylindrical crystals were taken from *International Tables for X-ray Crystallography* (1959).

## Structure refinement and discussion

Slight shifts in the C and O room-temperature fractional coordinates were indicated by several cycles of differential synthesis carried out on an Elea 6001 computer (Nardelli, Musatti, Domiano & Andreetti, 1965) applying an overall temperature factor $B=1{\cdot}7$ Å$^2$ obtained by a Wilson plot and atomic scattering factors from *International Tables for X-ray Crystallography* (1962*b*). The $R$ index changed from 0·12 to 0·115.

Refinement was then continued on an IBM 7094/7040 DCS computer, with the *X-ray* 63 *program system* (1965). Both the Cruickshank (1961) and the Hughes (1941) weighting schemes were applied in the full-matrix least-squares program *ORFLS*, giving very close final values of the positional and isotropic thermal parameters of C and O ($R=0{\cdot}089$). H atom coordinates from a model were kept constant. Refinement of individual layer scale factors did not result in any significant variation, and a difference synthesis did not show any evidence of anisotropic thermal vibrations. Two further cycles of least-squares with the weighting scheme of Mills & Rollett (1961) lowered the estimated standard deviations of C and O positional parameters to the values reported in Table 1 and the $R$ index to 0·073. The values $a=8$ $F_{\min}=24$, $b=5$ $F_{\min}=15$ and $k=1$ were used in the equation

$$w=1/(1+[(k|F_o|-b)/a]^2)\,.$$

Finally, H atom coordinates were localized on a difference-Fourier synthesis calculated with reflexions limited to $\sin\theta/\lambda=0{\cdot}7$ Å$^{-1}$. Observed peak heights of the H(1) and H(2) atoms were 0·3 and 0·6 e.Å$^{-3}$, respectively, the spurious peaks being lower than 0·15

Table 1. *Final atomic coordinates and temperature factors, with their e.s.d.'s (in parentheses) calculated by the ORFLS program*

| | $x/a$ | $y/b$ | $z/c$ | $B$(Å$^2$) |
|---|---|---|---|---|
| O | 0·1514 (4) | 0·0164 (4) | 0·0282 (4) | 1·52 (3) |
| C | 0·1357 (6) | 0·1521 (6) | −0·0282 (6) | 2·18 (5) |
| H(1) | 0·136 | 0·165 | −0·158 | 2·18 |
| H(2) | 0·237 | 0·252 | 0·031 | 2·18 |

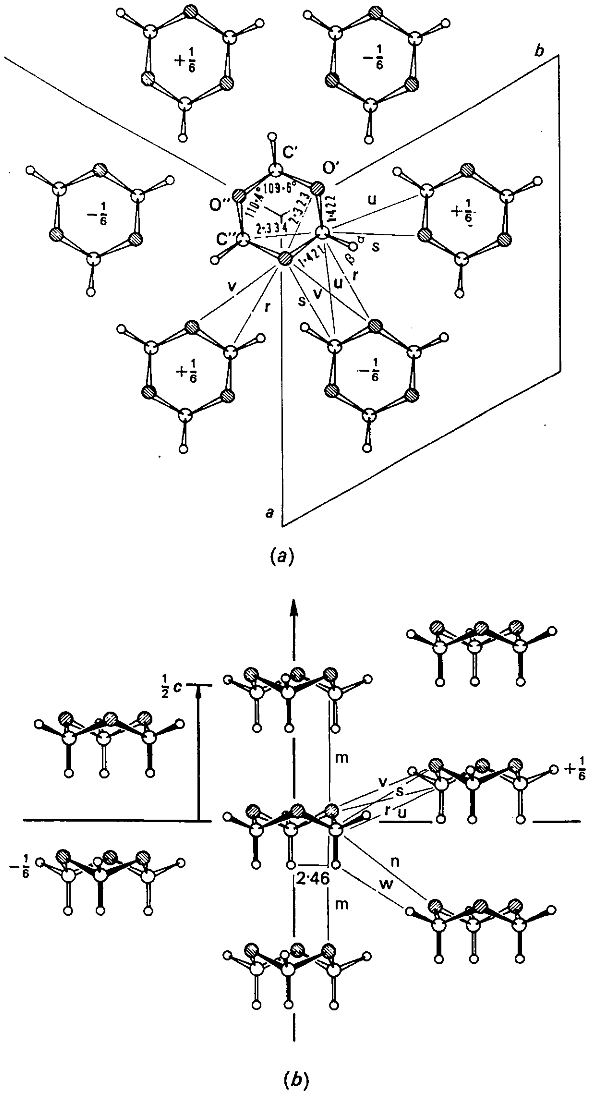

Fig. 2. Trioxane crystal packing. (*a*) Adjacent molecules shifted by $\pm\frac{1}{6}c$ and viewed down the $c$ axis. (*b*) View along the $a$ axis of three contiguous rows of molecules, whose threefold axes lie in the origin plane perpendicular to **a**. Shaded circles, oxygen atoms; open circles, carbon atoms; small circles, hydrogen atoms. The indicated intermolecular distances are (Å): $r=3{\cdot}321$, $s=3{\cdot}474$, $u=3{\cdot}607$, $v=3{\cdot}614$, $w=2{\cdot}55$, $m=3{\cdot}645$, $n=3{\cdot}869$.

Table 2. *Observed and calculated structure factors*

Columns are $H$, $K$, $10|F_o|$, $10|F_c|$, $\alpha$ in millicycles. The asterisk denotes unobserved reflexions, which were given half the minimum observed intensity and were not included in the least-squares refinement or in the $R$ calculation. The amplitudes of the reflexions cut off by the beam stop are reported in parentheses.

| | | | | |
|---|---|---|---|---|
| L = 0 | | | | |
| 3 | 0 | 475 | 465 | 10 |
| 6 | 0 | 510 | 519 | 998 |
| 9 | 0 | 19* | 30 | 854 |
| 12 | 0 | 24* | 22 | 772 |
| 15 | 0 | 26* | 28 | 994 |
| 1 | 1 | 709 | 707 | 999 |
| 4 | 1 | 181 | 175 | 44 |
| 7 | 1 | 325 | 339 | 3 |
| 10 | 1 | 114 | 119 | 40 |
| 13 | 1 | 72 | 67 | 13 |
| 2 | 2 | 730 | 702 | 0 |
| 5 | 2 | 140 | 145 | 3 |
| 8 | 2 | 69 | 66 | 984 |
| 11 | 2 | 24* | 8 | 70 |
| 14 | 2 | 26* | 16 | 117 |
| 3 | 3 | 347 | 320 | 999 |
| 6 | 3 | 58 | 71 | 923 |
| 9 | 3 | 64 | 67 | 972 |
| 12 | 3 | 26* | 18 | 140 |
| 4 | 4 | 141 | 163 | 0 |
| 7 | 4 | 76 | 83 | 937 |
| 10 | 4 | 24* | 10 | 141 |
| 13 | 4 | 27* | 20 | 898 |
| 5 | 5 | 149 | 168 | 0 |
| 8 | 5 | 76 | 73 | 33 |
| 11 | 5 | 26* | 30 | 45 |
| 6 | 6 | 52 | 55 | 0 |
| 9 | 6 | 46 | 36 | 955 |
| 12 | 6 | 27* | 26 | 76 |
| 7 | 7 | 120 | 126 | 999 |
| 10 | 7 | 49 | 44 | 94 |
| 8 | 8 | 26* | 5 | 0 |
| 9 | 9 | 34 | 28 | 999 |
| L = 1 | | | | |
| 2 | 1 | 153 | 150 | 923 |
| 5 | 1 | 137 | 150 | 25 |
| 8 | 1 | 72 | 71 | 24 |
| 11 | 1 | 23* | 33 | 32 |
| 14 | 1 | 49 | 50 | 935 |
| 3 | 2 | 237 | 249 | 315 |
| 6 | 2 | 231 | 243 | 932 |
| 9 | 2 | 33 | 43 | 944 |
| 12 | 2 | 86 | 92 | 997 |
| 15 | 2 | 26* | 13 | 15 |
| 1 | 3 | 277 | 269 | 904 |
| 4 | 3 | 105 | 112 | 6 |
| 7 | 3 | 54 | 50 | 996 |
| 10 | 3 | 45 | 33 | 887 |
| 13 | 3 | 71 | 62 | 967 |
| 2 | 4 | 269 | 261 | 940 |
| 5 | 4 | 133 | 140 | 911 |
| 8 | 4 | 123 | 127 | 971 |
| 11 | 4 | 25* | 26 | 902 |
| 3 | 5 | 114 | 130 | 74 |
| 6 | 5 | 20* | 24 | 181 |
| 9 | 5 | 112 | 106 | 1 |
| 12 | 5 | 26* | 12 | 835 |
| 1 | 6 | 164 | 168 | 15 |
| 4 | 6 | 19* | 41 | 756 |
| 7 | 6 | 83 | 60 | 933 |
| 10 | 6 | 25* | 35 | 74 |
| 2 | 7 | 134 | 136 | 12 |
| 5 | 7 | 78 | 77 | 20 |
| 8 | 7 | 39 | 31 | 43 |
| 11 | 7 | 26* | 9 | 66 |
| 3 | 8 | 20* | 28 | 209 |
| 6 | 8 | 35 | 37 | 10 |
| 9 | 8 | 26* | 5 | 13 |
| 1 | 9 | 59 | 53 | 945 |
| 4 | 9 | 89 | 86 | 50 |
| 7 | 9 | 57 | 38 | 972 |
| 2 | 10 | 50 | 51 | 894 |
| 5 | 10 | 62 | 62 | 977 |
| 8 | 10 | 26* | 14 | 929 |
| 3 | 11 | 47 | 41 | 10 |
| 6 | 11 | 26* | 13 | 902 |
| 1 | 12 | 53 | 60 | 998 |
| 4 | 12 | 26* | 29 | 128 |
| 2 | 13 | 66 | 75 | 40 |
| 5 | 13 | 26* | 11 | 26 |
| 3 | 14 | 26* | 15 | 60 |
| 1 | 15 | 26* | 22 | 33 |
| L = 2 | | | | |
| 2 | 0 | 322 | 306 | 989 |
| 5 | 0 | 224 | 209 | 973 |
| 8 | 0 | 245 | 269 | 9 |
| 11 | 0 | 31* | 50 | 158 |
| 14 | 0 | 72 | 59 | 33 |
| 0 | 1 | (363) | 363 | 4 |
| 3 | 1 | 382 | 350 | 35 |
| 6 | 1 | 379 | 375 | 14 |
| 9 | 1 | 49 | 42 | 112 |
| 12 | 1 | 59 | 40 | 932 |
| 15 | 1 | 37* | 7 | 961 |
| 1 | 2 | 327 | 323 | 993 |
| 4 | 2 | 95 | 91 | 58 |
| 7 | 2 | 25* | 35 | 120 |
| 10 | 2 | 63 | 58 | 44 |
| 13 | 2 | 36* | 25 | 119 |
| 2 | 3 | 460 | 447 | 2 |
| 5 | 3 | 67 | 84 | 963 |
| 8 | 3 | 120 | 120 | 981 |
| 11 | 3 | 34* | 11 | 856 |
| 14 | 3 | 37* | 22 | 905 |
| 0 | 4 | 374 | 373 | 967 |
| 3 | 4 | 101 | 106 | 18 |
| 6 | 4 | 158 | 174 | 981 |
| 9 | 4 | 32* | 19 | 865 |
| 12 | 4 | 36* | 24 | 963 |
| 1 | 5 | 187 | 200 | 23 |
| 4 | 5 | 117 | 131 | 33 |
| 7 | 5 | 30* | 21 | 245 |
| 10 | 5 | 35* | 10 | 923 |
| 2 | 6 | 191 | 198 | 990 |
| 5 | 6 | 57 | 41 | 81 |
| 8 | 6 | 80 | 92 | 18 |
| 11 | 6 | 36* | 29 | 157 |
| 0 | 7 | 472 | 461 | 10 |
| 3 | 7 | 54 | 48 | 139 |
| 6 | 7 | 107 | 118 | 4 |
| 9 | 7 | 36* | 21 | 871 |
| 1 | 8 | 74 | 75 | 37 |
| 4 | 8 | 30* | 32 | 849 |
| 7 | 8 | 60 | 54 | 35 |
| 10 | 8 | 37* | 23 | 172 |
| 2 | 9 | 107 | 112 | 3 |
| 5 | 9 | 33* | 46 | 0 |
| 8 | 9 | 36* | 39 | 972 |
| 0 | 10 | 142 | 165 | 971 |
| 3 | 10 | 32* | 15 | 102 |
| 6 | 10 | 36* | 45 | 938 |
| 1 | 11 | 72 | 73 | 960 |
| 4 | 11 | 35* | 5 | 215 |
| 7 | 11 | 37* | 48 | 942 |
| 2 | 12 | 34* | 43 | 985 |
| 5 | 12 | 36* | 31 | 2 |
| 0 | 13 | 34* | 60 | 25 |
| 3 | 13 | 36* | 23 | 888 |
| 1 | 14 | 36* | 46 | 997 |
| 0 | 16 | 36* | 26 | 925 |
| L = 3 | | | | |
| 1 | 1 | 130 | 124 | 958 |
| 4 | 1 | 154 | 148 | 870 |
| 7 | 1 | 112 | 117 | 10 |
| 10 | 1 | 35 | 35 | 898 |
| 13 | 1 | 71 | 60 | 11 |
| 2 | 2 | 478 | 480 | 926 |
| 5 | 2 | 169 | 183 | 10 |
| 8 | 2 | 16* | 24 | 793 |
| 11 | 2 | 19* | 32 | 94 |
| 14 | 2 | 49 | 50 | 3 |
| 3 | 3 | 251 | 232 | 921 |
| 6 | 3 | 192 | 198 | 982 |
| 9 | 3 | 120 | 117 | 965 |
| 12 | 3 | 78 | 83 | 993 |
| 1 | 4 | 299 | 278 | 954 |
| 4 | 4 | 140 | 148 | 936 |
| 7 | 4 | 58 | 49 | 3 |
| 10 | 4 | 48 | 36 | 16 |
| 13 | 4 | 21* | 20 | 961 |
| 2 | 5 | 153 | 154 | 35 |
| 5 | 5 | 113 | 122 | 937 |
| 8 | 5 | 122 | 125 | 1 |
| 11 | 5 | 21* | 24 | 875 |
| 3 | 6 | 51 | 53 | 203 |
| 6 | 6 | 17* | 2 | 976 |
| 9 | 6 | 57 | 50 | 62 |
| 1 | 7 | 79 | 91 | 40 |
| 4 | 7 | 33 | 27 | 39 |
| 7 | 7 | 19* | 0 | 103 |
| 10 | 7 | 21* | 7 | 139 |
| 2 | 8 | 77 | 91 | 981 |
| 5 | 8 | 55 | 75 | 59 |
| 8 | 8 | 20* | 10 | 908 |
| 3 | 9 | 36 | 49 | 862 |
| 6 | 9 | 111 | 77 | 8 |
| 9 | 9 | 21* | 13 | 910 |
| 1 | 10 | 52 | 67 | 961 |
| 4 | 10 | 19* | 35 | 41 |
| 7 | 10 | 21* | 12 | 988 |
| 2 | 11 | 60 | 67 | 990 |
| 5 | 11 | 21* | 36 | 941 |
| 3 | 12 | 41 | 39 | 111 |
| 1 | 13 | 20* | 43 | 55 |
| 4 | 13 | 21* | 10 | 759 |
| 2 | 14 | 21* | 33 | 88 |
| L = 4 | | | | |
| 1 | 0 | (728) | 729 | 42 |
| 4 | 0 | 91 | 82 | 203 |
| 7 | 0 | 310 | 311 | 36 |
| 10 | 0 | 30* | 50 | 838 |
| 13 | 0 | 80 | 51 | 28 |
| 2 | 1 | 123 | 113 | 97 |
| 5 | 1 | 192 | 181 | 17 |
| 8 | 1 | 71 | 82 | 17 |
| 11 | 1 | 33* | 32 | 859 |
| 14 | 1 | 37* | 24 | 102 |
| 0 | 2 | 85 | 95 | 82 |
| 3 | 2 | 221 | 224 | 59 |
| 6 | 2 | 69 | 66 | 101 |
| 9 | 2 | 77 | 62 | 52 |
| 12 | 2 | 36* | 13 | 167 |
| 1 | 3 | 370 | 354 | 10 |
| 4 | 3 | 83 | 86 | 23 |
| 7 | 3 | 137 | 137 | 987 |
| 10 | 3 | 34* | 32 | 994 |
| 13 | 3 | 37* | 28 | 926 |
| 2 | 4 | 95 | 94 | 11 |
| 5 | 4 | 131 | 147 | 9 |
| 8 | 4 | 68 | 73 | 966 |
| 11 | 4 | 36* | 15 | 968 |
| 0 | 5 | 42 | 52 | 246 |
| 3 | 5 | 26 | 26 | 869 |
| 6 | 5 | 75 | 78 | 999 |
| 9 | 5 | 34* | 27 | 68 |
| 12 | 5 | 37* | 18 | 89 |
| 1 | 6 | 256 | 277 | 28 |
| 4 | 6 | 28* | 43 | 187 |
| 7 | 6 | 73 | 69 | 50 |
| 10 | 6 | 37* | 28 | 890 |
| 2 | 7 | 84 | 91 | 991 |
| 5 | 7 | 77 | 70 | 974 |
| 8 | 7 | 57 | 55 | 25 |
| 0 | 8 | 146 | 162 | 44 |
| 3 | 8 | 30* | 29 | 203 |
| 6 | 8 | 77 | 70 | 35 |
| 9 | 8 | 37* | 14 | 221 |
| 1 | 9 | 108 | 114 | 989 |
| 4 | 9 | 36 | 38 | 958 |
| 7 | 9 | 37* | 35 | 944 |
| 2 | 10 | 73 | 72 | 10 |
| 5 | 10 | 36* | 12 | 935 |
| 8 | 10 | 37* | 46 | 980 |
| 0 | 11 | 145 | 144 | 985 |
| 3 | 11 | 35* | 23 | 959 |
| 6 | 11 | 59 | 60 | 982 |
| 1 | 12 | 35* | 15 | 118 |
| 4 | 12 | 37* | 9 | 783 |
| 2 | 13 | 48 | 49 | 991 |
| 0 | 14 | 37* | 55 | 29 |
| 1 | 15 | 37* | 4 | 855 |
| L = 5 | | | | |
| 3 | 1 | 279 | 280 | 959 |
| 6 | 1 | 98 | 96 | 34 |
| 9 | 1 | 51 | 46 | 943 |
| 12 | 1 | 25* | 29 | 74 |
| 1 | 2 | 258 | 262 | 973 |
| 4 | 2 | 122 | 119 | 914 |
| 7 | 2 | 95 | 90 | 31 |
| 10 | 2 | 72 | 74 | 955 |
| 13 | 2 | 62 | 71 | 24 |
| 2 | 3 | 432 | 417 | 972 |
| 5 | 3 | 207 | 214 | 998 |
| 8 | 3 | 94 | 99 | 982 |
| 11 | 3 | 25* | 31 | 38 |
| 3 | 4 | 49 | 42 | 48 |
| 6 | 4 | 113 | 116 | 978 |
| 9 | 4 | 113 | 104 | 7 |
| 12 | 4 | 59 | 51 | 989 |
| 1 | 5 | 137 | 135 | 15 |
| 4 | 5 | 169 | 169 | 959 |
| 7 | 5 | 73 | 69 | 19 |
| 10 | 5 | 26* | 19 | 244 |
| 2 | 6 | 36 | 52 | 163 |
| 5 | 6 | 67 | 59 | 978 |
| 8 | 6 | 64 | 49 | 51 |
| 11 | 6 | 27* | 12 | 899 |
| 3 | 7 | 20* | 20 | 83 |
| 6 | 7 | 24* | 17 | 148 |
| 9 | 7 | 26* | 13 | 232 |
| 1 | 8 | 55 | 62 | 21 |
| 4 | 8 | 23* | 35 | 829 |
| 7 | 8 | 36 | 34 | 17 |
| 2 | 9 | 102 | 107 | 971 |
| 5 | 9 | 56 | 55 | 68 |
| 8 | 9 | 27* | 1 | 178 |
| 3 | 10 | 53 | 46 | 945 |
| 6 | 10 | 26* | 46 | 6 |
| 1 | 11 | 60 | 56 | 994 |
| 4 | 11 | 26* | 30 | 940 |
| 2 | 12 | 42 | 37 | 100 |
| 5 | 12 | 27* | 18 | 937 |
| 3 | 13 | 27* | 23 | 247 |
| 1 | 14 | 26* | 19 | 150 |
| L = 6 | | | | |
| 0 | 0 | (455) | 453 | 73 |
| 3 | 0 | 47 | 49 | 802 |
| 6 | 0 | 170 | 175 | 49 |
| 9 | 0 | 71 | 83 | 994 |
| 12 | 0 | 67 | 51 | 969 |
| 15 | 0 | 24* | 16 | 80 |
| 1 | 1 | 102 | 131 | 65 |
| 4 | 1 | 56 | 55 | 916 |
| 7 | 1 | 86 | 98 | 79 |
| 10 | 1 | 50 | 54 | 901 |
| 13 | 1 | 24* | 20 | 161 |
| 2 | 2 | 140 | 154 | 68 |
| 5 | 2 | 31 | 25 | 110 |
| 8 | 2 | 57 | 40 | 22 |
| 11 | 2 | 23* | 4 | 822 |
| 0 | 3 | 169 | 200 | 21 |
| 3 | 3 | 81 | 88 | 69 |
| 6 | 3 | 102 | 108 | 996 |
| 9 | 3 | 57 | 54 | 20 |
| 12 | 3 | 24* | 27 | 947 |
| 1 | 4 | 115 | 132 | 8 |
| 4 | 4 | 55 | 53 | 51 |
| 7 | 4 | 118 | 113 | 1 |
| 10 | 4 | 23* | 14 | 948 |
| 2 | 5 | 68 | 66 | 34 |
| 5 | 5 | 59 | 60 | 65 |
| 8 | 5 | 22* | 22 | 840 |
| 11 | 5 | 24* | 12 | 845 |
| 0 | 6 | 123 | 136 | 70 |
| 3 | 6 | 66 | 70 | 960 |
| 6 | 6 | 21* | 20 | 54 |
| 9 | 6 | 24* | 38 | 18 |
| 1 | 7 | 121 | 131 | 52 |
| 4 | 7 | 62 | 65 | 939 |
| 7 | 7 | 64 | 52 | 80 |
| 10 | 7 | 24* | 38 | 913 |
| 2 | 8 | 19* | 11 | 194 |
| 5 | 8 | 78 | 63 | 15 |
| 8 | 8 | 24* | 3 | 146 |
| 0 | 9 | 89 | 73 | 969 |
| 3 | 9 | 21* | 18 | 817 |
| 6 | 9 | 24* | 18 | 874 |
| 1 | 10 | 137 | 125 | 9 |
| 4 | 10 | 23* | 19 | 985 |
| 7 | 10 | 71 | 60 | 997 |
| 2 | 11 | 23* | 7 | 26 |
| 5 | 11 | 49 | 28 | 17 |
| 0 | 12 | 54 | 49 | 973 |
| 3 | 12 | 49 | 34 | 986 |
| 1 | 13 | 46 | 39 | 52 |
| 0 | 15 | 24* | 11 | 151 |
| L = 7 | | | | |
| 2 | 1 | 183 | 215 | 989 |
| 5 | 1 | 48 | 37 | 908 |
| 8 | 1 | 22* | 15 | 839 |
| 11 | 1 | 26* | 29 | 938 |
| 14 | 1 | 28* | 26 | 68 |
| 3 | 2 | 307 | 325 | 985 |
| 6 | 2 | 110 | 114 | 29 |
| 9 | 2 | 94 | 100 | 983 |
| 12 | 2 | 54 | 40 | 74 |
| 1 | 3 | 225 | 259 | 993 |
| 4 | 3 | 18* | 23 | 66 |
| 7 | 3 | 22* | 17 | 66 |
| 10 | 3 | 55 | 52 | 991 |
| 2 | 4 | 170 | 132 | 3 |
| 5 | 4 | 183 | 196 | 994 |
| 8 | 4 | 97 | 94 | 18 |
| 11 | 4 | 54 | 37 | 992 |
| 3 | 5 | 109 | 104 | 958 |
| 6 | 5 | 46 | 41 | 970 |
| 9 | 5 | 53 | 35 | 104 |
| 1 | 6 | 19* | 25 | 141 |
| 4 | 6 | 103 | 93 | 976 |
| 7 | 6 | 50 | 31 | 41 |
| 10 | 6 | 28* | 22 | 892 |
| 2 | 7 | 21* | 22 | 195 |
| 5 | 7 | 25* | 16 | 819 |
| 8 | 7 | 28* | 12 | 859 |
| 3 | 8 | 70 | 76 | 977 |
| 6 | 8 | 27* | 26 | 129 |
| 1 | 9 | 62 | 65 | 1 |
| 4 | 9 | 51 | 40 | 894 |
| 7 | 9 | 28* | 25 | 43 |
| 2 | 10 | 88 | 84 | 989 |
| 5 | 10 | 46 | 41 | 39 |
| 3 | 11 | 27* | 9 | 221 |
| 1 | 12 | 27* | 21 | 93 |
| 4 | 12 | 28* | 32 | 932 |
| 2 | 13 | 28* | 26 | 809 |
| L = 8 | | | | |
| 2 | 0 | 46 | 52 | 46 |
| 5 | 0 | 99 | 79 | 17 |
| 8 | 0 | 21* | 55 | 114 |
| 11 | 0 | 100 | 82 | 959 |
| 14 | 0 | 28* | 17 | 768 |
| 0 | 1 | 91 | 94 | 165 |
| 3 | 1 | 51 | 61 | 902 |
| 6 | 1 | 19* | 46 | 189 |
| 9 | 1 | 44 | 57 | 964 |
| 12 | 1 | 27* | 16 | 53 |
| 1 | 2 | 53 | 51 | 50 |
| 4 | 2 | 17* | 19 | 884 |
| 7 | 2 | 49 | 45 | 958 |
| 10 | 2 | 26* | 21 | 871 |
| 2 | 3 | 57 | 65 | 90 |
| 5 | 3 | 49 | 51 | 9 |
| 8 | 3 | 80 | 63 | 31 |
| 11 | 3 | 27* | 19 | 934 |
| 0 | 4 | 106 | 119 | 21 |
| 3 | 4 | 18* | 12 | 764 |
| 6 | 4 | 82 | 83 | 31 |
| 9 | 4 | 26* | 33 | 986 |
| 1 | 5 | 17* | 25 | 842 |
| 4 | 5 | 21* | 31 | 883 |
| 7 | 5 | 41 | 46 | 978 |
| 10 | 5 | 28* | 13 | 3 |
| 2 | 6 | 62 | 68 | 43 |
| 5 | 6 | 40 | 33 | 937 |
| 8 | 6 | 27* | 22 | 192 |
| 0 | 7 | 62 | 69 | 147 |
| 3 | 7 | 71 | 72 | 966 |
| 6 | 7 | 26* | 32 | 109 |
| 9 | 7 | 28* | 31 | 990 |
| 1 | 8 | 22* | 20 | 855 |
| 4 | 8 | 63 | 58 | 981 |
| 7 | 8 | 27* | 16 | 801 |
| 2 | 9 | 25* | 30 | 95 |
| 5 | 9 | 27* | 14 | 112 |
| 0 | 10 | 125 | 110 | 17 |
| 3 | 10 | 26* | 15 | 934 |
| 6 | 10 | 28* | 40 | 8 |
| 1 | 11 | 48 | 56 | 19 |
| 4 | 11 | 28* | 9 | 966 |
| 2 | 12 | 27* | 22 | 43 |
| 0 | 13 | 27* | 14 | 235 |
| L = 9 | | | | |
| 1 | 1 | 59 | 70 | 937 |
| 4 | 1 | 126 | 130 | 990 |
| 7 | 1 | 25* | 18 | 147 |
| 10 | 1 | 48 | 50 | 959 |
| 2 | 2 | 233 | 262 | 999 |
| 5 | 2 | 22* | 21 | 190 |
| 8 | 2 | 73 | 50 | 975 |
| 11 | 2 | 32* | 25 | 932 |
| 3 | 3 | 149 | 150 | 0 |
| 6 | 3 | 92 | 87 | 30 |
| 9 | 3 | 80 | 78 | 18 |
| 1 | 4 | 120 | 127 | 9 |
| 4 | 4 | 126 | 121 | 999 |
| 7 | 4 | 29* | 12 | 78 |
| 10 | 4 | 32* | 9 | 233 |
| 2 | 5 | 22* | 24 | 845 |
| 5 | 5 | 112 | 111 | 1 |
| 8 | 5 | 29 | 35 | 103 |
| 3 | 6 | 108 | 90 | 971 |
| 6 | 6 | 30* | 2 | 991 |
| 9 | 6 | 32* | 24 | 881 |
| 1 | 7 | 25* | 21 | 874 |
| 4 | 7 | 29* | 13 | 927 |
| 7 | 7 | 32* | 0 | 982 |
| 2 | 8 | 45 | 48 | 26 |
| 5 | 8 | 31* | 37 | 906 |
| 3 | 9 | 77 | 80 | 983 |
| 6 | 9 | 32* | 22 | 129 |
| 1 | 10 | 61 | 50 | 12 |
| 4 | 10 | 32* | 9 | 785 |
| 2 | 11 | 32* | 24 | 75 |
| L = 10 | | | | |
| 1 | 0 | 79 | 71 | 858 |
| 4 | 0 | 94 | 83 | 973 |
| 7 | 0 | 60 | 59 | 861 |
| 10 | 0 | 95 | 83 | 980 |
| 2 | 1 | 37 | 37 | 949 |
| 5 | 1 | 15* | 18 | 202 |
| 8 | 1 | 19* | 14 | 171 |
| 11 | 1 | 35 | 42 | 980 |
| 0 | 2 | 36 | 36 | 949 |
| 3 | 2 | 56 | 50 | 913 |
| 6 | 2 | 49 | 51 | 952 |
| 9 | 2 | 21* | 25 | 901 |
| 1 | 3 | 23 | 37 | 126 |
| 4 | 3 | 16* | 10 | 768 |
| 7 | 3 | 43 | 50 | 42 |
| 10 | 3 | 22* | 11 | 76 |
| 2 | 4 | 15* | 12 | 137 |
| 5 | 4 | 18* | 22 | 150 |
| 8 | 4 | 34 | 43 | 23 |
| 0 | 5 | 48 | 56 | 981 |
| 3 | 5 | 27 | 36 | 988 |
| 6 | 5 | 20* | 23 | 78 |
| 9 | 5 | 22* | 12 | 867 |
| 1 | 6 | 16* | 41 | 830 |
| 4 | 6 | 64 | 62 | 966 |
| 7 | 6 | 22* | 27 | 889 |
| 2 | 7 | 19* | 31 | 49 |
| 5 | 7 | 21* | 33 | 29 |
| 0 | 8 | 47 | 46 | 887 |
| 3 | 8 | 54 | 48 | 966 |
| 6 | 8 | 22* | 19 | 817 |
| 1 | 9 | 32 | 40 | 47 |
| 4 | 9 | 22* | 24 | 19 |
| 2 | 10 | 22* | 16 | 152 |
| 0 | 11 | 77 | 60 | 50 |
| 3 | 11 | 22* | 14 | 22 |
| 1 | 12 | 22* | 13 | 944 |
| L = 11 | | | | |
| 3 | 1 | 101 | 115 | 11 |
| 6 | 1 | 20* | 17 | 857 |
| 9 | 1 | 45 | 36 | 1 |
| 1 | 2 | 80 | 94 | 15 |
| 4 | 2 | 77 | 88 | 997 |
| 7 | 2 | 23* | 16 | 807 |
| 10 | 2 | 48 | 47 | 16 |
| 2 | 3 | 140 | 147 | 20 |
| 5 | 3 | 54 | 52 | 63 |
| 8 | 3 | 46 | 41 | 35 |
| 3 | 4 | 20* | 15 | 919 |
| 6 | 4 | 49 | 49 | 33 |
| 9 | 4 | 26* | 24 | 138 |
| 1 | 5 | 19* | 19 | 116 |
| 4 | 5 | 102 | 102 | 9 |
| 7 | 5 | 25* | 12 | 219 |
| 2 | 6 | 68 | 61 | 963 |
| 5 | 6 | 25* | 22 | 43 |
| 3 | 7 | 24* | 11 | 926 |
| 6 | 7 | 26* | 18 | 948 |
| 1 | 8 | 23* | 9 | 198 |
| 4 | 8 | 63 | 53 | 977 |
| 2 | 9 | 64 | 55 | 24 |
| 3 | 10 | 26* | 29 | 15 |
| 1 | 11 | 26* | 17 | 84 |
| L = 12 | | | | |
| 0 | 0 | (120) | 120 | 934 |
| 3 | 0 | 54 | 60 | 982 |
| 6 | 0 | 45 | 53 | 914 |
| 9 | 0 | 25* | 29 | 51 |
| 1 | 1 | 35 | 38 | 934 |
| 4 | 1 | 50 | 43 | 992 |
| 7 | 1 | 64 | 54 | 934 |
| 10 | 1 | 55 | 52 | 990 |
| 2 | 2 | 48 | 48 | 933 |
| 5 | 2 | 21* | 24 | 959 |
| 8 | 2 | 25* | 7 | 797 |
| 0 | 3 | 14* | 17 | 217 |
| 3 | 3 | 27 | 31 | 928 |
| 6 | 3 | 24* | 27 | 66 |
| 9 | 3 | 26* | 10 | 222 |
| 1 | 4 | 18* | 18 | 119 |
| 4 | 4 | 22* | 22 | 926 |
| 7 | 4 | 25* | 27 | 95 |
| 2 | 5 | 21* | 12 | 862 |
| 5 | 5 | 24* | 27 | 915 |
| 0 | 6 | 74 | 67 | 940 |
| 3 | 6 | 33 | 41 | 11 |
| 6 | 6 | 26* | 9 | 919 |
| 1 | 7 | 55 | 43 | 902 |
| 4 | 7 | 36 | 46 | 2 |
| 2 | 8 | 25* | 17 | 968 |
| 0 | 9 | 35 | 33 | 20 |
| 3 | 9 | 26* | 23 | 973 |
| 1 | 10 | 26* | 26 | 143 |
| L = 13 | | | | |
| 2 | 1 | 47 | 53 | 39 |
| 5 | 1 | 27 | 33 | 992 |
| 8 | 1 | 27* | 18 | 974 |
| 3 | 2 | 50 | 59 | 38 |
| 6 | 2 | 25* | 19 | 825 |
| 1 | 3 | 58 | 58 | 49 |
| 4 | 3 | 23* | 11 | 936 |
| 7 | 3 | 27* | 7 | 885 |
| 2 | 4 | 26 | 29 | 107 |
| 5 | 4 | 55 | 48 | 70 |
| 3 | 5 | 64 | 57 | 7 |
| 6 | 5 | 23* | 17 | 34 |
| 1 | 6 | 29 | 25 | 956 |
| 4 | 6 | 27* | 34 | 38 |
| 2 | 7 | 32 | 27 | 961 |
| 1 | 9 | 23* | 15 | 97 |

e.Å$^{-3}$. Two least-squares cycles, using reflexions with $\sin\theta/\lambda < 0{\cdot}4$ Å$^{-1}$ and unitary weights, gave the H atom coordinates reported in Table 1. The H temperature factors were assumed to be equal to that of the carbon atom. Electron density sections through C,O and H atoms are shown in Fig. 1. Observed and calculated structure factors are collected in Table 2.

The final $R$ index, omitting unobserved reflexions, was 0·073, and was 0·082 not including the H atoms. These values are lowered to 0·032 and 0·052, respectively for the reflexions in the range $\sin\theta/\lambda < 0{\cdot}4$ Å$^{-1}$. The e.s.d.'s of all the C–O, C–C and O–O interatomic distances and of the angles between them are ±0·006, ±0·008, ±0·005 Å and ±0·3°, respectively. The standard deviations of distances and angles involving hydrogen atoms may be roughly estimated to be ±0·08 Å and ±4°.

Table 3. *Bond lengths, valence angles and intramolecular distances of trioxane*

The dash indicates atoms at $\bar{y}$, $x-y$, $z$. C″ is at $y-x$, $\bar{x}$, $z$.

| | | | |
|---|---|---|---|
| C—O | 1·421 Å | O–C–O′ | 109·6° |
| C—O′ | 1·422 | C–O–C″ | 110·4 |
| C—C″ | 2·334 | H(1)–C–O | 115 |
| O—O′ | 2·323 | H(1)–C–O′ | 106 |
| C—H(1) | 1·07 | H(2)–C–O | 101 |
| C—H(2) | 1·06 | H(2)–C–O′ | 110 |
| H(1)–H(1′) | 2·46 | H(1)–C–H(2) | 114 |

Bond lengths and angles and intramolecular distances are reported in Table 3. Apart from the obvious variation in the $B$ factors (from 4·38 Å$^2$), only minor changes are observed in the chair molecule with respect to the room temperature structure. The distance between the oxygen and carbon atom planes is

0·462 (6) Å, instead of 0·513 Å, and the ring valence angles are increased by about 2°. The distances of each C and O atom from the threefold axis are 1·348(6) Å and 1·341(4) Å, respectively and the internal rotation angle of both the independent C–O bonds is 58·8°. It appears, therefore, that trioxane retains its molecular symmetry $3m$, though its point symmetry in the crystal is 3. The maximum symmetry is also obeyed by the H atoms, which are both found insignificantly out of the plane containing the $c$ axis and the carbon atom, on opposite sides (+0·10 and −0·10 Å). The polar H atoms are 2·46 Å apart.

As shown in Fig. 2, the molecules are packed in rows parallel to the $c$ axis. In each row they are separated by $\frac{1}{2}c$ and alternately rotated from each other by ±48·6°, so that each carbon is only 11·4° from being exactly superimposed on an oxygen atom, at a distance $m=3{\cdot}645$ Å (3·671 Å at room temperature). Thus, each polar hydrogen H(1) points nearly towards an oxygen atom, with an H–C---O angle of 10° and an H---O distance of 2·59 Å.

Threefold screw axes relate adjacent rows, so that neighbouring molecules are shifted from each other by $\frac{1}{6}c$. From each C and O atom there are two intermolecular C---O distances, $r=3{\cdot}321$ Å and $s=3{\cdot}454$ Å, which define the approach between the rows (Fig. 2) and appear significantly shorter than in the room temperature structure (3·372 and 3·546 Å, respectively). These contacts involve the equatorial hydrogen H(2), which is 0·21 Å out of the plane defined by the C atom and by the two oxygen atoms with which the carbon atom is in contact at $r$ and $s$ (see Fig. 2(*a*)]. The C–H(2) bond makes angles $\alpha=27°$ and $\beta=51°$ with the directions of the longer ($s$) and the shorter ($r$) C---O distances, respectively, the corresponding H---O values being 2·56 Å and 2·79 Å. The observed C–H---O contacts have an important role in the crystalline state polymerization of trioxane (Bezzi, 1962) which takes place along the two crystallographic directions where these contacts are observed, connecting either superimposed molecules or those shifted by $\frac{1}{6}c$ (Busetti *et al.*, 1963; Carazzolo & Mammi, 1967). A longer C---O distance, $n=3{\cdot}869$ Å, between molecules displaced by $\frac{2}{6}c$, is ineffective for the solid state process.

Some intermolecular contacts between like atoms are also observed, *i.e.* two equivalent contacts for each C and O and one for each H (C---C, $u=3{\cdot}607$ Å; O---O, $v=3{\cdot}614$ Å; H---H, $w=2{\cdot}55$ Å). All the other intermolecular distances are larger than 4 Å (3 Å for the hydrogen atoms).

It may be concluded that the small change in the $a$ axis parameter (0·07 Å) from room temperature to −170°C is mainly a result of the closer approach between adjacent molecules. On the other hand, the larger variation in the $c$ axis length (0·15 Å) is mainly a result of the reduction of the molecular thickness, the H---O contacts within each row being in fact just at the limit of the van der Waals value. It appears from all the above considerations that the structure of trioxane at −170°C is on the whole highly ordered.

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