

## The Crystal Structure of the K Form of D-Mannitol

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The crystal structure of K-D-mannitol has been solved by use of a direct method procedure on a centrosymmetric projection and an interpretation of a Patterson-Harker section. The space group is  $P2_12_12_1$ , with four molecules in the unit cell of dimensions  $a=8.942$  (5),  $b=18.798$  (9) and  $c=4.893$  (4) Å. The molecules have the same conformation as in the B form with a carbon chain which is planar within 0.09 Å and a twofold axis of symmetry within 0.01 Å. The two polymorphs have nearly identical molecules, with similar systems of intermolecular hydrogen bonds in different steric arrangements.

### Introduction

The crystal structures of the A' and B forms of D-mannitol have been reported by Berman, Jeffrey & Rosenstein (1968)\*. This third form was obtained accidentally from an attempted crystallization of a mannitol-boric acid complex and advantage has been taken of this circumstance to determine the structure. Since the acyclic sugar molecules might be expected to have greater conformational flexibility than the cyclic compounds, it is of interest to observe to what extent conformational variety does in fact occur when the same molecule appears in the different hydrogen-bonding environments of the three polymorphs. In the case of the A' and B forms, it was found that the molecular conformations were the same, but this was not explored in detail because adequate crystals for a three-dimensional study were not obtained for the A' form. This study provides a detailed comparison between the structures of the B and K forms.

### Experimental

Crystals were obtained as colorless needles by slow evaporation of an aqueous solution of D-mannitol and boric acid in methanol. The crystal data are as follows:

$$a = 8.942 \text{ } (\sigma = 0.005) \text{ \AA}$$

$$b = 18.798 \text{ } (\sigma = 0.009)$$

$$c = 4.893 \text{ } (\sigma = 0.004)$$

$$Z = 4$$

$$D_x = 1.471 \text{ g.cm}^{-3}$$

$$D_m = 1.485 \text{ g.cm}^{-3} \text{ (by flotation)}$$

$$\mu_{\text{Cu } K\alpha} = 11.75 \text{ cm}^{-1}$$

$$\text{M.W. } 182.17$$

Space group,  $P2_12_12_1$ , from absences  $h00$  for  $h=2n+1$ ,  $0k0$  for  $k=2n+1$ ,  $00l$  for  $l=2n+1$ .

\* We have changed the nomenclature for these polymorphs from lower to upper case Greek letters to avoid confusion with  $\alpha$  and  $\beta$  which are commonly used in carbohydrate chemistry to denote particular molecular configurations.

This polymorph may be the same as the  $\Gamma$  form characterized by Rye & Sørum (1952) from powder data (see Berman, Jeffrey & Rosenstein, 1968). The lattice parameters were obtained from a series of general  $hkl$  diffractometer measurements using a least-squares program by Shiono (1966a). The three-dimensional intensity data were measured with a Picker four-angle automatic diffractometer in the  $\theta/2\theta$  scanning mode using Cu  $K\alpha$  radiation. The acicular crystal had dimensions  $0.03 \times 0.05 \times 0.5$  mm, and was mounted along the needle axis. Within the limit of  $2\theta < 130^\circ$ , 753 independent reflections were observed above background. The data were reduced to structure amplitudes without absorption corrections using a series of programs by Craven & Chu (1967).

### Determination of the structure

The structure was solved in the [001] projection by means of the IBM 1620 sign correlation program of Beurskens (1963), which is based on a systematic use of correlations between sign relations as given by the Sayre equation. The normalized structure amplitudes were calculated with scale and temperature factors obtained by the method of Wilson (1942). The first trial structure gave an  $R$  value of 0.50 for the 182  $hk0$  reflections, which was refined by difference syntheses to 0.13. The  $z$  parameters of the atoms were determined without ambiguity from the Harker section,  $P(\frac{1}{2}, v, w)$ .

### Refinement of the structure

The structure was refined in three-dimensions by the modified version (Shiono, 1966b) of the Busing, Martin & Levy (1962) full-matrix least-squares program for the IBM 7090 computer, with the Cruickshank (1961) weighting scheme. The function minimized was  $\sum w(F_o - F_c)^2$ , where  $w = 1/(A + BF + CF^2)$ . The factors  $A=1$ ,  $B=0.1$ ,  $C=0.01$  gave an essentially constant value of  $w(F_o - F_c)^2$  over all ranges of  $F$ . The fourteen hydrogen atoms were revealed unambiguously by difference Fourier syntheses. The final cycle of anisotropic least-squares varied all parameters except those of the

hydrogen atoms, with no shift as much as  $\sigma$ , and gave an  $R$  value of 0.049. The final positional and thermal parameters are given in Table 1, and the structure factors in Table 2.

### Description of the structure

The conformation of the molecule and the atomic numbering is shown in Fig. 1. The intramolecular distances and angles are given in Table 3. The average lengths of the C–C and C–O bonds are 1.519 and 1.426 Å respectively, and no bond length differs from the mean value by more than  $2\sigma$  except the C(6)–

O(6) bond, which had a trivially larger deviation. These values correspond closely with the mean values of 1.522 and 1.421 Å from some recent studies of the cyclic monosaccharides (Berman, Chu & Jeffrey, 1967). The corrections for 'riding' motion increase these lengths by about  $0.5\sigma$ , as shown in Table 3. When compared with the same distances in the structure of the B form, the mean C–C distance is 0.003 Å shorter and the mean C–O distance is 0.012 Å longer. The thermal parameters in the two structures are so similar that the larger discrepancy cannot be explained by inadequate thermal corrections (*cf.* the thermal ellipsoids given in Table 4 with those given by Berman,

Table 1. Fractional atomic coordinates and anisotropic thermal parameters in K-D-mannitol

Key to atomic numbering is given in Fig. 1. The temperature factor expression used was:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

The estimated standard deviations are given in parentheses.

Atom	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	0.4951 (5)	-0.0127 (2)	-0.1301 (9)	0.0117 (5)	0.0015 (1)	0.0329 (19)	0.0002 (2)	0.0005 (10)	0.0008 (4)
C(2)	0.4626 (4)	0.0516 (2)	0.0456 (8)	0.0089 (5)	0.0016 (1)	0.0169 (15)	0.0002 (2)	0.0023 (8)	0.0011 (3)
C(3)	0.4327 (4)	0.1184 (2)	-0.1204 (8)	0.0069 (4)	0.0018 (1)	0.0143 (15)	0.0001 (2)	-0.0002 (7)	0.0003 (3)
C(4)	0.4137 (4)	0.1849 (2)	0.0547 (8)	0.0075 (4)	0.0015 (1)	0.0158 (14)	0.0005 (2)	-0.0015 (7)	0.0005 (8)
C(5)	0.3950 (4)	0.2524 (2)	-0.1116 (8)	0.0088 (4)	0.0016 (1)	0.0158 (14)	-0.0003 (2)	-0.0029 (7)	0.0004 (3)
C(6)	0.3852 (4)	0.3195 (2)	0.0618 (9)	0.0094 (5)	0.0016 (1)	0.0299 (17)	0.0009 (2)	-0.0013 (9)	-0.0005 (4)
O(1)	0.6306 (3)	-0.0045 (1)	-0.2785 (6)	0.0119 (4)	0.0022 (1)	0.0189 (13)	0.0019 (1)	-0.0004 (6)	0.0007 (3)
O(2)	0.5822 (3)	0.0641 (1)	0.2314 (6)	0.0099 (4)	0.0024 (1)	0.0190 (12)	0.0016 (1)	-0.0008 (5)	0.0008 (3)
O(3)	0.3045 (3)	0.1073 (1)	-0.2905 (5)	0.0093 (3)	0.0019 (1)	0.0138 (10)	0.0001 (1)	-0.0012 (6)	-0.0007 (2)
O(4)	0.2835 (3)	0.1778 (1)	0.2212 (5)	0.0089 (3)	0.0019 (1)	0.0111 (9)	0.0008 (1)	0.0019 (5)	0.0014 (2)
O(5)	0.5149 (3)	0.2583 (1)	-0.3041 (5)	0.0096 (3)	0.0019 (1)	0.0166 (11)	-0.0009 (1)	-0.0006 (6)	0.0004 (2)
O(6)	0.5188 (3)	0.3307 (1)	0.2106 (6)	0.0109 (4)	0.0019 (1)	0.0167 (11)	-0.0014 (1)	-0.0004 (6)	-0.0003 (3)
H(O1)	0.611 (6)	0.016 (2)	-0.386 (10)						
H(O2)	0.670 (5)	0.053 (2)	0.143 (10)						
H(O3)	0.232 (5)	0.120 (2)	-0.194 (9)						
H(O4)	0.297 (5)	0.153 (2)	0.358 (9)						
H(O5)	0.594 (5)	0.277 (2)	-0.228 (9)						
H(O6)	0.500 (5)	0.313 (2)	0.350 (9)						
H(C1)	0.407 (5)	-0.027 (2)	-0.255 (10)						
H(C1')	0.501 (5)	-0.054 (2)	-0.027 (9)						
H(C2)	0.383 (4)	0.044 (2)	0.191 (10)						
H(C3)	0.517 (4)	0.124 (2)	-0.244 (9)						
H(C4)	0.506 (4)	0.186 (2)	0.159 (8)						
H(C5)	0.306 (5)	0.253 (2)	-0.200 (9)						
H(C6)	0.288 (5)	0.316 (2)	0.190 (10)						
H(C6')	0.368 (5)	0.359 (2)	-0.065 (10)						

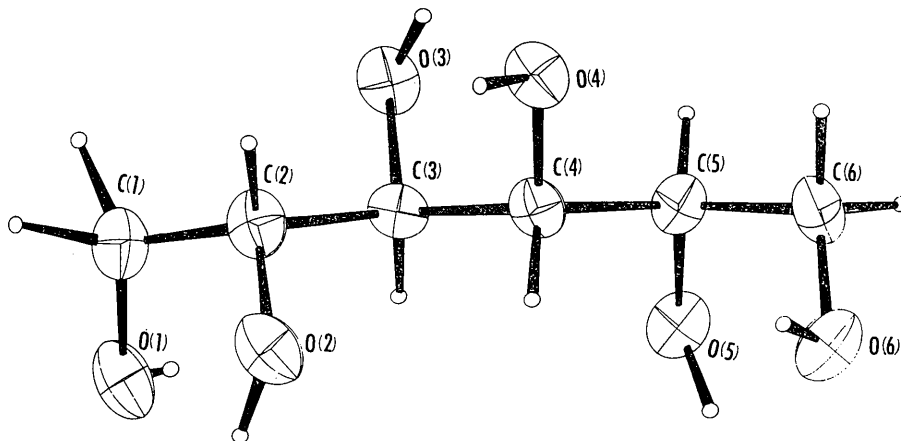


Fig. 1. Identification and numbering of the atoms in K-D-mannitol. The ellipsoids represent anisotropic thermal parameters.

Jeffrey & Rosenstein, 1968). It seems most likely that it is due to some unknown systematic errors in one or other of the structure determinations. The C-C-C bond angles are very constant at  $113.4^\circ$  and the C-C-O angles have a mean value of  $110.2^\circ$ , which is significantly closer to the ideal tetrahedral value. The same observation was made less precisely in the B structure.

The data on the conformation of the molecule with respect to the planarity of the carbon chain and the deviations from twofold axial symmetry normal to that

plane are shown in Table 5. An interesting aspect of the detailed structure is a small, but significant, bowing of the chain, as revealed by the distances from the best plane. The same result was observed in the B form, as shown in Table 5. The molecule with the exception of the hydrogen atoms has very nearly twofold axial symmetry, as shown in Table 5 by the distances of the mid-points of the appropriate pairs of atoms from the molecular twofold axis. The conformation angles are given in the Newman projections in Fig. 2.

Table 2. Observed and calculated structure factors

Columns are: Index,  $10|F_{\text{obs}}|$ ,  $10|F_{\text{calc}}|$ ,  $10A_{\text{calc}}$ ,  $10B_{\text{calc}}$ . (\* = unobserved).

2	761	871	871	0	0	0	64	60	0	60	2	165	162	4	161	0	27	20	0	20	0	297	288	0	288
2	126	133	133	0	1	97	103	73	71	0	3	111	110	92	60	0	114	113	83	79	2	296	299	295	31
6	12	15	15	0	2	64	60	36	48	5	71	72	60	41	2	139	131	125	36	3	179	175	70	174	
8	54	57	57	0	3	99	96	12	59	6	114	116	115	12	3	167	161	193	16	4	51	50	46	29	
10	132	138	138	0	4	55	51	16	59	7	144	143	117	11	4	125	121	117	11	5	28	28	65	27	
10	178	187	0	187	5	41	47	34	26	8	34	28	3	27	6	161	162	123	136	7	61	62	63	7	
2	597	606	0	606	0	185	185	103	0	0	39	39	0	39	0	54	52	44	50	9	115	111	7	111	
4	339	323	0	323	2	10	11	13	0	2	135	131	2	131	0	62	56	45	50	9	162	161	0	161	
5	41	29	0	29	3	286	323	0	323	3	147	147	146	17	3	139	135	0	135	2	225	214	157	145	
6	33	34	0	34	4	231	211	211	0	4	75	73	63	37	0	50	46	31	161	3	74	69	20	66	
7	150	147	0	147	5	11	17	0	17	5	51	50	49	10	1	234	234	170	23	4	130	132	124	79	
8	47	44	0	44	6	11	14	14	0	6	22	19	18	6	2	270	268	141	268	5	203	196	141	136	
9	124	8	0	8	7	294	314	0	314	7	69	71	70	6	3	174	172	153	79	6	32	27	25	10	
10	28	24	0	24	8	52	48	48	0	8	50	48	0	48	0	97	96	16	95	7	54	56	54	15	
0	818	907	907	0	10	75	74	74	0	10	60	60	32	5	1	105	109	8	108	7	28	32	9	31	
1	23	10	0	10	11	109	109	0	0	11	50	70	68	15	0	27	25	6	24	9	53	52	32	41	
2	78	60	60	0	12	48	56	11	55	4	34	28	22	18	0	60	60	0	60	0	123	119	0	119	
3	263	247	247	0	13	239	240	40	223	0	306	304	309	0	1	99	98	73	69	2	213	205	196	58	
4	222	204	204	0	14	118	117	115	17	1	650	637	0	637	0	50	48	1	46	3	374	370	46	368	
5	54	54	0	54	15	91	92	92	0	2	181	196	0	196	4	58	57	7	56	4	184	186	120	143	
6	125	108	108	0	16	221	208	175	113	2	451	469	469	0	5	129	133	92	96	5	72	71	12	71	
7	12	9	0	9	17	108	112	24	99	5	38	44	0	44	6	34	30	28	11	6	111	109	6	108	
8	124	17	17	0	18	102	107	107	0	6	92	104	104	0	7	21	21	21	11	7	54	55	32	44	
9	30	28	28	0	19	42	39	11	38	7	74	71	1	1	8	80	82	0	82	0	57	55	0	55	
0	124	117	0	117	10	34	23	23	0	9	29	27	0	27	1	43	44	6	43	0	141	141	136	10	
4	17	5	0	5	11	60	64	63	11	10	10	16	16	0	2	76	76	6	40	2	81	89	89	10	
5	12	0	0	0	12	133	123	123	0	12	198	202	202	0	4	77	84	18	82	3	27	27	25	10	
6	7	88	0	88	13	481	467	455	104	1	533	540	1	540	0	339	346	344	0	6	61	59	58	7	
8	13	7	0	7	14	178	164	148	72	3	232	191	63	180	1	114	112	0	112	6	10	10	4	9	
0	204	206	216	0	15	131	128	57	115	4	113	95	89	33	2	54	55	55	0	0	126	131	0	275	
1	12	1	1	0	16	12	14	2	14	5	124	20	19	8	3	9	5	0	5	1	154	131	111	68	
2	62	64	64	0	17	44	41	32	29	6	114	9	7	7	1	4	19	20	23	0	2	75	70	50	50
3	273	268	268	0	18	352	344	18	344	7	202	191	21	190	5	106	112	0	112	2	13	25	23	13	
4	35	33	33	0	19	48	45	27	34	8	48	48	41	19	6	53	52	52	0	3	75	75	0	75	
5	62	64	64	0	20	107	7	7	0	8	48	48	41	19	6	53	52	52	0	3	75	75	0	75	
6	13	14	14	0	21	44	41	32	29	9	140	135	62	120	7	101	94	38	86	0	144	7	7	0	
7	12	5	5	0	22	49	45	45	6	10	47	45	13	43	0	105	117	117	0	23	187	186	0	186	
0	202	198	0	198	23	153	148	8	148	0	58	47	47	0	10	15	1	1	1	2	22	10	10	1	
1	202	198	0	198	24	101	103	103	0	1	299	292	106	290	0	705	736	736	0	4	11	30	30	0	
2	75	74	0	74	25	152	153	125	88	2	170	174	172	290	0	705	736	736	0	4	11	30	30	0	
4	60	63	0	63	7	31	26	23	11	3	146	147	16	166	1	277	276	28	275	5	42	37	0	37	
5	40	34	34	0	8	14	9	7	4	4	142	144	14	14	0	142	144	14	14	0	153	168	168	0	
0	204	206	216	0	9	57	95	77	55	5	97	95	77	55	3	125	128	14	127	7	28	29	0	29	
1	109	122	0	122	10	52	56	56	0	6	33	34	12	32	4	84	77	59	50	8	54	58	58	0	
2	573	672	672	0	11	41	41	41	0	7	81	28	27	11	5	351	335	36	333	9	24	19	0	19	
3	248	248	0	248	12	43	43	43	0	8	87	74	75	38	6	69	71	61	57	0	136	137	137	0	
4	197	205	205	0	13	45	41	21	89	9	28	27	14	23	7	77	71	64	55	0	190	192	26	902	
5	201	283	0	283	14	204	198	165	110	10	114	7	3	0	8	85	84	61	58	0	136	137	137	0	
6	19	21	21	0	15	41	43	23	37	0	114	7	3	0	9	74	72	4	74	3	271	269	27	27	
7	195	196	0	196	16	40	88	72	50	1	180	172	125	118	0	48	35	35	0	4	45	38	32	21	
8	216	216	0	216	17	49	47	20	43	2	245	245	200	141	0	162	157	107	115	5	88	83	35	75	
9	24	20	0	20	18	44	41	32	29	3	67	67	67	67	1	162	157	107	115	5	88	83	35	75	
10	24	24	24	0	19	84	31	91	0	4	104	104	93	48	2	97	99	86	48	6	55	48	46	14	
0	383	651	0	651	20	64	62	36	51	6	84	80	80	1	4	180	177	83	155	8	68	65	62	23	
1	355	363	363	0	21	35	31	28	13	5	60	55	53	15	3	131	125	117	44	7	52	46	36	38	
2	101	198	47	151	4	27	27	8	20	8	33	27	21	16	0	92	90	73	53	9	88	86	12	85	
3	371	357	297	198	5	38	38	37	37	0	31	32	32	0	8	100	100	98	18	0	163	158	158	0	
4	246	237	85	221	6	1665	667	0	667	0	151	148	106	133	0	62	59	57	9	1	241	234	230	121	
5	59	51	46	24	7	111	116	116	0	1	51	51	21	86	4	36	41	60	12	2	88	86	86	0	
6	209	194	96	167	8	3	66	69	0	2	85	84	12	83	0	93	95	75	0	4	108	104	72	74	
7	43	42	36	21	9	81	81	81	0	3	65	67	56	40	1	39	38	17	34	5	74	71	61	37	
8	17	69	68	8	10	118	122	0	122	5	144	15	8	13	2	154	135	135	9	6	82	84	81	21	
9	54	49	25	42	11	225	230	230	0	6	94	61	29	54	3	227	215	137	166	7	57	59	58	0	
10	93	94	90	27	12	124	116	116	0	7	57	58	55	19	4	136	141	67	86	8	45	46	46	15	
0	84	84	0	84	13	136	145	145	0																

Table 2 (cont.)

5	11*	7	0	7	6	22	17	14	9-	7	28	27	21	17	0	12*	22	22-	0	0	25	23	0	23	
6	88	88	88-	0	7	31	42	26-	17	0	53	47	47-	0	1	35	28	6	28	0	61	66	63-	23	
7	12*	7	0	7-	0	4	10	10	0	0	28	29	29-	29	3	25	30	17-	25	1	59	57	6	57-	
8	12*	6	6-	0	0	12*	17	17	0	1	28	29	29-	29	3	25	20	0	20	2	59	57	6	57-	
9	107	117	0	117-	0	1	45	43	15	4	2	77	77	58-	50	4	35	23	5-	43-	3	96	90	66-	61
0	113	114	0	114-	2	115	120	118-	22-	3	63	57	36	45	5	28	30	23	18-	4	119	120	54-	107-	
1	116	108	0	108	3	61	61	31-	53	4	38	36	22-	31-	0	11*	1	4	14	5	30	29	20-	21-	
2	72	71	21	47-	5	93	76	73	62-	6	11*	17	0	17	1	49	57	55-	12	0	59	65	4-	65-	
3	82	83	70-	44-	0	41	48	48	0	0	68	63	63	0	3	84	82	82	1	1	30	26	10	24-	
4	108	100	92	39-	0	78	83	71	43	2	74	79	7-	79-	1	171	172	0	172-	1	96	102	50	89	
5	48	48	7	47-	1	65	59	0	59	3	57	61	57-	22	2	221	213	413-	0	4	21	21	7-	23-	
6	255	247	246-	14-	2	176	165	165	0	4	38	36	4	36	3	31	31	0	31-	5	23	23	18	14-	
7	99	94	38-	86-	4	79	80	80	0	1	246	243	0	243-	5	12*	17	0	17-	0	11*	10	0	13	
8	26	24	7-	23-	0	95	106	0	106	2	232	227	227	0	6	30	29	29-	0	1	25	22	13	18	
9	41	41	17-	37-	3	153	156	0	156-	0	128	123	0	123-	7	22	27	0	27-	2	64	73	40-	67	
0	97	96	0	96-	4	79	80	80	0	1	246	243	0	243-	4	29	22	22-	0	3	41	41	19	37-	
1	70	64	62-	14	6	90	98	98	0	3	128	123	0	123-	7	22	27	0	27-	2	64	73	40-	67	
2	156	156	67-	140-	7	25	26	0	26	4	92	92	92-	0	4	100	96	82-	46	3	57	60	6	60	
3	171	176	167	30-	8	11*	29	0	29-	0	246	245	0	245-	0	246	245	0	245-	3	41	41	19	37-	
4	144	134	102-	95-	9	77	86	0	86-	6	85	91	91-	0	1	57	56	55-	12	0	156	157	157	0	
5	179	176	158	79-	0	95	106	0	106	7	12*	9	0	9	2	117	115	21	113-	1	78	79	0	79	
6	120	111	101	46	0	95	101	0	101-	8	153	192	192-	0	3	36	37	17-	53-	2	12*	14	14	0	
7	100	107	92	51-	1	123	116	86	80	7	12*	9	0	9	2	117	115	21	113-	1	78	79	0	79	
8	49	46	37	26	2	147	152	152	4-	0	28	21	0	21	5	12*	12	5	11-	4	57	56	56	0	
9	38	40	0	40	4	39	39	32	2-	2	111	108	88	62-	6	73	78	30-	71	5	54	62	0	62	
0	98	100	100	100	5	124	111	8	8	3	124	111	8	8	8	12*	12	5	11-	4	57	56	56	0	
1	96	93	70-	60	6	51	48	40	26-	4	139	138	64-	123-	0	33	36	0	36	0	154	151	151-	0	
2	300	305	241	188	7	73	69	30	62	5	90	85	58-	62-	1	155	156	18-	155-	1	63	60	1-	60-	
3	214	211	163-	133	8	41	37	6-	36-	6	83	81	25-	77-	2	107	110	80-	75	2	27	26	6-	26	
4	41	39	16	16	7	51	62	58-	22	3	78	83	40	72	3	78	83	40	72	3	110	111	11	111-	
5	99	93	50	79	0	11*	14	0	14	8	34	34	18	29	4	158	146	164-	2	3	28	28	12-	12-	
6	65	62	41	47-	1	103	101	66-	77-	7	29	31	19	25-	5	11*	12	12	2	0	92	94	94	0	
7	84	84	0	87-	2	176	177	163-	69-	0	43	45	0	45-	6	33	31	27	14	0	106	104	104-	0	
8	93	96	89-	61-	4	60	60	59	4-	1	169	164	93	135	0	12*	12	10	10-	0	106	104	104-	0	
9	60	61	44-	42-	5	108	106	6-	106-	1	64	66	62	24-	1	26	21	16	13-	2	34	35	35	7-	
0	57	56	47-	31-	6	59	54	44-	32-	4	126	124	66	105-	2	12*	15	7-	13-	3	45	41	17	37-	
1	21	19	17	17	7	70	68	14	67-	5	128	126	101	76-	3	38	35	10	33	4	26	29	28	7-	
2	47	47	35	31-	8	32	32	4-	32-	6	90	92	61	92	6	62	62	61	12	3	62	61	18	18	
3	45	51	18-	48-	0	75	73	0	73	0	12*	19	0	19	0	38	35	0	35-	1	29	25	21	14	
4	73	77	0	77-	1	73	74	56-	51-	0	12*	19	0	19	0	38	35	0	35-	2	36	37	26-	26-	
5	43	50	42	27	2	119	114	109-	48-	1	23	29	22	19	1	75	74	7-	74-	1	33	33	25-	17-	
6	44	46	28	30-	3	77	78	6	77	2	40	38	4-	38	2	95	96	36	89-	1	12*	1	0	1-	
7	12*	8	8-	0	4	12*	8	1-	8	3	31	31	30	10-	0	397	399	399	0	3	11*	15	0	15-	
8	80	74	0	74	6	67	66	23	62	4	43	36	36	2-	1	34	30	26	30	4	35	40	40-	0	
9	309	304	304-	30-	0	7	30	25	10-	22	6	22	21	6	20	2	124	125	125	0	5	19	19	0	15-
0	31	35	0	35-	0	107	107	0	107-	0	29	32	0	32	4	91	84	84-	0	0	12*	8	0	8	
1	126	127	127-	0	0	174	174	31-	31-	1	74	79	89	60-	5	49	51	0	51	1	21	18	14-	12	
2	12	15	15	0	4	80	80	69	40	2	26	30	28	11-	6	76	83	83-	2	2	11*	8	8-	2-	
3	46	46	0	46-	3	73	79	66	43-	3	71	70	69-	14	7	58	83	0	83-	3	85	83	8-	82	
4	27	25	25-	0	4	20	18	6	16-	4	61	61	27-	54	0	11*	16	0	0	4	42	41	41	3-	
5	70	70	0	70	5	57	55	18-	52	0	370	372	372-	0	1	113	98	98-	0	4	42	41	41	3-	
6	67	59	59	0	0	399	402	402	0	1	388	385	0	385	2	153	148	49-	140-	0	47	43	0	43	
7	142	139	7	139	1	61	60	0	60	2	14*	4	6-	0	3	98	86	31	47	2	10	12	6	10	
8	283	283	283-	0	7	132	95	95	0	3	204	195	0	195	4	86	82	23	78-	3	35	31	1-	32	
9	125	125	39-	119-	3	116	112	0	112	4	93	97	97-	0	5	65	62	61	12	0	11*	0	0	0	
0	63	60	59-	8	4	12*	14	14	0	5	38	33	0	33	6	25	24	22-	10	5	11*	8	8	0	
1	32	28	25	14	5	126	130	0	130-	6	26	27	27	0	0	67	53	53-	0	1	20	17	0	17-	
2	165	160	153-	46	6	75	82	62	0	6	11*	6	0	6	0	67	53	53-	0	2	11*	13	13	0	
3	29	28	24	15	7	78	82	0	82	8	26	25	25-	0	1	67	69	24	50	3	39	36	0	36	
4	125	126	122-	32	8	124	130	150	0	0	57	51	51-	0	3	163	159	46	152	1	27	24	0	24	
5	26	25	0	25-	0	194	204	204	0	1	38	37	36	7-	4	32	31	7-	30	0	50	50	50	0	
6	64	65	65-	0	1	38	36	7-	36	2	142	135	5-	135	3	11*	16	13	9	1	82	82	1	82	
7	109	112	105-	51-	2	98	97	72	65-	3	93	92	90	19-	6	42	46	10-	45-	2	11*	10	8-	4	
8	174	174	174	3-	3	42	41	35-	21-	4	100	95	12-	94	0	32	22	22	0	0	10*	12	12	0	
9	92	94	29-	89	4	44	46	16-	43	5	72	74	70	23	0	11*	11	4-	11-	0	10*	12	12	0	
0	86	84	29-	87-	2	71	65	33-	57-	6	94	86	36	14-	31-	4	38	34	36	0	0	53	41	0	51-
1	57	54	12	7	6	74	75	2-	75	7	54	56	24	50	2	25	24	22	11-	4	11*	15	15-	0	
2	82	80	43-	67-	7	93	96	27	92	0	50	51	51-	0	3	163	159	46	152	1	27	24	0	24	
3	49	50	33	34	8	63	70	57	49	0	50	51	51-	0	4	28	25	22-	13-	1	27	24	0	24	
4	12*	8	16	7	0	255	253	253-	0	2	94	88	76-	44	1	39	38	0	38						

Table 4. Principal axes of thermal ellipsoids

The root mean square displacement  $U_i$  corresponds to the  $i$ th principal axis of the ellipsoid and  $\theta_{ia}$ ,  $\theta_{ib}$ ,  $\theta_{ic}$  are angles between the  $i$ th axis and the crystallographic axes  $a$ ,  $b$ ,  $c$ .

	$i$	$U_i$	$\theta_{ia}$	$\theta_{ib}$	$\theta_{ic}$
C(1)	1	0.1604 Å	93.33°	14.47°	104.07°
	2	0.2012	77.62	103.04	161.86
	3	0.2183	12.83	83.83	78.79
C(2)	1	0.1313	78.14	67.78	154.51
	2	0.1701	67.01	151.33	106.18
	3	0.1969	26.17	72.82	70.86
C(3)	1	0.1313	87.55	95.14	5.70
	2	0.1667	170.63	81.21	86.78
	3	0.1804	80.96	10.20	85.29
C(4)	1	0.1304	108.79	69.05	151.22
	2	0.1599	69.80	144.85	117.41
	3	0.1815	28.18	63.18	98.05
C(5)	1	0.1298	71.46	94.61	19.13
	2	0.1677	109.58	160.31	88.13
	3	0.1973	27.51	109.09	109.04
C(6)	1	0.1569	119.11	29.24	87.48
	2	0.1859	113.66	100.29	153.93
	3	0.2098	39.10	62.95	115.92
O(1)	1	0.1457	105.47	66.65	151.45
	2	0.1701	56.86	133.50	118.46
	3	0.2471	37.46	52.59	88.11
O(2)	1	0.1444	109.24	69.15	150.98
	2	0.1736	47.67	124.10	118.80
	3	0.2346	48.55	41.61	86.85
O(3)	1	0.1258	83.55	80.20	11.76
	2	0.1843	71.98	160.44	82.63
	3	0.1959	19.20	73.24	99.11
O(4)	1	0.1073	95.42	104.02	15.08
	2	0.1685	45.66	134.97	96.25
	3	0.2092	44.85	48.35	76.33
O(5)	1	0.1413	88.31	96.15	6.38
	2	0.1680	126.32	143.38	93.96
	3	0.2112	143.62	54.07	84.99
O(6)	1	0.1409	82.46	78.69	13.63
	2	0.1651	123.72	142.89	76.36
	3	0.2303	145.21	55.21	90.24

The dihedral angles of the C-C-bonds range from 51° to 65°. In general, the detailed structure of the molecule in the K form differs almost insignificantly from that in the B form despite the different hydrogen-bonding environment of the molecules. This suggests that the detailed shape of the molecule is determined almost entirely by intramolecular forces and that the effect of intermolecular forces on planarity and conformation angles is trivial in comparison.

The hydrogen-bonding is shown in Fig. 3. All the hydroxyl groups donate and accept one hydrogen bond with O(H)···O distances ranging from 2.716 to 2.835 Å. The angles at the donor oxygens vary between 111° and 128° and are invariably smaller than those at the corresponding acceptor oxygen (Table 6). For the two longest hydrogen bonds O(2)···O(1) and O(3)···O(6), the observed hydrogen atom positions deviate by as

Table 5. Least squares plane and twofold axis in K-D-mannitol

Equation for plane:  $Ax + By + Cz = D$ , where  $x$ ,  $y$ ,  $z$  are in Å and  $A = 0.9876$ ,  $B = 0.1565$ ,  $C = -0.0151$  and  $D = 4.2543$ . This plane makes an angle of 9° with (100).

Atoms included in plane	Distance from best plane	
	K form	B form
C(1)	+0.090 Å	+0.065 Å
C(2)	-0.021	-0.010
C(3)	-0.076	-0.073
C(4)	-0.061	-0.036
C(5)	-0.015	+0.005
C(6)	+0.083	+0.048

Parametric equation of the best twofold axis in Å,

$$x = 4.038 + 0.988t$$

$$y = 2.894 + 0.153t$$

$$z = -0.167 + 0.002t$$

Atom pairs		Distance of mid-point of atom pairs from molecular twofold axis
C(1)	C(6)	0.005 Å
C(2)	C(5)	0.008
C(3)	C(4)	0.008
O(1)	O(6)	0.004
O(2)	O(5)	0.011
O(3)	O(4)	0.006

The angle between the plane and the axis is 89°6'.

much as 0.4 Å from the line of the O···O centers towards the nearest intramolecular oxygen atoms, O(1) and O(4), respectively, possibly forming weak bifurcated hydrogen bonds. The intramolecular distances are 2.841 Å for O(2)···O(1) and 2.839 Å for O(3)···O(4). The other deviations of hydrogen atom positions from the line of O···O centers are less than 0.25 Å and are probably not significant.

The hydrogen-bonding scheme, illustrated in Figs. 3 and 4, consists of four-link infinite spirals about the screw axes, *i.e.*  $\rightarrow O(1) \rightarrow O(2) \rightarrow O(1) \rightarrow O(2) \rightarrow$ , and four-link closed circuits, *i.e.*  $\rightarrow O(6) \rightarrow O(5) \rightarrow O(4) \rightarrow O(3) \rightarrow$ . The molecules lie in planes approximately

Table 6. Intermolecular distances and angles in K-D-mannitol

		Symmetry code					
$a$	$x$	$y$	$z$				
$b$	$1\frac{1}{2} - x$	$-y$	$-\frac{1}{2} + z$				
$c$	$x$	$y$	$-1 + z$				
$d$	$-\frac{1}{2} + x$	$\frac{1}{2} - y$	$-z$				
$e$	$x$	$y$	$1 + z$				
$f$	$\frac{1}{2} + x$	$\frac{1}{2} - y$	$-z$				
$g$	$1\frac{1}{2} - x$	$-y$	$\frac{1}{2} + z$				
$h$	$-\frac{1}{2} + x$	$\frac{1}{2} - y$	$1 - z$				
$j$	$\frac{1}{2} + x$	$\frac{1}{2} - y$	$1 - z$				
$\rightarrow$ : direction O-H···O bond.							
$i$	$j$	$k$	$l$	$D_{jk}$	$\angle ijk$	$\angle jkl$	
C(1)	O(1)→O(2) $c$	C(2) $c$		2.756 Å	111.2°	126.6°	
C(2)	O(2)→O(1) $g$	C(1) $g$		2.802	127.7	136.8	
C(3)	O(3)→O(6) $d$	C(6) $d$		2.835	125.5	153.2	
C(4)	O(4)→O(3) $e$	C(3) $e$		2.739	119.2	119.4	
C(5)	O(5)→O(4) $f$	C(4) $f$		2.716	126.7	139.9	
C(6)	O(6)→O(5) $e$	C(5) $e$		2.737	111.2	128.2	

parallel to (001). There are marked similarities to the molecular packing in the B form, which is also illustrated in Figs. 3 and 4. Both structures have the same number of hydrogen bonds per molecule and each hydroxyl group is involved in two bonds. In both unit cells, there is an infinite chain or spiral and a closed circuit of hydrogen bonds, which repeat after four links.

The infinite chains involve only the oxygen atoms O(1), O(2) at one end of the molecule, while the remainder form the closed circuits in the sequence O(6), O(5), O(4), O(3). The donor direction of the closed circuits is reversed in the two structures. The hydrogen bonds in the K form are longer and make a wider range of C-O(H)-O angles than the B form; *i.e.* 2.716–2.835

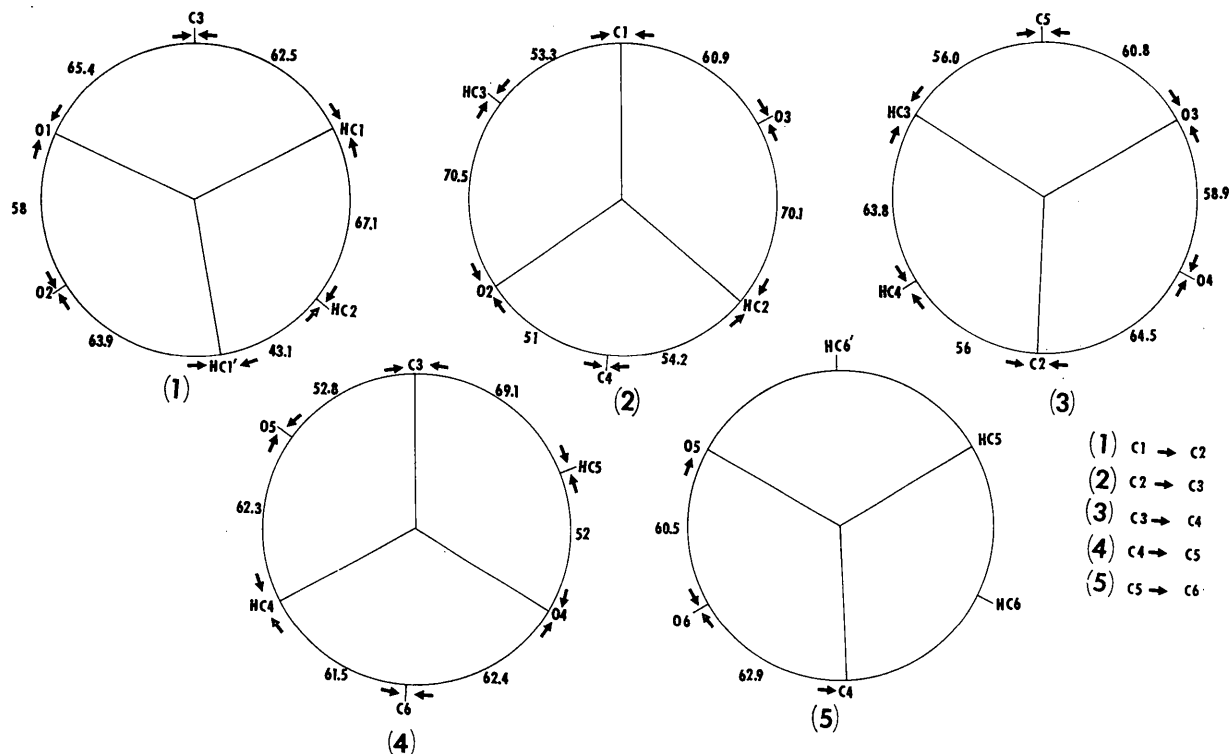


Fig. 2. The conformation angles of the carbon-carbon bonds in K-D-mannitol, shown in Newman projections.

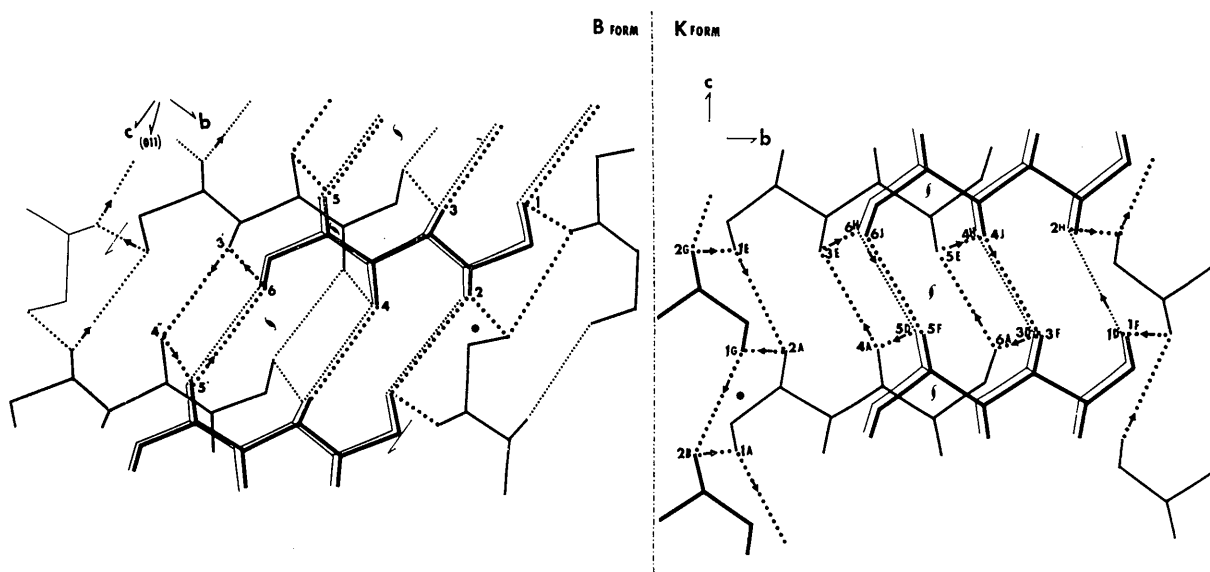


Fig. 3. The structures of the B and K forms of D-mannitol viewed down the *a* axis.

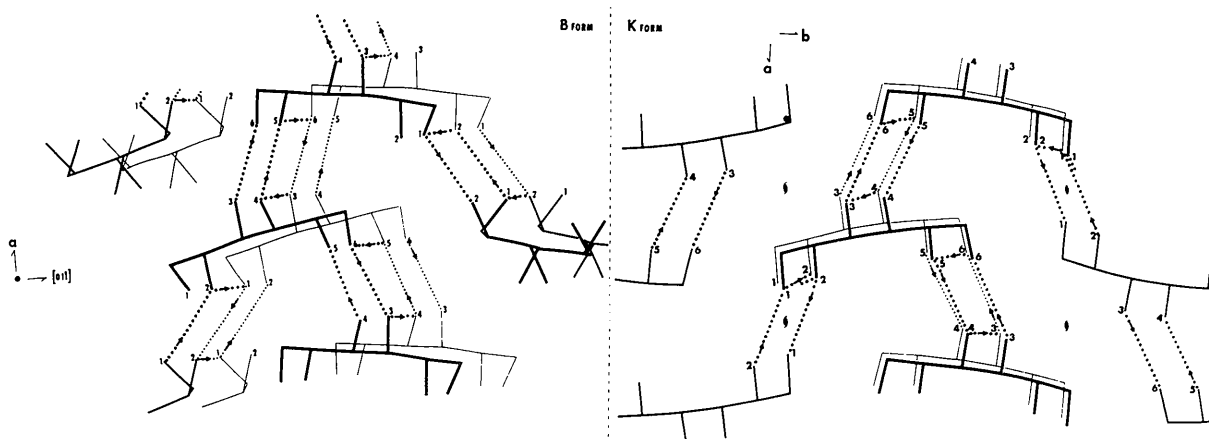


Fig. 4. The structures of the B and K forms of D-mannitol projected on the  $(01\bar{1})$  and  $(001)$  planes, respectively.

versus  $2.692\text{--}2.766 \text{ \AA}$ ,  $111.2\text{--}153.2$  versus  $108.3\text{--}124.9^\circ$ . The unit cell volume of the K form is one per cent larger. Hence it is the metastable form, obtained only under special circumstances such as those described in this paper.

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