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Crystal and molecular structures of D-*glycero*-L-*gulo*-heptitol, *meso*-*glycero*-*allo*-heptitol, and *meso*-*glycero*-*allo*-heptitol heptaacetate

Peter Köll [a,*], Manfred Bischoff [a], Martina Morf [b], Bärbel Zimmer [b] and Jürgen Kopf [b,*]

[a] *Department of Chemistry, The University, Carl-von-Ossietzky-Str. 9-11, D-26111 Oldenburg (Germany)*
[b] *Institute of Inorganic and Applied Chemistry, The University, Martin-Luther-King-Platz 6, D-20146 Hamburg (Germany)*

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ABSTRACT

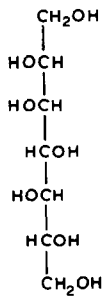
The molecular structures of the title compounds were determined by X-ray crystallography, using direct methods, and refined to final residual parameters of $R = 0.040$, 0.063, and 0.044, respectively. All the compounds investigated adopt bent conformations, the molecules of *meso* configuration thus becoming chiral conformers. For *meso-glycero-allo*-heptitol, this involves a 1,3-parallel interaction between C-5 and O-2. The derived heptaacetate is found in a different conformation with O-3/C-6 and O-4/C-7 aligned 1,3-parallel. The reported solution for *meso-glycero-allo*-heptitol is conventional, but with regard to the optimum in crystallography has to be considered as preliminary.

INTRODUCTION

Heptitols can occur as ten diastereomers, of which four are *meso* forms and the others are found as six enantiomeric pairs. As yet, the crystal structures of *meso-glycero-gulo*-heptitol[1], D-*glycero*-L-*allo*-heptitol[2], D-*glycero*-D-*galacto*-heptitol (D-perseitol)[3] and the racemate[4], D-*glycero*-D-*manno*-heptitol (α-sedoheptitol, volemitol)[5], D-*glycero*-D-*gluco*-heptitol (β-sedoheptitol)[5], and D-*glycero*-L-*galacto*-heptitol[6] have been determined.

So far as chiral isomers are concerned (racemates excluded), the title compound D-*glycero*-L-*gulo*-heptitol (**1**) is the only member of this group of compounds remaining for X-ray structure determination. The other title compound, *glycero*-*allo*-heptitol (**2**), is the second of the four isomers with *meso* configuration for which such an investigation can be reported. Both **1** and **2** were expected to adopt sickle (bent) conformations in the solid state in order to avoid 1,3-parallel O//O

* Corresponding authors.



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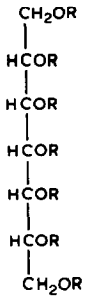

2 R = H
3 R = Ac

interactions which would occur in the planar zigzag arrangement. Only recently, it was realized that such interactions, nevertheless, can be observed frequently, as well as 1,3-parallel C//O interactions in bent conformations[2,5,7–10]. Whereas **1** on acetylation yielded a heptaacetate which has resisted crystallization, the heptaacetate **3** derived from **2** gave suitable crystals for an X-ray investigation. Recently, the structures of the isomeric heptaacetates with *meso-glycero-gulo*, D-*glycero*-D-*manno*, and D-*glycero*-D-*galacto* configuration have been reported[11].

RESULTS AND DISCUSSION

Suitable crystals of D-*glycero*-L-*gulo*-heptitol[12] (**1**) and of *meso-glycero-allo*-heptitol[13] (**2**) were obtained from methanol and ethanol, respectively. Compound **3**[14] crystallized from ethanol. The relevant crystallographic data for **1**, **2**, and **3** are given in Table I. The structures were solved by direct methods with the help of the programs SHELXS-90[15] (solution) and SHELXL-92[16] (refinement).

All atoms, with hydrogens introduced at theoretical positions using the AFIX option[16], were refined. The final fractional coordinates of C and O with equivalent isotropic thermal parameters are listed in Table II for compounds **1** and **2**, and in Table III for **3** *. Selected torsion angles are given in Table IV, and perspective views of compounds **1**, **2**, and **3** are presented in Figs. 1–3 (SCHAKAL-88 plots[17]) which show the atom numbering schemes as well.

In order to avoid two 1,3-parallel interactions which would occur in a planar zigzag conformation of the central carbon chain, molecules of **1** adopt, by rotation

* Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE I

Crystallographic data for **1**, **2** and **3**[a,b]

Data	**1**	**2**	**3**
Formula	$C_7H_{16}O_7$	$C_7H_{16}O_7$	$C_{21}H_{30}O_{14}$
Mol wt	212.20	212.20	506.45
Mp (°C)	127	143–144	62–63
Crystal dimensions (mm)	0.6×0.5×0.4	0.6×0.4×0.4	0.5×0.4×0.3
Space group	$P22_12_1$	$P2_12_12_1$	$P\bar{1}$
Cell parameters (pm, degrees)			
a [α]	465.9(1)	500.5(1)	986.8(1) [101.99(1)]
b [β]	1019.0(1)	1020.0(2)	1069.2(1) [108.14(1)]
c [γ]	1929.8(1)	1805.2(2)	1395.7(2) [102.78(1)]
Volume V (pm^3)	916.2(2)×10^6	921.6(2)×10^6	1302.5(3)×10^6
Z	4	4	2
F(000)	456	456	536
Calculated density (D_x) ($g\ cm^{-3}$)	1.538	1.529	1.291
λ (Cu $K\alpha$) (pm)	154.178	154.178	154.178
μ (cm^{-1})	12.1	12.0	9.5
2θ range (degrees)	4.5–153	4.5–153	4.5–153
Reflections measured	2385	2379	11556
Symmetry independent reflections	1915	1916	5481
Symmetry independent reflections with $F_o > 2\sigma(F_o)$	1910	1203	4556
Number of refined parameters	148	151	354
Final residual factor R_{obsd}	0.040	0.063	0.044
Goodness of fit S_{obsd}	1.09	1.25	1.10

[a] Standard deviations in parentheses. [b] Diffractometer: Enraf-Nonius CAD 4.

TABLE II

Fractional positional parameters of C and O atoms (×10^4) and the temperature factors U_{eq} [a] (×10^3) for **1** and **2** [b]

Atom	**1**				**2**			
	x	y	z	U_{eq}	x	y	z	U_{eq}
O-1	1802(3)	7029(1)	−4070(1)	29(1)	−1483(10)	14297(4)	1703(2)	49(3)
O-2	6992(3)	6821(1)	−3287(1)	28(1)	−3899(8)	11853(4)	2250(2)	33(2)
O-3	1694(3)	4264(1)	−2889(1)	26(1)	−2419(8)	12348(4)	290(2)	37(2)
O-4	6678(3)	3792(1)	−2222(1)	27(1)	−5034(7)	9933(4)	703(2)	34(2)
O-5	5974(3)	4716(1)	−919(1)	33(1)	1135(8)	9771(4)	1794(2)	33(2)
O-6	5471(3)	7466(1)	−1307(1)	31(1)	−1119(8)	7236(4)	2068(2)	35(2)
O-7	216(3)	7720(1)	−435(1)	40(1)	−412(10)	6092(4)	645(2)	50(3)
C-1	3505(3)	5860(1)	−4077(1)	30(1)	−4084(13)	13825(6)	1515(3)	40(3)
C-2	5288(3)	5671(1)	−3421(1)	23(1)	−4169(10)	12359(5)	1519(3)	29(3)
C-3	3533(3)	5361(1)	−2769(1)	21(1)	−2064(9)	11742(5)	992(3)	26(2)
C-4	5535(3)	5094(1)	−2151(1)	21(1)	−2310(9)	10258(5)	887(3)	27(2)
C-5	4067(4)	5161(2)	−1444(1)	24(1)	−1500(10)	9415(5)	1547(3)	26(2)
C-6	3169(4)	6551(2)	−1245(1)	24(1)	−1677(10)	7935(5)	1401(3)	27(2)
C-7	1876(4)	6553(2)	−518(1)	31(1)	157(11)	7413(5)	815(3)	34(3)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [b] Standard deviations in parentheses.

TABLE III

Fractional positional parameters of C and O atoms ($\times 10^4$) and the temperature factors U_{eq} [a] ($\times 10^3$) for **3** [b]

Atom	x	y	z	U_{eq}
O-1	5041(1)	6448(1)	8841(1)	71(1)
O-2	1942(1)	6124(1)	8260(1)	54(1)
O-3	4147(1)	9117(1)	8017(1)	57(1)
O-4	1983(1)	8056(1)	5984(1)	64(1)
O-5	−828(1)	7735(1)	6431(1)	59(1)
O-6	438(1)	10466(1)	8016(1)	58(1)
O-7	928(2)	11623(1)	6499(1)	71(1)
O-11	6517(1)	6290(2)	10363(1)	92(1)
O-21	1420(1)	6560(1)	9723(1)	76(1)
O-31	5450(2)	8567(2)	7034(2)	121(1)
O-41	2044(3)	6039(2)	5196(1)	121(2)
O-51	−1422(2)	6719(2)	7546(1)	119(1)
O-61	2165(1)	10319(1)	9434(1)	61(1)
O-71	3035(2)	11615(2)	6258(2)	116(1)
C-1	4512(2)	7375(2)	9410(1)	65(1)
C-2	3063(2)	7423(1)	8652(1)	52(1)
C-3	3187(2)	7749(1)	7666(1)	51(1)
C-4	1682(2)	7594(1)	6819(1)	52(1)
C-5	700(1)	8338(1)	7189(1)	50(1)
C-6	1118(2)	9853(1)	7343(1)	51(1)
C-7	516(2)	10194(2)	6325(1)	69(1)
C-11	6054(2)	5972(2)	9418(2)	74(1)
C-12	6472(3)	5013(3)	8714(2)	105(2)
C-21	1193(2)	5810(2)	8885(1)	59(1)
C-22	110(2)	4440(2)	8394(2)	79(1)
C-31	5238(2)	9393(2)	7632(2)	75(1)
C-32	6062(3)	10853(2)	8016(2)	99(1)
C-41	2201(2)	7187(2)	5237(1)	81(1)
C-42	2687(4)	7894(3)	4527(2)	111(2)
C-51	−1793(2)	6950(2)	6721(1)	68(1)
C-52	−3324(2)	6413(2)	5886(2)	83(1)
C-61	1124(2)	10704(1)	9062(1)	54(1)
C-62	412(2)	11471(2)	9669(2)	81(1)
C-71	2214(2)	12214(2)	6430(1)	76(1)
C-72	2438(4)	13676(2)	6572(2)	105(2)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [b] Standard deviations in parentheses.

around the C-4/5 bond, a sickle conformation free of 1,3-parallel interactions between the heavy atoms. This is the predicted topology[18]. The 7-deoxy-7-nitro derivative of **1** behaves similarly[19].

The molecules of **1** are interlinked in the crystal by a complex network of hydrogen bonds (Table V), which involves all hydroxyl groups as donors with O-5 supporting a bifurcated bond. O-1 And O-4 are acceptors for two such bonds, whereas O-5 is not an acceptor and the others accept one bond each.

Molecules of *meso-glycero-allo*-heptitol(**2**) were predicted[18] to be found in a doubly bent symmetric conformation retaining in the centre one of the three

TABLE IV

Selected torsion angles (degrees) in **1**, **2**, and **3** [a]

Angle	1	2	3
(a) Angles in the chain			
O-1–C-1–C-2–C-3	69.1(3)	−56.6(6)	−54.6(2)
C-1–C-2–C-3–C-4	176.0(1)	−171.7(4)	171.3(1)
C-2–C-3–C-4–C-5	163.5(1)	−71.7(5)	52.6(2)
C-3–C-4–C-5–C-6	−69.4(2)	−177.6(4)	77.8(2)
C-4–C-5–C-6–C-7	−176.8(1)	63.7(6)	82.9(2)
C-5–C-6–C-7–O-7	−160.8(1)	−171.5(4)	179.9(3)
(b) Angles between vicinal oxygen atoms			
O-1–C-1–C-2–O-2	−53.5(2)	68.6(5)	62.6(2)
O-2–C-2–C-3–O-3	177.0(2)	−177.5(4)	172.4(1)
O-3–C-3–C-4–O-4	45.1(2)	−68.7(5)	55.3(2)
O-4–C-4–C-5–O-5	51.6(2)	−175.4(4)	78.1(1)
O-5–C-5–C-6–O-6	69.5(2)	60.5(5)	77.0(1)
O-6–C-6–C-7–O-7	73.7(2)	65.8(5)	60.6(2)
(c) Angles between vicinal hydrogen atoms			
H-11–C-1–C-2–H-2	−49(1)	−53(1)	−57(1)
H-12–C-1–C-2–H-2	68(1)	65(1)	63(1)
H-2–C-2–C-3–H-3	175(1)	−177(1)	172(1)
H-3–C-3–C-4–H-4	−77(1)	−70(1)	53(1)
H-4–C-4–C-5–H-5	174(1)	−175(1)	77(1)
H-5–C-5–C-6–H-6	−55(1)	61(1)	82(1)
H-6–C-6–C-7–H-71	76(1)	71(1)	64(1)
H-6–C-6–C-7–H-72	−164(1)	−171(1)	−178(1)

[a] Standard deviations in parentheses.

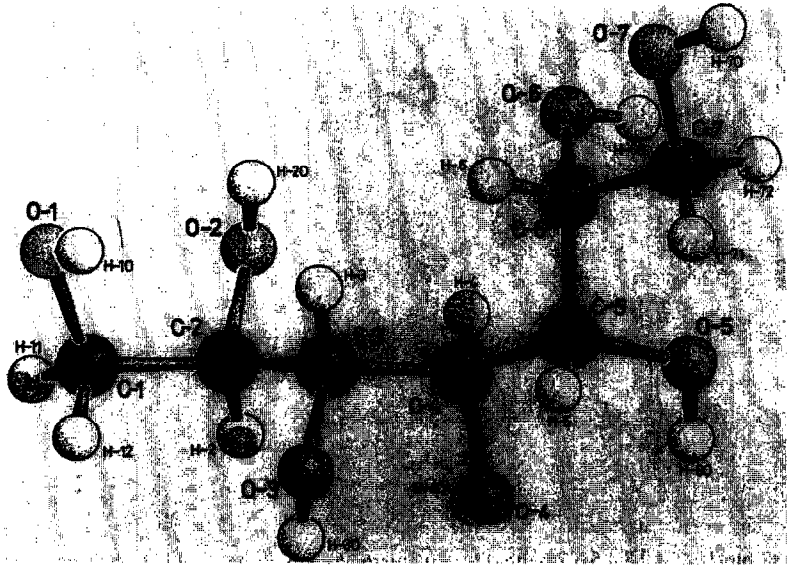

Fig. 1. SCHAKAL-88 plot[17] of D-*glycero*-L-*gulo*-heptitol (**1**), showing atom numbering.

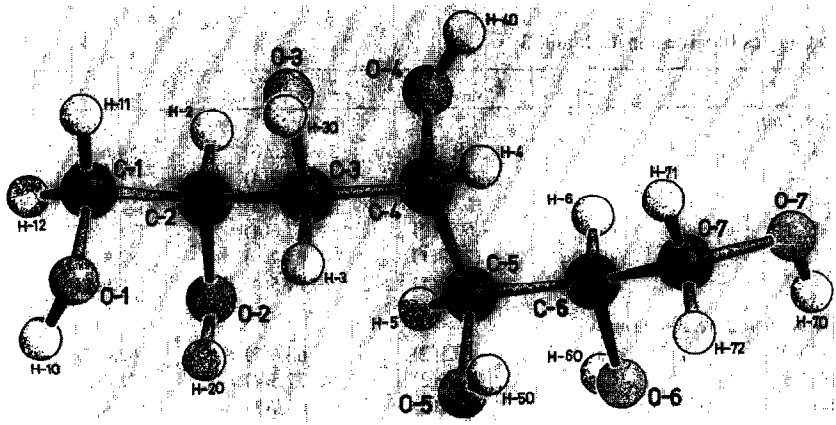

Fig. 2. SCHAKAL-88 plot[17] of *meso-glycero-allo*-heptitol (**2**), showing atom numbering.

O//O interactions which would occur in the planar zigzag arrangement, thus resembling the overall geometry that was observed for D-*glycero*-D-*gluco*-heptitol in the solid state[5]. Contrary to this expectation, molecules of **2** are found to be asymmetric (Fig. 2 and Table IV), involving a 1,3-interaction between atoms C-5 and O-2 with a distance between these atoms of 303.6 pm. This situation parallels that observed for D-*glycero*-L-*allo*-heptitol[2]. Considering other results[7,9,10], in cases of three contiguous centres of the same chirality (*ribo* configuration), such topology is an obvious alternative to other ones, even to those without any 1,3-parallel interactions between C and O atoms in certain cases.

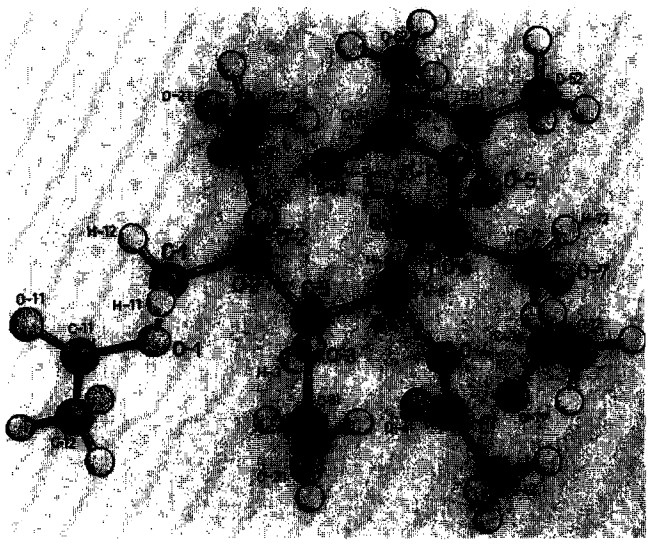

Fig. 3. SCHAKAL-88 plot[17] of 1,2,3,4,5,6,7-hepta-*O*-acetyl-*meso-glycero-allo* heptitol (**3**), showing atom numbering.

TABLE V

Hydrogen-bond patterns [a] in **1** and **2** (bond lengths in pm, angles in degrees) [b]

Compound	Distances *D-H* ··· *A*	Symmetry operation on A	Distance D ··· A	Angle D-H ··· A	Angle of bifurcation A ··· H ··· A′
1	O-1 $\overset{85(2)}{\text{——}}$ H-1O$^{186(2)}$O-2	$-x, y, z$	271.1(2)	173(2)	
	O-2 $\overset{85(1)}{\text{——}}$ H-2O$^{197(1)}$O-4	$-x+1, 1/2+y, 1/2-z-1$	281.5(2)	177(1)	
	O-3 $\overset{85(1)}{\text{——}}$ H-3O$^{193(2)}$O-6	$-x+1, 1/2+y-1, 1/2-z-1$	274.1(2)	159(2)	
	O-4 $\overset{85(1)}{\text{——}}$ H-4O$^{188(1)}$O-3	$x+1, y, z$	271.1(2)	167(1)	
	O-5 $\overset{85(2)}{\text{——}}$ H-5O$^{231(1)}$O-4	intramolecular	270.4(2)	109(1)	
	O-5 $\overset{85(2)}{\text{——}}$ H-5O$^{211(2)}$O-1	$-x+1, 1/2+y-1, 1/2-z-1$	292.8(2)	160(1)	91(1)
	O-6 $\overset{85(2)}{\text{——}}$ H-6O$^{200(2)}$O-7	$x+1, y, z$	279.1(2)	154(2)	
	O-7 $\overset{85(2)}{\text{——}}$ H-7O$^{196(1)}$O-1	$-x, 1/2-y+1, 1/2+z$	280.8(2)	175(2)	
2	O-1 $\overset{85(2)}{\text{——}}$ H-1O$^{191(1)}$O-5	$-x, 1/2+y, 1/2-z$	276.1(5)	179(2)	
	O-2 $\overset{85(5)}{\text{——}}$ H-2O$^{199(4)}$O-6	$-x, 1/2+y, 1/2-z$	282.4(6)	168(8)	
	O-3 $\overset{85(4)}{\text{——}}$ H-3O$^{194(3)}$O-3	$1/2+x, 1/2-y+2, -z$	273.0(6)	153(6)	
	O-4 $\overset{85(2)}{\text{——}}$ H-4O$^{182(3)}$O-7	$1/2+x-1, 1/2-y+1, -z$	265.5(5)	166(6)	
	O-5 $\overset{85(1)}{\text{——}}$ H-5O$^{191(1)}$O-4	$x+1, y, z$	275.4(5)	170(2)	
	O-6 $\overset{85(3)}{\text{——}}$ H-6O$^{196(3)}$O-2	$-x-1, 1/2+y-1, 1/2-z$	280.8(6)	173(5)	
	O-7 $\overset{85(4)}{\text{——}}$ H-7O$^{254(4)}$O-6	intramolecular	284.4(5)	102(3)	
	O-7 $\overset{85(4)}{\text{——}}$ H-7O$^{193(6)}$O-1	$x, y-1, z$	269.9(6)	150(9)	86(2)

[a] A, Acceptor oxygen; D, Donor oxygen. [b] Standard deviations in parentheses.

If this sequence is alternating (*xylo* configuration), O//O interactions are often tolerated instead in zigzag conformations[8–11]. Until now, no explanations can be given for these findings.

The single crystals of **2** are composed of asymmetric conformers of the same chirality, as can be derived from the observed space group $P2_12_12_1$. Such a conglomerate is also encountered[20] in the case of *meso*-xylitol, but not in the case of the more related *meso*-ribitol[21] which also is chiral in the crystalline state but forms racemic single crystals.

The network of hydrogen bonds for **2** is given in Table V. All hydroxyl groups are involved as donors with O-7 supporting a bifurcated bond. All oxygens are acceptors with O-6 accepting two such bonds.

Considering the high quality of the crystals investigated, as documented for instance by excellent diffractive properties, the comparatively poor R value of 0.063 is surprising. We cannot give an explanation for this finding. A possibility could be that single crystals contain a certain amount of the other conformational enantiomer. Also, in the case of xylitol a comparatively poor solution was reported[20]. The result for **2** therefore should be considered as preliminary only. The possibility of a crystallographically more appropriate description of the nature of the crystals investigated cannot be excluded.

The heptaacetate **3** derived from **2** crystallized in the space group $P\bar{1}$, which indicates that the observed chiral conformers are accompanied by a symmetry-related enantiomer in the crystal. In Fig. 3, only one of the enantiomeric conformers is shown. Individual molecules differ considerably in shape from those of the free compound **2**. Again, it adopts a bent (sickle) conformation, but it is one in which **two** C//O interactions are observed. Both C-7/O-4 and C-6/O-3 are found in a 1,3-parallel arrangement. The distances are 299.8(3) and 316.8(2) pm, respectively. Until now, only for the configurationally related *meso*-allitol hexaacetate[9] has such a situation been reported. Nevertheless, the geometries are different. In *meso*-allitol hexaacetate, the observed two C//O interactions with a distance of 282.0 pm are symmetry-related[9], whereas this is not the case for **3**.

Comparison of the conformations of **2** and the acetylated derivative **3** in the crystal provides another example where considerable differences are observed in the shape of the central carbon chain for the parent alditols and the aforementioned derivatives. So far, reported examples are the acetates of xylitol[22,23], allitol[9], D- and DL-iditol[9], D- and DL-glucitol[9], *meso-glycero-gulo*-heptitol[11], and D-*glycero*-D-*manno*-heptitol[11].

EXPERIMENTAL

Compounds **1** and **2** were prepared by the procedures cited[12,13]. Acetate **3**[14] was obtained in the usual way by acetylating **2** with Ac_2O and a catalytic amount of trifluoromethanesulfonic acid. The X-ray structure determinations were performed at ~20°C, and the methods and results are given in Table I or have been

deposited. Calculations of geometries were executed by using the PLATON program[24]. Standard deviations for bond lengths and angles involving H-atoms as deposited are probably an order of magnitude too low, due to the AFIX option[16] which was used to calculate and refine the position of these atoms.

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