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Crystal Structure of the 1:1 Molecular Compound 1,4-Dioxan, Sulphuric Acid

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The 1:1 addition compound 1,4-dioxan, sulphuric acid crystallizes in the monoclinic system — space group $P2_1/c$ — with lattice parameters:

$$a = 13.22 \text{ Å};\ b = 7.73 \text{ Å};\ c = 7.71 \text{ Å};\ \beta = 92°.$$

Hydrogen bonds link each sulphuric acid unit to two neighbouring dioxan molecules, thus producing endless chains of alternating dioxan and sulphuric acid molecules. Two sets of non-equivalent dioxan molecules are present in the structure, and two sets of hydrogen bonds are therefore also present. The lengths of these bonds are found equal to 2.51 and 2.59 Å, respectively.

In order to establish the crystal structure of one solid compound formed by an ether and a strong mineral acid, an X-ray analysis of the 1:1 compound 1,4-dioxan, sulphuric acid has been carried out. This compound has a melting point of 101°C (Faworski[1]). The possible structure of the isolated complex has been discussed on the basis of dipole moment measurements by Syrkin and Anisimova[2] who have concluded that both hydrogen atoms of the sulphuric acid molecule are linked to one particular ether oxygen atom. The angle between the two hydrogen bonds thus established would, however, appear to be rather small and we would therefore prefer a model in which both ether oxygen atoms are involved in hydrogen bond formation. In this case the dioxan molecule would of course be present in the »boat» form. Both models would lead to a rather high dipole moment. In the crystal the possibility of chains built up of alternating sulphuric acid and dioxan molecules would also have to be considered. In this case centrosymmetrical dioxan molecules might be expected.

EXPERIMENTAL

The compound was prepared as described by Faworski[1]. Sulphuric acid was added to a solution of dioxan in benzene and the reaction mixture cooled slowly. The needle-shaped crystals thus obtained turned out to be well fitted for X-ray examination. The procedure of bringing a crystal into a capillary tube without admitting small traces of moisture which would eventually liquefy the crystal after the tube had been sealed, turned out to be difficult. By careful handling this could, however, be achieved. The cross section of the crystals used in the X-ray work was approximately 0.15 × 0.15 mm².

The experimental material on which the analysis was based consisted of integrated Weissenberg (Wiebenga) diagrams (CuK_α-radiation) with rotation about the c-axis (needle-axis) and precession diagrams (MoK_α-radiation, $\mu = 30°$) of the ($h0l$)- and ($0kl$)-zones. The number of reflexions recorded in the ($hk0$)-zone was 113 (theor. 135), in the ($h0l$)-zone 101 (theor. 129) and in the ($0kl$)-zone 49 (theor. 72). The intensities in the Wiebenga diagrams were recorded photometrically, whereas the precession diagram intensities were estimated visually. Most of the computation work was performed using a Ferranti Mercury machine.

The crystals are monoclinic, space group $P2_1/c$, and the parameters obtained are as follows:

$$a = 13.22 \text{ Å};\ b = 7.73 \text{ Å};\ c = 7.71 \text{ Å};\ \beta = 92°.$$

These figures are believed to be accurate to within 0.03 Å and 0.5°. The calculated density, assuming the unit cell to contain four molecules of either kind, is 1.57.

STRUCTURE DETERMINATION

If the dioxan and sulphuric acid molecules take up fourfold general positions no symmetry requirements for the single molecules have to be fulfilled. On the other hand, the dioxan molecules may occupy two two-fold positions involving centers of symmetry, in this case two types of dioxan molecules are present in the structure.

Projection along the c*-axis.* From the Weissenberg data a two-dimensional Patterson synthesis was worked out. This synthesis made possible the localization of the sulphur atom and the determination of approximate coordinates of the sulphuric acid oxygen atoms. The atoms belonging to dioxan molecules could not be determined, but it became obvious that two non-equivalent sets of dioxan molecules are present in the structure having their centers of symmetry

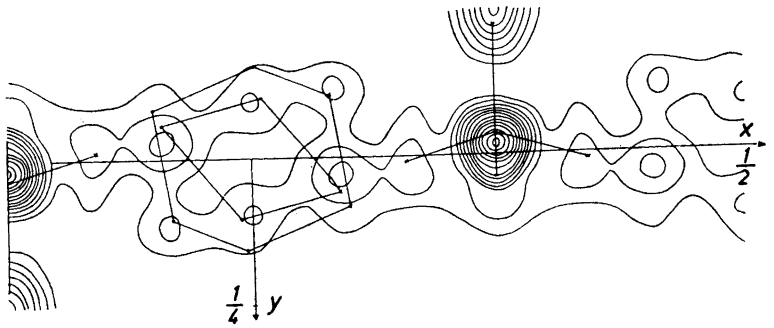

Fig. 1. Fourier map based on the ($hk0$)-reflexions using F_{hk0} with $h+k = 2n$ only.

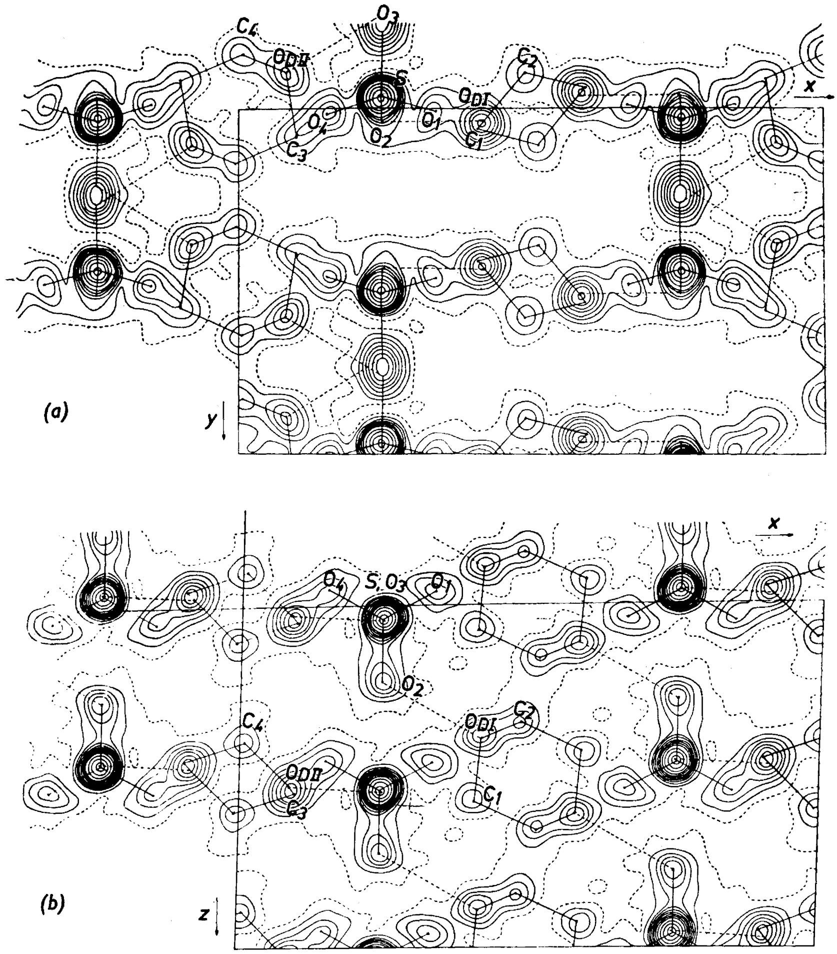

Fig. 2. Electron density projection along the *c*-axis (a) and *b*-axis (b). Contour lines at intervals of 2e. Å^{-2} from 2—16 e. Å^{-2} and 4 e. Å^{-2} from 16 e. Å^{-2} upwards.

in (0,0) and (1/2,0), respectively. The approximate coordinates of the sulphur and oxygen atoms of the sulphuric acid group were as follows: S: (0.250, —0.013) ; O_1: (0.345, 0) ; O_2: (0.250, 0) ; O_3: (0.250, —0.208) and O_4: (0.155, 0). On the basis of these coordinates only the structure factor signs of reflexions with $h + k = 2n$ could be determined. The neglection of other reflexions introduced an extra line of symmetry ($x = 1/4$) in the resulting Fourier synthesis (reproduced in Fig. 1). Here the sulphuric acid molecule therefore exhibits a symmetry line which is not real and the peaks around (0,0) indicate two overlapping dioxan molecules rather than one molecule. Using a reasonable

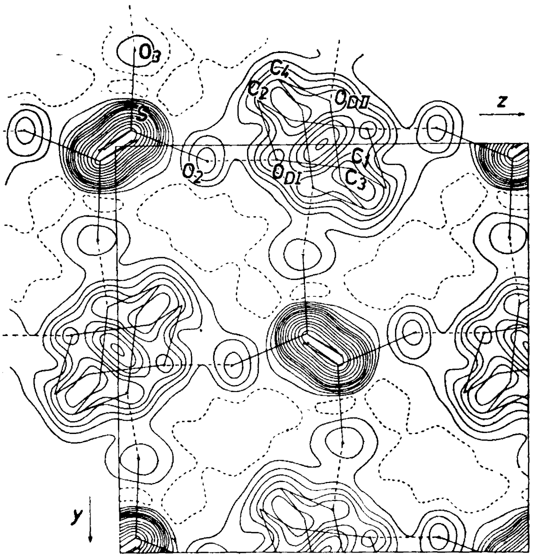

Fig. 3. Electron density projection along the *a*-axis. Contour lines as in Fig. 2.

model of the dioxan ring it was possible to split up the "double molecule" into two molecules, the centers of which were placed in (0,0) and (1/2, 0) thus bringing the symmetry in accordance with the true symmetry requirements of the plane group *pgm*. (The dioxan rings drawn in Fig. 1 are based on the ultimate, refined coordinates).

The *R* factor of the [001] projection at this preliminary stage of the analysis was 0.32. Successive refinements brought it down to 0.19 and after employing difference syntheses and least squares refinements it dropped to 0.13. At this stage further refinements of this projection were not attempted.

Projection along the b-*axis.* From a Patterson synthesis based on the (*h0l*) intensities and the coordinates obtained from the [001] projection a preliminary spatial model of the structure could be set up. It was assumed that hydrogen bonds are established between the hydroxy oxygens of the sulphuric acid molecules and the ether oxygen atoms of dioxan corresponding to "equatorial" directions in the dioxan molecules. After refinements the *R* factor was 0.14.

Projection along the a-*axis.* Using parameters derived from the two earlier projections the Fourier projection along the *a*-axis was refined until an *R* factor of 0.16 was obtained.

In all three projections overlapping of atoms occurred preventing further direct refinements. Nearly all coordinates could be determined, however, from at least one of the projections. Combining parameters obtained from different projections, and also (at this stage) introducing hydrogen parameters determined by projection of a model it was possible to perform least squares refinements on all three data sets alternatingly. The mean value of the atomic

Table 1. Atomic coordinates as fractions of the cell edges.

Atom	*x*	*y*	*z*
S	0.2446	−0.0355	0.0383
O_1	0.3354	0.0118	−0.0401
O_2	0.2450	0.0358	0.2212
O_3	0.2479	−0.2322	0.0494
O_4	0.1505	0.0133	−0.0481
O_{DI}	0.4182	0.0344	0.3894
O_{DII}	0.0830	−0.1069	0.5226
C_1	0.410	0.060	0.573
C_2	0.487	−0.106	0.343
C_3	0.098	0.072	0.559
C_4	0.008	−0.156	0.397

coordinates thus obtained are listed in Table 1. Estimates of the standard deviations [3] for the positions of resolved atoms were as follows:

$$\begin{array}{l} \text{Oxygen: } \sigma(x) = 0.014 \text{ Å} \; ; \; \sigma(y) = 0.016 \text{ Å} \; ; \; \sigma(z) = 0.018 \text{ Å} \\ \text{Carbon: } \sigma(x) = 0.018 \text{ Å} \; ; \; \sigma(y) = 0.020 \text{ Å} \; ; \; \sigma(z) = 0.023 \text{ Å} \end{array}$$

A comparison between observed and calculated structure factors is given in Table 3. In the calculations the analytical approximation to the atomic scattering factors computed by Forsyth and Wells [4] was employed.

The final R factors not including unobserved reflexions were as follows: $R_{hk0} = 0.09$; $R_{h0l} = 0.12$ and $R_{0kl} = 0.09$. The Fourier maps are reproduced in Figs. 2 and 3.

DISCUSSION OF THE STRUCTURE

The structure is built up of chains of alternating sulphuric acid and dioxan molecules. Two dioxan molecules are linked to a particular sulphuric acid

Table 2. Angles and interatomic distances.

$$\begin{array}{ll} \angle \text{ S } O_2O_{DI} & = 115.8^\circ \\ \angle \text{ S } O_3O_{DII}' & = 117.1^\circ \\ \angle\, O_{DI}'O_{DI}O_2 & = 166^\circ \\ \angle\, O_{D'II}O_{DII}O_3' & = 172^\circ \end{array} \left.\begin{array}{l} \\ \\ \\ \\ \end{array}\right\} \text{"equatorial"} = 153^\circ$$

Hydrogen bonds:

$O_2\text{—H— —}O_{DI}$: 2.59 Å
$O_3'\text{—H— — —}O_{DII}$: 2.51 Å

Distances in the sulphuric acid molecule:

SO_1 : 1.41 Å
SO_2 : 1.51 Å
SO_3 : 1.52 Å
SO_4 : 1.44 Å
O_1O_2 : 2.39 Å

O_1O_3 : 2.33 Å
O_1O_4 : 2.44 Å
O_2O_3 : 2.46 Å
O_2O_4 : 2.39 Å
O_3O_4 : 2.40 Å

Bond lenghts in the dioxan molecules:

$O_{DI}C_1$: 1.44 Å
$O_{DI}C_2$: 1.47 Å
$C_1'C_2$: 1.53 Å

$O_{DII}C_3$: 1.42 Å
$O_{DII}C_4$: 1.41 Å
$C_3'C_4$: 1.59 Å

Table 3. Observed and calculated structure factors.

hkl	F_o	F_c
1 0 0	6	5
2 0 0	51	−43
3 0 0	13	−12
4 0 0	44	44
5 0 0	4	5
6 0 0	63	−66
7 0 0	< 3	0
8 0 0	48	49
9 0 0	15	17
10.0 0	21	−20
11.0 0	12	−12
12.0 0	47	48
13.0 0	10	10
14.0 0	11	−11
15.0 0	6	−7
16.0 0	7	7
1 1 0	27	28
2 1 0	17	16
3 1 0	31	−31
4 1 0	11	10
5 1 0	37	38
6 1 0	7	6
7 1 0	10	−9
8 1 0	12	−10
9 1 0	18	16
10.1 0	7	−5
11.1 0	8	−7
12.1 0	< 4	−2
13.1 0	9	8
14.1 0	4	5
15.1 0	3	−3
16.1 0	< 2	1
0 2 0	133	136
1 2 0	26	−27
2 2 0	36	−39
3 2 0	13	−14
4 2 0	18	−18
5 2 0	4	4
6 2 0	34	−31
7 2 0	4	4
8 2 0	14	13
9 2 0	7	5
10.2 0	16	−17
11.2 0	15	−17
12.2 0	23	23
13.2 0	< 3	3
14.2 0	9	−7
15.2 0	8	−6
16.2 0	< 2	0
1 3 0	25	−25
2 3 0	19	18
3 3 0	10	−11
4 3 0	20	21
5 3 0	7	8
6 3 0	9	7
7 3 0	7	6
8 3 0	16	−15
9 3 0	12	11
10.3 0	12	−10
11.3 0	< 4	1
12.3 0	3	−6
13.3 0	< 3	1
14.3 0	5	6
15.3 0	< 3	2
0 4 0	35	38
1 4 0	21	−20
2 4 0	60	−63
3 4 0	5	−3
4 4 0	15	15
5 4 0	23	20
6 4 0	20	−19
7 4 0	11	11
8 4 0	17	15
9 4 0	6	3
10.4 0	27	−28
11.4 0	14	−14
12.4 0	10	10
13.4 0	< 3	1
14.4 0	8	−9
15.4 0	< 2	−1
1 5 0	12	9
2 5 0	7	7
3 5 0	43	−43
4 5 0	4	4
5 5 0	18	18
6 5 0	6	5
7 5 0	17	−15
8 5 0	10	−11
9 5 0	24	23
10.5 0	< 4	−2
11.5 0	10	−12
12.5 0	< 3	−3
13.5 0	4	5
14.5 0	4	5
0 6 0	< 4	1
1 6 0	4	3
2 6 0	10	−9
3 6 0	6	6
4 6 0	3	5
5 6 0	16	11
6 6 0	16	12
7 6 0	9	9
8 6 0	5	4
9 6 0	6	2
10.6 0	9	−8
11.6 0	5	−2
12.6 0	4	0
13.6 0	2	3
1 7 0	6	6
2 7 0	< 4	2

hkl	F_o	F_c
3 7 0	22	−24
4 7 0	< 4	1
5 7 0	11	10
6 7 0	5	4
7 7 0	11	−11
8 7 0	4	− 5
9 7 0	11	14
10. 7 0	3	4
11. 7 0	4	− 5
0 8 0	< 3	− 1
1 8 0	7	3
2 8 0	< 3	2
3 8 0	< 3	− 1
4 8 0	< 3	1
5 8 0	< 3	− 3
6 8 0	8	7
7 8 0	4	− 2
8 8 0	< 3	0
9 8 0	2	− 2
1 9 0	10	9
2 9 0	3	3
3 9 0	10	−10
4 9 0	< 3	2
5 9 0	9	10
6 9 0	4	2
0 0 2	122	128
0 0 4	26	24
0 0 6	8	− 8
0 0 8	7	− 8
0 0 10	9	− 6
1 0 −10	8	5
1 0 − 8	8	8
1 0 − 6	25	31
1 0 − 4	37	44
1 0 − 2	57	62
1 0 2	< 3	3
1 0 4	10	8
1 0 6	26	−28
1 0 8	12	− 8
1 0 10	< 6	− 3
2 0 −10	10	10
2 0 − 8	12	12
2 0 − 6	< 5	1
2 0 − 4	35	−43
2 0 − 2	< 3	− 3
2 0 2	56	−56
2 0 4	59	−59
2 0 6	< 5	− 4
2 0 8	< 6	3
2 0 10	< 6	1
3 0 −10	9	− 5
3 0 − 8	8	− 4
3 0 − 6	16	−22
3 0 − 4	< 5	− 6
3 0 − 2	36	−40
3 0 2	47	45
3 0 4	< 5	1
3 0 6	< 6	4
3 0 8	7	6
3 0 10	15	8
4 0 −10	< 6	1
4 0 − 8	< 6	2
4 0 − 6	7	− 3
4 0 − 4	11	13
4 0 − 2	8	− 6
4 0 2	42	−34
4 0 4	< 5	5
4 0 6	7	7
4 0 8	< 6	− 4
4 0 10	8	− 4
5 0 −10	12	8
5 0 − 8	12	12
5 0 − 6	24	26
5 0 − 4	16	20
5 0 − 2	21	24
5 0 2	42	−38
5 0 4	66	−58
5 0 6	52	−52
5 0 8	12	−10
5 0 10	< 5	− 3
6 0 − 8	7	6
6 0 − 6	7	10
6 0 − 4	18	−20
6 0 − 2	21	−20
6 0 2	47	−44
6 0 4	25	−26
6 0 6	< 6	− 3
6 0 8	< 6	0
7 0 − 8	9	−10
7 0 − 6	39	−42
7 0 − 4	48	−52
7 0 − 2	46	−44
7 0 2	40	36
7 0 4	16	12
7 0 6	19	19
7 0 8	12	10
8 0 − 6	< 6	− 5
8 0 − 4	7	2
8 0 − 2	< 5	3
8 0 2	23	24
8 0 4	26	22
8 0 6	9	5
9 0 − 6	6	6
9 0 − 4	7	9
9 0 − 2	22	20
9 0 2	< 6	4
9 0 4	< 6	1
9 0 6	9	− 9
10. 0 − 6	< 6	− 1
10. 0 − 4	24	−22
10. 0 − 2	16	−16
10. 0 2	10	− 8
10. 0 4	17	−13
10. 0 6	6	− 4
11. 0 − 6	9	− 8
11. 0 − 4	< 6	− 2

hkl	F_o	F_c
11.0 − 2	11	−10
11.0 2	13	8
11.0 4	10	4
11.0 6	12	11
12.0 − 6	6	− 4
12.0 − 4	< 6	5
12.0 − 2	18	20
12.0 2	23	24
12.0 4	10	10
12.0 6	< 6	0
13.0 − 6	12	14
13.0 − 4	15	17
13.0 − 2	13	12
13.0 2	< 6	2
13.0 4	7	− 5
13.0 6	14	−10
14.0 − 4	7	− 6
14.0 − 2	< 6	− 2
14.0 2	11	−11
14.0 4	10	−10
15.0 − 2	9	− 9
15.0 2	9	7
0 1 1	12	12
0 1 2	6	− 4
0 1 3	50	46
0 1 4	14	18
0 1 5	34	31
0 1 6	9	10
0 1 7	5	− 6
0 1 8	3	6
0 1 9	< 5	− 5
0 2 1	23	26
0 2 2	50	47
0 2 3	30	31
0 2 4	26	23
0 2 5	9	9
0 2 6	< 5	− 3
0 2 7	< 5	6
0 2 8	5	− 5
0 2 9	< 5	2
0 3 1	69	68
0 3 2	7	− 5
0 3 3	33	31
0 3 4	15	14
0 3 5	16	18
0 3 6	6	7
0 3 7	< 5	− 4
0 3 8	6	8
0 3 9	< 5	− 3
0 4 1	4	− 6
0 4 2	24	23
0 4 3	17	19
0 4 4	14	13
0 4 5	19	20
0 4 6	3	− 4
0 4 7	15	15
0 4 8	< 5	− 4
0 5 1	48	43
0 5 2	22	23
0 5 3	21	19
0 5 4	19	19
0 5 5	10	9
0 5 6	< 5	5
0 5 7	< 5	0
0 5 8	7	6
0 6 1	< 4	− 4
0 6 2	< 4	2
0 6 3	16	16
0 6 4	< 5	− 2
0 6 5	20	20
0 6 6	< 5	− 4
0 6 7	14	13
0 7 1	< 5	4
0 7 2	10	11
0 7 3	6	5
0 7 4	6	10
0 7 5	< 5	3
0 7 6	< 5	2
0 8 1	< 5	− 1
0 8 2	< 5	3
0 8 3	8	6
0 8 4	< 5	0
0 8 5	9	9
0 9 1	< 5	1
0 9 2	6	7
0 9 3	< 5	2

unit by hydrogen bonds,the direction of which is roughly "equatorial" (Fig. 4). Both dioxan molecules are centrosymmetrical, but they are not crystallographically equivalent. The two O—H—O distances as computed from the coordinates listed in Table 1 are 2.51 Å and 2.59 Å, respectively, the standard deviation is 0.025 Å. It is obvious that two different types of S—O distances are present in the sulphuric acid group, one of which (involving the "keto" oxygen atom) is 1.42 Å, the other 1.51 Å. Some of the atomic distances computed have been listed in Table 2. (Compare also Fig. 5).

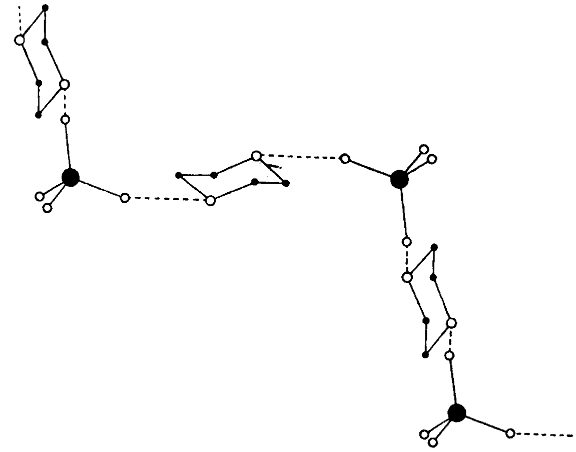

Fig. 4. Structure of the sulphuric acid-dioxan chains.

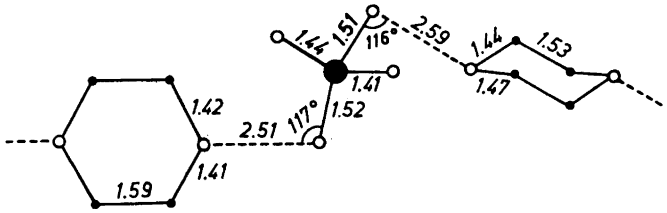

Fig. 5. Distances and angles. Open circles indicate oxygens, closed circles sulphur (large) and carbon (small) atoms.

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