

*The crystalline structure of pentaerythritol tetranitrate*

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**P**ENTAERYTHRITOL tetranitrate,  $C(CH_2ONO_2)_4$ , is an interesting compound structurally, since there is, in the molecule, a carbon atom with four like groups ( $-CH_2ONO_2$ ) attached to it. The molecule is therefore of the type  $CX_4$ . It was hoped that an examination of the crystals by means of X-rays would show how far the molecule retains its form and symmetry in the crystalline state; also that some light would be thrown on the configuration of the nitro- ( $-NO_2$ ) group, especially the equivalence or otherwise of the two oxygen atoms of the group—a question which it has not yet been found possible to settle by chemical methods.

The following crystallographic data for this compound have already been published:<sup>1</sup>

Ditetragonal bipyramidal,  $a : c = 1 : 0.506$ .

$D_4^{20} = 1.773$ . Refractive indices,  $\omega = 1.554$ ,  $\epsilon = 1.553$ .

Cleavage, (100) imperfect.

The crystals, which were very kindly supplied by Sir William Pope, are of excellent quality and size (those selected for use being about 3 mm. in length and 2 mm. in breadth) and the forms developed are the prism (100) and the bipyramid (111).

The X-ray examination was made on a Bragg ionization spectrometer, using a Coolidge X-ray bulb of rhodium anticathode. The spacings for the (100) and (001) planes were found to be 6.60 Å. and 3.33 Å. respectively. Observations of spacings on other planes showed that these represented half-spacings, there being a true halving in the case of the (100) planes and an accidental halving in the case of the (001) planes. (This will be referred to later.) So that the dimensions of the unit cell are  $13.2^{\circ} \times 6.66$  Å. Since none of the (*hhl*) planes were found

<sup>1</sup> I. E. Knaggs, Journ. Chem. Soc., London, 1923, Trans. vol. 123, p. 77.

to be halved, the crystals must be built on the simple tetragonal lattice  $\Gamma_t$ . The halving of the (100) planes (which include (010)) must be due to a reflection molecule lying half-way between the (100) and the (010) planes.

$N$ , the number of molecules per unit cell, may be found, as follows:

$13.2^2 \times 6.66 \times \rho = N \times M \times 1.65$ , where  $\rho$  = density,  $M$  = molecular weight referred to oxygen as 16.

Then  $13.2^2 \times 6.66 \times 1.77 = N \times 316 \times 1.65$ , hence  $N = 3.94$ .

That is, the number of molecules per unit cell is 4. The following table gives the results obtained by X-ray reflections from the various planes. The calculated spacings are based on a simple tetragonal lattice of the dimensions found.

Plane.	Spacings in Å.		Relative intensities of reflections.
	Calculated.	Observed.	
(100)	13.2*	6.60	Moderate ( $IV^{th} > II^{nd}$ ).
(001)	6.66*	3.33	Small.
(110)	9.33	4.66	Moderate.
(210)	5.90	2.97	Moderate.
(101)	5.95	2.96	Small.
(102)	3.23	3.21	Moderate.
(201)	4.69	2.34	Small.
(301)	3.67	3.70	Moderate.
(111)	5.42	5.38	Small.
(112)	3.14	3.13	Large.
(331)	2.82	2.82	Fairly large.

A consideration of the spacings shows that the only true halvings are for planes ( $hk0$ ), where ( $h + k$ ) is odd. The only space-group<sup>1</sup> in the holohedral class of the tetragonal system, which, based on a simple tetragonal lattice, would lead to this result is  $D_{4h}^7$ . This space-group has 16-fold symmetry, and, since it has already been shown that there must be four molecules per unit cell, each molecule must have four-fold symmetry. Two types of four-fold symmetry are possible in this case: (1) the molecule may have two planes parallel to (100) and (010) respectively intersecting in a digonal axis, or (2) a plane parallel to (110) with a digonal axis at right angles to it. Only by assuming the molecular symmetry (1) was it found possible to obtain a reasonable structure for the crystals. This structure is, moreover, in accordance with the known facts, as far as they can be interpreted.

The molecule has the appearance shown in fig. 1. It may be regarded

<sup>1</sup> See W. T. Astbury and K. Yardley, Tabulated data for the examination of the 230 space-groups by homogeneous X-rays. Phil. Trans. Roy. Soc. London, 1924, ser. A, vol. 224, p. 242. [Min. Abstr., vol. 2, p. 366.]

as taking the form of a modified tetrahedron in which only one of the three digonal axes and only two of the six planes of symmetry, namely, those two which intersect in the one digonal axis, are retained. The angles between the  $-\text{CH}_2\text{ONO}_2$  chains attached to the central carbon atom have not the value of the tetrahedral angle ( $109^\circ 28'$ ), but two of them are  $126^\circ 27'$  and four of them  $101^\circ 40'$ . The relationship between the molecule as built into the crystal and the molecule in the free state, as known to the chemist, is, that the former may be derived from the latter by compression along the one remaining digonal axis. This digonal axis is, moreover, a simple digonal axis and not a tetragonal alternating axis, as is the case in a regular tetrahedron. The arrange-

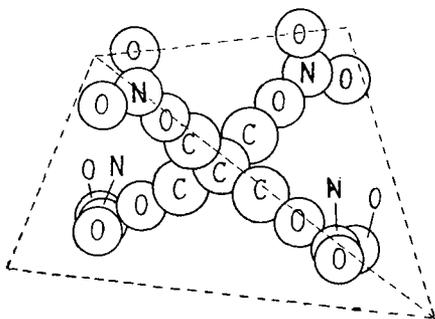
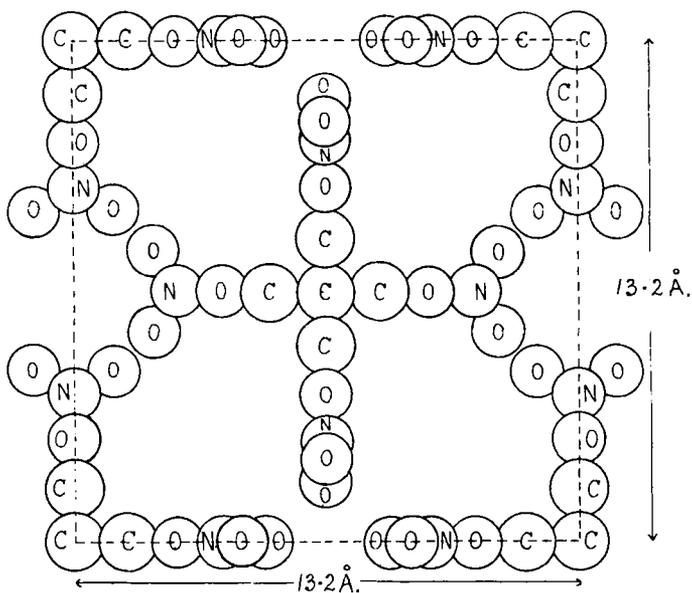
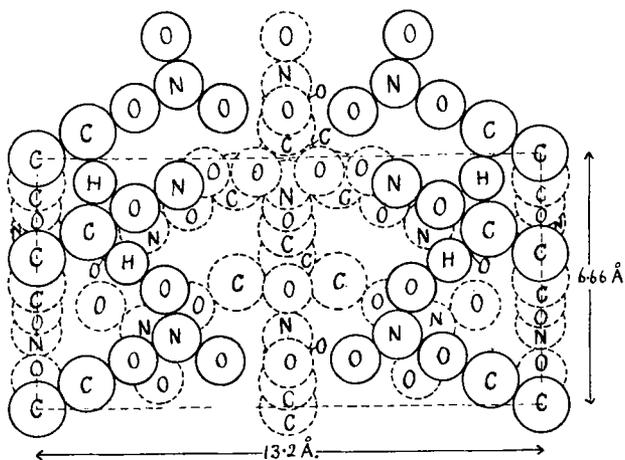


Fig. 1. Diagrammatical representation of the molecule of pentaerythritol tetranitrate.

ment (as shown in fig. 1) of the oxygen atoms of the nitro-group ensures that this shall be so. The hydrogen atoms are omitted from the figure for the sake of clearness. It is obvious that two hydrogen atoms will be attached to the carbon atom of each chain, but as far as the symmetry of the molecule is concerned, it is immaterial whether the hydrogen atoms in any chain lie in the same plane as, or in one at right angles to, the

plane containing the oxygen atoms in that chain. But from a consideration of the structure of the crystal as a whole, it is seen that a proper linking together of the successive layers of atoms can only be attained by arranging the hydrogen atoms in planes at right angles to the planes containing the oxygen atoms (see fig. 2).

Figs. 2 and 3 indicate the way in which the molecules are arranged in the cell. Again, in order to simplify the diagrams, hydrogen atoms are not shown except that, in the case of fig. 2, those hydrogen atoms which actually lie in the plane of projection (100) are inserted in order to show the way in which they serve to link up successive layers of atoms. It will be seen from the diagrams that one molecule is associated with each corner of the cell, and that lying at the centre of the (001) plane is a molecule derived from any of these by reflection across a (110) plane. At an indeterminate distance down the cell lie other molecules



FIGS. 2 and 3. Projections (elevation and plan) of the atoms of pentarythritol tetranitrate on (100) and (001) respectively. (In Fig. 2 continuous circles represent atoms lying in the plane (100), and broken circles atoms lying below the plane (100); atoms lying above the plane are not shown.)

directly under those in the (001) plane and derived from them by reflection across the (001) plane combined with a rotation through  $90^\circ$ .

From the table it will be seen that only a small or a moderate reflection of X-rays was obtained from most of the planes. The planes measured in the zones of the faces ( $h\bar{k}0$ ) and ( $h0l$ ), and which are given in the table, are the only ones, in those zones, from which it was found possible to observe reflections.

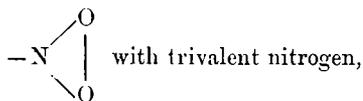
In the structure described above there is a very sparse distribution of atoms on the (001) plane and a considerable number of atoms lying in planes at right angles to it, hence it is not surprising to find a small reflection of X-rays from the (001) plane. Reference has already been made to the accidental halving of the spacing for this plane. This is evidently due to the molecules, which lie at an indeterminate distance between the (001) planes, and whose positions appear to be not very far from half-way down the cell.

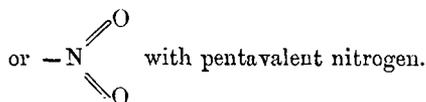
The proposed structure would lead to the expectation of a larger reflection from the (100) planes than from the (001) plane, and this has been observed. The fourth-order reflection being larger than the second for the (100) planes also appears to be in accordance with the structure, since there are atoms lying at approximately one-quarter and three-quarters of the distance between the (100) planes, and atoms in such positions would tend to decrease the second-order and increase the fourth-order reflections.

It is readily seen also, that the densest distribution of atoms, in the structure, is on the (112) planes, along which lie the  $-\text{CH}_2\text{ONO}_2$  chains, and that there are extremely few atoms lying between these planes. This agrees well with the fact that the most intense reflections of X-rays were obtained from these planes.

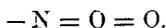
Owing to the explosive nature of pentaerythritol tetranitrate, it has been difficult to examine the crystals for cleavage, and although an imperfect (100) cleavage has been observed, it would be unwise to attach much importance to it. The structure suggests a possible (110) cleavage, but this has not been observed.

With regard to the configuration of the  $-\text{NO}_2$  group, it seems evident that the oxygen atoms are equivalent, and that the structure of the group is as follows :





The only other structure possible is that in which three atoms of the group lie in one straight line, thus :



The last would make the length of the  $-\text{CH}_2\text{ONO}_2$  chain 6.74 Å. (accepting the values of the atomic diameters given by W. L. Bragg), whereas the space available in the crystal-cell is only 6.58 Å., necessitating some compression of the atoms in the chain. As already stated, it is necessary that the digonal axis shall be a simple one and not a tetragonal alternating axis. Allowing the straight-line arrangement of the  $-\text{NO}_2$  group, this condition would need to be secured by the arrangement of the hydrogen atoms alone, which is unlikely. Another objection to the straight-line arrangement of the  $-\text{NO}_2$  group is evident from a consideration of the crystal-structure as a whole, for it would necessitate four oxygen atoms meeting so as to touch closely, and it seems highly probable that the repulsion of these oxygen atoms for one another would be too great to allow of the existence of the structure.

The evidence, therefore, appears to be in favour of one of the first two formulae for the nitro-group, but it is not possible to say which of the two is the more likely for this compound. Adopting the arrangement of the oxygen atoms resulting from either of these formulae, as has been done in the structure described in this paper, some instability might still be expected from the comparative proximity of eight oxygen atoms. It is suggested that this, combined with the strain due to the considerable departure from the true tetrahedral angle of the bonds from the central carbon atom of the molecule, may contribute to the explosive nature of the compound.

#### *Summary.*

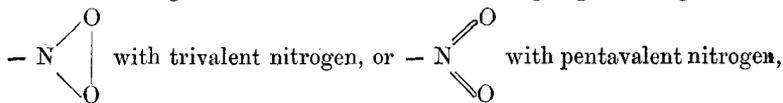
1. Pentaerythritol tetranitrate has been examined with X-rays by the Bragg ionization spectrometer method.

2. It has been found to be built on the simple tetragonal lattice  $\Gamma_t$ , to belong to the space-group  $D_{4h}^7$ , and to have four molecules per unit cell.

3. The molecule is believed to have one simple digonal axis parallel to the axis  $c$ , and two planes of symmetry parallel to (100) and (010) intersecting in it. There is considerable departure from the tetrahedral angle ( $109^\circ 28'$ ) between the bonds from the central carbon atom, the

values of the angles between these bonds being two of them  $126^{\circ} 27'$  and four of them  $101^{\circ} 40'$ .

4. The arrangement of the atoms in the nitro-group is thought to be



and not  $-\text{N} = \text{O} = \text{O}$ .

5. It is thought that the strain due to the departure from the tetrahedral angle of the bonds from the central carbon atom of the molecule, and the comparative proximity of eight oxygen atoms at intervals in the structure, and the consequent repulsion, may be contributory causes of the explosive nature of the compound.

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