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X-Ray Investigations of Reductone, Reductonates and Bromomalonic dialdehyde

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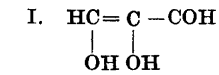
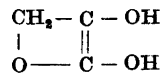
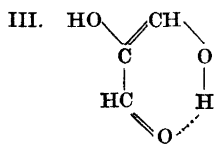
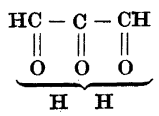
X-ray investigations have been made on reductone and on a series of related compounds. Only the main results are given in this paper. The crystal structure for bromomalonic dialdehyde, $C_3H_3O_2Br$, has been solved and a Fourier projection ϱ (xyp) has been calculated for rubidium reductonate, $C_3H_3O_3Rb \cdot H_2O$. Both compounds showed the same general form of the organic molecule. Therefore we expect a similar arrangement for reductone itself and are now attacking the problem of solving its structure from this point of view.

In his book "Reduktone" von Euler [1] has given four possible structure formulae for reductone, $C_3H_4O_3$, namely:

I. 

II. 

III. 

IV. 

where formula IV implies that all oxygen atoms in the molecule are equivalent by resonance. Formula III was originally proposed by Arndt [3]. All these formulae were considered as equally possible from a chemical point of view. A determination of the crystal structure of reductone might, however, show which of them is correct. At Professor von Euler's request we therefore started a crystallographic investigation of reductone.

Single crystals of reductone (kindly supplied by Professor von Euler and Mr. Hasselquist) were investigated by rotation and Weissenberg photographs (*hk*0, *hk*1, *h*0*l*, *h*1*l*, 0*kl*, and 1*kl*) using Cu-*K* radiation. They were found to be of orthorhombic symmetry with the following unit cell dimensions:

$$a = (10.5 \pm 0.1)\ \text{Å}$$
$$b = (10.0 \pm 0.1)\ \text{Å}$$
$$c = (3.6 \pm 0.1)\ \text{Å}$$
$$V = 380\ \text{Å}^3$$

In the photographs the following reflections were systematically absent:

$hk0$ with h = odd
$0kl$ with $k + l$ = odd

which is characteristic of the space groups No. 33 $Pn2_1a$ [4] and No. 62 $Pnma$ [4]. The density, as given in the monograph "Reduktone" [2] is 1.38, indicating that there are 3.59 (~ 4) formula units per unit cell.

From Patterson projections ($P(upw)$, $P(uvp)$ and $P(pvw)$) and "trial and error" calculations we found that the intensities of the reflections could not be explained assuming $Pnma$. The correct space group should then be $Pn2_1a$ which is non-centrosymmetric. The determination of the structure would therefore be rather difficult, as there was no previous knowledge about the spatial arrangement of reductone.

We therefore tried some related compounds, *viz.* reductonates and bromomalonic dialdehyde (kindly supplied by Professor von Euler and Mr. Hasselquist), in the hope of finding crystals which have more favourable symmetry. Table 1 summarizes the crystallographic data obtained from rotation and Weissenberg photographs of these compounds.

Of these compounds there are only two, $C_3H_3O_3Na$ and $C_3H_3O_3Rb \cdot H_2O$, that unambiguously have centres of symmetry. However, it was thought to

Table 1.

Compound	Crystal system	Unit cell dimensions	Characteristic space groups	Formula units per unit cell
Reductone ($C_3H_4O_3$)	Orthorhombic	$a = 10.5$ Å $b = 10.0$ Å $c = 3.6$ Å $V = 380$ Å^3	No. 62 $Pnma$ No. 33 $Pn2_1a$ **	4
Sodium reductonate ($C_3H_3O_3Na$)	Monoclinic	$a = 9.8$ Å $b = 11.6$ Å $c = 3.5$ Å $\beta = 96°$ $V = 397$ Å^3	No. 14 $P2_1/n$ **	4 *
Potassium reductonate ($C_3H_3O_3K$)	Triclinic	$a = 10.0$ Å $b = 11.3$ Å $c = 3.9$ Å $\alpha = 92°$ $\beta = 98°$ $\gamma = 96°$ $V = 440$ Å^3	No. 2 $P\bar{1}$ No. 1 $P1$	4 *
Rubidium reductonate ($C_3H_3O_3Rb \cdot H_2O$)	Monoclinic	$a = 8.3$ Å $b = 18.3$ Å $c = 4.0$ Å $\beta = 93°$ $V = 607$ Å^3	No. 14 $P2_1/a$	4 *
Bromomalonic dialdehyde ($C_3H_3O_3Br$)	Orthorhombic	$a = 6.4$ Å $b = 10.7$ Å $c = 6.3$ Å $V = 431$ Å^3	No. 63 $Cmcm$ No. 40 $C2cm$ ** No. 36 $Cmc2_1$	4 *

* By comparison with reductone.
** Orientation, different from that given in the International Tables.

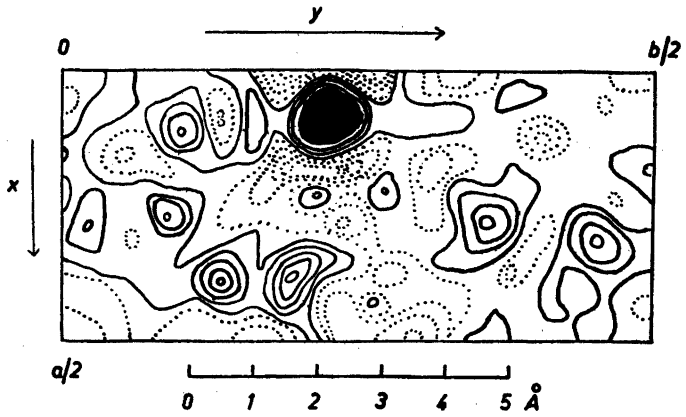


Fig. 1. Electron density projection on (001) of the crystal structure of $C_3H_3O_3Rb \cdot H_2O$.

be easier to find the structure of the rubidium salt, and this was therefore chosen as a suitable subject for the investigation. A full report of the calculations will be published later on; in this paper we are only giving the results obtained.

Fig. 1 shows the final electron density projection $\varrho\,(xyp)$ of $C_3H_3O_3Rb \cdot H_2O$. Only this projection was calculated, as the c axis is very short and the general shape of the molecule should appear rather well resolved there. Fig. 2 shows a diagram of the structure, projected on the xy plane. It is seen that the alternative structures I and IV for reductone are the only ones compatible with the projection, if it is assumed that the reductonate ion has the same configuration as reductone itself. It is also seen that, in the molecules, all three oxygen atoms are situated on the same side of the C—C chain. However, we could not decide between I and IV, as the z parameters of the atoms were not determined

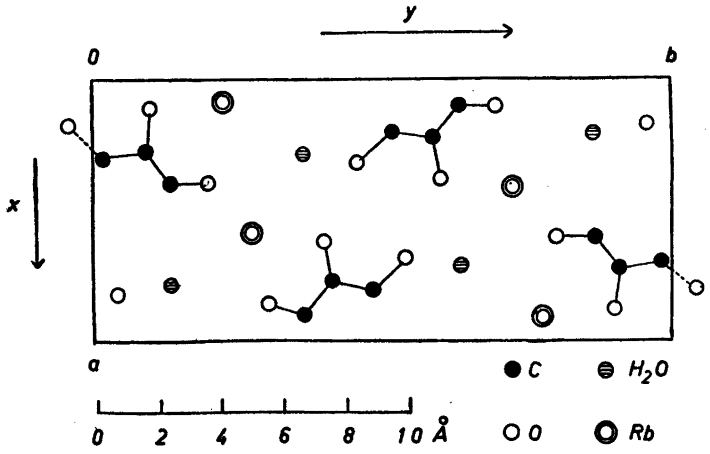


Fig. 2. Diagram of the crystal structure of $C_3H_3O_3Rb \cdot H_2O$ *projected on (001).*

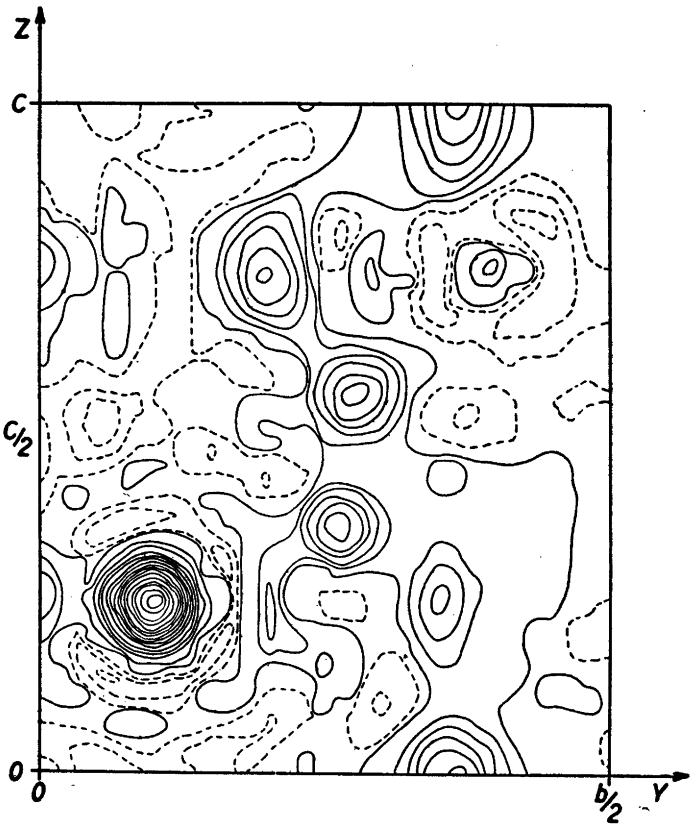


Fig. 3. Electron density in the plane $x = 0$ for bromomalonic dialdehyde.

and consequently the distances and bond angles within the reductonate ion could only be roughly estimated.

To see if this general appearance of the C_3O_3 skeleton was restricted to rubidium reductonate or if it could also be found in other reductone compounds, we investigated the crystal structure of a reductone derivative in which one of the OH groups had been substituted by a bromine atom. Its unit cell, Laue symmetry and characteristic space groups were obtained from single crystal photographs with Cu-K radiation and are given in Table 1. The correct space group was found to be $Cmc2_1$, which is non-centrosymmetric and thus rather unfavourable from our point of view. However, we could show that the C_3O_2Br skeleton in this compound is planar and that it is situated in a plane of symmetry. It was then possible to determine its structure.

Fig. 3 shows the electron density ϱ $(0yz)$ in the plane $x = 0$, which is the plane of the molecule. A diagram of the molecular arrangement is shown in Fig. 4. It is seen that the general arrangement of the C_3O_2Br skeleton is the same as in rubidium reductonate, *i. e.* 2 O + 1 Br are situated on the same side of the C—C chain.

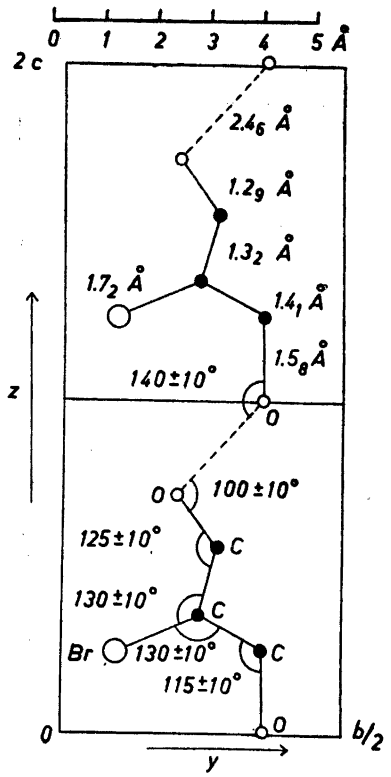


Fig. 4. Diagram of the crystal structure of bromomalonic dialdehyde, giving the bond angles and interatomic distances within a molecule.

The distances and bond angles within a molecule are also given in Fig. 4. Owing to the large scattering power of the bromine atom the accuracy in the determination of the carbon and oxygen parameters is too low to enable us to make a decision between the alternative structures I and IV for reductone. A detailed description of the structure of bromomalonic dialdehyde will appear elsewhere.

As both $C_3H_3O_3Rb \cdot H_2O$ and $C_3H_3O_2Br$ show the same general shape of the organic molecule, we might expect that a similar arrangement would also be found in reductone itself, and we are now attacking the problem of solving its crystal structure from this point of view.

We are much indebted to Professor Hans von Euler for his suggesting the problem and for his kind continuous interest. We also wish to thank Professor Lars Gunnar Sillén for valuable discussions.

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