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On the Crystal Structure of Bromo-malonic Dialdehyde

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The crystal structure of bromo-malonic dialdehyde has been determined. Its unit cell is orthorhombic with the following dimensions: $a = 6.45 \pm 0.05$ Å, $b = 10.70 \pm 0.05$ Å, $c = 6.36 \pm 0.05$ Å. A structure is proposed with atomic positions according to space group No. 36 $Cmc2_1$. The parameters are given on p. 1649. A schematic drawing of the structure is shown in Fig. 10.

The crystals are built up of molecules $C_3H_3O_2Br$ held together by hydrogen bonds in the z direction and with van der Waals' contacts in the x and y directions. The molecules are planar and therefore appear in their enolic form in the structure.

In a series of investigations on hydroxy-malonic dialdehyde ("reductone") and related compounds undertaken by the authors, a crystal structure determination of bromo-malonic dialdehyde was performed. A crystalline sample of this compound was kindly supplied by Professor Hans von Euler and Mr. H. Hasselquist. It had been prepared according to the method described by Dieckmann and Platz.[1]

Single crystals were picked out, and rotation and Weissenberg photographs ($0kl - 3kl$, $hk0 - hk1$, $h0l - h1l$) were taken using CuK radiation. The crystals were found to be of orthorhombic symmetry with the following cell dimensions (determined from the Weissenberg photographs):

$$a = (6.45 \pm 0.05) \text{ Å}$$
$$b = (10.70 \pm 0.05) \text{ Å}$$
$$c = (6.36 \pm 0.05) \text{ Å}$$
$$V = 439 \text{ Å}^3$$

The following reflections are systematically absent:

$$hkl \text{ with } h + k = \text{odd}$$
$$h0l \text{ with } l = \text{odd}$$

This is characteristic of the space groups No. 63 $Cmcm$, No. 40 $C2cm$ * and No. 36 $Cmc2_1$.[2] By comparing the cell volume of bromo-malonic dialdehyde with

* Orientation differing from that given in the *International Tables*.[2]

that of hydroxy-malonic dialdehyde, we found that the two compounds must contain the same number of formula units per unit cell,[3] *e.g.* there must be 4 $C_3H_3O_2Br$ per cell, corresponding to a calculated density of 2.28 g/ml for bromo-malonic dialdehyde.

POSITIONS OF THE BROMINE ATOMS

The fourfold positions available for the four bromine atoms in the unit cell are 4(*a*), 4(*b*), 4(*c*) in *Cmcm*, or 4(*a*), 4(*b*) in *C*2*cm*, or 4(*a*) in *Cmc*2_1. Without making any conditions, we only need to consider the two positions 4(*a*) and 4(*c*) in *Cmcm*.

The Patterson-Harker section *P*(0*vw*) (Fig. 1) was calculated using the $|F|^2$ values obtained from the Weissenberg photographs 0*kl* — 3*kl*. It could be

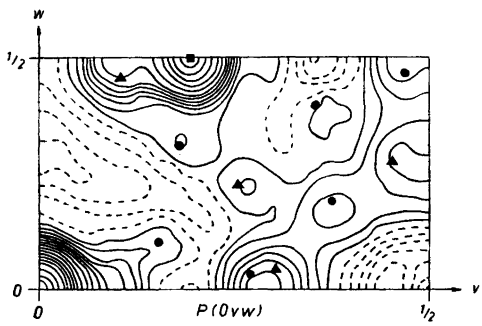

Fig. 1. The Patterson-Harker section *P*(0*vw*). The final positions of the Br-Br (■), Br-O (▲), and Br-C (●) vectors have been indicated.

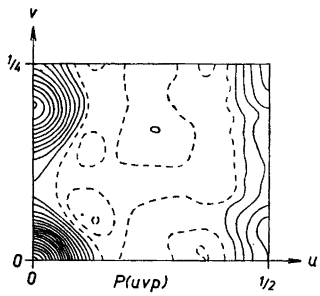

Fig. 2. The Patterson projection *P*(*uvp*).

seen from the large maximum at $v = 0.194$, $w = \frac{1}{2}$ that the correct positions of the bromine atoms should be 4(*c*) with $y = 0.097$, *e.g.*

4 Br in *Cmcm*, 4(*c*) : $(0,0,0;\ \frac{1}{2},\frac{1}{2},0) \pm (0,y,\frac{1}{4})$ with $y = 0.097$

POSITIONS OF THE CARBON AND OXYGEN ATOMS

From the Patterson projection *P*(*uvp*) in Fig. 2, it is seen that all the maxima fall on the lines $u = 0$ and $u = \frac{1}{2}$. Since the x coordinates of the bromine atoms are 0 and $\frac{1}{2}$, the oxygen and carbon atoms must be situated in, or close to, the planes $x = 0$ and $x = \frac{1}{2}$. The molecule should then be planar, or roughly planar, since no distance between neighbouring atoms in the molecule could be as large as $a/2 = 3.23$ Å. The possible point positions for the light atoms should be

$(0,0,0;\ \frac{1}{2},\frac{1}{2},0)\ +$

in $Cmcm$ $4(a)$ $(0,0,0);\ (0,0,\frac{1}{2})$

$4(b)$ $(0,\frac{1}{2},0);\ (0,\frac{1}{2},\frac{1}{2})$

$4(c)$ $\pm\ (0,y,\frac{1}{4})$

$8(f)$ $\pm\ (0,y,z)\ ;\ \pm\ (0,y,\frac{1}{2}-z)$

in $C2cm$ $4(a)$ $(x,0,0);\ (x,0,\frac{1}{2})$ with $x \approx 0$

$4(b)$ $(x,y,\frac{1}{4});\ (x,\bar{y},\frac{3}{4})$ with $x \approx 0$

$8(c)$ $(x,y,z)\ ;\ (x,\bar{y},\bar{z})\ ;\ (x,y,\frac{1}{2}-z);\ (x,\bar{y},\frac{1}{2}+z)$ with $x \approx 0$

in $Cmc2_1$ $4(a)$ $(0,y,z)\ ;\ (0,\bar{y},\frac{1}{2}+z)$

If $x = 0$, all the possible point positions in $C2cm$ become identical with some of those in $Cmcm$. Therefore, it is only necessary to consider the space groups $Cmcm$ and $Cmc2_1$ and, consequently, the projection of the structure on the xy plane should possess a centre of symmetry.

The electron density projection on the xy plane was calculated (Fig. 3), the signs of the F-values being determined by the known positions of the

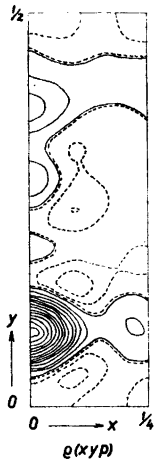

Fig. 3 The electron density projected on the xy plane.

bromine atoms. As is seen, most of the maxima outside the diffraction ring around the bromine atom fall on the line $x = 0$, which is in agreement with the Patterson projection $P(uvp)$ (Fig. 2). The bromine maximum stood out clearly, but some superimposed peaks from $y = 0.18$ to $y = 0.45$ indicating the positions of the light atoms could also be seen. The carbon and oxygen atoms could then be situated in the positions $4(c)$ or $8(f)$ in $Cmcm$, or $4(a)$ in $Cmc2_1$. However, their maxima are not resolved in $\varrho(xyp)$, and we could not determine their y parameters from this projection only.

We also calculated the electron density projection $\varrho(pyz)$ assuming that it had a centre of symmetry, *i.e.* that the correct space group should be $Cmcm$. The results are shown in Fig 4; the bromine atoms are seen clearly. The small maxima that might be ascribed to the light atoms are, however, rather distorted. Moreover, the heights of the peaks are smaller than could be expected.

We suspected then that the correct space group should be $Cmc2_1$, which has no centre of symmetry in the yz projection. Therefore the investigation was continued assuming $Cmc2_1$ since this space group also includes $Cmcm$ as a special case: each position 8(c) in $Cmcm$ corresponding to two positions 4(a) in $Cmc2_1$.

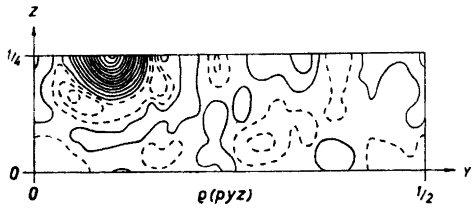

Fig. 4. The electron density projected on the yz plane assuming that the correct space group for bromo-malonic dialdehyde is $Cmcm$.

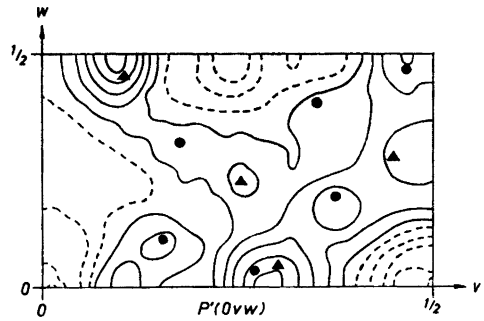

Fig. 5. The Patterson-Harker section $P'(0vw)$ with the Br-Br vectors subtracted. The final Br-O (▲) and Br-C (●) vectors have been indicated.

To get a clear view of the Br—C and Br—O vectors we subtracted the dominating Br—Br vectors from the Patterson section $P(0vw)$. The following function was then calculated:

$$P'(0vw) = \sum_h \sum_k \sum_l |F_{hkl}|_{\mathrm{obs}}^2 \cdot \cos 2\pi(kv + lw) - \sum_h \sum_k \sum_l |F_{hkl}|_{\mathrm{Br}}^2 \cdot \cos 2\pi(kv + lw) \cdot \exp(-2B\sin^2 \Theta/\lambda^2)$$

$|F_{hkl}|_{\mathrm{Br}}$ is the structure factor calculated from the known bromine positions and B is the mean "temperature factor" calculated by the ordinary procedure to be $\approx$ 2.85 Å^2.

Table 1.

Max. No.	$P'(0vw)$			$P(0vw)$		
	v	w	Height (in arbitrary units)	v	w	Height (in arbitrary units)
I	0.097	½	230	0.104	½	230
II	0.290	0	230	0.288	0	170
III	0.470	½	160	0.464	½	120
IV	0 483	0.294	150	0 483	0.283	120
V	0.375	0.164	125	0.382	0.179	80
VI	0.141	0.091	80			
VII	0.108	0	80			
VIII	0.258	0.225	70	(0.266)	(0.225)	(40)
(IX)	(0.183)	(0.292)	(50)	(0.180)	(0.324)	(40)

The functions $P'(0vw)$ is shown in Fig. 5, and Table 1 gives the parameters of the maxima observed in it. The maxima should correspond to the Br—C and Br—O vectors in the unit cell, whereas the C—C, C—O and O—O peaks should be too weak to be observed. The table also contains the corresponding maxima in $P(0vw)$ (Fig. 1).

The peaks corresponding to maxima Nos. VI and VII fall close to the big peak at the origin in $P(0vw)$ and could not be determined there. The vectors VIII in $P(0vw)$ and IX in $P(0vw)$ and $P'(0vw)$ are rather low and have been given only in brackets.

If we consider a carbon or an oxygen atom, A, situated in the point position $4(a)$ in $Cmc2_1$ the Br—A vectors in $P(0vw)$ and $P'(0vw)$ should be

a) $v = \pm(0.097 - y_A)$, $w = \pm(0.250 - z_A)$
b) $v = \pm(0.097 + y_A)$, $w = \pm(0.750 - z_A)$.

For y_A we must consider the whole range $0 \leq y_A \leq 1$, but for z_A we could make the restriction $0 \leq z_A \leq \frac{1}{2}$.

By identifying these vectors at first with the large maximum I and then with the large maximum II, we could ascertain that there are two light atoms in the unit cell having the position

A_1: $y_1 = 0.80$, $z_1 = 0.25$
A_2: $y_2 = 0.37$, $z_2 = 0.25$

These parameters give Br—A vectors at $\pm(0.70;0)$ (A_1), $\pm(0.90;0.50)$ (A_1), $\pm$ $(0.27;0)$ (A_2), and $\pm(0.47;0.50)$ (A_2) corresponding to the observed maxima I, II, and III.

Point positions for the light atoms could also be obtained from IV—IX using one of the two vectors a) and b). The remaining vector was then situated

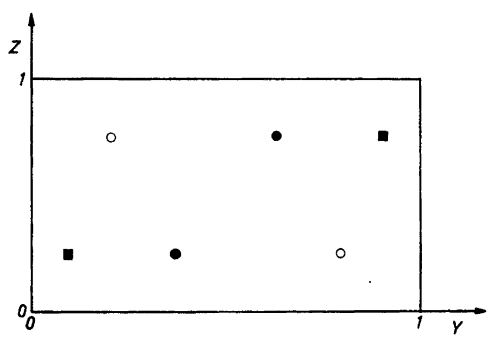

Fig. 6. The positions of the Br (■), A_1 (○), and A_2 (●) atoms in the plane $x = 0$.

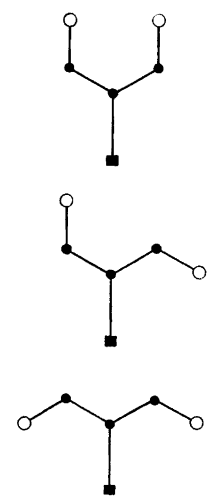

Fig. 7. The three possible configurations of the molecule of bromo-malonic dialdehyde. Br = ■, C = ●, and O = ○.

in positive regions but not at any decided maximum. To get reliable coordinates for the light atoms in question we thought it worth while to introduce geometrical arguments in the discussion.

GEOMETRICAL DISCUSSIONS

From $P(0vw)$ and $P'(0vw)$ we have obtained parameters for the bromine and for two of the light atoms. Their positions have been indicated in Fig. 6, which shows a section through the unit cell at $x = 0$.

Furthermore we might observe that from the mode of preparation [1] it is quite clear that the bromine atom is bonded to the central carbon atom in a C—C—C chain. Knowing that the molecule is planar (*cf.* $P(uvp)$ in Fig. 2) there are now basically only three possible arrangements for it. They are shown in Fig. 7, where the following mean values were used for distances and angles within the molecule, which should appear in its enolic form (*cf.* above):

C — C = 1.4 Å	∠ C — C — C = 120°
C — O = 1.3 Å	∠ Br — C — C = 120°
Br — C = 1.8 Å	∠ O — C — C = 120°

We then tried to fill in the three models from Fig. 7 with the known atomic positions of Br, A_1, and A_2. Only two possibilities were found to be possible,

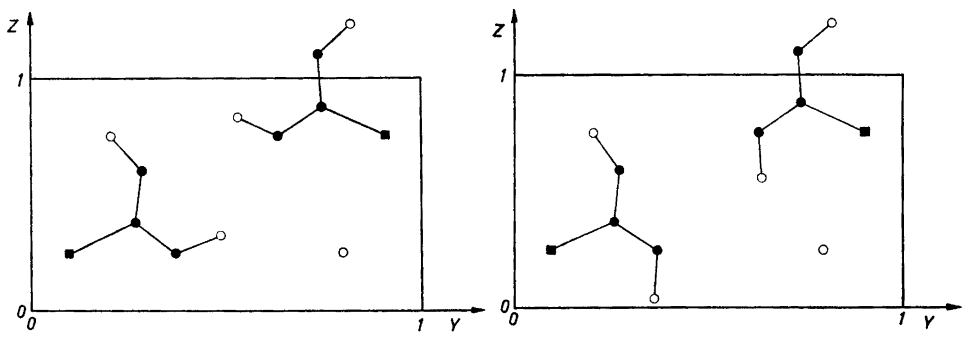

Fig. 8. The two possible arrangements of the molecules of bromo-malonic dialdehyde in the plane $x = 0$. (I to the left, II to the right).

and they are drawn in Fig. 8. The approximate parameters of the C and O atoms would be:

I)	C_1 :	$y = 0.26$	$z = 0.59$	II)	C_1 :	$y = 0.26$	$z = 0.59$
	C_2 :	$y = 0.25$	$z = 0.37$		C_2 :	$y = 0.25$	$z = 0.37$
	C_3 (= A_2) :	$y = 0.37$	$z = 0.25$		C_3 (= A_2) :	$y = 0.37$	$z = 0.25$
	O_1 (= A_1) :	$y = 0.80$	$z = 0.25$		O_1 (= A_1) :	$y = 0.80$	$z = 0.25$
	O_2 :	$y = 0.47$	$z = 0.33$		O_2 :	$y = 0.35$	$z = 0.04$

Table 2.

	I.	*II.*
$Br-C_1$		
	$v = 0.16$ $w = 0.34$	$v = 0.16$ $w = 0.34$
	$v = 0.36$ $w = 0.16$	$v = 0.36$ $w = 0.16$
$Br-C_2$		
	$v = 0.15$ $w = 0.12$	$v = 0.15$ $w = 0.12$
	$v = 0.35$ $w = 0.38$	$v = 0.35$ $w = 0.38$
$Br-C_3$		
	$v = 0.27$ $w = 0$	$v = 0.27$ $w = 0$
	$v = 0.37$ $w = \frac{1}{2}$	$v = 0.47$ $w = \frac{1}{2}$
$Br-O_1$		
	$v = 0.30$ $w = 0$	$v = 0.30$ $w = 0$
	$v = 0.10$ $w = \frac{1}{2}$	$v = 0.10$ $w = \frac{1}{2}$
$Br-O_2$		
	$v = 0.37$ $w = 0.08$	$v = 0.25$ $w = 0.21$
	$v = 0.43$ $w = 0.42$	$v = 0.45$ $w = 0.29$

The parameters of the two cases were then tested against $P'(0vw)$ in Fig. 5. The calculated vectors are shown in Table 2.

As is seen, all the $Br-C_1$, $Br-C_2$, $Br-C_3$, and $Br-O_1$ vectors are situated at well defined peaks in $P'(0vw)$. Only in alternative II are the maxima due to the $Br-O_2$ vectors in agreement with this function. For alternative I, the vectors are certainly situated at positive regions but at the slopes of other maxima explained earlier. Therefore we prefer alternative II since otherwise the distinct peaks IV and VIII in $P'(0vw)$ and $P(0vw)$ (*cf.* Table 1) could not be explained. (The Br—O vectors are the most pronounced of the vectors in $P'(0vw)$).

The Br—C and Br—O vectors calculated according to alternative II have been indicated in Figs. 1 and 5.

REFINEMENT OF THE ATOMIC PARAMETERS

To refine the parameters obtained by the previous considerations, we calculated four successive Fourier sections $\varrho(0yz)$. The phase angles were then determined from atomic parameters, starting with the approximate structure given above for alternative II. In this way $\varrho(0yz)$ as given in Fig. 3 of Ref.[3] was obtained.

To get a further refinement by reducing the diffraction effects as much as possible, we subtracted the bromine atom from $\varrho(0yz)$. In these calculations we used the same temperature factor as earlier at the calculation of $P'(0vw)$ (*cf.* p. 1645). The function was called $\varrho'(0yz)$.

The following table gives the parameters as obtained from $\varrho(0yz)$ and $\varrho'(0yz)$:

4 Br in $Cmc2_1$: 4(a) with $y = 0.098 \pm 0.002$, $z = 0.250$
4 C_1 » » » $y = 0.279 \pm 0.005$, $z = 0.564 \pm 0.005$
4 C_2 » » » $y = 0.262 \pm 0.005$, $z = 0.360 \pm 0.005$
4 C_3 » » » $y = 0.360 \pm 0.005$, $z = 0.258 \pm 0.005$
4 O_1 » » » $y = 0.799 \pm 0.005$, $z = 0.220 \pm 0.005$
4 O_2 » » » $y = 0.357 \pm 0.005$, $z = 0.006 \pm 0.005$

Finally, we refined these parameters with a least-squares program for FACIT EDB.[4] The R value according to Booth[5] then dropped from 0.221 to 0.155 after 7 cycles of refinement (absent reflections not included). This must be considered as satisfactory for a structure without a centre of symmetry, when no correction has been made for specimen absorption, *cf.* Table 3.

Thus the following structure is proposed for bromo-malonic dialdehyde; Space group: $Cmc2_1$, 4 formula units per unit cell.

4 Br in 4(a) with $y = 0.0981$, $z = 0.2500$
4 C_1 » 4(a) » $y = 0.275_3$, $z = 0.558_5$
4 C_2 » 4(a) » $y = 0.252_8$, $z = 0.354_4$
4 C_3 » 4(a) » $y = 0.369_2$, $z = 0.283_5$
4 O_1 » 4(a) » $y = 0.796_3$, $z = 0.205_6$
4 O_2 » 4(a) » $y = 0.352_1$, $z = 0.240_1$

The standard deviations in the coordinates and the isotropic temperature factors are

for Br: $\sigma_y = \pm 0.0007$		$B = 2.00$ Å^2
for C_1: $\sigma_y = \pm 0.006$	$\sigma_z = \pm 0.011$	$B = 2.04$ Å^2
for C_2: $\sigma_y = \pm 0.004$	$\sigma_z = \pm 0.008$	$B = 0.03$ Å^2
for C_3: $\sigma_y = \pm 0.006$	$\sigma_z = \pm 0.011$	$B = 2.05$ Å^2
for O_1: $\sigma_y = \pm 0.005$	$\sigma_z = \pm 0.007$	$B = 2.20$ Å^2
for O_2: $\sigma_y = \pm 0.006$	$\sigma_z = \pm 0.013$	$B = 4.44$ Å^2

The temperature factors for C_2 and O_2 deviate from each other and from those of the other atoms. This difference can, however, probably not be considered as significant since the values of the temperature factors are strongly influenced by the absorption.

DISCUSSION OF THE STRUCTURE

The bond distances and bond angles between the atoms in the molecule are shown in Fig. 9. (In the preliminary paper[3] all distances were calculated with the parameters obtained from $\varrho(0yz)$. Owing to a miscalculation the distances Br—C_2 and C_2—C_3 were there given as 1.72 Å and 1.41 Å, whereas they should have been 1.91 Å and 1.16 Å.)

As is seen from the figure the distances C_1—C_2 and C_2—C_3 are shorter and C_3—O_2 longer than could be expected. However, with the heavy bromine atom and the low symmetry of the structure, the accuracy of interatomic distances including light atoms is rather low. The standard deviation of C—C and C—O distances is ± 0.05 Å, which means that the statistical error (corresponding to a reliability of 95 %) is ± 0.12 Å.

Table 3. Observed and calculated structure factors *h k l* for bromo-malonic dialdehyde.

h	*k*	*l*	F_{obs}	$\|F_{calc}\|$	*h*	*k*	*l*	F_{obs}	$\|F_{calc}\|$
0	0	2	105.7	114.1	1	5	4	46.2	49.9
0	0	4	79.6	84.1	1	5	6	31.2	36.8
0	0	6	50.2	42.2	1	7	0	41.7	43.3
0	0	8	20.4	23.9	1	7	1	66.7	74.7
0	2	0	25.1	32.7	1	7	2	34.1	33.1
0	2	1	85.8	78.5	1	7	3	41.7	53.9
0	2	2	38.3	29.3	1	7	4	19.6	26.7
0	2	3	64.9	69.6	1	7	5	24.0	27.5
0	2	4	29.0	23.8	1	9	0	44.0	35.1
0	2	5	56.2	46.4	1	9	1	27.8	16.6
0	2	6	25.1	22.2	1	9	2	46.2	36.5
0	2	7	38.3	32.6	1	9	3	27.8	25.8
0	4	0	66.7	74.1	1	9	4	34.1	28.9
0	4	1	52.3	80.1	1	9	5	24.0	23.8
0	4	2	52.3	63.1	1	9	6	13.9	16.3
0	4	3	64.9	57.5	1	11	0	60.5	43.5
0	4	4	64.9	62.4	1	11	2	36.7	29.6
0	4	5	41.1	32.0	1	11	3	19.6	17.0
0	4	6	32.5	34.9	1	11	4	27.8	26.5
0	4	7	14.5	17.6	1	13	1	27.8	30.8
0	6	0	68.1	69.0	2	0	2	115.6	97.8
0	6	1	50.4	43.5	2	0	4	70.8	74.1
0	6	2	48.2	62.9	2	0	6	42.9	38.8
0	6	3	45.9	43.6	2	2	0	25.8	20.9
0	6	4	45.9	33.4	2	2	1	59.2	68.1
0	6	5	14.5	17.9	2	2	2	31.6	25.1
0	6	6	20.4	26.6	2	2	3	56.3	62.1
0	6	7	14.6	15.1	2	2	4	22.3	22.1
0	8	0	29.0	25.4	2	2	5	44.7	42.6
0	8	1	72.7	55.4	2	2	6	25.8	20.6
0	8	3	48.2	40.5	2	2	7	25.8	30.0
0	8	5	41.1	39.4	2	4	0	57.7	63.6
0	10	0	50.2	38.1	2	4	1	64.7	68.5
0	10	2	50.2	45.9	2	4	2	54.8	56.4
0	10	4	41.1	37.5	2	4	3	46.6	51.2
0	12	0	14.5	12.7	2	4	4	57.7	56.4
0	12	1	41.1	28.7	2	4	5	34.1	29.0
0	12	2	14.5	12.0	2	4	6	22.3	32.7
0	12	3	32.5	25.9	2	6	0	54.8	62.5
1	1	0	60.7	75.4	2	6	1	48.3	38.5
1	1	1	88.1	71.0	2	6	2	57.7	56.3
1	1	2	109.6	92.9	2	6	3	34.1	38.8
1	1	3	59.0	55.1	2	6	4	22.3	30.7
1	1	4	59.0	51.1	2	6	6	22.3	24.4
1	1	5	27.8	23.0	2	8	0	25.8	23.2
1	1	6	36.7	34.0	2	8	1	57.7	50.3
1	1	7	13.9	20.5	2	8	3	50.0	37.3
1	3	1	100.2	118.8	2	8	5	38.8	36.4
1	3	2	57.3	47.7	2	10	0	50.0	34.7
1	3	3	89.1	80.9	2	10	2	48.3	42.0
1	3	4	27.8	22.0	2	10	4	34.1	35.0
1	3	5	76.3	64.8	2	12	1	28.9	26.7
1	3	7	24.0	27.8	3	1	0	63.3	58.3
1	5	0	68.2	71.0	3	1	1	53.0	50.4
1	5	1	27.8	26.2	3	1	3	63.1	42.5
1	5	2	46.2	56.3	3	1	4	59.2	42.3

h k l	F_{obs}	$\lvert F_{calc}\rvert$	h k l	F_{obs}	$\lvert F_{calc}\rvert$
3 1 6	26.5	29.4	3 7 1	76.6	61.3
3 3 2	34.1	34.0	3 7 2	40.4	27.6
3 3 3	68.5	65.1	3 7 3	53.0	44.7
3 3 5	48.4	54.9	3 7 4	26.5	22.2
3 5 0	61.3	58.1	3 7 5	21.5	22.8
3 5 1	30.6	17.9	3 9 0	26.5	28.9
3 5 2	68.5	47.0	3 9 2	26.5	30.9
3 5 4	34.3	41.8	3 9 3	15.3	22.3
3 5 6	15.3	31.4	3 9 4	15.3	24.7
3 7 0	37.5	33.3	3 11 0	26.5	37.1

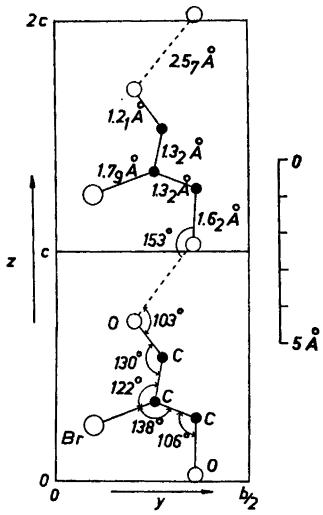

Fig. 9. Bond distances and bond angles within the molecule of bromo-malonic dialdehyde.

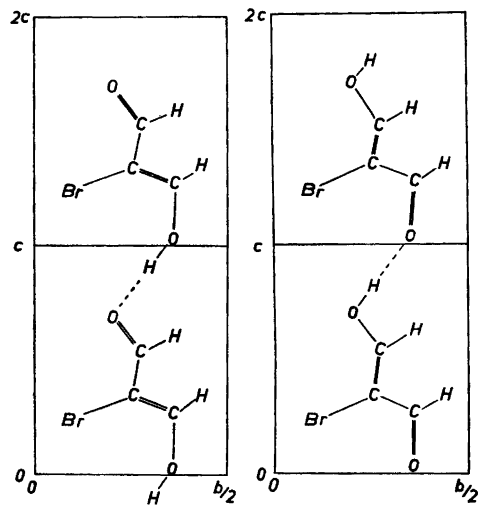

Fig. 10. The bond systems within the molecule of bromo-malonic dialdehyde.

However, irrespective of the actual positions of the light atoms, we could by $P(uvp)$ ascertain that the molecule is planar. This should imply that the molecules of bromo-malonic dialdehyde in the crystals appear in their enolic form. The enolic hydrogen atoms should then form hydrogen bonds between O_1 and O_2 atoms belonging to different molecules. The crystal thus contains strings of molecules along the z axis. In the x and y directions the molecules form van der Waals' contacts with each other.

The molecular strings are shown in Fig. 10. The bond system may then either be as given in Fig. 10a or Fig. 10b, or we might have a resonance structure of the two systems. In the latter case the distances C_1-C_2 and C_2-C_3 should be equal and C_1-O_1 and C_3-O_2 should also be equivalent. However, as said above, the accuracy of our determination is too low to enable us with certainty to decide between the two possibilities.

According to Grard,[6] who investigated the equilibria between the enolic and keto form of bromo-malonic dialdehyde in solutions, the solid form has the enolic structure. This was shown by dissolving crystals of $BrC_3H_3O_2$ in a suitable solvent at temperatures ranging from $-33°C$ to $-78°C$ and immediately indicating the enolic form by the colour it forms with iron(III) chloride. His observations are thus confirmed by the results of our X-ray analysis.

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