[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION][1]

The Crystal Structure of Metaldehyde

BY LINUS PAULING AND D. C. CARPENTER

Metaldehyde is described by Groth[2] as crystallizing in tetragonal needles with the axial ratio $a:c = 1:0.2761$. A preliminary x-ray investigation of the crystal was carried out by Hassel and Mark,[3] who determined the size of the unit of structure and reported the space group to be either C_{4v}^9 or C_4^5, the location of the atoms in the unit not being found. We have reinvestigated this crystal, finding the space group to be C_4^5—I_4, and making a complete determination of the atomic arrangement. The unit of structure contains two molecules of the tetramer, $(CH_3CHO)_4$, each molecule consisting of an eight-membered –O–C–O–C– ring with H and CH_3 attached to each carbon atom of the ring. The interatomic distances and bond angles were found to be the same as in paraldehyde,[4] $(CH_3CHO)_3$.

The Unit of Structure and Space-Group Symmetry

Metaldehyde was recrystallized from absolute alcohol by the method of slow cooling, and dried on a Büchner funnel. The crystals were in the form of needles with dimensions about 0.5 × 0.5 × 20 mm. Laue photographs taken with crystal orientations differing only by rotation through a multiple of 90° about the needle axis were found to be identical, verifying the tetragonal symmetry of the crystal. Several Laue photographs were prepared with the incident beam in the plane normal to the *c*-axis. Each of these photographs showed a horizontal plane of symmetry, but none showed a vertical plane of symmetry (photographs with the incident beam parallel to [100] and [110] of the unit of structure, among others, were prepared). Consequently the point-group symmetry of the crystal cannot be that of D_{4h}, D_4, C_{4v}, or D_{2d}, but must be instead that of C_{4h}, C_4, or S_4. Of these C_{4h} and S_4 are eliminated by our observation of a strong pyroelectric effect along the needle axis, the liquid-air method[5] being used. The crystal is thus definitely allocated[6] to the point group C_4.

The pronounced prismatic cleavage of the crystal was strikingly shown by its behavior on cooling with liquid air, the strains resulting from temperature gradients during cooling causing each crystal to separate into a large number of fibers.

Oscillation and rotation photographs were prepared with [001] as axis of rotation, Mo $K\alpha$ radiation filtered through zirconia being used. These led to the values $a_0 = 10.40$ Å. and $c_0 = 4.11$ Å. for the edges of the unit of structure, in approximate agreement with the values of Hassel and Mark, $a_0 = 10.34$ Å., $c_0 = 4.10$ Å. All of the reflections on a complete set of oscillation photographs about [001] and on a completely-indexed Laue photograph were found to be compatible with this unit (the axes of which are 45° from those used by Groth). No reflections (*hkl*) with $h + k + l$ odd were observed; the lattice is accordingly body-centered. Of the body-centered space groups isomorphous with C_4 all but C_4^5 are eliminated by the observation that all types of prism planes give reflections; C_4^5—I_4 is accordingly the space group of the crystal.

The Atomic Arrangement

There are 8 CH_3CHO in the unit of structure (density calculated, 1.31; observed, 1.27). As pointed out by Hassel and Mark, these are formally combined by the four-fold axes into polymers $(CH_3CHO)_4$. It seems highly probable that these groups have a structure closely similar to that of paraldehyde, each oxygen atom being attached to two carbon atoms by single bonds. We made the preliminary assumptions that the interatomic distances have the values C—C = 1.54 Å. and C—O = 1.43 Å. and the bond angles all have the tetrahedral value 109° 28′, as in paraldehyde. There are only two configurations of the molecule compatible with these assumptions. In one of these the four methyl groups are directed along the *c*-axis, and in the other they

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[2] P. Groth, "Chemische Krystallographie," Vol. III, p. 47.

[3] O. Hassel and H. Mark, *Z. physik. Chem.*, **111**, 357 (1924).

[4] D. C. Carpenter and L. O. Brockway, THIS JOURNAL, **58**, 1270 (1936).

[5] A. J. P. Martin, *Mineral. Mag.*, **22**, 519 (1931).

[6] Hassel and Mark prepared only complete rotation photographs, and so were unable to distinguish between the point groups C_4 and C_{4v} and the space groups C_4^5 and C_{4v}^9.

are directed outward from the center of the ring. (The four-fold axis eliminates intermediate configurations.) The first of these is at once ruled out by the consideration of interatomic distances in the *c* direction, in which molecules are only 4.11 Å. apart. The metaldehyde molecule accordingly has the configuration shown in Fig. 1. The atomic arrangement is then completely determined by one additional parameter φ, corresponding to rotation of the molecule about the four-fold axis through its center (see Fig. 6).

The intensity data used in evaluating this parameter and in verifying the assumed values for the others were obtained in the following way. Using the same crystal and the same exposure, oscillation photographs about [001] were prepared with the incident beam covering the ranges 0–15, 15–30, 30–45, 45–60, 60–75, 75–90 and 90–105° with the axis [100] (the first and last photographs being identical). Microphotometer records of the equatorial reflections were then prepared with a Krüss microphotometer, and interpreted in terms of intensities with the aid of similar records of a set of 0–15° photographs taken with different exposure times. The intensity values so obtained for thirty prismatic forms are given in Table I, together with relative values of F calculated from them by use of the equation

$$F_{hkl} = \left(\frac{2I_{hkl}\sin 2\vartheta}{1+\cos^2 2\vartheta}\right)^{1/2} \quad (1)$$

in which I_{hkl} is the observed intensity and ϑ the angle of reflection.

TABLE I

EQUATORIAL REFLECTIONS FOR METALDEHYDE

hkl	Intensity of reflection Obsd.	Intensity of reflection Calcd.	*F*, obsd.
110	275	230	5.0
200	33	18	2.1
220	78	62	−3.8
130	60	74	−4.1
310	13	0	1.6
400	51	63	−3.8
330	36	32	−3.2
240	11	9	1.9
420	46	57	−3.8
150	19	8	−2.7
510	25	18	−3.0
350	13	8	2.4
600	9	3	−2.0
260	8	9	1.9
620	20	21	3.0
550	9	11	2.2
710	10	7	2.3
170	9	6	2.2
460	8	5	−2.0
370	5.6	5	1.8
730	7	7	2.0
800	4	2	−1.6
820	8	10	2.2
750	7	6	−2.2
480	10	14	2.6
190	9	10	−2.6
930	8	14	2.5
680	8	1	−2.5
860	3.6	3	−1.7
2.10.0	9	13	−2.8

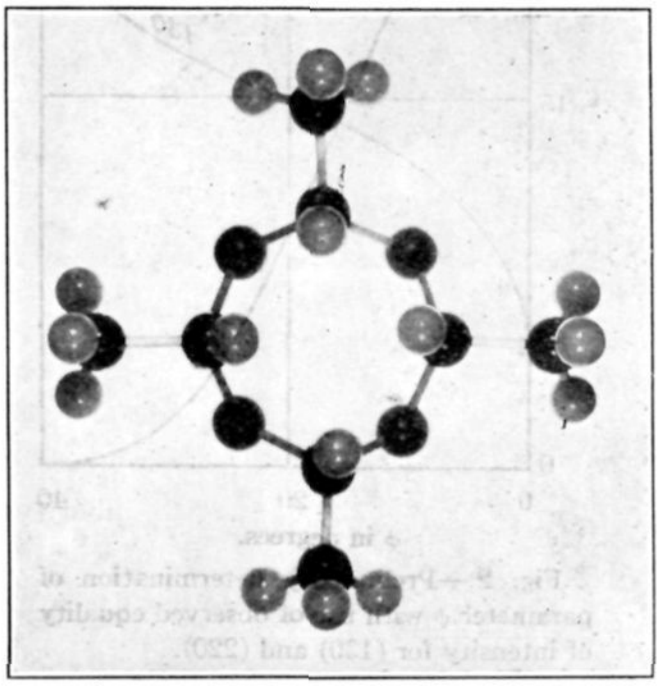

Fig. 1.—Configuration of metaldehyde molecule.

The observed intensity values were compared with intensity values calculated by replacing F_{hkl} in Equation 1 by

$$F_{hkl} = \Sigma_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (2)$$

Pauling–Sherman *f*-values[7] being used for f_j, and the coördinates $x_j\ y_j\ z_j$ being calculated as a function of φ for the molecular model described above.

The observed approximate equality in intensity of reflection from {130} and {220} limits φ to values in the neighborhood of 16° (Fig. 2). The comparisons of {150} with {510} ($F_{150}/F_{510} = 0.87$) and {260} with {620} ($F_{260}/F_{620} = 0.63$) shown in Fig. 3, as well as other similar comparisons, lead to values near 16° 40′ for φ.

In order to investigate the possibility that the molecular parameter values differ slightly from those assumed, a two-dimensional Fourier analysis of the distribution of scattering power in the crystal projected on the plane (001) was made, using the equation

$$\rho(x,y) = \text{constant}\ \Sigma_h\Sigma_k\ F_{hk0}\cos 2\pi(hx + ky) \quad (3)$$

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[7] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

the sum being extended over all planes ($hk0$) for which reflections were observed. The experimental F-values for the corresponding forms are given in Table I, together with their assumed algebraic signs, these being as calculated for $\varphi = 16° 40'$ and the original molecular model. The resultant distribution function $\rho(x,y)$ is shown in Fig. 4. It is seen that the function corresponds to well-defined molecules of the type described. In order to obtain some information as to the reliability of the distribution function and especially as to the effect of breaking off the Fourier series, the calculations were repeated three times: first, with use of the F values of Table I except for omission of the form {2.10.0}; second, the same except for omission also of the forms {860} and {680}; and third, with inclusion of all forms, the F-values of Table I being multiplied by a factor decreasing from 1 for forms with $\sin \vartheta/\lambda$ less than 0.75 to 0.20 for the forms with largest $\sin \vartheta/\lambda$, in order to force a gradual termination of the series. The atomic coördinates given by the four treatments deviate from their average values by a mean of 0.002, or 0.02 Å. The average values of the atomic coördinates given by the four treatments are

$\mathrm{O}:\ x = 0.074,\ y = 0.143$
$\mathrm{C_1}:\ x_1 = 0.149,\ y_1 = 0.050$
$\mathrm{C_2}:\ x_2 = 0.291,\ y_2 = 0.091$

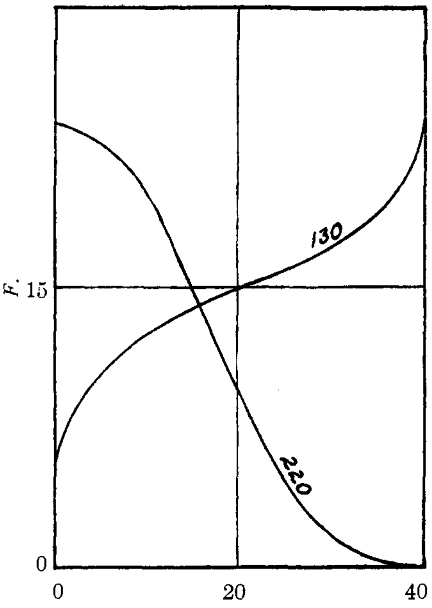


Fig. 2.—Preliminary determination of parameter ϕ with use of observed equality of intensity for (130) and (220).

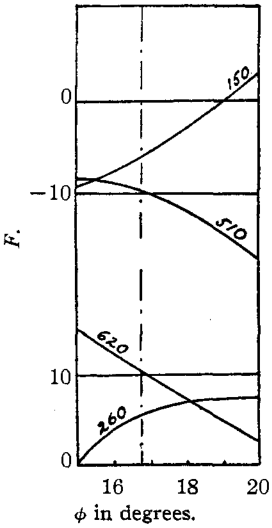


Fig. 3.—Determination of parameter ϕ.

These correspond to the projected interatomic distances C–O = 1.24 Å. and 1.28 Å. and C–C = 1.53 Å. (all ± 0.03 Å.), in excellent agreement with the originally assumed values C–O = 1.27 Å. and C–C = 1.54 Å.

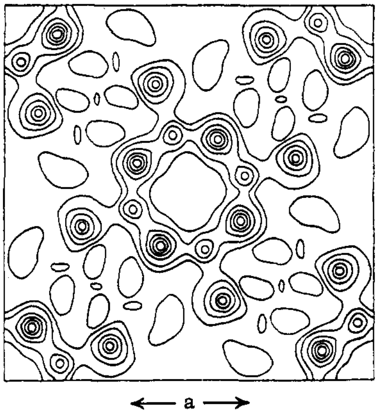


Fig. 4.—Distribution function $\rho(x,y)$ for metaldehyde (projection on (100)).

The value of φ given by the distribution function is about 17° 30′, and that given by our original treatment is 16° 40′. Inasmuch as the projected interatomic distances agree with those originally assumed to within 0.02 Å., we shall accept the original molecular model as verified by experiment, and take for φ the average of the two determined values, 17° 0′ ± 30′. The atomic arrangement of the crystal is then described by the parameters

$\mathrm{O}:\ x = 0.074,\ y = 0.140,\ z = -0.163$
$\mathrm{C_1}:\ x_1 = 0.151,\ y_1 = 0.047,\ z_1 = 0.000$
$\mathrm{C_2}:\ x_2 = 0.293,\ y_2 = 0.090,\ z_2 = 0.000$

The values of the z parameters are those corresponding to the original model. Verification of these values is provided by the general agreement of calculated and visually estimated observed intensities of layer-line reflections (Table II).

TABLE II

LAYER-LINE REFLECTIONS FOR METALDEHYDE

First layer line	Intensity		Second layer line	Intensity	
hkl	Obsd.	Calcd.	*hkl*	Obsd.	Calcd.
121	40	71	222	10	10
211	10	10	312	60	50
301	9	8	402	15	17
231	18	17	142	25	27
321	18	32	332	7	5
141	10	12	242	8	5
411	40	55	422	27	24
341	18	8	512	20	22
431	40	55	152	6	8
501	46	39	352	15	18
251	20	15	532	8	4
521	15	17	602	4	1
161	0	2	622	8	17
611	9	10	262	9	8
451	9	13	552	3	2
361	6	15	192	4	1
631	5	7	772	3	1
701	0	1			
271	6	8			
721	15	23			
471	5	9			
901	6	9			
921	9	7			
491	2	4			
1.10.1	3	6			

Description and Discussion of the Structure

The crystal of metaldehyde is found to consist of molecules with the configuration shown in Fig. 1 arranged as shown in Fig. 5. The single-bond distances 1.43 Å. (C–O) and 1.54 Å. (C–C) and the tetrahedral bond angle 109° 28′ for both carbon and oxygen are verified within the accuracy of the investigation (±0.03 Å. and ±3°, respectively). The molecules are piled in columns along the *c*-axis. We expect the forces between adjacent molecules in a column to be large, because of the apposition of the negatively charged face of each molecule (formed by the four oxygen atoms of the staggered ring) to the positively charged face of the next molecule (formed by the hydrogen atoms attached to the ring carbon atoms).[8] On the other hand, the forces between columns are small, the molecules in one column presenting their relatively inactive methyl groups to those of the surrounding columns. In consequence the crystal cleaves easily into fibers.

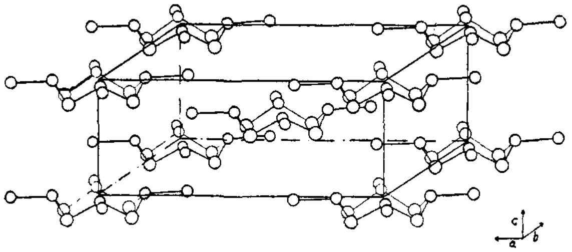
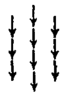


Fig. 5.—Arrangement of metaldehyde molecules in the unit cell.

It is interesting that the translation by $c_0/2$ of each column relative to its four nearest neighbors brings the molecule dipole into an electrostatically stabilized configuration in which the positive poles of one column are closer to the negative poles of neighboring columns than to their positive poles.



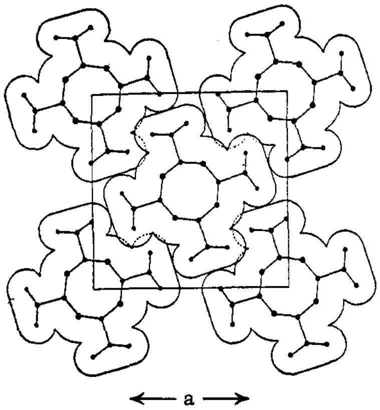


Fig. 6.—Packing diagram of metaldehyde molecules in the unit cell.

The packing of the molecules is shown in Fig. 6, drawn with packing radii of 1.0 Å. for hydrogen and 1.5 Å. for oxygen, the C–H distance being taken as 1.06 Å. and the methyl groups being assumed to rotate about the C–C bonds. Each methyl group is approximately equidistant from eight methyl groups of surrounding molecules, there being two at a distance of 3.90 Å., four at 4.03 Å., and two at 4.11 Å. (directly above and below), corresponding to a packing radius for the methyl group of 2.01 ± 0.06 Å. The variation observed in the methyl–methyl distances is not accidental; it is clearly the result of the shape of the methyl group. Interatomic distances between hydrogen atoms are found to be very closely equal, showing that a hydrogen atom attached to carbon can be assigned a packing radius and con-

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(8) The parallel dipole moments of the molecules give rise to the observed pyroelectric effect.

sidered to behave as a sphere (so far as contacts in directions away from the carbon atom are concerned). This point of view has been especially emphasized by Mack[9] in connection with his interesting work on the packing of organic molecules. In metaldehyde, assuming rotation of methyl groups, the hydrogen–hydrogen distances corresponding to the methyl–methyl contacts mentioned above are 2.16 Å. (two), 2.15 Å. (four), and 2.11 Å. (two), giving for hydrogen the packing radius 1.07 ± 0.01 Å.

There may also be contact between oxygen and hydrogen atoms. Each oxygen atom is 2.68 Å. from two hydrogen atoms attached to ring carbons of the molecule below, and 2.70 Å. from a hydrogen atom in an adjacent column. These distances correspond to a packing radius for oxygen of 1.6 Å., which is somewhat larger than the ionic crystal radius 1.40 Å.

It is interesting to note that metaldehyde, like paraldehyde, contains no aldehyde groups, the oxygen atoms being ethereal in type.

We are indebted to Dr. S. Weinbaum for much assistance in the course of this investigation.

Summary

The tetragonal crystal metaldehyde is shown by x-ray examination to have a body-centered unit of structure with $a_0 = 10.40$ Å. and $c_0 = 4.11$ Å., containing two molecules of the tetramer, $(CH_3CHO)_4$. The atomic arrangement involves all atoms in general positions of the space group C_4^5–I_4, with the following parameter values: oxygen, $x = 0.074$, $y = 0.140$, $z = -0.163$; ring carbon, $x_1 = 0.151$, $y_1 = 0.047$, $z_1 = 0.000$; methyl carbon, $x_2 = 0.293$, $y_2 = 0.090$, $z_2 = 0.000$. The molecule contains an eight-membered –C–O–C– ring, with the carbon–oxygen distance 1.43 ± 0.03 Å., and methyl groups attached to ring carbon atoms, with the carbon–carbon distance 1.54 ± 0.03 Å. The bond angles of oxygen and carbon have the value 109.5 ± 3°. A discussion of the packing of the molecules and of the packing radii of the methyl group and hydrogen atom is given.

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[9] E. Mack, Jr., THIS JOURNAL, **54**, 2141 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE B. F. GOODRICH COMPANY]

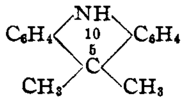
The Preparation of Acridanes by the Grignard Reaction

BY W. L. SEMON AND DAVID CRAIG

In previous publications[1a] *o-t*-butyldiphenylamine (III) has been identified as one of the two main products from the reaction of methylmagnesium iodide with methyl N-phenylanthranilate (I). The other product[1b] is shown here to be 5,5-dimethylacridane (IV) formed as indicated in reactions 1 and 3 by the dehydration of *o*-anilinophenyldimethylcarbinol (II).

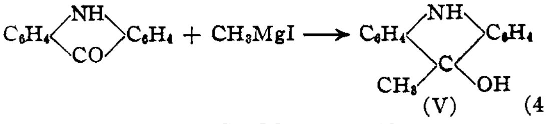
$$C_6H_5—NH—C_6H_4\text{-}o—CO—OCH_3\ \text{(I)} + CH_3MgI \longrightarrow C_6H_5—NH—C_6H_4\text{-}o—C(OH)(CH_3)_2 \quad \text{(II)} \quad (1)$$

$$\text{(II)} + CH_3MgI \longrightarrow C_6H_5—NH—C_6H_4\text{-}o—C(CH_3)_3 \quad \text{(III)} \quad (2)$$



$$\text{(II)} \quad -H_2O \longrightarrow C_6H_4\overset{NH}{\underset{CH_3\diagup C \diagdown CH_3}{<\ {}^{10}_{5}\ >}}C_6H_4 \quad \text{(IV)} \quad (3)$$

The acridane (IV) has not previously been described and identified although some may have been contained in the material isolated following the action of sodium on commercial acridine.[2] The 5,5-diphenylacridane[3] and certain amino derivatives of acridane[4] have been prepared by reactions similar to the ones used here. While this method of formation is strong evidence for the accuracy of the formula assigned to IV, it is not beyond the realm of possibility that the product might have been *o*-isopropenyldiphenylamine. A more conclusive proof for the presence of an *o,o'*-carbon bridge was found in the synthesis of IV from compounds such as acridone or 5-methylacridine already containing the heterocyclic nucleus. This was accomplished by reactions 4 and 6



$$C_6H_4\overset{NH}{\underset{CO}{<\ >}}C_6H_4 + CH_3MgI \longrightarrow C_6H_4\overset{NH}{\underset{CH_3\diagup C \diagdown OH}{<\ >}}C_6H_4 \quad \text{(V)} \quad (4)$$

$$V + CH_3MgI \longrightarrow IV$$

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[1] (a) Craig, THIS JOURNAL, **57**, 195 (1935); (b) Semon, British Patent 405,797, Jan. 30, 1933, and French Patent 750,474, May 29, 1933.

[2] Bergmann and Blum-Bergmann, *Ber.*, **63**, 759 (1930).

[3] (a) Baeyer and Villiger, *ibid.*, **37**, 3191 (1904); (b) Gilman, THIS JOURNAL, **51**, 2260 (1929); (c) Kehrmann, and Tschui, *Helv. Chim. Acta*, **8**, 28 (1925).

[4] Goldstein and others, *ibid.*, **11**, 486 (1928), and previous papers especially *ibid.*, **11**, 478 (1928).