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The Crystal and Molecular Structure of Diketene

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The structure of diketene has been a matter of debate since the compound was first prepared in 1907. This study shows that the structure in the solid state is 3-buteno-β-lactone.

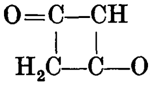
Diketene crystallizes in the monoclinic system. The space group is $P2_1/c$ and there are four molecules per unit cell. Unit cell dimensions are $a = 4{\cdot}00$, $b = 20{\cdot}67$, $c = 5{\cdot}11$ Å; $\beta = 101{\cdot}8°$.

Introduction

A year after diketene was first prepared, the acetylketene structure,

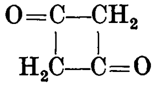
$$CH_3COCH{=}C{=}O\ , \qquad \text{(I)}$$

was postulated for it (Chick & Wilsmore, 1908). This postulate was based on the reactions of diketene with water to form acetoacetic acid and with aniline to form acetoacetanilide. Soon after (Staudinger & Bereza, 1909), objections were raised to this structure, and the monoenolic form of cyclobutadione-1,3,



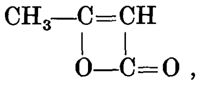
(II)

was proposed. Later, the reaction between bromine and diketene to give the γ-bromo acid bromide was used as evidence for the 1,3 cyclobutadione structure,



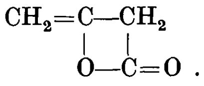
(III)

(Chick & Wilsmore, 1910). Still another structure, 2-buteno-β-lactone,



(IV)

was proposed as a possibility when the product of an ozonolysis reaction was reported to be pyruvic aldehyde (Hurd & Williams, 1936). A. L. Wilson (see Boese, 1940) advanced a fifth structure, 3-buteno-β-lactone,



(V)

This structure was capable of explaining the chemistry of diketene satisfactorily, with the exception of the results obtained above for the ozonolysis reaction.

Since that time, an ultra-violet study (Calvin, Magel & Hurd, 1941) has been interpreted as fovoring IV; a Raman study (Taufen & Murray, 1945) as favoring V or I; an infra-red study (Whiffen & Thompson, 1946), which considered the Raman data as well, as favoring IV, V or a mixture—some preference being expressed for V; and an electron-diffraction study (Bauer, Bregman & Wrightson, to be published) as favoring IV or V without being able to distinguish between them. Another infra-red study (Miller & Koch, 1948) provided good evidence that diketene was an equilibrium mixture, presumably of IV and V, though perhaps containing some III.

In view of the evidence for the 3-buteno-β-lactone structure (V), and the apparently strong contradiction to it provided by the ozonolysis reaction, this reaction was reinvestigated (Hurd & Blanchard, 1950). The previous conclusion that pyruvic aldehyde was formed was shown to be in error, the chief products actually being formaldehyde and malonic acid. These would be expected from V. The authors pointed out, however, that their evidence did not prove that diketene was homogeneously represented by this structure. The X-ray investigation was undertaken to find an unequivocal answer—at least for the solid-phase problem —by an independent method.

Experimental

Since diketene freezes at —6·5 °C., the substance lent itself readily to the techniques already described (Abrahams, Collin, Lipscomb & Reed, 1950) for growing and photographing crystals of substances which are liquids at room temperature. The method consists essentially in sealing off under vacuum a sample of the liquid in a glass capillary, mounting this capillary on a goniometer head, and growing a crystal by controlling the temperature of a stream of cold air directed on the capillary. Zero-level Buerger precession photographs were obtained of five different zones using Mo $K\alpha$ radiation; for each of four of these zones three intensity pictures were taken—one each of 40 min., 2 hr., and 6 hr. exposure. The pictures were taken individually, rather than in packs of three, to prevent spot splitting. First-level photographs were also taken but these were of too poor a quality for intensity work and were used only to establish n-level symmetries for the determination of the space group. Precession angles for the above were between 22·5° and 24·5°. A standard strip of intensity spots made from a reflection of the diketene crystal was used to estimate the intensities visually, and spots common to the four zones were used to put them all on a single intensity scale. Lorentz and polarization corrections were made, although the revised expression (Waser, 1951) was not used; this work was done prior to the receipt of that communication. No correction was made for absorption because the atoms in diketene are light and the radiation used was penetrating, and no correction for extinction was made. This latter was justified later, at least partially, by the agreement between observed and calculated intensities for the more intense reflections.

Unit cell and space group

One of the zones showed C_2 symmetry in both the zero and first levels. The others showed C_{2l} symmetry in the zero levels and C_l symmetry in the first levels.* From these facts and the absence of any higher symmetry, the centro-symmetric crystal class was found to be C_{2h}. The four zero-level pictures with C_{2l} symmetry were indexed as $hk0$, $0kl$, hkh, $hk\bar{h}$; the one exhibiting C_2 symmetry as $h0l$. The extinctions of $h0l$ reflections with l odd and of $0k0$ reflections with k odd showed the presence of a c glide plane and a two-fold screw axis so that the space group is C_{2h}^5–$P2_1/c$. The unit cell dimensions were found to be

$$a = 4{\cdot}00 \pm 0{\cdot}02,\ b = 20{\cdot}67 \pm 0{\cdot}06,\ c = 5{\cdot}11 \pm 0{\cdot}02\ \text{Å},$$
$$\beta = 101{\cdot}8° \pm 0{\cdot}5°.$$

The density of the solid was not known, but was estimated from the density of the liquid ($D_{20}^{20} = 1{\cdot}090$), and the observed contraction on freezing, to be about 1·30 g.cm.$^{-3}$. The number of molecules per unit cell is thus 4, and, since this is the multiplicity of the general position of the space group, no molecular symmetry is demanded.

Determination of the structure

Our first attempt at discovering something about the structure of diketene was made using the molecular-structure-factor method (Knott, 1940). The calculations were made for a four-membered ring structure with a center of symmetry. The method readily yielded the information that for a structure even approaching the above, the y coordinate of the 'center' of a molecule (the other three would be positioned by the space group) would be about 0·113 or about 0·137. The ambiguity arises from the fact that it is the $\cos 2ky_{\text{ave.}}$ which is found and for even k this is symmetrical in absolute magnitude about $y = 0{\cdot}125$. (The final average y for the molecule in the first quarter of the cell is 0·135.) The method could have yielded many more results, but it was not pushed, largely because of some misgivings at that time as to the validity of the approximations.

Unsharpened Patterson projections were made using the $hk0$ data and the $0kl$ data. Very few peaks showed up and almost nothing which could be ascribed to intramolecular vectors were found. However, on the $0kl$ projection a large peak showed up on the $z=\frac{1}{2}$ line.

An attempt was then made by the Banerjee method (Banerjee, 1933; Hughes, 1949). This method seemed to hold promise because of the long b axis and the consequent presence of comparatively long rows of reflections with the same h and l indices. The intensities were put on an absolute scale using Wilson's method (Wilson, 1942) and the $0k0$ signs were calculated. Unfortunately, six different combinations of signs gave reasonable fit for the equations. Since this would mean six different sets of constants with which to attempt to determine the remaining signs in a zone, the amount of work was prohibitive. However, the constants calculated from the two sets of $0k0$ signs which were considered best were used to determine the remaining $hk0$ signs, but when Fouriers were plotted with them it was apparent that either the $0k0$ signs were incorrect or the $hk0$ signs determined from them were incorrect, or both. It should be noted that of the six different Fourier projections on the b axis computable from the six different sets of $0k0$ signs, three were mirror images of the other three about the line $y = 0{\cdot}125$. This was equivalent to the same ambiguity which arose in the molecular-structure-factor treatment.

At this point it was decided that the large peak on the $0kl$ Patterson at $z = \frac{1}{2}$ must be due to the action of the glide plane on the molecule as a whole, and that its y coordinate could be used to resolve the ambiguity in the y coordinate of the mass center. This calculation showed the 0·137 value to be correct. This then reduced the number of projections to be considered to three. Structure-factor calculations based on these three projections were made, and the best fit was obtained for a curve which had a single-weight peak at about $b = 0{\cdot}063$, a double-weight peak at about $b = 0{\cdot}108$ and a triple-weight peak at about $b = 0{\cdot}170$. The misleading thing about this projection was that its three peaks of about single, double and triple weights seemed to suggest an acetylketene structure for the molecule with the ketene group almost perpendicular to the b axis, thus accounting for the triple-weight peak. Because of this, several attempts were made to fit the acetylketene structure to the data, but always without success.

A sharpened-up $0kl$ Patterson projection was now made; this showed considerably more detail than the unsharpened one. Although it was possible to reconcile an acetylketene structure with many of its features, the projection also suggested how a four-membered

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* Symmetry symbols according to Buerger (1942, p. 469).

ring could be distorted from a model with a 'center of symmetry' so as to give the desired projection on the *b* axis. When a fourmembered-ring model was built from the vectors indicated by the Patterson without too serious an attempt to impose structural principles on it, a Fourier was obtained which not only refined to a projection of reasonable appearance, but permitted reasonable structure factors to be calculated from it. In addition, although only an average atomic scattering factor was used, one of the ring atoms showed up with about 25% higher density than the others, indicating the location of one of the oxygen atoms.

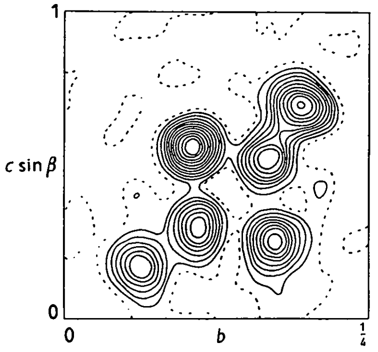


Fig. 1. Projection of the electron density along [100]. Contours are approximately in e.Å^{-2}, the one-electron contour being broken.

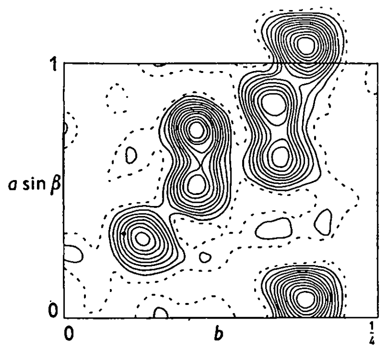


Fig. 2. Projection of the electron density along [001]. Contours are approximately in e.Å^{-2}, the one-electron contour being broken. In both Fig. 2 and Fig. 3 the natural temperature factor has been divided out of the F_0.

Advantage was now taken of the fact that the $\bar{1}21$ reflection was very intense—about 60% of the maximum possible if everything were in phase. The assumption was then made that the molecule lay in this plane, and [101] projection was made. This showed the molecule edge-on and indicated that the molecule was indeed planar, or nearly so, and that the plane of the molecule in the quarter of the cell bounded by $y = 0$ and $y = 0{\cdot}25$ was the $\bar{1}21$ plane.

Approximate x coordinates were then obtained by combining the 0*kl* projection coordinates and the condition on the plane of the molecule, and a [001] projection was made. In this case, again using an average atomic scattering factor, two of the atoms showed up more dense than the other four. Assuming that these were the oxygen atoms, the Fouriers were repeated to account for the different scattering of oxygen from that of carbon, and general improvement was achieved both in the background of the Fouriers (Figs. 1 and 2) and in the agreement between observed and calculated structure factors. A [10$\bar{1}$] projection was also made in a similar manner.

Final parameters and discussion of results

With the arrangement of oxygen and carbon atoms settled, the structural possibilities had been narrowed to the 2-buteno-β-lactone and the 3-buteno-β-lactone structures. These two differ only in the interchange of a single and a double bond and the shift of a hydrogen atom. No attempt was made to locate the hydrogen atoms in this study, or to correct for them in the calculation of the structure factors. The decision was made on the basis of the bond lengths.

The critical bonds are the carbon–carbon bond outside the ring and the ring carbon–carbon bond adjacent to it. Calculation of these two bonds from the Fourier parameters gave 1·35 Å for the first and 1·42 Å for the second. The first result is the accepted double-bond distance, but the second is somewhere between any expected single- or double-bond values, and the one-third double-bond character would be hard to account for. A least-squares treatment of all the data (Hughes, 1941) was then undertaken without first applying backshift corrections (Booth, 1946). The corrections calculated from the least-squares treatment were generally about 0·01–0·02 Å, with the exception of two of the x parameters which changed 0·06–0·08 Å. Upon applying the corrections and calculating the bond lengths, the critical C–C bond in the ring was calculated to be 1·42 Å. Because of this somewhat improbable C–C bond value and the large corrections in two of the x parameters, it was felt advisable to make the backshift corrections on the 0*kl* and the *hk*0 zones, from which all of the parameters could be found. The shifts were large; the maximum backshift was 0·06 Å and the average backshift was 0·03 Å. However, they did corroborate the correctness of the least-squares x parameters, differing from these by a maximum of 0·03 Å and by an average of less than 0·02 Å. In addition, they combined to act in such a way as to make the 1·42 Å distance jump to 1·54 Å, which is the accepted single-bond distance. Needless to say, this meant that agreement between the least-squares and back-shift y and z parameters was not very good. In the case of the y parameters, the maximum difference in the parameters was 0·004 and the average was 0·002; because of the length of the b axis, however, these values correspond to distances of 0·08 and 0·04 Å. The disagreement in the z parameters is quite striking, for here, although the axis is short (5·11 Å), the maximum difference between the two determinations was 0·085 Å and the average 0·045 Å.

Possible reasons for these discrepancies include the following. The least-squares method, as applied to the X-ray problem, calls for the use of nearly correct parameters; if this condition is inadequately satisfied, the results may be expected to be correspondingly inadequate. This closeness of fit also applies to the values of the scale and temperature factors. In the Fourier method coupled with the backshift correction, an incorrect sign is more sensitively reflected. In addition, although the sampling was at 3° intervals, the length of the b axis meant that the interval of sampling was about 0·17 Å in this direction, making it somewhat more difficult than usual to fix the positions of the atomic centers. Both methods are affected by the omission of the hydrogen atoms; indeed this may be the most serious source of error. In both cases there is, of course, the possibility of computational error. This possibility seems somewhat greater in the case of the least-squares method. Finally, the weighting of the structure factors is different in the two methods. That the back-shift results were not completely self consistent can be seen by a comparison of the y parameters obtained from the $hk0$ and $0kl$ projections, since they are determinable from both. The maximum difference in these parameters is 0·0025 and the average is 0·0015; these correspond to 0·05 and 0·03 Å.

It may be remarked that during all of these calculations the carbon–carbon distance outside of the ring remained within ±0·02 of the normal C=C distance of 1·35 Å. Furthermore, the same value was indicated from the resolved peaks of the hkh Fourier, which is not presented here because of overlap in other portions of the molecule.

Undoubtedly, further work would have revealed methods for reducing the discrepancies described above. However, the primary purpose of this study was to determine the correct molecular structure rather than to determine highly accurate atomic parameters; and, since it was felt that there was insufficient reason for abandoning the results of either method, their values were averaged. These average values are:

	x	y	z
C_1	0·310	0·063	0·161
O_1	0·725	0·104	0·553
C_2	0·519	0·108	0·300
C_3	0·838	0·167	0·515
C_4	0·637	0·173	0·245
O_2	0·063	0·193	0·688

To get an idea as to the probable errors in these parameters, it was assumed that the determinant of the coefficients in the normal equations of the least-squares treatment was diagonal. Thereafter, the method outlined by Whittaker & Robinson (1944, p. 240 ff.) was followed and yielded about the same probable error, 0·02 Å, for each of the parameters. This would result in probable errors of approximately 0·03 Å in the bond lengths and 1° in the angles. In view of the previous results, however, it was felt that the bond lengths should be considered to be accurate to about a limit of 0·06 Å and the angles to about 2°. The picture of the molecule in Fig. 3 is the key to the following set of data:

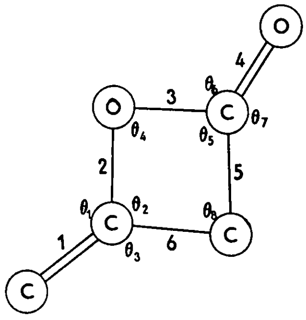
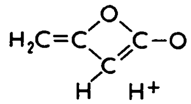


Fig. 3. The molecule of diketene.

1 = 1·35 Å
2 = 1·39 Å
3 = 1·40 Å
4 = 1·24 Å
5 = 1·46 Å
6 = 1·48 Å

θ_1 = 130°
θ_2 = 94°
θ_3 = 136°
θ_4 = 89°
θ_5 = 94½°
θ_6 = 121°
θ_7 = 145°
θ_8 = 83°

The angles attest to the planarity of the molecule (a fact previously determined by the [$10\bar{1}$] projection) well within the limits of error ascribed to them, and the bond lengths are probably all to be considered normal, again taking account of the limits of error, with the possible exception of the 1·46 Å C–C bond distance. The shortening here could be real, entirely or in part, and could be accounted for by resonance with the structure,



The attendant lengthening of the C=O bond would be completely covered up by the limit of error since it would amount to about 0·01 or 0·02 Å (Pauling, 1940). Resonance of this sort would make the angle labeled θ_6 smaller than θ_7, and this is observed. Similar remarks may apply to a lesser degree to bond 6.

The structure factors in Table 1 have the same scale factor and the same temperature-factor constant throughout. The scale and temperature factors were initially approximated by using Wilson's method for establishing the absolute scale, and the final values used were found by including them as unknowns in the least-squares determination. The reliability factor, $\Sigma||F_c|-|F_o||\div\Sigma|F_o|$, calculated for all the observed reflections, is 17·2%.

Table 1. *Comparison of structure factors*

hkl	F_c	F_o
020	−18	18
040	−52	60
060	6	12
080	−27	38
0,10,0	25	28
0,12,0	7	11
0,14,0	−22	24
0,16,0	5	< 5
0,18,0	12	16
100	− 3	8
110	24	24
120	−23	24
130	13	8
140	16	18
150	−26	38
160	21	25
170	−13	13
180	−16	19
190	− 1	< 3
1,10,0	2	< 3
1,11,0	6	4
1,12,0	− 1	< 3
1,13,0	22	25
1,14,0	3	5
1,15,0	− 3	4
1,16,0	4	4
1,17,0	−14	15
1,18,0	− 9	10
200	− 7	7
210	−13	13
220	−11	15
230	5	4
240	8	7
250	8	8
260	9	7
270	− 2	< 4
280	− 1	< 4
290	9	11
2,10,0	6	11
2,11,0	−11	12
2,12,0	− 6	7
2,13,0	− 6	7
2,14,0	− 1	< 4
2,15,0	6	6
2,16,0	3	< 4
2,17,0	− 2	< 4
2,18,0	− 6	7
300	5	7
310	− 6	5
320	1	< 4
330	0	< 4
340	2	< 4
350	2	< 4
360	1	< 4
370	2	< 4
380	− 8	8
390	5	8
3,10,0	0	< 4
3,11,0	− 8	9
3,12,0	1	< 4
3,13,0	− 2	< 4
3,14,0	2	< 4
3,15,0	− 2	< 4
3,16,0	5	6
400	1	< 3
410	− 6	5
420	5	6
430	− 1	< 3
440	− 3	< 3
450	0	< 3
460	− 8	10
470	6	6
480	5	6
490	2	3
4,10,0	5	7
011	−28	24
021	−14	20
031	38	38
041	−24	23
051	8	10
061	11	6
071	− 4	8
081	− 8	10
091	−12	13
0,10,1	4	4
0,11,1	−16	19
0,12,1	10	8
0,13,1	10	8
0,14,1	− 6	6
0,15,1	13	16
0,16,1	− 7	10
0,17,1	− 1	< 4
0,18,1	− 4	5
002	−12	20
012	−21	28
022	10	8
032	− 7	7
042	− 8	8
052	− 3	< 5
062	− 8	11
072	− 8	12
082	15	17
092	14	13
0,10,2	8	6
0,11,2	− 1	< 4
0,12,2	4	5
0,13,2	1	< 4
0,14,2	0	< 5
0,15,2	4	6
0,16,2	−10	10
013	− 7	5
023	17	24
033	− 5	5
043	2	4
053	10	10
063	−12	13
073	− 2	5
083	− 3	5
093	5	10
0,10,3	− 1	< 4
0,11,3	2	5
0,12,3	8	10
0,13,3	−10	10
0,14,3	6	8
0,15,3	4	7
0,16,3	11	12
004	9	13
014	0	< 5
024	− 7	5
034	−11	12
044	− 7	8
054	5	7
064	8	8
074	15	14
084	− 1	< 4
094	− 4	4
0,10,4	2	< 4
0,11,4	− 5	5
0,12,4	6	8
0,13,4	− 8	11
0,14,4	− 7	7
015	− 4	< 4
025	4	4
035	7	7
045	7	7
055	− 2	5
065	1	5
111	− 9	15
121	1	6
131	− 6	10
141	−25	27
151	5	< 4
161	−20	20
171	5	7
181	1	< 4
191	7	7
1,10,1	− 4	6
1,11,1	7	7
1,12,1	7	10
1,13,1	4	5
1,14,1	11	12
1,15,1	4	5
1,16,1	5	5
1,17,1	1	< 4
1,18,1	3	6
202	−17	19
212	−15	15
222	8	9
232	− 7	7
242	9	11
252	8	10
262	− 1	< 4
272	3	5
282	− 2	5
292	− 5	< 4
2,10,2	−16	19
2,11,2	− 3	5
2,12,2	2	< 4
2,13,2	8	9
2,14,2	10	10
2,15,2	− 5	5
2,16,2	2	4
2,17,2	− 6	7
$11\bar{1}$	5	11
$12\bar{1}$	70	84
$13\bar{1}$	27	34
$14\bar{1}$	− 7	7
$15\bar{1}$	−36	44
$16\bar{1}$	− 1	< 6
$17\bar{1}$	8	7
$18\bar{1}$	−11	14
$19\bar{1}$	14	21
$1,10,\bar{1}$	−12	15
$1,11,\bar{1}$	− 9	12
$1,12,\bar{1}$	19	20
$1,13,\bar{1}$	4	< 6
$1,14,\bar{1}$	− 1	< 6
$1,15,\bar{1}$	− 1	< 6
$1,16,\bar{1}$	13	15
$1,17,\bar{1}$	0	< 6

Table 1 (*cont.*)

hkl	F_c	F_o
$20\bar{2}$	−19	22
$21\bar{2}$	−12	12
$22\bar{2}$	− 3	< 6
$23\bar{2}$	25	25
$24\bar{2}$	13	15
$25\bar{2}$	16	20
$26\bar{2}$	6	< 8
$27\bar{2}$	−27	27
$28\bar{2}$	− 3	< 6
$29\bar{2}$	5	6
$2,10,\bar{2}$	− 6	6
$2,11,\bar{2}$	− 3	6
$2,12,\bar{2}$	− 1	< 6
$2,13,\bar{2}$	− 6	6
$2,14,\bar{2}$	7	6
$2,15,\bar{2}$	2	< 6
$2,16,\bar{2}$	2	< 5
$31\bar{3}$	− 6	6
$32\bar{3}$	2	< 7
$33\bar{3}$	− 8	9
$34\bar{3}$	− 6	< 7
$35\bar{3}$	16	15
$36\bar{3}$	− 8	6
$37\bar{3}$	4	6
$38\bar{3}$	3	6
$39\bar{3}$	8	10
$3,10,\bar{3}$	− 6	6

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The Diffraction of X-rays by Distorted-Crystal Aggregates. IV. Diffraction by a Crystal with an Axial Screw Dislocation

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In the reciprocal-lattice representation, the regions of high intensity become discs perpendicular to the dislocation axis. The variation of amplitude of reflexion across a disc can be represented either as an integral or as a finite series involving Bessel functions. Expressions for the integral breadths of lines on powder photographs are obtained in closed form.

1. Introduction

The hypothesis of dislocations explains many of the properties of cold-worked metals and the ease of crystal growth from vapour or solution. At the time when the work described below was begun (Wilson 1949*a*) there was no direct evidence of their existence, and it was hoped that some might be found through study of the details of diffraction by cold-worked metals, preferably of single crystals deformed in a way that would make it reasonable to suppose that most of the dislocation axes were parallel. This interest in the effect of a dislocation on the X-ray diffraction patterns of a crystal has now largely disappeared, as growth spirals give an ample direct indication of the existence of dislocations, but it is perhaps worth while to place the results on record, as the dislocated crystal and the