The crystal used for this investigation came from Ilmen Mt. Ural; it showed slight radioactivity (72 αmg.hr.$^{-1}$) and the specific gravity was 4·67 g.cm.$^{-3}$. These results showed that this specimen was 'normal' zircon, i.e. not affected by metamictization. The unit-cell dimensions were determined from a Straumanis powder photograph using Cu filtered radiation ($\lambda = 1·54050$ Å). The following results were obtained

$$a = 6·6164 \pm 0·0005, \quad c = 6·0150 \pm 0·0005 \text{ Å} .$$

Single-crystal photographs (taken with Cu-filtered radiation) included zero, first and second level normal Weissenberg c-axis photographs and first, second and third level a-axis photographs. Systematic absences confirmed the space group $I4_1/amd$; $Z = 4$.

To determine the oxygen parameters an electron-density projection on (100) with the origin at a symmetry centre $(2/m)$ was made. The intensities of 90 $0kl$ reflexions were obtained (using Mo filtered radiation) with an integrating Weissenberg goniometer. The intensities of the spots were measured with a Kipp (Delft) photometer. After allowing for Lorentz and polarization factors and for absorption, F values were placed on an absolute scale by scaling them to the calculated structure amplitudes for various regions of $\sin \theta/\lambda$. To calculate structure amplitudes Vegard's parameters were used, the atomic scattering factors being taken from *Internationale Tabellen* (1935).

For the refinement of the oxygen parameters both F_o and F_o-F_c syntheses were used. After the third F_o-F_c synthesis it was concluded that the error due to series termination was largely eliminated; the final parameters for oxygen atoms were $y = 0·067$, $z = 0·198$. The value of the reliability index R is 0·07.

Interatomic distances in the SiO_4 tetrahedron are as follows

O–O $= 2·42$ Å (two), O–O $= 2·73$ Å (four), Si–O $= 1·61$ Å , with $\sigma(x)$ estimated to be 0·02 Å (Cruickshank, 1949).

As can be seen there is a distorted tetrahedron with the length of the Si–O bond in good agreement with the values found in other silicates; each atom of zirconium is surrounded by four atoms of oxygen at 2·15 Å, and by another four at 2·29 Å. These values are nearer to the sum of the ionic radii of Zr and O than those given by the previous investigators (2·05 and 2·41 Å respectively), and the distribution of oxygen atoms around zirconium is more regular. The first set of these distances is close to the sum of the Goldschmidt ionic radii corrected for coordination (2·16 Å) while the other set is larger by 0·14 Å. This may be of some significance in connexion with the process of metamictization in zircon but it is interesting to note here that the same irregular oxygen polyhedra occur in the structure of Xenotime[*] (YPO_4); this is of the same structural type as zircon, but, although it is sometimes strongly radioactive, it is never found in the metamict state. Corresponding distances in Xenotime are 2·32 and 2·56 Å, while the sum of the corrected ionic radii for yttrium and oxygen is 2·35 Å. Some authors (e.g. Pellas, 1954) claim a high degree of covalent bonding as one of the causes of the metamict state but the interatomic distances zirconium–oxygen in this structure would not suggest this.

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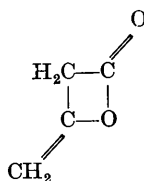
[*] To be published later.

A refinement of the crystal structure of ketene dimer.

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The structure of ketene dimer in the solid state was determined by Katz & Lipscomb (1952). They found the molecule to have the 3-butenoic acid β-lactone structure.

$$
\begin{array}{c}
\text{O} \\
\nearrow \\
\text{H}_2\text{C—C} \\
| \quad | \\
\text{C—O} \\
\nearrow \\
\text{CH}_2
\end{array}
$$

The emphasis of their study was on finding the correct molecular configuration rather than on determining 'highly accurate atomic parameters'. Thus, when the C–C single bond lengths were found to be unusually short, it was not known whether this was due simply to

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inaccuracy in the structure determination, or whether it would be necessary to invoke a significant amount of double bond character to explain the shrinkage. Electron-diffraction results (Bauer & Bregman, 1955) showed normal values of 1·52 Å for the ring C–C bond lengths.

A refinement of the structure determination was considered worth while when an I.B.M. 704 least-squares program and computer time became available. The data

Table 1. *New co-ordinates, temperature factors, and standard deviations for diketene*

Atom	x	y	z	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C_1	0·3049	0·0599	0·1652	3·324	0·007	0·0010	0·0006
O_1	0·7211	0·1033	0·5565	3·156	0·005	0·0007	0·0004
C_2	0·5032	0·1062	0·2884	2·964	0·007	0·0010	0·0004
C_3	0·8409	0·1650	0·5223	2·664	0·006	0·0010	0·0004
C_4	0·6399	0·1738	0·2412	2·356	0·006	0·0009	0·0004
O_2	0·0584	0·1920	0·6901	3·629	0·005	0·0007	0·0006

Fig. 1. Dimensions of diketene molecule.

Table 2. *Bond lengths and angles from old X-ray determination (K and L), electron diffraction (B and B), this refinement (K and K)*

Bond lengths	K and L	B and B	K and K
C_1-C_2	1·35 Å	1·31 Å	1·32 Å
C_2-C_4	1·48	1·52	1·54
C_3-C_4	1·46	1·52	1·51
C_3-O_2	1·24	1·19	1·22
C_3-O_1	1·40	1·41	1·39
C_2-O_1	1·39	1·41	1·47
Bond angles			
C_1-C_2-O_1	130°	130°*	126·9°
C_1-C_2-C_4	136	136*	141·6
C_4-C_2-O_1	94	95	91·3
C_2-C_4-C_3	83	81	83·0
C_4-C_3-O_1	94·5	95	95·8
C_4-C_3-O_2	145	145*	140·9
O_2-C_3-O_1	121	121*	123·1
C_3-O_1-C_2	89	89	90·0

* Assumed value.

of Katz and Lipscomb were used for the refinement (non-observed reflections were omitted). R dropped from 0·14 to 0·11 in 6 cycles. Numbering the atoms as in Fig. 1, the new coordinates are listed in Table 1. The new bond lengths and angles are indicated in Fig. 1 and, together with the old values of Katz and Lipscomb and the electron diffraction results of Bauer & Bregman, are given in Table 2. Standard deviations for the new results are about 0·03 Å for bond lengths, 1·5° for bond angles.

The C–C single bond lengths are in the usual range, confirming the absence of an appreciable amount of double bond character. The C_2-O_1 and the C_3-O_1 single bonds are, however, shorter and longer, respectively, than the normal C–O single bond distance of 1·42 Å. While the differences fall within twice the standard deviations, it should be noted that such shortening and lengthening of C–O single bonds α and β to a C–O double bond have been observed in methyl acetate, methyl formate, and methyl chloroformate (O'Gorman, Shand & Schomaker, 1950); in dimethyl terephthalate (Bailey, 1949); and in dimethyl oxalate (Dougill & Jeffrey, 1953). This effect in esters is probably a result of the usual resonance in carboxyl groups (Pauling, 1940). It is also of interest to note that the temperature factors for the atoms outside the ring are higher than those for the atoms in the ring.

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Space group of *o*-tolidine.

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Clark & Pickett (1931) examined *o*-tolidine $C_{14}H_{16}N_2$ with structural formula
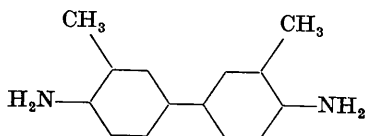
by both X-ray and optical methods and found it to be orthorhombic with cell dimensions: $a = 6·50$; $b = 7·48$ and $c = 23·62$ Å, with four molecules per unit cell. The space group was found to be either Q^3 or Q^4 depending upon the presence or absence of $(0k0)$ with k odd. The present work was undertaken to find out the correct space group of *o*-tolidine in preparation for complete structure determination.

Good crystals of *o*-tolidine, slightly brown in colour, were obtained from distilled alcohol. They exhibited extinctions parallel to the axes under the polarizing microscope. Employing unfiltered Co $K\alpha$ radiation, rotation and Weissenberg zero-layer and equi-inclination photographs were taken. The crystal was found to be orthorhombic. The systematic absenses are: $(h00)$ when h is odd, $(00l)$ when l is odd. Over-exposed a axis zero-layer Weissenberg photograph showed a sharp reflexion in the (050) position and very weak impression of a reflexion in the (010) position; these, however, did not