596. *The Crystal Structure of Dimethylketen Dimer.*

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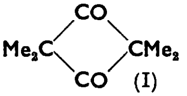
The crystal structure of dimethylketen dimer has been studied by *X*-ray analysis. The probable space group is C2/m (C^3_{2h}) with 2 molecules per cell and molecular symmetry 2/m. This implies a planar *cyclo*butane ring, although considerable out-of-plane vibrations are possible. The temperature factor is high. The mean C–C bond length in the ring is 1·56 Å; $C-CH_3$ is 1·49 Å and C=O 1·20 Å. Probable errors are at least ±0·02 Å, but the results are in good agreement with a previous electron-diffraction investigation and with other studies on *cyclo*butane derivatives.

The structure of the carbon ring in *cyclo*butane and a number of its derivatives has now been studied in detail by both spectroscopy and diffraction, with results which differ rather widely in different compounds. In *cyclo*butane itself the electron-diffraction results [1] show a non-planar ring, but are unable to distinguish between the symmetry $\bar{4}$ 2m (D_{2d}) applicable to a puckered ring, and 4/mmm (D_{4h}) for a planar ring with large amplitude of out-of-plane bending. In octafluoro*cyclo*butane [2] and octachloro*cyclo*butane [3] the diffraction evidence definitely indicates a puckered ring with symmetry at least approximately D_{2d}, although certain spectroscopic evidence [4] appears to be consistent with a planar ring in the former. In tetraphenyl*cyclo*butane [5] and diacenaphthaleno*cyclo*butane (acenaphthylene dimer) [6] the *X*-ray evidence requires a molecular centre of symmetry and hence a strictly planar ring. Dimethylketen dimer (2 : 2 : 4 : 4-tetramethyl*cyclo*buta-1 : 3-dione) (I), which is the subject of this investigation, has already been studied by electron diffraction; [7] the results point to a planar model of symmetry D_{2h}, although there is evidence of a large temperature factor which may arise from out-of-plane vibrations of the ring atoms and attached groups.



(I)

Although the geometry of the *cyclo*butane ring varies in different compounds, in all of them the carbon–carbon distance is consistently greater than the standard single-bond distance of 1·54 Å, the values reported ranging from 1·55 Å in methylene*cyclo*butane [8] to 1·60 Å in octafluoro*cyclo*butane. Reasons for this lengthening have been discussed by

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[1] Dunitz and Schomaker, *J. Chem. Phys.*, 1952, **20**, 1703.
[2] Lemaire and Livingston, *ibid.*, 1950, **18**, 569.
[3] Owen and Hoard, *Acta Cryst.*, 1951, **4**, 172.
[4] Claassen, *J. Chem. Phys.*, 1950, **18**, 543.
[5] Dunitz, *Acta Cryst.*, 1949, **2**, 1.
[6] Dunitz and Weissman, *ibid.*, 1949, **2**, 62.
[7] Lipscomb and Schomaker, *J. Chem. Phys.*, 1946, **14**, 475.
[8] Shand, Schomaker, and Fischer, *J. Amer. Chem. Soc.*, 1944, **66**, 636.

Dunitz and Schomaker [1] who attribute it mainly to repulsion of the non-bonded carbon atoms, which are only 2·22 Å apart in *cyclo*butane. Their calculations also show that it is difficult to predict whether the equilibrium configuration of the ring is planar or slightly non-planar.

The electron-diffraction investigation of dimethylketen dimer [7] gave a C–C distance in the ring of 1·56 Å and a C–CH_3 distance of 1·54 Å, although both these values are subject to a fairly large possible error of about ±0·05 Å. The crystal-structure study which we have now undertaken confirms the existence of long bonds in the ring, but indicates that the C–CH_3 distances are shortened to well below the standard value of 1·54 Å. Our results also indicate a strictly planar *cyclo*butane ring. The crystal structure is comparatively simple, but unfortunately the arrangement of the molecules in the unit cell precludes any clear projections of the *cyclo*butane ring in our present two-dimensional analysis. The volatile nature of the crystals and high temperature factor also create experimental difficulties, and it seems likely that the finer details of the structure will only be obtained from a low-temperature three-dimensional analysis.

Crystal Data.—Dimethylketen dimer, $C_8H_{12}O_2$; *M*, 140·2; m. p. 113°; *d*, calc. 1·110, found 1·10. Monoclinic, $a = 6{\cdot}55 \pm 0{\cdot}01$, $b = 10{\cdot}26 \pm 0{\cdot}03$, $c = 6{\cdot}43 \pm 0{\cdot}01$ Å, $\beta = 104{\cdot}0° \pm 0{\cdot}5°$. Absent spectra, *hkl* when $h + k$ is odd. Space group, C2 (C_2^3), Cm (C_s^3), or C2/m (C_{2h}^3). C2/m is assumed in this analysis. Two molecules per unit cell. Molecular symmetry (for C2/m), two-fold axis perpendicular to a plane. Volume of the unit cell, 419 Å^3. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}54$ Å), $\mu = 7{\cdot}38$ per cm. Total number of electrons per unit cell = F(000) = 152.

The colourless, wax-like crystals were irregular in shape, and very volatile. No pyroelectric effect was observed.

Structure Analysis.—The observed spectral absences do not lead to a positive identification of the space group. C2 with molecular symmetry 2 parallel to *b*, Cm with molecular symmetry *m* parallel to (010) and C2/m with molecular symmetry 2/m must all be considered possible, although the absence of pyroelectric effect is perhaps slightly in favour of the last.

As a basis for the evaluation of the structure factors it is convenient to construct a model with the maximum permitted symmetry 2/m, and place its centre in the special positions required by the space group C2/m, *viz.* (000, $\tfrac{1}{2}\tfrac{1}{2}0$). Each ring carbon and ketonic oxygen then lies on a symmetry plane and has the co-ordinates (000, $\tfrac{1}{2}\tfrac{1}{2}0$) + x0z; $\bar{x}0\bar{z}$, while the methyl groups occupy the general positions (000, $\tfrac{1}{2}\tfrac{1}{2}0$) + xyz; $x\bar{y}z$; $\bar{x}y\bar{z}$; $\bar{x}\bar{y}\bar{z}$. The asymmetric crystal unit thus consists of one quarter of the chemical molecule, made up of one methyl group, one half of each of two ring carbons, and one half of each of the two ketonic oxygen atoms. The justification for the space group C2/m will depend on how well such a model can explain the observed *X*-ray intensities.

A simple model based on a square ring with C–C = 1·54 Å, and C–O = 1·20 Å was now tested. It immediately led to excellent agreements with the observed structure factors. In particular, the strong axial series of reflections (00*l*) and (0*k*0) were accounted for almost quantitatively, to the seventh and tenth order respectively, and at this stage the overall agreement for some 70 structure factors was about 26%. Refinements by the double Fourier series method were then applied, giving projections of the structure along the *a* and the *b* axis. Unfortunately, the resolution is poor in these projections, except for the methyl group in the *a*-axis projection (Fig. 1). In the *b*-axis projection (Fig. 2) two co-ordinates of the ring atom C (1) can be determined.

Owing to the high temperature factor and comparatively small number of reflections observed (Table 3) it did not seem profitable to apply the usual difference synthesis refinement methods and the remaining 5 co-ordinates were determined chiefly by trial and error. The final discrepancy between calculated and observed structure factors over all zones was about 18%. The co-ordinates and bond lengths are given in Tables 1 and 2.

TABLE 1. *Co-ordinates.*

x, *y*, *z* are expressed as fractions of the axial lengths, *X*, *Y*, *Z*, *X′*, *Z′* are in Å, *X′* and *Z′* being referred to the *a* and *c′* crystal axes where *c′* is taken perpendicular to *a* and *b*.

Atom or group	*x*	*y*	*z*	*X*	*Y*	*Z*	*X′*	*Z′*
C(1)	0·117	0	−0·100	0·764	0	−0·643	0·920	−0·624
C(2)	0·125	0	0·147	0·819	0	0·947	0·590	0·919
CH_3	0·222	0·119	0·260	1·455	1·225	1·669	1·051	1·619
O	0·242	0	−0·208	1·583	0	−1·339	1·907	−1·299

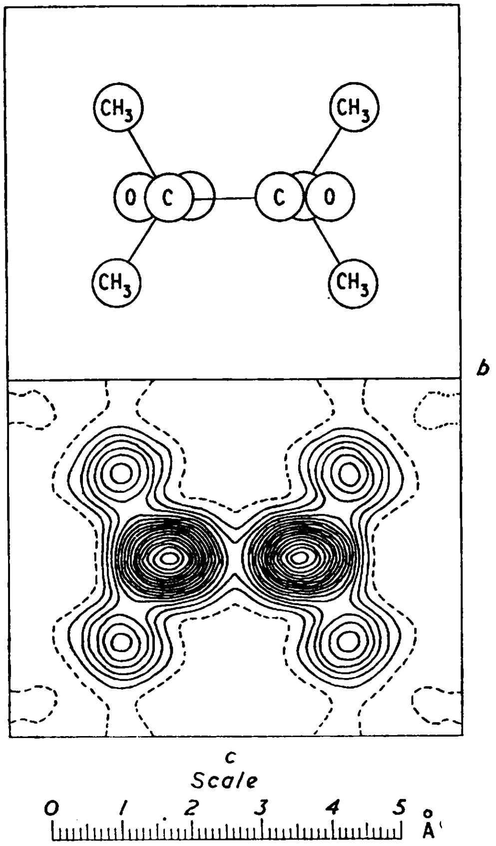

FIG. 1. *Electron-density projection along the* a *axis, showing resolution of the methyl groups. All the ring atoms and attached oxygen atoms lie in a plane normal to this projection, and are unresolved.*

FIG. 2. *Electron-density projection along the* b *axis, showing heavy overlap of adjoining molecules. The ring atoms lie in the plane of this projection, and the diagonal* C (1) . . . C (1′) *is inclined at about* 34° *to the* a *axis.*

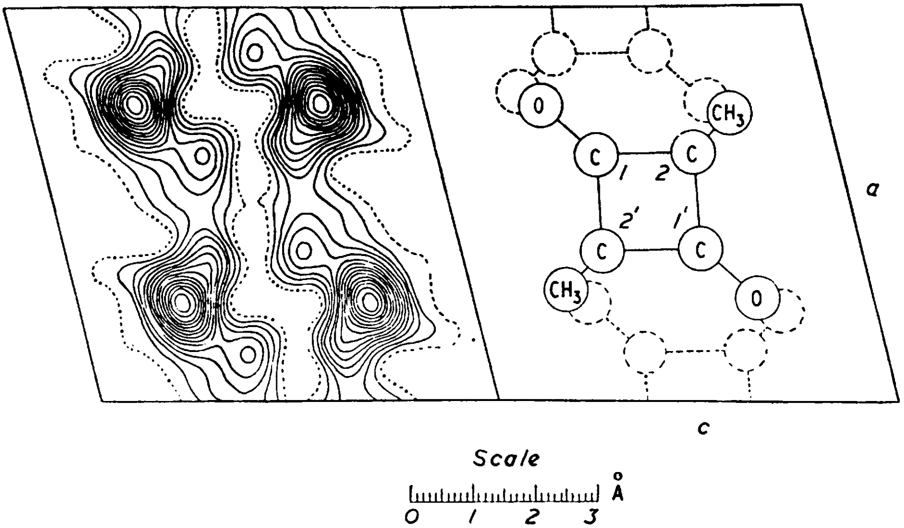

TABLE 2. *Bond lengths and angles.*

C(1)–C(2) = 1·58 Å
C(1)–C(1′) = 1·54 Å
Mean ring C–C = 1·56 Å
C(2)–CH_3 = 1·49 Å
C(1)–O = 1·20 Å

∠C(2)–C(1)–C(2′) = 89·5°
∠CH_3–C(2)–CH_3 = 111°
∠C(2)–C(1)–O = 138°

Discussion.—The agreements obtained show that the assumptions made regarding the symmetry of the molecule (2/m) are at least approximately correct. Calculation shows that distortions up to about 0·05 Å from a planar ring are possible, but any greater distortion would lead to serious structure-factor disagreements. The most likely situation is a planar ring with fairly large out-of-plane vibrations, a conclusion which is in agreement with the results of the electron-diffraction investigation.[7] The structure is a very open one of low density and appears to be governed mainly by contacts between the methyl groups and ketonic oxygen atoms. The distance between these groups on adjoining molecules along the *b* axis (where the overlap is shown in Fig. 2) is about 3·9 Å.

It is difficult to estimate accurately the errors in bond lengths on the data available, but probable errors of at least ±0·02 Å must be accepted. The difference between the two independent C–C ring bond lengths is not significant, but their mean value of 1·56 Å is in excellent agreement with the electron-diffraction measurements, and confirms a small increase over the standard value of 1·54 Å. On the other hand, the C–C bonds from the ring to the methyl groups, which are measured as 1·49 Å, appear to be slightly shortened.

These results are not unusual and agree with previous measurements, particularly those on tetraphenyl*cyclo*butane.[5] Owing to the strain imposed by the formation of the four-membered ring, it is to be expected that the usual sp^3 hybridization will be modified with an increase in the *p* character of the orbitals involved in the formation of the ring, and in the *s* character in the orbitals directed away from the ring. A tendency in this direction may explain the observed bond lengths.

EXPERIMENTAL

Photographic methods were employed with filtered Cu-*K*α radiation (λ = 1·54 Å), and intensities were estimated visually from moving film photographs, the multiple-film technique[9] being employed to correlate strong and weak reflections. Ilford fast film with an absorption factor of 3·3 was used. The crystals were extremely volatile and had to be sealed in thin capillary glass tubes. Even with this precaution the specimen often volatilised and deposited

TABLE 3. *Measured and calculated values of the structure factor.*

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
001	35·3	39·0	043	22·7	−18·8	401	<4·0	0·0
002	57·0	−50·0	044	17·6	−18·8	402	12·5	−14·8
003	31·3	−19·5	045	<4·0	2·7	403	4·0	−0·5
004	6·2	6·1	061	17·6	14·8	404	13·1	15·4
005	<4·0	−3·5	062	<4·0	−3·0	405	5·6	7·5
006	6·8	−7·0	063	14·7	−12·1	$40\bar{1}$	13·6	−19·7
007	<4·0	1·6	064	8·5	−6·6	$40\bar{2}$	16·5	−19·0
020	67·1	72·5	081	8·5	8·4	$40\bar{3}$	<4·0	12·0
040	14·2	15·2	082	11·3	−10·0	$40\bar{4}$	14·8	18·5
060	23·9	23·5	083	7·9	−6·0	$40\bar{5}$	7·9	1·7
080	26·7	28·4	201	10·2	7·8	601	<4·0	−5·9
0,10,0	11·4	13·4	202	34·1	32·1	602	5·1	7·7
200	43·8	−48·8	203	14·2	12·4	$60\bar{1}$	4·0	2·9
400	4·5	4·4	204	7·4	−8·5	$60\bar{2}$	4·6	5·2
600	8·0	−8·2	205	<4·0	−0·4	110	40·9	40·7
800	3·4	5·7	206	5·6	6·0	130	23·3	22·1
021	40·9	32·8	$20\bar{1}$	5·1	13·2	150	19·9	13·7
022	16·5	−15·1	$20\bar{2}$	35·3	40·8	170	14·2	13·2
023	23·3	−21·1	$20\bar{3}$	5·1	−9·4	220	14·7	−16·1
024	10·8	−7·4	$20\bar{4}$	23·3	−26·5	240	13·6	11·0
025	<4·0	−2·6	$20\bar{5}$	13·0	−5·2	260	<4·0	−3·8
041	27·8	24·4	$20\bar{6}$	<4·0	4·4	310	17·0	−25·8
042	13·6	13·0	$20\bar{7}$	5·1	2·7	330	13·6	−8·3
						350	<4·0	−4·4

[9] Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

on the walls of the tube unless the temperature was kept below 16°. Absorption corrections were not applied, but the specimens used were cut to nearly uniform cross-sections of about 0·3 × 0·3 mm. The F values were derived by the usual formula for mosaic type crystals and are collected in Table 3 ($F_{obs.}$). The scale is approximately absolute and was obtained by correlation with the final calculated values.

The Fourier syntheses were carried out by the three-figure numerical method.[10] In deriving the calculated structure factors ($F_{calc.}$) the temperature factor was not separately evaluated, but an averaged empirical scattering curve based on anthracene[11] was found to fit the results reasonably well. The (*hk*0) spectra are particularly difficult to observe, and in spite of very long exposures only seventeen F values could be obtained. For greater accuracy and more complete results it will probably be necessary to work at low temperatures with molybdenum radiation.

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[10] Robertson, *J. Sci. Instr.*, 1948, **25**, 28.
[11] Mathieson, Robertson, and Sinclair, *Acta Cryst.*, 1950, **3**, 245.