

The Crystal Structure of Ethylene Carbonate

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The structure of crystalline ethylene carbonate has been determined by the X-ray method. The dimensions of the monoclinic unit cell, which contains four molecules of $(\text{CH}_2)_2\cdot\text{CO}_2$, are $a = 8.92$, $b = 6.25$, $c = 6.94$ Å, $\beta = 100.5^\circ$. The space group is $C2/c$. X-ray intensity data were obtained from Weissenberg moving-film photographs for all layers of the three principal axes, and structure amplitudes were deduced for 372 separate planes. The approximate structure was derived by means of Patterson F^2 syntheses, and refinement of atomic coordinates was achieved by successive three-dimensional Fourier syntheses. The five-membered dioxolan ring is not planar, but the molecule possesses a twofold axis of symmetry which coincides with the twofold axis of symmetry in the unit cell. Although the other bond lengths are approximately normal, those associated with the CO_2 group are somewhat shorter than were expected, C = O being 1.15 Å and C—O 1.33 Å.

Introduction

Ethylene carbonate was chosen for a crystal-structure determination because it belongs to a class of compounds which possess particularly good solvent action for certain high polymers (Hill, New & Todd, 1950), and it was thought possible that a knowledge of its internal structure might shed some light on this property. Further, there is little accurate published information on the structures and bond lengths of heterocyclic ring systems involving oxygen; in particular no organic carbonate appears yet to have been determined. It was considered that a full three-dimensional determination of ethylene carbonate would fill these gaps in knowledge.

Experimental

Partly on account of the low melting point (39°C) of ethylene carbonate, and partly because of its high solubility in most solvents, it was somewhat difficult to prepare suitable crystals for accurate X-ray intensities. The crystals used in this investigation were obtained by slow cooling of a saturated alcoholic solution (slow evaporation was useless as the ethylene carbonate vaporized with the solvent). A variety of massive forms were generally produced, but occasionally well-formed needles, elongated along $[c]$, were grown; from these appropriate sections were cut with a sharp edge. Owing to the high vapour pressure of the crystals, the faces tarnished rapidly, and no goniometry was attempted. For the same reason, it was necessary to protect the crystals during exposure to X-rays, and this was done by enclosing them in thin polythene tubes, sealed at both ends. With a little practice, the correct orientation could be attained rapidly. The unit-cell dimensions were obtained by

measurement of layer lines on rotation photographs taken with $\text{Cu } K\alpha$ radiation.

$$a = 8.92, b = 6.25, c = 6.94 \text{ \AA}, \beta = 100^\circ 34'.$$

The angle β was calculated from the unit lengths of a , c and $[10\bar{1}] = 12.27$ Å. The best observed specific gravity, determination of which by flotation was difficult owing to the solubility of the crystals in all suitable solvents, was 1.47, sufficiently close to the calculated value (1.53) to indicate the presence of four molecules in the unit cell. Absent reflexions were $\{hkl\}$ for $(h+k)$ odd, and $\{h0l\}$ for l odd, whence the space group is either Cc or $C2/c$. Four molecules could be placed in Cc in general positions, or in the special position in $C2/c$ if the possible twofold molecular axis would coincide with the twofold axis of symmetry in the unit cell.

The result of a statistical survey of the distribution of intensities was inconclusive in fixing the space group, the curve lying midway between the ideal curves for centro-symmetrical and non-centro-symmetrical structures. There was no evidence of pyroelectricity when the crystals were tested in liquid nitrogen so the question of space group was left open until after the structure had been found. No molecular arrangement in the space group Cc could be found which gave structure-factor agreement, the only promising position being that in which the possible twofold axis of the molecule coincided with the twofold axis of symmetry in the unit cell, as required in the space group $C2/c$. Nothing arose later in the work to cast doubts on this choice, so the centro-symmetrical space group $C2/c$ may be regarded as established.

X-ray intensity data were obtained from Weissenberg moving-film photographs, taken with $\text{Cu } K\alpha$ radiation, about $[a]$ (zero and three layers), $[b]$ (zero and two layers) and $[c]$ (zero and two layers). As the

temperature coefficient of the structure amplitudes was fairly high, all the reflexions obtainable (372) at room temperature were recorded on these photographs. Batches of six films were exposed at each setting in the usual way, and the intensities of the reflexions were estimated by comparison with a time-exposure calibrated film strip. The usual corrections were applied for geometrical and polarization factors, and the experimental structure amplitudes were placed on the absolute scale by comparison with the calculated values obtained later. Owing to the rather large size of some of the crystals used, and the neglect of any correction for absorption, the experimental intensities may not have been as reliable as is usual in this class of work.

The structure determination

The b -axis projection was considered first, partly because b was the shortest axis, and partly because the $\{h0l\}$ zone contained three reflexions, (002), (200) and (20 $\bar{2}$), which were several times stronger than any of the others. Assuming a planar molecule, it seemed that the atoms would be grouped closely around the symmetry axis and would lie approximately in the plane (20 $\bar{2}$). A Patterson projection, using $F^2(h0l)$ terms, confirmed this, and the phases of about thirty structure amplitudes were fixed without ambiguity. Refinement of this projection was impossible owing to the overlap of atoms and to the limited number (fewer than forty) of $\{h0l\}$ reflexions observed.

In considering the c -axis projection, as values of x were known, it only remained to determine y for four atoms. The relatively high value of $F(060)$ was a good guide in this, all the atoms having to make contributions of the same phase for this plane; nevertheless it was found that there were several positions of the molecule which gave equally good agreements for the $\{hk0\}$ structure amplitudes. Refinement was again out of the question owing to the overlap of molecules related by the c glide plane. Indeed, using $F(hk0)$ terms alone, it was not possible to fix the y coordinates with certainty.

This was done by three-dimensional methods. Agreement was first sought for the $\{h1l\}$ terms, and when the y coordinates had thereby been settled, refinement of all the coordinates was carried out by successive syntheses along lines parallel to, and on sections perpendicular to, the b axis. Since x and z for atoms C_3 and O_3 were fixed by the space group, only three lines and two sections were needed at each stage of the refinement process. The final one used all the 372 experimental structure amplitudes.

At the conclusion of the work, an $F(\text{exp.}) - F(\text{calc.})$ synthesis was computed in an endeavour to locate the two unrelated hydrogen atoms. One of these was found, but not very accurately, at a position 1.1 Å from C_1 , but no very satisfactory peak was found for the other. This was probably an effect due to the lack of accuracy in the intensity measurements, and, in

view of this, no further work was done on the hydrogen coordinates, and they were omitted from the structure-amplitude calculations. The experimental and calculated structure amplitudes are listed in Table 1. Those where $F(\text{exp.}) = 0$ have been left out for economy in space; in each case they gave zero or very small calculated values.

The value of B in the temperature factor applied to the calculated structure amplitudes was taken as 5 Å². This resulted in a rather high discrepancy factor, $R = 0.25$. This may be due to inaccurate intensities, but another possibility is that the atomic vibrations may be anisotropic. In particular, the unshared electron pairs of the carbonyl oxygen atom (O_3) which show up by the elliptical shape of the peak in the bounded electron-density projection (Fig. 1) indicate

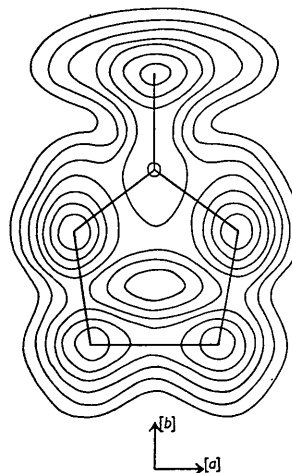


Fig. 1. Bounded projection from $z = 0.1$ to $z = 0.4$ to show the electron density associated with a single molecule of ethylene carbonate.

that the scattering curve for this atom is not spherically symmetrical. The calculated structure amplitudes are too low for the $\{0k0\}$ planes and for other planes vicinal to these, showing that 5 Å² is too high a value of B to apply. Better agreement would be obtained by using a value $B = 2$ Å² for planes perpendicular to $[b]$, and gradually increasing B with angle of inclination until a value 5 Å² is reached for planes parallel to $[b]$. A quantitative treatment along these lines would certainly reduce the value of the residual R , but was not carried out because it was felt that the uncertainty regarding the reliability of the experimental intensities did not warrant it.

Description of the structure

The crystal structure of ethylene carbonate consists of discrete molecules lying in layers almost parallel to the (001) face. All the molecules in a layer have their carbonyl group directed in the same way, but alternate layers have them pointing in opposite directions

Table 1. *Experimental and calculated structure amplitudes*

<i>hkl</i>	<i>F</i> (exp.)	<i>F</i> (calc.)	<i>hkl</i>	<i>F</i> (exp.)	<i>F</i> (calc.)	<i>hkl</i>	<i>F</i> (exp.)	<i>F</i> (calc.)
000	—	+184	51 $\bar{3}$	8	+11	424	7	+ 7
002	74	-71	51 $\bar{2}$	5	- 2	425	4	+ 3
004	6	+ 7	51 $\bar{1}$	25	-24	426	5	- 4
006	1	- 1	510	12	+ 7	427	1	- 1
008	1	+ 3	511	21	+21	62 $\bar{8}$	1	0
20 $\bar{8}$	1	+ 2	512	3	+ 5	62 $\bar{6}$	2	- 2
20 $\bar{6}$	4	- 6	513	8	-10	625	2	- 1
204	27	+30	514	10	- 9	62 $\bar{3}$	7	- 5
20 $\bar{2}$	78	-82	515	3	+ 4	62 $\bar{2}$	3	+ 3
200	62	+64	516	3	+ 3	62 $\bar{1}$	7	+ 8
202	5	0	517	1	- 2	620	2	+ 1
204	5	- 3	71 $\bar{7}$	1	+ 2	621	1	- 1
206	2	- 5	71 $\bar{6}$	2	+ 4	622	8	- 7
208	2	+ 3	71 $\bar{5}$	4	- 7	623	5	- 3
40 $\bar{8}$	3	+ 3	714	2	+ 1	624	6	+ 4
40 $\bar{6}$	10	- 8	71 $\bar{3}$	9	+13	625	1	0
404	25	+26	712	3	- 3	626	1	+ 1
40 $\bar{2}$	16	-18	71 $\bar{1}$	10	-15	82 $\bar{7}$	1	0
400	20	-10	710	5	- 5	82 $\bar{6}$	1	- 1
402	12	+ 7	711	4	+ 7	82 $\bar{5}$	3	+ 2
404	3	+ 6	712	9	+ 9	82 $\bar{3}$	3	- 4
406	3	- 5	714	3	- 3	82 $\bar{2}$	3	0
60 $\bar{8}$	3	+ 4	91 $\bar{5}$	3	- 5	82 $\bar{1}$	2	0
60 $\bar{6}$	6	- 8	91 $\bar{3}$	3	+ 5	820	6	+ 3
604	3	+ 4	91 $\bar{2}$	3	+ 3	821	3	+ 2
60 $\bar{2}$	10	+ 9	91 $\bar{1}$	1	- 2	822	3	- 2
600	8	- 5	910	6	- 6	824	1	- 2
602	6	- 8	911	2	0	10,2,4	1	- 1
604	6	+ 8	912	2	+ 2	10,2,3	1	0
606	2	- 2	913	1	- 1	10,2,2	3	- 1
804	4	- 4	914	2	+ 1	10,2,1	1	- 1
80 $\bar{2}$	2	+ 1	11,1,2	3	+ 3	10,2,0	1	0
800	7	+ 8	11,1,1	2	+ 1	10,2,1	1	- 1
802	6	- 9	11,1,0	1	- 1	10,2,2	2	+ 3
804	2	+ 4	020	12	- 8	13 $\bar{7}$	3	+ 3
10,0,2	3	- 6	021	1	+ 1	135	7	- 8
10,0,0	4	+ 7	022	15	+15	134	4	- 3
10,0,2	2	- 3	023	11	+11	133	1	+ 3
11 $\bar{7}$	3	+ 3	024	14	-16	132	18	+13
11 $\bar{6}$	3	- 5	025	8	- 9	131	14	+ 8
115	4	- 4	026	4	+ 6	130	22	-15
114	3	0	027	2	+ 2	131	1	+ 2
113	1	- 4	028	1	+ 1	132	3	+ 1
11 $\bar{2}$	29	+34	22 $\bar{8}$	1	- 3	133	10	- 9
11 $\bar{1}$	18	+18	227	3	- 5	134	2	+ 3
110	47	-47	226	5	+10	135	3	+ 3
111	1	+ 2	225	3	+ 5	136	1	- 1
112	1	- 2	224	3	- 8	137	1	+ 3
113	13	-15	223	3	+ 2	33 $\bar{7}$	2	+ 4
114	8	+ 8	222	1	+ 2	336	2	+ 2
115	8	+10	221	3	- 2	334	8	- 7
117	2	- 4	220	14	-12	333	8	- 6
118	2	- 3	221	17	-14	332	10	+ 8
31 $\bar{7}$	1	+ 1	222	23	+17	331	1	+ 2
31 $\bar{6}$	3	+ 1	223	14	+13	330	3	+ 2
31 $\bar{5}$	1	+ 3	224	5	- 4	331	10	+ 6
314	15	-16	225	3	- 2	332	8	- 6
31 $\bar{3}$	2	- 3	226	3	- 4	333	2	+ 1
31 $\bar{2}$	20	+23	227	1	- 2	334	2	+ 1
31 $\bar{1}$	13	-12	228	2	+ 3	335	4	- 7
310	5	+ 3	42 $\bar{8}$	1	- 3	336	1	+ 1
311	28	+29	427	2	- 2	337	2	+ 4
312	13	-10	425	1	- 2	53 $\bar{2}$	3	- 3
313	18	-19	424	2	+ 2	53 $\bar{1}$	6	- 2
314	1	- 4	423	1	+ 1	530	11	+ 6
315	6	+ 9	422	4	+ 2	531	1	- 3
316	4	+ 6	421	13	+10	532	3	- 1
317	1	- 3	420	13	- 9	73 $\bar{2}$	3	- 4
51 $\bar{8}$	1	- 1	421	13	-12	73 $\bar{1}$	2	0
51 $\bar{6}$	6	+ 7	422	2	+ 1	730	2	0
514	6	- 9	423	2	+ 1	731	7	- 7

Table 1 (cont.)

<i>hkl</i>	<i>F</i> (exp.)	<i>F</i> (calc.)	<i>hkl</i>	<i>F</i> (exp.)	<i>F</i> (calc.)	<i>hkl</i>	<i>F</i> (exp.)	<i>F</i> (calc.)
732	2	+ 2	841	2	+ 2	062	11	+ 7
931	3	+ 3	842	2	- 2	063	6	+ 4
930	3	- 2	10,4,1	2	- 2	064	4	- 2
931	1	- 2	157	3	+ 3	065	4	- 3
932	2	+ 1	155	4	- 5	266	2	+ 2
040	29	+17	154	3	+ 3	265	2	+ 3
041	18	+10	152	7	- 6	264	6	- 5
042	19	-13	151	5	+ 6	263	1	0
043	3	+ 4	150	8	+ 6	262	8	+ 9
044	6	+ 5	151	3	+ 1	261	1	0
045	8	- 7	152	3	- 2	260	7	- 6
046	1	- 2	153	9	-10	261	6	- 4
047	2	+ 2	155	4	+ 6	262	2	+ 1
247	2	- 3	156	2	0	263	4	+ 4
246	3	- 4	357	2	+ 2	264	1	0
245	1	+ 1	356	2	- 1	462	3	+ 3
244	9	+ 9	354	4	+ 3	461	3	+ 3
243	8	+ 8	353	2	- 3	461	4	- 3
242	17	-13	352	3	- 3	661	2	+ 2
241	11	- 8	351	6	- 4	661	2	+ 1
240	15	+10	350	1	0	662	3	+ 2
241	12	- 8	351	16	+13	174	1	- 1
242	5	- 4	352	2	+ 2	173	1	0
243	13	+11	353	10	-10	172	1	- 2
244	1	0	354	1	- 1	171	3	+ 2
245	3	- 3	355	2	+ 3	170	1	+ 2
246	1	0	552	1	+ 1	171	2	- 1
442	4	- 4	551	15	-12	172	1	+ 1
441	13	+ 9	550	3	- 3	174	1	- 1
440	1	0	551	14	+10	374	1	+ 1
441	18	-13	552	2	+ 2	373	2	- 2
442	3	+ 1	752	2	+ 2	372	1	- 3
642	2	+ 2	751	7	- 8	371	2	+ 1
641	13	+11	750	1	- 1	370	1	0
640	3	- 2	751	1	+ 2	371	1	0
642	2	0	752	2	0	571	1	0
842	2	0	951	1	0	570	1	0
841	2	+ 2	060	17	-11	080	3	- 1
			061	1	- 1	081	3	+ 2

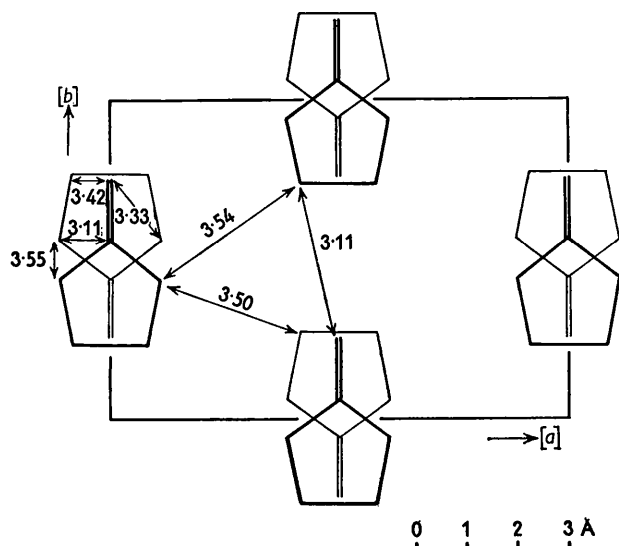


Fig. 2. Diagrammatic projection of contents of one unit cell on to the (001) face, showing packing and inter-molecular contacts. The thick-lined molecules lie approximately in the plane $z = 0.25$; the thin-lined in the plane $z = 0.75$.

(see Fig. 2). The final atomic coordinates are listed in Table 2.

The bond lengths and inter-bond angles are shown in Fig. 3. The normal aliphatic single bonds for C-C and C-O are usually regarded as 1.54 and 1.42 Å respectively, so those found in the ethylenic part of the molecule are not significantly different from the standard values. In the carbonate portion, though, the bond lengths are rather more unusual. The C-O distances in a true carbonate ion are generally equal at about 1.24 Å, as in calcite and sodium sesquicarbonate. When two of the oxygen atoms are bonded,

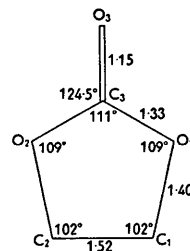


Fig. 3. Dimensions of a single molecule.

Table 2. *Atomic coordinates*

	x/a	y/b	z/c
C ₁	0.085	0.230	0.290
C ₃	0	0.564	0.250
O ₁	0.110	0.443	0.351
O ₃	0	0.748	0.250

as in this case, it might be expected that in the CO₃ group, there would be one double and two single bonds of about 1.24 and 1.42 Å respectively. Each of these bonds in ethylene carbonate is 0.09 Å short at 1.15 Å (for the 'double' bond) and 1.33 Å (for the 'single' bond). The system of electronic orbits which cause this shortening has not yet been worked out, but it is probably of general occurrence in this class of compound. In furoic acid (Goodwin & Thomson, 1953), for example, two of the C-O bonds in the ring have lengths 1.30 and 1.31 Å, and in the analogous ethylene thiourea (Wheatley, 1953), the corresponding C-N bonds shorten to 1.32 Å.

The C=O distance of 1.15 Å at first sight seems abnormally short. It is difficult to see why it should be less than the accepted double-bond value whereas the corresponding C=S bond in ethylene thiourea (Wheatley, 1953) is appreciably longer than a double bond. On the other hand distances of 1.15 Å for C=O have been observed by electron diffraction (Allen & Sutton, 1950) in a wide variety of compounds containing a carbonyl group. If the C=O in ethylene carbonate is considered as belonging to this class, it becomes necessary to explain why the C=S in ethylene thiourea has such a vastly different bond order. For the purpose of checking the reliability of the 1.15 Å distance, a section of a three-dimensional Fourier synthesis using calculated structure amplitudes as coefficients was computed along the line $0, y, \frac{1}{4}$. The results of this gave the C₃ and O₃ peaks at 0.564 and 0.746 compared with the values 0.564 and 0.748 (Table 2) obtained when experimental F 's were used. It would therefore appear that no correction needs to be applied to this bond length, which is probably correct to ± 0.01 Å.

The ethylene carbonate molecule is not planar. The CO₃ group is of necessity planar on account of the twofold axis of symmetry, but the line joining C₁ to C₂ makes an angle of 20° with the plane containing the

CO₃ group. This should be compared with the strict planarity found in the rings of ethylene thiourea and furoic acid, and the non-planarity of five-membered rings such as occur in furanose sugars (e.g. sucrose, cytidine). Despite this non-planarity and the wide range of bond lengths and angles, the distances between next-but-one atoms show a fair degree of constancy, e.g. O₁-O₂ 2.19; O₂-O₃ 2.20; C₁-C₃ 2.22; and C₁-O₂ 2.27 Å.

The nearest intermolecular contacts in the layers are 3.11 Å between the carbonyl oxygen (O₃) and the pair of CH₂ atoms belonging to the next molecule along the b axis; there are also distances of 3.54 and 3.76 Å between the CH₂ and other oxygen atoms. Between the layers there are short approaches of 3.11 Å from C₃ to O₁ and O₂ of neighbouring molecules, and also 3.33 Å between O₃ and O₁ and O₂. These and other contacts are shown in Fig. 2. The particularly close approach between the CH₂ groups and the neighbouring carbonyl oxygen suggests either strong dipole interaction or hydrogen-bond formation. Carbon does not usually form hydrogen bonds and no very definite examples can be quoted. Whether in this case sufficient electrons have drifted from other atoms in the ring to give the carbon enough electronegativity to cause hydrogen-bond formation is a matter for speculation. In other recent structures, e.g. threonine (Shoemaker, Donohue, Schomaker & Corey, 1950) and glycyl tyrosine hydrochloride (Smits & Wiebenga, 1953) short distances of the same order as this are exhibited between carbon and oxygen atoms in similar circumstances, and it would be an interesting study to determine exactly the role of the hydrogen atom in these surroundings.

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