BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 928—933 (1971)

The Molecular and Crystal Structure of 3,4-Furandicarboxylic Acid Dimethylester

Yasuyoshi OKADA,* Kazumi NAKATSU,** and Akira SHIMADA

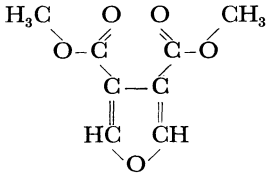
Department of Chemistry, Faculty of Science, Osaka City University, Sugimotocho, Osaka

(Received September 9, 1970)

The crystals of 3,4-furandicarboxylic acid dimethylester are monoclinic of the space group $P2_1/a$, with unit cell dimensions $a=12.64$, $b=8.16$, $c=7.97$ Å, and $\beta=100.0°$. An approximate structure was determined by application of the symbolic addition phase determining procedure. After several cycles of least-squares refinement, the discrepancy index for the 901 observed reflections was reduced to 14%. In the molecule the furan ring is planar, and one carbomethoxy group is almost on the same plane as the furan ring, while the other makes an angle of 10.5° with the ring. The bond lengths and angles do not differ appreciably from the values found in the other compounds, except for those of C(3)–C(4)=1.41 Å, C(4)–C(3)–C(6)=131° and C(3)–C(4)–C(7)=132°, the latter two being larger than normal values probably because of interaction between the carbonyl-oxygens. The mode of packing of the molecules and a scheme of twinning found in this crystal is discussed.

3,4-Furandicarboxylic acid dimethylester (I) (MW 184, mp 47°C) was studied by means of X-ray crystal analysis to elucidate its molecular structure and the mode of packing in the crystal. Several structures similar to that of the present molecule were studied. They include 3,4-furandicarboxylic acid,[1] furan-α,α'-dicarboxylic acid[2] (or 2,5-furandicarboxylic acid), and 3,4-thiophendicarboxylic acid dimethylester.[3] It would be of interest to compare the present structure with the others, especially about the configurations of the two substituents with respect to the furan ring and the bond distances and angles inside it.

(I)



Experimental

Specimens of suitable size for X-ray work were crystallized from the aqueous solution in the form of a transparent, colorless column elongated along the c axis.[4] The crystals have a cleavage plane normal to the a^* axis.

The compound crystallizes always in a twinned form; the twinning is found to be such that the twins have common a^* and b^* but different c^* direction. Twinning made the accurate intensity determinations difficult, for partial or heavy overlappings of the reflections from the twins occurred in some zones.

Since the crystals sublime readily in the air at room temperature, the specimen was enclosed in a capillary tube during exposure to X-rays. Multiple Weissenberg intensity data were collected with Ni-filtered Cu $K\alpha$ radiation along axis c from zeroth to fifth layer and along axes a and b for zeroth layer only. The intensities were estimated visually with the use of a calibrated scale. Altogether 1239 independent reflections were observed, and 338 of them were too weak to be

* Present address: NIKKI Chemical Co., Ltd., 4-51 Kitahama, Osaka.

** Present address: Faculty of Science, Kwansei Gakuin University, 1-2 Uegahara, Nishinomiya.

1) D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 660 (1964).

2) E. Martuscelli and C. Pedone, *Acta Crystallogr.*, **B24**, 175 (1968).

3) H. Yoshioka, K. Nakatsu, and A. Shimada, to be published.

4) The crystals were kindly prepared by Professor S. Oae, Faculty of Technology of Osaka City University.

measured. No correction was made for absorption and extinction. After the Lorentz and the polarization corrections were made, intensities were placed on a same relative scale.

The crystal data are as follows:
Monoclinic,
$a=12.64\pm0.04$ Å
$b=8.16\pm0.02$
$c=7.97\pm0.02$
$\beta=100.0\pm0.1°$
Systematic Absences, $h0l$ with h odd and $0k0$ with k odd
Space Group, $P2_1/a$
Density, $D_m=1.50$ g cm^{-3}, $D_x=1.51$ g cm^{-3}
Z 4
Absorption Coefficient, $\mu=12.7$ cm^{-1} (for Cu $K\alpha$).

Structure Determination

Since attempts to solve the Patterson map were not successful, the direct phase determining method, or so-called symbolic addition method[5] by Karle *et al.*, was applied. Professor Y. Okaya of State University of New York kindly supplied us with a copy of his program.[6]

In this procedure normalized structure factors may be used, being defined as

$$E_h^2 = F_h^2/\varepsilon \sum_{j=1}^{N} f^2{}_j h^2, \qquad (1)$$

where F_h is the observed structure factor for the reflection $\boldsymbol{h}$, and N is the number of atoms in the unit cell. ε is a factor that depends on the space group extinctions, and $\varepsilon=1$ in the space group $P2_1/a$ except for the $h0l$ and $0k0$ reflections, where $\varepsilon=2$. The distribution and the statistical averages of the normalized structure factor are given in Table 1. The experimental values imply that the crystal is centrosymmetric.

To initiate the symbolic addition procedure, three linearly independent reflections were chosen to specify the origin. The signs of two other reflections were specified symbolically by letters. These five reflections forming the basic starting set are as follows:

Table 1. Statistical averages and distribution of the normalized structure factors

	Experimental	Theoretical	
		Centric	Acentric
$\langle\|E^2\|\rangle$	1.000[a]	1.000	1.000
$\langle\|E^2-1\|\rangle$	1.059	0.968	0.736
$\langle\|E\|\rangle$	0.726	0.798	0.886
$\|E\|>3$	0.26%	0.3%	0.01%
$\|E\|>2$	5.1	5.0	1.8
$\|E\|>1$	31.0	32.0	36.8

a) Normalized to the unity.

$h\ k\ l$	$\|E\|$	sign	$h\ k\ l$	$\|E\|$	sign
1 1 2	3.63	+	3 5 0	3.53	A
5 3 1	2.76	+	8 2 0	2.72	B
3 4 1	2.67	+			

These reflections were chosen on the basis of the large number of interactions obtained from application of the Σ_2 formula and on their relatively high $|E|$ values. The Σ_2 formula is

$$sE_h \approx s\sum_{k} E_k \cdot E_{h-k}, \qquad (2)$$

where s means "sign of". The probability $P_s(E_h)$ that a symbolic phase s determined by the Σ_2 formula is valid is given by[6]

$$P_s(E_h) = 1/2 + 1/2 \tanh\left(\frac{\sigma_3}{\sigma_2^{3/2}}|E_h|\cdot R_s\right), \qquad (3)$$

where $\sigma_n=\sum_{j=1}^{N} Z_j{}^n$, Z_j is the atomic number of the jth atom and R_s is the difference between the sum of the products $E_k \cdot E_{h-k}$ associated with the dominant symbol(s) and the sum of the products of all other symbols.

Table 2. A typical sigma-2 list

Reflection $\boldsymbol{h}=(3\ 6\ 3)$ $|E|=1.69$

k			$\|E_k\|$	$h-k$			$\|E_{h-k}\|$	T[a]	s_k[b]	s_{h-k}	s_h
9	4	3	3.41	−6	2	0	2.13	12.27	−A B		
9	5	1	2.61	−6	1	2	1.82	8.03	B	−A B	−A
1	8	1	3.11	2	−2	2	1.95	10.25	A	− B	−A B
10	3	5	2.49	−7	3	−2	2.41	10.14	−A B		
10	3	1	2.48	−7	3	2	2.90	12.15		B	
0	8	2	2.35	3	−2	1	2.17	8.62		B	
0	9	3	2.16	3	−3	0	1.72	6.28	+	−A	−A
2	7	1	1.85	1	−1	2	3.63	11.35	−A B	+	−A B
8	1	2	1.82	−5	5	1	1.66	5.11	−		
8	−1	2	1.82	−5	7	1	1.61	4.95	+		
6	1	−2	1.82	−3	5	5	2.49	7.66	A B	−	−A B
4	0	3	1.82	−1	6	0	1.70	5.20	B	−A	−A B

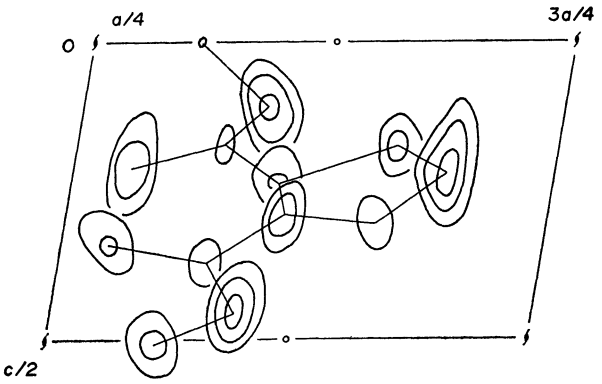
$R_s=11.91$ $P_s(E_h)=0.9965$ Phase $=-$AB

a) $T=|E_h \cdot E_k \cdot E_{h-k}|$
b) s's mean sign or phase of $\boldsymbol{h}$, $\boldsymbol{k}$, or $(\boldsymbol{h}-\boldsymbol{k})$.

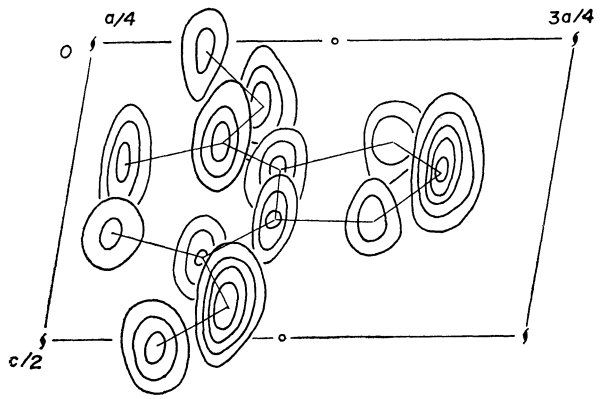
5) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
6) Y. Okaya and A. Bednowitz, *ibid.*, **22**, 111 (1967).

Only 220 reflections with $|E|$ greater than 1.5 were considered. As many terms in Σ_2 as possible were used to determine each phase. An example of Σ_2 list is given in Table 2, which contains all the interaction pairs giving the index triplet for which a phase should be assigned. Some of these terms seem to indicate a relationship between the unknown symbols. After four cycles of iterations, the phases for 138 reflections were expressed by the combinations of A and B. Inspection of all the Σ_2 interaction lists showed that there was only one possible assignment for the unknown A and B, that is, A=+ and B=+. Any other assignment would have resulted in discrepancies in a number of contributors to Σ_2. This relation was taken into account and 29 additional phases of the reflections were determined. Thus 167 phases were settled.

E maps (Fourier map with E rather than F values for coefficients) were computed with both the 138 and 167 reflections. All the thirteen non-hydrogen atoms in the asymmetric unit were resolved. Sections from these maps are illustrated in Figs. 1(a) and (b). On the E map shown in Fig. 1(b), the peak values for all the atoms exceeded 220 (on an arbitrary scale), while the maximum value of the rapidly varying background was 193.



(a)



(b)

Fig. 1. E maps computed with 138 terms (a) and 167 terms (b).

Coordinates for the thirteen non-hydrogen atoms as read from the E map were subjected to a least-squares refinement, using all the reflection data. After three cycles of diagonal least-squares calculations, the discrepancy index $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was reduced to 0.21 for the non-zero reflections only. Successive two cycles of block-diagonal calculations lowered R only by 2%.

Electron density and difference Fourier syntheses were calculated at this stage of refinement. Sections of the three-dimensional electron density map projected on (010) are given in Fig. 2. Since remarkable anisotropic thermal vibration of the atoms were implied from the difference Fourier map, further refinement was carried out with the anisotropic temperature factors applied to the thirteen non-hydrogen atoms. Two more cycles of block-diagonal least-squares calculations improved R to 0.135. The peaks of hydrogen atoms did not appear in the difference map even at this stage.

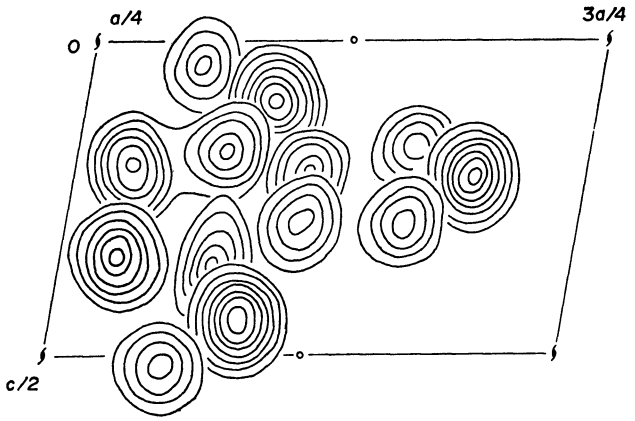


Fig. 2. Sections of electron density distribution projected onto (010) plane. Contours are drawn at intervals of 1 e·Å^{-3}, starting at 2 e·Å^{-3}.

Results and Discussion

The final coordinates and temperature factors of the atoms are listed in Table 3(a) and (b), respectively, and the intramolecular distances and angles are given in Table 4 and Fig. 3. In Table 5 the bond distances and angles inside the furan ring found in the several similar molecules are compared with the mean values in the present one, where the furan ring has approximately a mirror symmetry through O(1) and the midpoint of C(3)–C(4) bond.

The ring C–O lengths of 1.36 and 1.35 Å are very close to the values found in various compounds. The double bond lengths of 1.37 and 1.38 Å in the ring are nearly equal to the value of 1.361 Å found in furan, but greater than the values 1.351 and 1.35_4 Å found in 3,4-acid and α,α'-acid, respectively. The single bond distance 1.41 Å in the ring appears to be significantly shorter than the value 1.462 Å found in 3,4-acid. The single bonds between the ring and the carbonyl group are 1.45 and 1.47 Å long, the former

Table 3. Atomic parameters

(a) Fractional Coordinates and Their Standard Deviations

Atom	x	$10^4\sigma(x)$	y	$10^4\sigma(y)$	z	$10^4\sigma(z)$
O (1)	0.6383	6	0.0405	9	0.2204	10
C (2)	0.5794	8	−0.0929	14	0.1699	15
C (3)	0.4782	8	−0.0739	12	0.2128	13
C (4)	0.4783	8	0.0802	12	0.2934	14
C (5)	0.5785	9	0.1448	13	0.2973	16
C (6)	0.3949	9	−0.1991	13	0.1734	15
C (7)	0.3958	8	0.1673	12	0.3676	14
O (8)	0.4320	6	−0.3240	9	0.0954	10
O (9)	0.3059	6	−0.1923	11	0.2059	12
O (10)	0.3032	6	0.1293	11	0.3453	12
O (11)	0.4350	6	0.2979	9	0.4465	10
C (12)	0.3567	10	−0.4578	16	0.0345	18
C (13)	0.3621	9	0.4007	14	0.5227	16

(b) Thermal Parameters and Their Standard Deviations ($\times 10^4$)

Temperature factor $=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

Atom	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
O (1)	53	5	172	13	211	18	−18	14	96	15	−76	25
C (2)	52	8	151	18	187	25	−11	20	62	21	−35	36
C (3)	43	7	127	15	146	22	−6	17	57	18	−12	31
C (4)	46	7	108	15	167	23	4	17	62	19	−10	31
C (5)	53	8	142	18	240	27	10	20	83	23	−49	36
C (6)	56	8	125	16	193	26	−2	16	45	21	−20	34
C (7)	53	7	126	16	153	23	−3	18	62	20	1	32
O (8)	57	6	161	13	232	19	−14	15	89	16	−142	26
O (9)	59	6	193	16	355	23	−50	17	144	19	−143	31
O (10)	55	6	204	16	336	23	−2	17	102	19	−147	31
O (11)	56	5	160	13	194	17	2	14	73	15	−81	25
C (12)	71	10	185	22	272	32	−63	25	72	27	−151	44
C (13)	72	9	166	19	195	27	40	22	80	24	−188	39

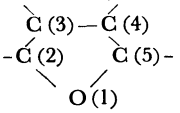
Table 4. Interatomic distances and bond angles in a molecule (standard deviations in parenthesis)

Interatomic distances (Å)		Bond angles (°)	
O(1)–C(2)	1.364 (0.014)	C(2)–O(1)–C(5)	108.9 (0.9)
C(2)–C(3)	1.383 (0.016)	O(1)–C(2)–C(3)	108.9 (1.0)
C(3)–C(4)	1.412 (0.015)	C(2)–C(3)–C(4)	106.7 (1.0)
C(4)–C(5)	1.374 (0.017)	C(3)–C(4)–C(5)	106.7 (1.0)
C(5)–O(1)	1.362 (0.015)	C(4)–C(5)–O(1)	108.8 (1.0)
C(3)–C(6)	1.454 (0.016)	C(2)–C(3)–C(6)	121.9 (1.0)
C(4)–C(7)	1.468 (0.016)	C(4)–C(3)–C(6)	131.4 (1.0)
C(6)–O(8)	1.323 (0.015)	C(5)–C(4)–C(7)	121.1 (1.0)
C(6)–O(9)	1.210 (0.015)	C(3)–C(4)–C(7)	132.2 (1.0)
C(7)–O(10)	1.197 (0.015)	C(3)–C(6)–O(8)	110.0 (1.0)
C(7)–O(11)	1.294 (0.014)	C(3)–C(6)–O(9)	126.5 (1.1)
O(8)–C(12)	1.477 (0.016)	O(8)–C(6)–O(9)	123.5 (1.1)
O(11)–C(13)	1.459 (0.015)	C(4)–C(7)–O(10)	123.9 (1.1)
		C(4)–C(7)–O(11)	110.9 (0.9)
C(2)–O(8)	2.639 (0.014)	O(10)–C(7)–O(11)	124.8 (1.1)
C(5)–O(11)	2.642 (0.015)	C(6)–O(8)–C(12)	117.9 (1.0)
O(9)–C(12)	2.700 (0.017)	C(7)–O(11)–C(13)	117.6 (0.9)
O(9)–O(10)	2.849 (0.013)		
O(10)–C(13)	2.672 (0.016)		

Table 5. Comparison of bond lengths and angles in furan ring with similar substances

	3,4-ester[a]	2,5-acid[b]	3,4-acid[c]	furan[d]
O(1)–C(2)[e]	1.36_3 Å	1.36_8 Å	1.361 Å	1.3621 Å
C(2)–C(3)	1.37_9	1.35_4	1.351	1.3609
C(3)–C(4)	1.41_2	1.44_2	1.462	1.4309
$\sigma \times 10^3$(Å)	14—17	6—8	3—5	1—2
C(2)–O(1)–C(5)	108.9°	104.4°	107.2°	106.55°
O(1)–C(2)–C(3)	108.9	112.3	110.3	110.68
C(2)–C(3)–C(4)	106.7	105.4	105.7	106.05
σ(°)	0.9—1.1	0.5	0.2—0.3	0.067

a) Present work. The mean values are shown. b) 2,5-furandicarboxylic acid (furan-α,α'-dicarboxylic acid)[2]. c) 3,4-furandicarboxylic acid[1]. d) Results from microwave spectroscopy[7]. e) Key;



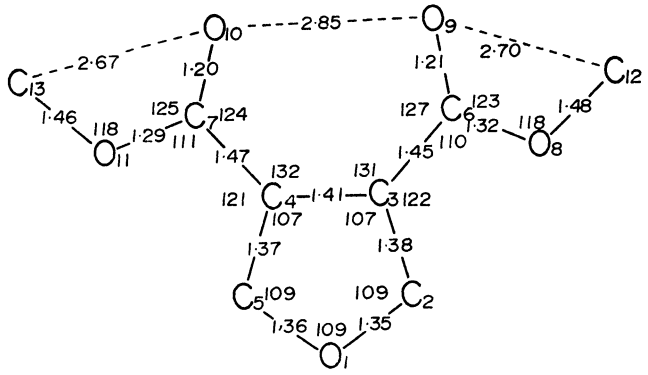


Fig. 3. The molecular structure projected on the plane of furan ring. Standard deviations are about 0.016Å and 1.0°.

is slightly shorter than the usual value.

The furan ring is accurately planar, and the equation of the mean plane and the deviations of the atoms from this plane are given in Table 6, in which the planes of carbonyl groups are also described. The oxygen atoms in one of the carboxyl group, O(10) and O(11), are markedly out of the plane of furan ring; the twist angle of the carboxyl group with respect to the ring plane is 10.5°. The other carboxyl oxygen atoms, O(8) and O(9), on the other hand, are almost completely on the same plane as the ring.

The distance between the two carboxyl oxygen atoms is 2.85 Å, which is just the twice of the van der Waals radius of oxygen atom and should be compared to the value of 2.91 Å found in 3,4-thiophendicarboxylic acid dimethylester.[3] The angles C(4)–C(3)–C(6)= 131° and C(3)–C(4)–C(7)=132° deviate considerably from the ideal value 126°. This would be due to the steric hindrance between the two substituents. The interaction would also cause the distortion of the bond angles around C(6) and C(7), *viz.*, C(3)–C(6)–O(9) and C(4)–C(7)–O(10) are increased, while C(3)–C(6)–O(8) and C(4)–C(7)–O(11) are reduced by several degrees each.

The mode of packing of the molecules in the crystal can be seen in Figs. 4 and 5. The furan rings incline

Table 6. Mean plane parameters and deviations of the atoms from the plane

Plane 1. Furan ring defined by O(1), C(2), C(3), C(4), and C(5).

$-0.1718X+0.4360Y-0.8834Z+2.7242=0$

Atom	Deviation	Atom	Deviation
O(1)	+0.0060 Å	O(8)	−0.0064 Å
C(2)	−0.0022	O(9)	−0.0036
C(3)	−0.0024	O(10)	+0.2138
C(4)	+0.0060	O(11)	−0.1501
C(5)	−0·0074	C(12)	+0.0881
C(6)	−0.0034	C(13)	−0.1360
C(7)	−0.0013		

Plane 2. Carboxyl group defined by C(3), C(6), O(8), and O(9).

$-0.1716X+0.4346Y-0.8841Z+2.7251=0$

Atom	Deviation	Atom	Deviation
C(3)	−0.0002 Å	O(9)	−0.0002 Å
C(6)	+0.0005	C(12)	+0.0964
C(8)	−0.0002		

Plane 3. Carboxyl group defined by C(4), C(7), O(10), and O(11).

Atom	Deviation	Atom	Deviation
C(4)	+0.0081 Å	O(11)	+0.0086 Å
C(7)	−0.0294	C(13)	+0.0209
O(10)	+0.0132		

Dihedral angles between the planes.

Plane 1—Plane 2 0.1°

Plane 1—Plane 3 10.5°

by 64° to the (010) plane, and contact each other alternatively with the interplanar separation of 3.28 Å across the center of symmetry at (1/2, 0, 1/2) and 2.83 Å across that at (1/2, 0, 0). Hence, the molecules are thought to be stacked along the *c* direction with their planes parallel to each other but in opposite orientation. There are gaps between the molecular layers parallel to the *bc* plane. This explains for the crystals showing a cleavage parallel to this plane. The intermolecular distances less than 3.7 Å are listed in Table

7) B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaad, J. R. Andersen, and M. Schottlander, *J. Mol. Spectrosc.*, **9**, 124 (1962).

Table 7. Intermolecular distances less than 3.7 Å

From	To	At	Distance	From	To	At	Distance
O(1)	C(3)	IV	3.52 Å	C(2)	C(13)	VII	3.50 Å
	C(6)	IV	3.35	C(3)	C(7)	VII	3.53
	C(8)	IV	3.42		O(11)	VII	3.30
	O(9)	III	3.56	C(4)	C(4)	VII	3.50
	O(10)	VII	3.68	C(5)	C(7)	VII	3.66
	C(12)	III	3.42		O(8)	IV	3.44
	O(10)	IX	3.45		O(10)	IX	3.35
	C(13)	IX	3.42	C(6)	O(11)	VII	3.49
C(2)	C(2)	IV	3.42	O(8)	C(12)	V	3.51
	C(3)	IV	3.30		C(13)	VII	3.70
	C(4)	IV	3.63	O(9)	C(13)	VIII	3.37
	C(6)	IV	3.68		C(12)	II	3.19
	C(7)	VII	3.70	O(10)	C(13)	VIII	3.12
	O(9)	III	3.33		C(12)	II	3.41
	O(11)	VII	3.52	O(11)	C(13)	VI	3.53

I	x	y	z	VI	$1-x$	$1-y$	$1-z$
II	$1/2-x$	$1/2+y$	$-z$	VII	$1-x$	$-y$	$1-z$
III	x	$-1+y$	z	VIII	$1/2-x$	$-1/2+y$	$1-z$
IV	$1-x$	$-y$	$-z$	IX	$1/2+x$	$1/2-y$	z
V	$1-x$	$-1-y$	$-z$				

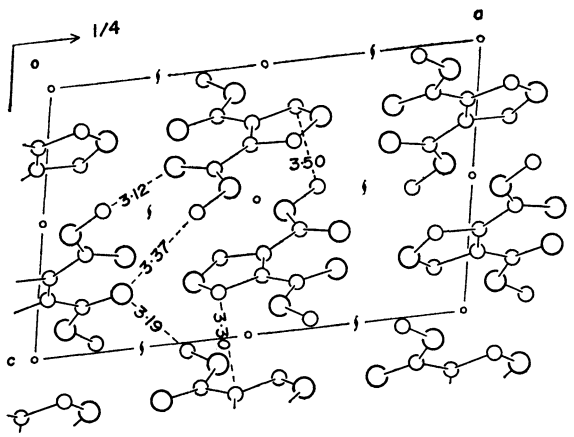


Fig. 4. The crystal structure viewed along the b axis.

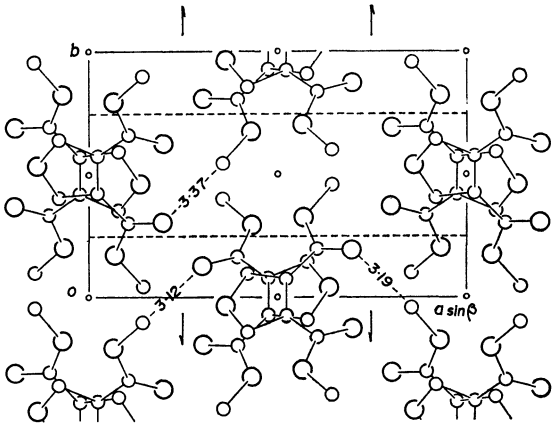


Fig. 5. The crystal structure viewed along the c axis.

7, in which several close approaches are found between the carbonyl oxygen atom and the methyl group, and between the furan ring carbon atoms.

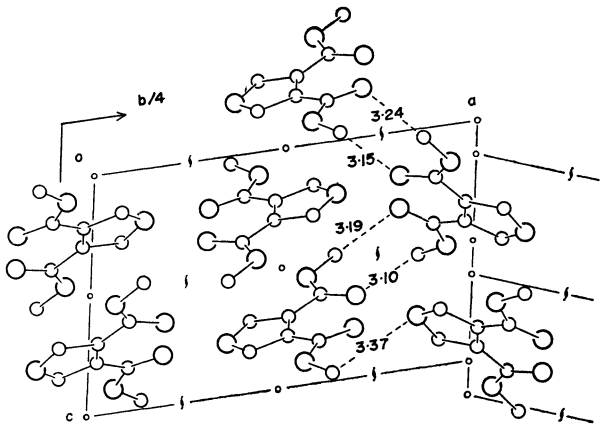


Fig. 6. Proposed scheme of twinning.

A submicroscopic scheme of twinning is proposed, as shown in Fig. 6. The boundary surface of the twin components is assumed on the crevice that lies between the molecular layers parallel to the bc plane, and the layer on $x=a$ is inverted and translated along axes b and c so that the twins have common a^* and b^* directions but different c^* direction. Thus, the resultant intermolecular distances across the crevice on $x=a/2$ and $x=a$ take reasonable values as shown in the figure.

The authors wish to express their sincere thanks to Professor Yoshiharu Okaya of State University of New York and Professor Tamaichi Ashida of Osaka University who kindly gave us computing facilities.

Tables of the observed and calculated structure factors are kept as Document No. 7104 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥ 600 for photoprints. Pay by check or money order payable to: Chemical Society of Japan,