Recent electron microscope studies of crystalline Nylon-6 specimens prepared from single crystals of the monomer reveal that twinning is of frequent occurrence in the polymer crystals (Fischer, 1965). The twinning appears to involve rotation of successive layers, or groups of layers, of the type shown in Fig. 3, by 55° relative to one another. Such twinning is not observed in Nylon specimens prepared from the melts (Macchi, 1966). Although the detailed mechanism of the twinning is not known, it is not difficult to relate the 55° twin angle of the polymer to the 55° by which molecular chains in successive layers of the monomer are inclined to one another.

References

Bednowitz, A. & Post, B. (1966). *Acta Cryst.* **21**, 566.
Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.
Fischer, E. (1965). Unpublished work.
Hahn, T. (1957). *Z. Kristallogr.* **109**, 438.
Hamilton, W. C. (1965). *Norelco Reporter*, **12**, 33.
Hauptman, H. & Karle, J. (1953). *The Solution of the Phase Problem.* Amer. Cryst. Assoc. Monograph No. 3.
Holmes, D. R., Bunn, C. W. & Smith, D. J. (1955). *J. Polymer Science*, **17**, 159.
Johnson, C. K. (1965). Report no. 3794. Oak Ridge National Laboratory, Tennessee.
Karle, I. & Karle, J. (1963). *Acta Cryst.* **16**, 969.
Macchi, E. (1966). Private communication.
Morosoff, N., Lim, D. & Morawetz, H. (1964). *J. Amer. Chem. Soc.* **86**, 3167.
Muller, E. (1952). *Methoden der Anorganischen Chemie, Makromoleculare Stoffe*, II, 14/2, pp. 105–6.
Okaya, Y. & Bednowitz, A. (1967). *Acta Cryst.* **22**, 111.
Simpson, H. J. & Marsh, R. E. (1966). *Acta Cryst.* **20**, 550.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151.
Woolfson, M. (1954). *Acta Cryst.* **7**, 721.
Wright, D. E. & Marsh, R. E. (1962). *Acta Cryst.* **15**, 54.

Acta Cryst. (1967). **23**, 491

The Crystal Structure of Thiodiglycollic Acid*

By Sukla Paul†‡

Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32, India

(*Received* 13 *June* 1966 *and in revised form* 3 *January* 1967)

Thiodiglycollic acid, $S(CH_2COOH)_2$, crystallizes in space group *Pnam* with 4 molecules in the unit cell of dimensions $a = 5{\cdot}050 \pm 0{\cdot}005$, $b = 6{\cdot}701 \pm 0{\cdot}003$, $c = 17{\cdot}742 \pm 0{\cdot}004$ Å. The structure has been solved from two-dimensional photographic data and has been refined by least squares with three-dimensional diffractometer data. The structure consists of parallel infinite chains of hydrogen bonded molecules. Hydrogen bonding takes place between carboxyl groups around the centre of symmetry; they are coplanar within experimental error.

Introduction

Thiodiglycollic acid, $S(CH_2COOH)_2$ (also known as methyl sulphide α,α-dicarboxylic acid or thiodiacetic acid), is of importance because of its use as a precipitating organic reagent for zirconium (Sant & Sant, 1959). It is used for the detection of copper, lead, mercury and silver, and also for the estimation of cadmium.

A preliminary report of the structure has already been published (Roy, 1965).

Experimental

Single crystals of thiodiglycollic acid were grown by slow evaporation of a concentrated aqueous solution at room temperature. The crystals appeared as thin plates elongated in the [100] direction. The unit-cell dimensions determined by means of a General Electric Single Crystal Orienter are: $a = 5{\cdot}050 \pm 0{\cdot}005$, $b = 6{\cdot}701 \pm 0{\cdot}003$, $c = 17{\cdot}742 \pm 0{\cdot}004$ Å.

Systematic absences as found on Weissenberg photographs about the *a* and *b* axes were consistent with the space groups *Pnam* and $Pna2_1$. The density as determined by flotation is 1·66 g.cm^{-3}, and the calculated density for four molecules per unit cell is 1·70 g.cm^{-3}.

The structure was solved from the two projections along [100] and [010]. The $0kl$ and $h0l$ intensities were estimated visually from the integrated Weissenberg photographs. The three-dimensional data used for the refinement of the structure were collected with a General Electric diffractometer equipped with a scintillation counter using β-filtered Cu *Kα* radiation and discrimination.

Peak intensities were measured which were converted to integrated intensities in the following way. For a set of 30 reflexions of θ values, distributed over the accessible θ range, both peak intensities and inte-

---

* Part of this work was done in the laboratory of the Department of Molecular Biophysics, Yale University, New Haven, Connecticut, U.S.A.

† née Roy.

‡ Present address: Laboratory for Crystallography, University of Amsterdam, The Netherlands.

grated intensities were measured. Plotting the ratio of integrated intensity to peak intensity *versus* θ resulted in a graph which was used for converting peak intensities to integrated intensities.

To decide between the two possible space groups *Pnam* and *Pna*2_1, the $0kl$ reflexions were subjected to the $N(z)$ test (Howells, Phillips & Rogers, 1950). Though the results seemed to indicate centrosymmetry they were not altogether convincing. The choice of *Pnam* was confirmed by the successful solution and refinement of the structure in terms of this space group.

Structure determination and refinement

Approximate y and z parameters for sulphur were derived from the $0kl$ Patterson projection. The fact that sulphur was found to occupy a special position on a mirror plane perpendicular to **c**, together with a large concentration of peaks along the c axis supported our choice of space group.

Starting from the sulphur parameters the projection was solved by the heavy atom technique. Successive Fourier and difference Fourier calculations reduced the R index to 20%.

The x coordinate of sulphur was found from the $h0l$ Patterson projection. Approximate x coordinates of the remaining atoms (except hydrogen) were obtained from bond length and bond angle considerations. This projection was refined as described above to an R index value of 27%. The [010] electron density projection is shown in Fig. 1.

The coordinates thus obtained were used as the starting point of a three-dimensional least-squares refinement with the diffractometer intensities, using Busing & Levy's (1962) program. One overall scale factor was used and each observation assigned unit weight. Four cycles of refinement with individual isotropic temperature factors reduced R from 22·5 to 14·5%. Another four cycles, this time with individual anisotropic temperature factors, brought the discrepancy factor down to 11·2%. The temperature factor used was of the form

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

The positions of the three hydrogen atoms in the asymmetric unit were now located from two-dimensional difference Fourier maps. Four more cycles of refinement were done with the hydrogen atoms included, the thermal parameters of which were kept fixed. This reduced R to 10·0%.

Inspection of the observed and calculated structure factors showed that three reflexions, 020, 110, and 111, suffered from extinction effects: these were omitted from further refinement. Another cycle of refinement resulted in an R value of 7·0%.

Since the crystal was of appreciable dimensions (0·061 cm × 0·020 cm × 0·015 cm; $\mu = 44{\cdot}4\ \text{cm}^{-1}$) an absorption correction was applied (Wehe, Busing & Levy, 1962). One more cycle of refinement with the corrected structure factor gave no appreciable change in the R value. Also a correction for anomalous dispersion was made (*International Tables for X-ray Crystallography*,

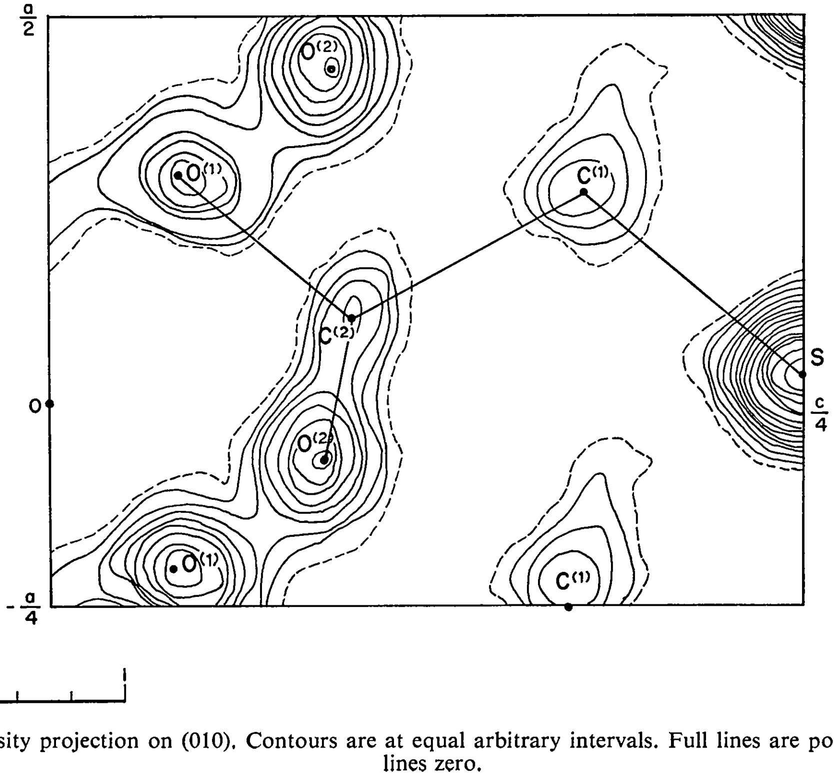


Fig. 1. Electron density projection on (010). Contours are at equal arbitrary intervals. Full lines are positive contours, broken lines zero.

Table 1. *Final atomic coordinates with estimated standard deviations*

Atom	*x/a*	e.s.d.	*y/b*	e.s.d.	*z/c*	e.s.d.
C(1)	0·2813	0·0014	−0·0228	0·0013	0·1749	0·0003
C(2)	0·1508	0·0012	−0·0088	0·0011	0·0991	0·0002
O(1)	0·2931	0·0008	−0·0873	0·0008	0·0458	0·0001
O(2)	−0·0641	0·0008	0·0691	0·0008	0·0896	0·0002
S	0·0566	0·0004	0·0374	0·0004	0·2500	0·0000
H(1)	0·2254		−0·0692		−0·0107	
H(2)	0·3198	0·0147	−0·1663	0·0112	0·1785	0·0034
H(3)	0·4057	0·0137	0·0742	0·0109	0·1722	0·0034

Table 2. *Anisotropic thermal vibration parameters with estimated standard deviations*

Atom	β_{11}	e.s.d.	β_{22}	e.s.d.	β_{33}	e.s.d.	β_{12}	e.s.d.	β_{13}	e.s.d.	β_{23}	e.s.d.
C(1)	0·0320	0·0023	0·0200	0·0022	0·0011	0·0001	−0·0023	0·0028	−0·0003	0·0005	0·0000	0·0005
C(2)	0·0259	0·0026	0·0186	0·0024	0·0012	0·0001	0·0009	0·0024	0·0007	0·0005	0·0002	0·0004
O(1)	0·0322	0·0020	0·0370	0·0020	0·0009	0·0001	0·0069	0·0018	0·0010	0·0003	−0·0007	0·0003
O(2)	0·0339	0·0021	0·0319	0·0022	0·0011	0·0001	0·0080	0·0019	−0·0006	0·0006	−0·0013	0·0003
S	0·0269	0·0009	0·0192	0·0007	0·0010	0·0000	0·0019	0·0008				

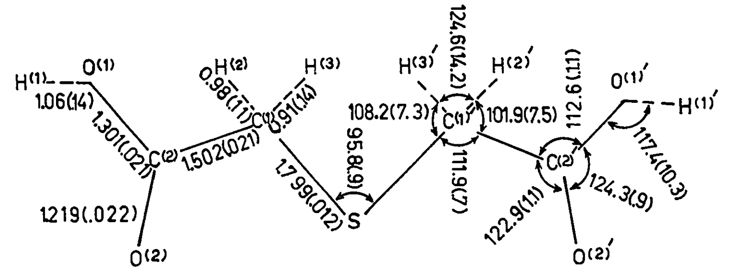


Fig. 2. Bond distances and bond angles. Standard deviations are given in brackets.

1962). This reduced the discrepancy index to 6·8%. The final positions of all the atoms and their thermal parameters together with estimated standard deviations are given in Tables 1 and 2 respectively. A comparison of the observed and calculated structure factors is given in Table 3. The standard deviations of all the atoms were estimated from the diagonal elements of the inverse matrix.

Table 3. *Observed and calculated structure factors*

h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_c$	$10F_o$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$
0	0	2	36	22	0	6	4	16	-33	1	3	10	56	-57	2	2	8	257	244	3	2	10	204	198	4	2	0	18	11
0	0	4	24	28	0	6	6	25	15	1	3	11	45	46	2	2	9	135	-128	3	2	11	33	23	4	2	1	141	-134
0	0	6	740	-758	0	6	8	52	39	1	3	12	179	171	2	2	10	76	-78	3	2	12	17	35	4	2	2	63	-64
0	0	8	107	-92	0	6	10	44	38	1	3	13	178	-179	2	2	11	48	48	3	2	13	81	-81	4	2	3	222	-223
0	0	10	179	-178	0	7	1	64	-59	1	3	14	154	-154	2	2	12	160	148	3	2	14	105	110	4	2	4	71	75
0	0	12	441	429	0	7	3	92	92	1	3	15	80	83	2	2	13	123	-117	3	2	15	51	-49	4	2	5	130	-131
0	0	14	548	-541	0	7	5	138	132	1	3	16	53	57	2	2	14	34	-8	3	2	16	91	-95	4	2	6	82	83
0	0	18	131	-138	0	7	7	90	102	1	3	17	21	11	2	2	15	77	81	3	2	17	57	-60	4	2	7	25	-25
0	0	20	246	251	0	7	9	117	-115	1	3	18	102	-105	2	2	16	78	79	3	3	0	21	17	4	2	8	37	-29
0	1	1	69	-77	1	1	2	194	-214	2	0	0	90	-100	2	2	17	67	-66	3	3	1	67	-69	4	2	9	167	-197
0	1	3	102	98	1	1	3	132	-131	2	0	1	45	-45	2	2	18	158	-180	3	3	2	124	-123	4	2	10	78	-84
0	1	5	24	19	1	1	4	35	34	2	0	2	357	-346	2	2	19	86	84	3	3	3	119	110	4	2	11	142	154
0	1	7	395	376	1	1	5	209	-207	2	0	3	411	395	2	3	0	60	-54	3	3	4	139	135	4	2	12	14	14
0	1	9	83	90	1	1	6	751	-723	2	0	4	101	81	2	3	1	-281	-284	3	3	5	176	-175	4	2	13	48	-59
0	1	11	64	61	1	1	7	300	-270	2	0	5	73	-64	2	3	2	103	100	3	3	6	44	37	4	2	14	17	-22
0	1	13	154	-149	1	1	8	372	-359	2	0	6	515	-515	2	3	3	124	-122	3	3	7	157	154	4	3	0	71	66
0	1	15	89	-88	1	1	9	141	-140	2	0	7	427	407	2	3	4	218	-224	3	3	8	26	20	4	3	1	24	12
0	1	17	102	-105	1	1	10	51	53	2	0	8	389	388	2	3	5	245	-249	3	3	9	142	-141	4	3	2	171	163
0	1	19	48	42	1	1	11	91	99	2	0	9	215	-211	2	3	6	19	-13	3	3	10	133	-135	4	3	3	20	19
0	2	2	142	-143	1	1	12	421	404	2	0	10	42	34	2	3	7	30	28	3	3	11	68	75	4	3	4	115	-116
0	2	4	18	13	1	1	13	146	-139	2	0	11	57	50	2	3	8	43	-46	3	3	12	56	51	4	3	5	13	7
0	2	6	457	-467	1	1	14	203	-199	2	0	12	317	309	2	3	9	44	-46	3	3	13	45	-37	4	3	6	34	35
0	2	8	87	86	1	1	15	279	-277	2	0	13	139	-136	2	3	10	230	222	3	3	14	42	-36	4	3	7	59	60
0	2	10	76	-71	1	1	16	39	33	2	0	14	17	32	2	3	11	118	113	3	3	15	65	68	4	3	8	142	-157
0	2	12	371	353	1	1	17	90	99	2	0	15	82	93	2	3	12	37	32	3	3	16	82	90	4	3	9	14	9
0	2	14	404	-387	1	1	18	225	-231	2	0	16	72	77	2	3	13	131	-119	4	0	0	81	65	4	3	10	56	65
0	2	16	38	37	1	1	19	62	55	2	0	17	102	-110	2	3	14	93	94	4	0	1	193	-167	4	3	11	11	2
0	2	18	109	-107	1	1	20	181	184	2	0	18	217	-235	2	3	15	99	106	4	0	2	30	-26	4	3	12	49	-59
0	2	20	171	168	1	2	0	400	466	2	0	19	72	79	2	3	16	108	-117	4	0	3	316	-267	4	3	13	12	-10
0	3	1	183	-213	1	2	1	286	-309	2	0	20	88	89	2	3	17	11	4	4	0	4	107	99	5	1	0	146	-143
0	3	3	149	150	1	2	2	304	335	2	1	0	46	-47	3	1	0	239	252	4	0	5	224	-194	5	1	1	73	-86
0	3	5	63	-67	1	2	3	134	-131	2	1	1	204	-195	3	1	1	27	-24	4	0	6	93	79	5	1	2	12	-7
0	3	7	506	510	1	2	4	28	-13	2	1	2	53	-45	3	1	2	69	-70	4	0	7	98	-80	5	1	3	202	222
0	3	9	66	58	1	2	5	275	-276	2	1	3	145	-140	3	1	3	407	393	4	0	8	64	-53	5	1	4	25	-16
0	3	11	144	140	1	2	6	49	-11	2	1	4	135	-128	3	1	4	200	186	4	0	9	297	-276	5	1	5	77	-86
0	3	12	245	-243	1	2	7	178	-183	2	1	5	184	-180	3	1	5	120	-108	4	0	10	124	-116	5	1	6	19	20
0	3	15	79	-78	1	2	8	224	-222	2	1	6	35	-31	3	1	6	39	-27	4	0	11	182	182	5	1	7	13	-6
0	3	17	181	-186	1	2	9	20	12	2	1	7	34	-29	3	1	7	291	264	4	0	12	13	-6	5	1	8	44	45
0	3	19	117	108	1	2	10	66	-58	2	1	8	13	0	3	1	8	45	-58	4	0	13	41	-39	5	1	9	151	-168
0	4	0	235	234	1	2	11	129	123	2	1	9	24	-14	3	1	9	250	-242	4	0	14	32	-38	5	1	10	37	48
0	4	2	252	-251	1	2	12	83	-92	2	1	10	133	126	3	1	10	246	-228	4	0	15	200	239	5	1	11	85	122
0	4	4	29	-11	1	2	13	155	-144	2	1	11	61	59	3	1	11	113	108	4	0	16	48	58	5	2	0	12	4
0	4	6	103	-99	1	2	14	72	-65	2	1	12	40	37	3	1	12	61	54	4	1	0	67	71	5	2	1	14	-8
0	4	8	158	-148	1	2	15	49	37	2	1	13	62	-46	3	1	13	65	-63	4	1	1	21	8	5	2	2	62	81
0	4	10	35	27	1	2	16	53	-58	2	1	14	65	49	3	1	14	92	-90	4	1	2	93	91	5	2	3	30	-38
0	4	12	204	203	1	2	17	57	-49	2	1	15	74	59	3	1	15	96	94	4	1	3	23	17	5	2	4	52	-62
0	4	14	167	-183	1	2	18	45	54	2	1	16	70	-59	3	1	17	140	-157	4	1	4	60	-53	5	2	5	16	-18
0	4	16	41	48	1	2	19	114	113	2	1	17	11	19	3	1	18	43	-45	4	1	5	27	18	6	0	0	32	-51
0	5	1	158	-152	1	3	0	327	344	2	1	18	14	-10	3	2	0	123	-124	4	1	6	19	2	6	0	1	12	-7
0	5	3	133	124	1	3	1	262	-246	2	1	19	61	63	3	2	1	31	-24	4	1	7	53	40	6	0	2	22	52
0	5	5	192	-179	1	3	2	137	-147	2	2	0	19	10	3	2	2	73	66	4	1	8	92	-85					
0	5	7	261	246	1	3	3	15	20	2	2	1	107	-111	3	2	3	52	54	4	1	9	26	15					
0	5	9	100	-99	1	3	4	88	95	2	2	2	161	-181	3	2	4	200	-198	4	1	10	20	21					
0	5	11	125	123	1	3	5	43	39	2	2	3	183	187	3	2	5	18	16	4	1	11	17	2					
0	5	13	119	122	1	3	6	306	-314	2	2	4	159	150	3	2	6	38	-41	4	1	12	25	-27					
0	5	15	43	44	1	3	7	75	52	2	2	5	99	-101	3	2	7	180	176	4	1	13	18	-11					
0	6	0	17	24	1	3	8	201	203	2	2	6	319	-327	3	2	8	32	-29	4	1	14	21	7					
0	6	2	103	-90	1	3	9	17	19	2	2	7	273	276	3	2	9	37	32	4	1	15	21	-20					

Results and discussion

Molecular structure

The molecule has mirror symmetry, sulphur being on the mirror plane. The bond distances and angles in the molecule with their standard deviations are shown in Fig. 2. Standard errors in bond angles were calculated by the method of Darlow (1960). Bond lengths and angles were calculated without correction for anisotropic thermal motion.

The sulphur–carbon bond length is 1·80 Å, which does not differ significantly from the single bond value of 1·82 Å mentioned by Abrahams (1956). At the sulphur atom the valency angle is 96°. This is considerably smaller than the corresponding angle in similar non-ring compounds (Abrahams, 1956; Stam, 1962). If we assume a van der Waals radius of 1·2 Å for H, there is no contact between the H atoms on C(1) and C(1′), the distances H(2)–H(2′) and H(3)–H(3′) being 2·76 and 2·54 Å respectively.

The carbon–carbon single bond length is 1·50 Å, which is in agreement with the values recently obtained for carboxylic acids (Eichhorn & MacGillavry, 1959; Nardelli, Fava & Giraldi, 1962; Higgs & Sass, 1963; Okaya, 1965; van Eijck, Kanters & Kroon, 1965). Within limits of error the configuration about C(1) is tetrahedral.

As can be seen from Fig. 2, C=O is 1·22 Å and C–O is 1·30 Å. The angle O–C=O is 124°. This is in good agreement with the most recently published X-ray measurements on the carboxylic acids, as mentioned earlier.

It is not certain to what degree the structure of the carboxyl group is dependent on the molecular environment and hydrogen bond system. It has been suggested by Vaughan & Donohue (1952) that the relative contributions of the two resonance forms depend upon the two oxygen atoms in the crystal structure, *i.e.* upon the number and strength of the hydrogen bonds. But considering other substances it is evident that this group will have very nearly the same structure in all carboxylic acids regardless of environment. In some acids there is no direct hydrogen bonding between the carboxylic groups.

Crystal structure

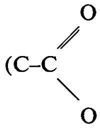
The projection of the structure along [100] is shown in Fig. 3. The structure consists of parallel infinite chains of molecules as shown in the Figure. The chains are formed by hydrogen bonding between pairs of carboxyl groups around the centre of symmetry. The O···O distance is 2·66 Å.

The equations of the plane containing the atoms C(2), O(1), O(2) and that containing C(1), C(2), O(1), O(2), together with their centrosymmetrically related ones (across the center of symmetry 000), are given in Table 4. The deviations of the atoms from these

Table 4. *Least-squares planes*

Plane *A* (two carboxyl groups connected by hydrogen bonds)

$$0{\cdot}4317x+0{\cdot}8872y-0{\cdot}1630z=0.$$

Plane *B* 
$\left(\mathrm{C{-}C}\begin{matrix}{/\!\!/}\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}\right.$ group, with the centrosymmetrically related one)

$$0{\cdot}4337x+0{\cdot}8870y-0{\cdot}1568z=0.$$

Deviations from the planes

	Plane *A*	Plane *B*
C(1)	−0·0262 Å	−0·0100 Å
C(2)	−0·0138	−0·0047
O(1)	0·0095	0·0159
O(2)	0·0104	−0·0165

(each atom has been given unit weight.)

Table 5. *Analysis of anisotropic temperature factors*

	Axis vector	Direction cosines (relative to the *a*, *b* and *c* axes respectively)			Mean square amplitude
S	1	−0·918	0·397	0·000	0·03372 Å^2
	2	0·397	0·918	0·000	0·04495
	3	0·000	0·000	1·000	0·01752
C(1)	1	−0·763	−0·621	0·183	0·03902
	2	−0·419	0·905	0·076	0·04807
	3	0·019	0·003	0·999	0·01882
C(2)	1	0·146	0·961	0·233	0·04290
	2	0·062	0·018	−0·998	0·01940
	3	−0·781	0·232	−0·580	0·03377
O(1)	1	0·276	0·946	−0·167	0·08452
	2	−0·034	0·020	−0·999	0·01868
	3	−0·667	0·236	−0·707	0·03788
O(2)	1	0·270	0·893	0·360	0·07921
	2	0·014	0·051	0·999	0·01756
	3	0·881	0·473	0·013	0·03832

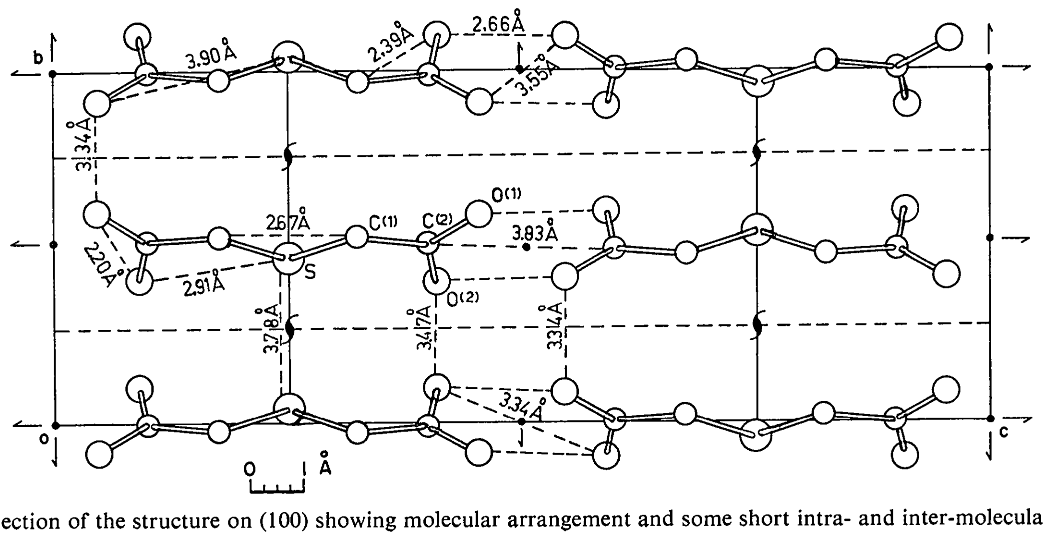


Fig. 3. Projection of the structure on (100) showing molecular arrangement and some short intra- and inter-molecular distances.

planes are also given in the Table 4. These are least-squares planes obtained by the method suggested by Schomaker, Waser, Marsh & Bergman (1959). The atoms are co-planar within experimental error.

The β_{ij} were used to calculate the displacements along the principal axes. At the same time the principal axes of the atomic ellipsoids and their direction cosines were determined. These data seem compatible with a libration of the carboxyl groups about the carbon–carbon bonds. This is given in Table 5.

I am much indebted to Dr Sankar K. Dutta for suggesting the problem. Thanks are due to my husband, Dr Ranjit Paul, for many suggestions, help in calculations and constant encouragement. Finally I wish to express my gratitude to Dr C. H. Stam and Prof. C. H. MacGillavry for going through the manuscript very carefully and suggesting valuable improvements.

Financial support from the Government of India, New Delhi, and the National Science Foundation, U.S.A., is also acknowledged.

References

Abrahams, S. C. (1956). *Quart. Rev. Chem. Soc. Lond.* **10**, 407.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS, Fortran Crystallographic Least Squares Program* (for IBM 7090). Oak Ridge National Laboratory, Tennessee.

Darlow, S. F. (1960). *Acta Cryst.* **13**, 683.

Eichhorn, E. L. & MacGillavry, C. H. (1959). *Acta Cryst.* **12**, 872.

Eijck, B. P. van, Kanters, J. A. & Kroon, J. (1965). *Acta Cryst.* **19**, 435.

Higgs, M. A. & Sass, R. L. (1963). *Acta Cryst.* **16**, 657.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Nardelli, M., Fava, G. & Giraldi, G. (1962). *Acta Cryst.* **15**, 737.

Okaya, Y. (1965). *Acta Cryst.* **19**, 879.

Roy, S. (1965). *Indian J. Phys.* **39**(1), 49.

Sant, S. B. & Sant, B. R. (1959). *Anal. Chem. Acta*, **21**, 221.

Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Stam, C. H. (1962). *Acta Cryst.* **15**, 317.

Vaughan, P. & Donohue, J. (1952). *Acta Cryst.* **5**, 430.

Wehe, D. J., Busing, W. R. & Levy, H. A. (1962). *ORABS, A Fortran Program for Calculating Single Crystal Absorption Corrections.* Oak Ridge National Laboratory, Tennessee.

Acta Cryst. (1967). **23**, 494

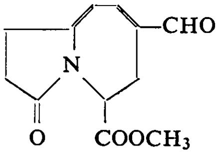
The Identification and Crystal Structure of L-5-Methoxycarbonyl-7-formyl-1,2,5,6-tetrahydro-3*H*-pyrrolo[1,2-a]azepin-3-one, $C_{12}H_{13}NO_4$, a Photolysis Product

By I. L. Karle, J. Karle and J. A. Estlin

U.S. Naval Research Laboratory, Washington, D.C. 20390, *U.S.A.*

(*Received* 13 *March* 1967)

The irradiation of *N*-chloroacetyl-*p*-*O*-methyl-L-tyrosine resulted in the production of an unusual rearrangement product, m.p. 225°. The methyl ester of this product, m.p. 145°, has been identified by an X-ray analysis of its crystal structure to be



It crystallizes in the orthorhombic system, space group $P2_12_12_1$ with four molecules per unit cell. The cell parameters are $a = 7{\cdot}17$, $b = 10{\cdot}08$, $c = 15{\cdot}99$ Å. A partial structure was obtained by determining phases directly from the structure factor magnitudes by the use of the symbolic addition procedure as applied to noncentrosymmetric crystals. The complete structure evolved by the use of the tangent formula in a recycling procedure.

Introduction

In the study of the effects of irradiation on *N*-chloroacetyl derivatives of amino acids Yonemitsu, Cerutti & Witkop (1966) found that *N*-chloroacetyl-L-tryptophan