Crystal Structure of Tetramethyl-β-oxoglutaric Acid. Monoclinic Modification

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ABSTRACT: Tetramethyl-β-oxoglutaric acid ($C_9H_{14}O_5$) in its monoclinic modification crystallizes in the space group $P2_1/c$. The unit cell constants are $a = 11.266 \pm 0.009$ Å, $b = 6.199 \pm 0.008$ Å, $c = 15.273 \pm 0.010$ Å, $\beta = 105° 45' \pm 5'$, $Z = 4$, $D_x = 1.322$ g cm^{-3}, $D_{meas} = 1.31 \pm 0.01$ g cm^{-3}. Intensities were collected at room temperature on a Picker automated diffractometer. The structure was solved by direct methods and refined by least-squares calculations. The molecular conformation is different from that of the triclinic modification of the same compound. This conformation was predicted by conformational analysis. The molecules form rows through hydrogen bonds between the carboxylic groups. These rows do not contain inversion centers as usually occur, but are characterized by a helicoidal 2_1 symmetry.

Tetramethyl-β-oxoglutaric acid is a model compound of polydimethylketene with ketonic enchainment.[2] In a previous paper we reported the crystal structure of the triclinic modification of this acid.[3] The molecular conformation was found to be very close to one of those yielded by the conformational analysis of the grouping $-C(=O)-C(CH_3)_2-COC(CH_3)_2C(=O)$. Conformational analysis also revealed the existence of other nonequivalent minima with nearly the same energy.[4] It seemed likely that the molecular conformation of the acid in its monoclinic modification corresponds to one of these minima. We also believed that this conformation could represent a model of another chain structure of polydimethylketene, *e.g.*, the β-modification.[4] To this end we undertook a crystal analysis of the monoclinic modification of tetramethyl-β-oxoglutaric acid. In this paper we report our results of this investigation.

Experimental Section

Needle-shaped crystals of tetramethyl-β-glutaric acid were obtained as described in ref 2. The crystals were sealed in Lindemann capillaries in carbon dioxide atmosphere to prevent decarboxylation. Weissenberg photographs indicated the space group $P2_1/c$ with four units $C_9H_{14}O_5$ per unit cell. The intensities of 1349 reflections, of which 1232 were nonzero, were measured with a Picker four-circle automated diffractometer. The unit cell constants were refined from the accurate setting of 12 reflections with a least-squares program. The unit cell parameters are reported in Table I.

TABLE I
UNIT CELL CONSTANTS OF TETRAMETHYL-β-OXOGLUTARIC ACID

a	$= 11.266 \pm 0.009$ Å
b	$= 6.199 \pm 0.008$ Å
c	$= 15.273 \pm 0.010$ Å
β	$= 105° 45' \pm 5'$
Mol wt	$= 202$
Z	$= 4$
D_x	$= 1.322$ g cm^{-3}
D_{meas}	$= 1.31 \pm 0.01$ g cm^{-3}

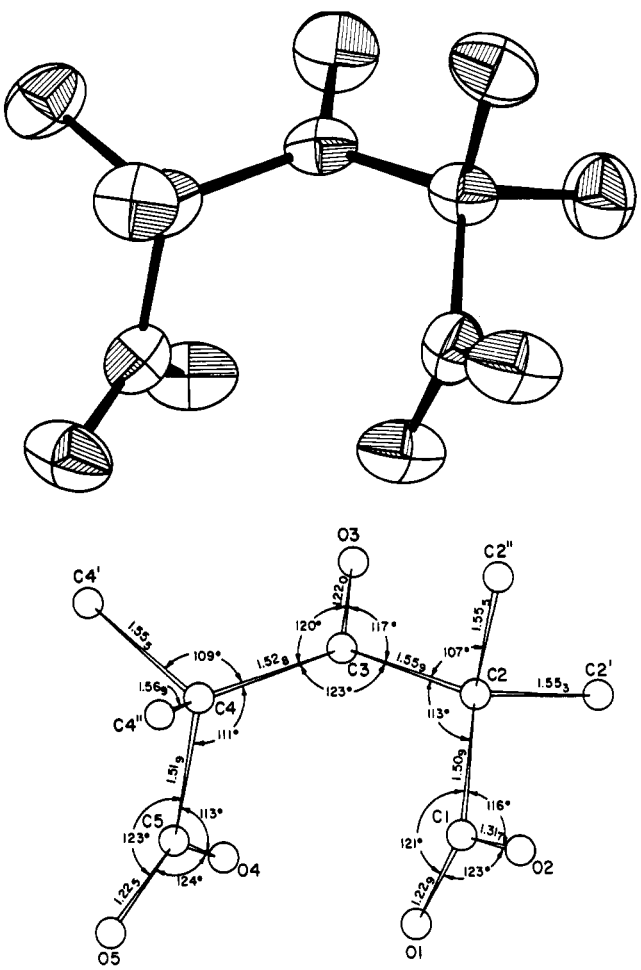

Figure 1. Molecular geometry of tetramethyl-β-oxoglutaric acid. The most important conformational parameters and the mode of thermal vibration of the atoms are shown.

Structure Determination and Refinement

The crystal structure was solved by direct methods using a new program written by one of us.[5] From the Fourier calcu-

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(2) P. Ganis, A. Panunzi, and C. Pedone, *Ric. Sci.*, **38**, 801 (1968).
(3) G. Avitabile, P. Ganis, and E. Martuscelli, *Acta Crystallogr., Sect. B*, **25**, 2378 (1969).
(4) P. Ganis and P. A. Temussi, *Eur. Polym. J.*, **2**, 401 (1966).
(5) G. Avitabile, in preparation.

TABLE II
POSITIONAL AND TEMPERATURE PARAMETERS OF THE NONHYDROGEN ATOMS OF TETRAMETHYL-β-OXOGLUTARIC ACID

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C1	0.6104 (3)	0.2278 (5)	0.4082 (2)	3.1 (1)	2.8 (1)	3.1 (1)	0.3 (1)	1.2 (1)	0.3 (1)
C2	0.7278 (3)	0.1338 (5)	0.4662 (2)	2.6 (1)	2.0 (1)	2.8 (1)	0.1 (1)	0.4 (1)	0.3 (1)
C2′	0.6897 (3)	−0.0228 (6)	0.5336 (2)	4.6 (2)	4.0 (2)	3.6 (2)	−0.2 (1)	1.3 (1)	0.8 (1)
C2″	0.8144 (3)	0.3109 (5)	0.5224 (2)	4.1 (2)	2.9 (1)	3.7 (2)	−0.1 (1)	−0.1 (1)	−0.5 (1)
C3	0.8000 (2)	0.0039 (5)	0.4102 (2)	2.2 (1)	1.7 (1)	3.2 (1)	−0.3 (1)	0.3 (1)	0.2 (1)
C4	0.7981 (3)	0.0635 (4)	0.3131 (2)	2.5 (1)	1.1 (1)	3.6 (1)	0.2 (1)	0.7 (1)	0.4 (1)
C4′	0.9084 (3)	−0.0461 (6)	0.2873 (2)	3.2 (1)	3.4 (2)	5.0 (2)	1.0 (1)	1.4 (1)	0.5 (1)
C4″	0.8066 (3)	0.3138 (5)	0.2991 (2)	4.1 (1)	1.4 (1)	4.4 (2)	−0.5 (1)	0.8 (1)	0.7 (1)
C5	0.6849 (3)	−0.0282 (5)	0.2465 (2)	2.7 (1)	2.1 (1)	3.5 (1)	0.1 (1)	1.1 (1)	−0.1 (1)
O1	0.5430 (2)	0.1232 (3)	0.3468 (2)	3.1 (1)	2.6 (1)	4.2 (1)	0.6 (1)	−0.2 (1)	−0.9 (1)
O2	0.5798 (2)	0.4212 (4)	0.4325 (2)	4.0 (1)	3.0 (1)	5.2 (1)	1.6 (1)	−0.1 (1)	−1.5 (1)
O3	0.8684 (2)	−0.1390 (4)	0.4492 (2)	4.5 (1)	2.8 (1)	4.6 (1)	1.8 (1)	1.0 (1)	1.4 (1)
O4	0.6580 (2)	−0.2272 (3)	0.2666 (2)	3.4 (1)	1.3 (1)	5.2 (1)	−0.1 (1)	0.0 (1)	0.3 (1)
O5	0.6274 (2)	0.0691 (4)	0.1784 (2)	3.9 (1)	3.2 (1)	3.4 (1)	−0.9 (1)	−0.3 (1)	1.1 (1)

TABLE III
SOME RELEVANT INTERNAL GEOMETRIC AND CONFORMATIONAL PARAMETERS OF TETRAMETHYL-β-OXOGLUTARIC ACID

Bond	Bond distance, Å	Bond	Bond angle, deg	Intramolecular nonbonded distance	Å	Internal rotation	Angle, deg
C1–C2	1.509 (4)	O1–C1–O2	123.3 (1)	C2″····C4″	3.39	C1–C2–C3–C4	32.7
C2–C2′	1.553 (5)	C2–C1–O1	120.6 (2)	C1····C4″	3.14	C2–C3–C4–C5	−83.0
C2–C2″	1.555 (5)	C2–C1–O2	116.0 (1)	C1····C5	3.23	C3–C2–C1–O1	41.5
C2–C3	1.559 (4)	C1–C2–C3	112.7 (1)	O1·····O4	2.96	C3–C4–C5–O4	−41.5
C3–C4	1.528 (4)	C3–C2–C2′	107.9 (1)	O1····C5	2.66		
C4–C4′	1.555 (5)	C3–C2–C2″	108.6 (1)	O1····O5	2.99		
C4–C4″	1.569 (4)	C2–C3–C4	122.6 (1)				
C4–C5	1.519 (4)	C2–C3–O3	117.4 (1)				
C1–O1	1.229 (4)	C4–C3–O3	119.7 (1)				
C1–O2	1.317 (4)	C3–C4–C4′	109.2 (1)				
C3–O3	1.220 (4)	C3–C4–C4″	112.1 (1)				
C5–O4	1.319 (4)	C3–C4–C5	110.6 (1)				
C5–O5	1.225 (4)	C4–C5–O4	113.5 (1)				
		C4–C5–O5	122.7 (1)				
		O4–C5–O5	123.7 (1)				

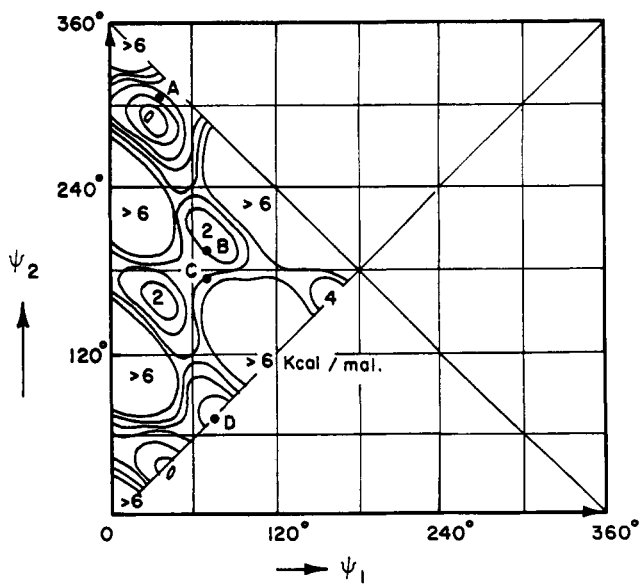

Figure 2. Internal conformational energy *vs.* ψ_1 and ψ_2 for the grouping $-C(=O)C(CH_3)_2COC(CH_3)_2C(=O)-$. A indicates the location on the diagram of the conformation of tetramethyl-β-oxoglutaric acid (monoclinic modification), B indicates the position of the triclinic modification of the same compound,[3] C indicates the conformation of the above-mentioned grouping in polydimethylketene (α-modification),[5] and D indicates the conformation of the same group in polydimethylketene (β modification).

lated with the normalized factors of 231 reflections, we obtained a model which yielded a discrepancy factor $R = 0.24$. This model was refined by least-squares programs[6] to $R = 0.13$ with isotropic temperature factors and from this value to the final $R = 0.078$ with anisotropic temperature factors. The hydrogen atoms were placed in the geometrically calculated positions and included in the structural factor calculations with a temperature factor $B = 3.50$, but not refined. We used the atomic scattering factors of Moore.[7] Unit weights were given to all reflections. In Table II the final coordinates and temperature parameters of the nonhydrogen atoms are reported.[8]

Results and Discussion

In Figure 1 and Table III the most relevant parameters of tetramethyl-β-oxoglutaric acid are reported. Bond lengths and angles are very similar to those found in the case of the triclinic modification of this compound. Internal rotation angles about the bonds of the molecular backbone are very different. As shown in Figure 1 the internal rotation angles

(6) A. Immirzi, *Ric. Sci.*, 37, 743, 846, 850 (1967).
(7) F. H. Moore, *Acta Crystallogr.*, 16, 1169 (1963).
(8) A list of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

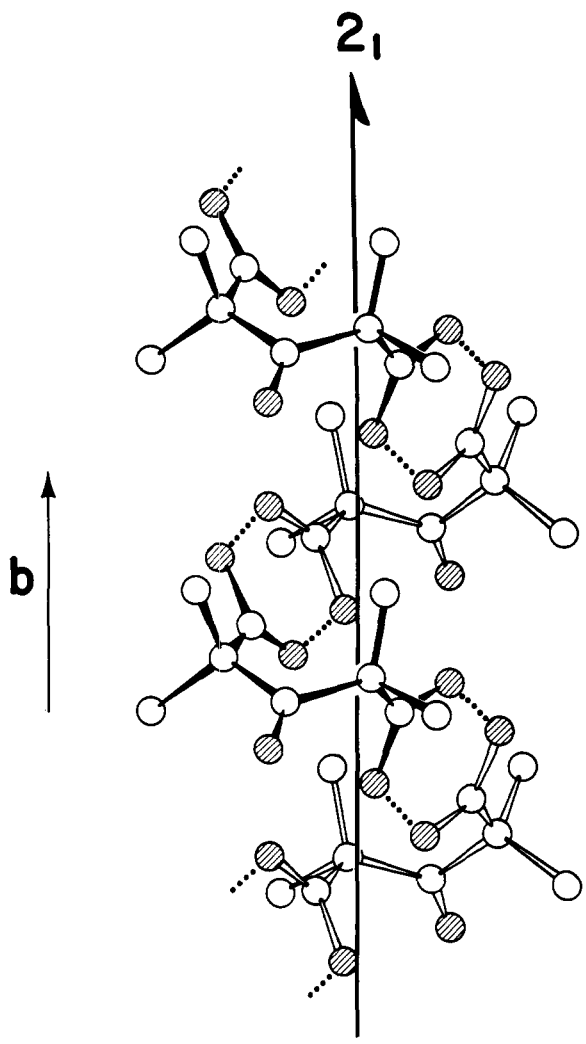

Figure 3. The figure shows one row of molecules of tetramethyl-β-oxoglutaric acid bonded through hydrogen bonds. The row has the helicoidal symmetry 2_1.

ψ_1 = C_1–C_2–C_3–C_4 and ψ_2 = C_2–C_3–C_4–C_5 are 32° (328°) and 277° (83°), respectively. The corresponding angles in the triclinic modification are 66° (294°) and 205° (155°), respectively. From these results we have shown that the conformation of the monoclinic form of tetramethyl-β-oxoglutaric acid does not correspond to the conformation of the β modification of polydimethylketene ($\psi_1 = \psi_2 \simeq 72°$ [4]). However, this conformation is extremely close to one of the minima indicated in the plot of the conformational energy as a function of ψ_1 and ψ_2 (Figure 2).[9] We emphasize that this conformation was theoretically predicted by our conformational analysis. Incidentally, we note that among the six nonequivalent minima of the diagram $E = f(\psi_1, \psi_2)$ three are represented by actual structures; the minimum corresponding to ψ_1 and ψ_2 both nearly 165° seems to be unlikely because of its higher energy.

(9) Energy calculations are fully described in ref 4.

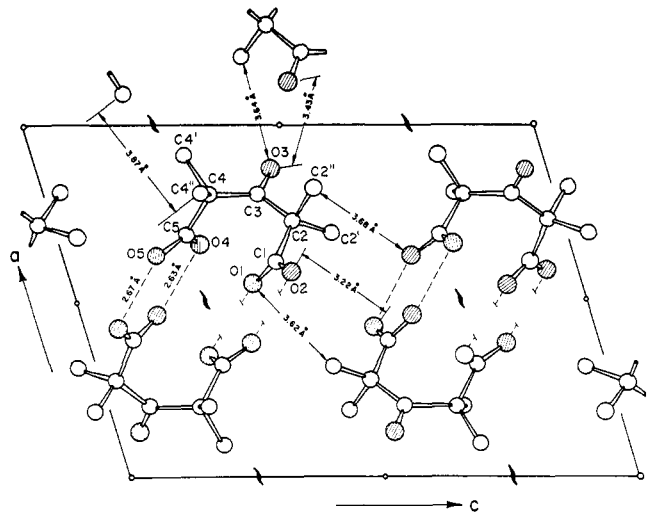

Figure 4. Projection of the packing of tetramethyl-β-oxoglutaric acid on 010.

The intramolecular C····C nonbonded distances in the monoclinic modification are slightly longer (minimum value ~3.15 Å) than in the case of the triclinic form (minimum value ~3.05 Å). However, the carboxyl groups are closer in the present case: O····O ≃ 2.95 Å, O····C ≃ 2.66 Å. Similar intermolecular nonbonded distances were found in the structure of the polydimethylketene α modification. This fact could explain the facile decomposition of this modification by decarboxylation even if the internal conformational energy is not very different between the two crystalline forms (Figure 2).

The molecules of the acid are bonded in rows through hydrogen bonds between carboxyl groups (Figure 3). The rows are characterized by the symmetry 2_1 (or $s(2/1)1$ according to the Corradini nomenclature[10] for linear repetition groups), while for almost all the dicarboxylic acids forming rows the symmetry is usually *ti*;[10] the only known exception to this behavior was previously found in the case of β-phenylglutaric acid (symmetry *tc*).[11]

In Figure 4 the projection of the structure on 010 is reported; the shortest intermolecular distances are shown. The distances C····C, C····O, and O····O between molecules translated by *b* are longer than 4.0, 3.3, and 3.2 Å, respectively.

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(10) P. Corradini, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **28** (5), 632 (1960).

(11) G. Avitabile, P. Ganis, and E. Martuscelli, *Chem. Commun.*, in press.