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## Crystal and Molecular Structure of $\alpha,\alpha',\alpha,\alpha'$ -Tetramethyl- $\beta$ -ketoglutaric Acid (Triclinic Modification). A Model of Polydimethylketene with Ketonic Enchainment

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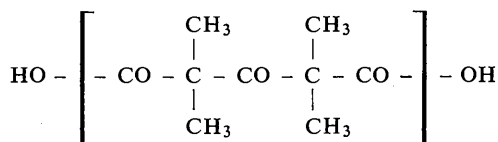
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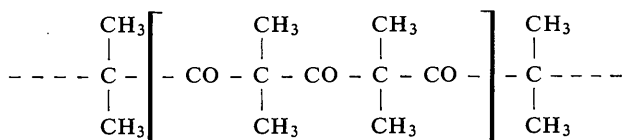
The crystal and molecular structure of the title compound has been determined. The space group is  $P\bar{1}$ , with unit-cell parameters:  $\bar{a}=7.07\pm 0.01$ ,  $\bar{b}=6.13\pm 0.01$ ,  $\bar{c}=13.13\pm 0.02$  Å;  $\alpha=81^\circ 23' \pm 30'$ ,  $\beta=96^\circ 42' \pm 30'$ ,  $\gamma=118^\circ 23' \pm 30'$ . Three-dimensional X-ray diffraction data were collected by photographic methods. Signs of structure factors were determined by the direct methods of Sayre, Cochran and Zachariasen (*Acta Cryst.* (1952), 65, 68). Refinement was carried out by least-squares methods. The values of the rotation angles around the C-C bonds adjacent to the central carbonylic group are  $66^\circ$  and  $-155^\circ$  ( $G+$ ,  $T$  type). Some valence angles on carbon atoms are larger than the expected normal values because of strong intramolecular interactions. The molecular conformation is similar to that found for the chain of ketonic polydimethylketene.

### Introduction

This paper describes the structural analysis of  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl- $\beta$ -ketoglutaric acid (TMKGA),



The part of the molecule in brackets is a fragment of the chain of polydimethylketene,



a polymer whose crystal structure has been recently studied in our laboratory (Bassi, Ganis & Temussi, 1967).

The molecular structure of polydimethylketene is characterized by very short intramolecular distances, e.g.  $\text{CH}_3\text{---CH}_3$  distances of the order of 3 Å and  $\text{O---O}$  distances of the order of 2.8 Å, which are certainly surprising, even considering the limited accuracy inherent in fibre spectra crystal structure analyses.

Our interest in the X-ray study of TMKGA originated in part from the possibility of finding similar intramolecular distances in a model compound. From a more general point of view it was our purpose to gain new data on some conformational parameters (bond lengths, valence angles, torsional angles) in overcrowded open-chain aliphatic molecules, since very few values are available in the literature. In this connexion it is worth mentioning that the choice of such conformational parameters in order to build preliminary molecular models for the structural analysis, and for the calculation of the internal conformational energy of polydimethylketene (Ganis & Temussi, 1966) has been particularly difficult owing to the lack of reliable values for valence angles of the type present in TMKGA

### Experimental and unit-cell parameters

$\alpha, \alpha', \alpha'$ -Tetramethyl- $\beta$ -ketoglutaric acid crystallizes from ethyl acetate or heptane in either the monoclinic or the triclinic system (Ganis, Panunzi & Pedone, 1968). The present paper is concerned with the triclinic modification.

The space group and unit-cell dimensions were determined from oscillation and Weissenberg photographs taken about the crystallographic axes with Cu  $K\alpha$  radiation. The density of the crystals was measured by the flotation method.

#### Crystal data

$C_8O_4H_{14}$  M.W. = 202.1

$a = 7.07 \pm 0.01$ ,  $b = 6.13 \pm 0.01$ ,  $c = 13.13 \pm 0.02$  Å;  
 $\alpha = 81^\circ 23' \pm 30'$ ,  $\beta = 96^\circ 42' \pm 30'$ ,  $\gamma = 118^\circ 23' \pm 30'$ .

$U = 501.76$  Å<sup>3</sup>,  
 $Z = 2$ .  $\mu = 9.4$  cm<sup>-1</sup>.

Density  $\left\{ \begin{array}{l} \text{experimental } 1.35 \pm 0.01 \text{ g.cm}^{-3} \\ \text{X-rays } 1.35 \text{ g.cm}^{-3} \end{array} \right.$

Possible space groups  $P1$  or  $P\bar{1}$ . Space group  $P\bar{1}$  was assumed tentatively; this was confirmed during the structure analysis.

The intensities were evaluated from Weissenberg spectra (Cu  $K\alpha$ ) by the multiple-film method with a standard scale of blackening. Photographs were collected of layers from  $0kl$  to  $4kl$  in one set and from  $h0l$  to  $h3l$  in another. 1314 independent reflexions were measured; the intensities were put on a common arbitrary scale by examination of the common reflexions of different sets.

Lorentz, polarization and Phillips corrections were applied. No correction was applied for absorption,

Table 1. Final fractional atomic coordinates and their standard deviations

|       | $x/a$   | $y/b$  | $z/c$   | $\sigma(x/a)$ | $\sigma(y/b)$ | $\sigma(z/c)$ |
|-------|---------|--------|---------|---------------|---------------|---------------|
| C(1)  | 0.3735  | 0.6885 | 0.0855  | 0.0017        | 0.0020        | 0.0007        |
| C(2)  | 0.2848  | 0.4427 | 0.1531  | 0.0017        | 0.0018        | 0.0007        |
| C(3)  | 0.4701  | 0.4074 | 0.2081  | 0.0019        | 0.0020        | 0.0008        |
| C(4)  | 0.1519  | 0.2371 | 0.0826  | 0.0021        | 0.0021        | 0.0008        |
| C(5)  | 0.1295  | 0.4507 | 0.2223  | 0.0019        | 0.0020        | 0.0007        |
| C(6)  | 0.0744  | 0.2984 | 0.3260  | 0.0017        | 0.0018        | 0.0007        |
| C(7)  | -0.0130 | 0.0120 | 0.3186  | 0.0021        | 0.0019        | 0.0008        |
| C(8)  | 0.2584  | 0.3772 | 0.3992  | 0.0021        | 0.0019        | 0.0008        |
| C(9)  | -0.1020 | 0.3264 | 0.3734  | 0.0023        | 0.0024        | 0.0009        |
| O(1)  | 0.3403  | 0.7141 | -0.0045 | 0.0014        | 0.0013        | 0.0005        |
| O(2)  | 0.5039  | 0.8784 | 0.1353  | 0.0014        | 0.0014        | 0.0006        |
| O(3)  | 0.0398  | 0.5787 | 0.1916  | 0.0015        | 0.0015        | 0.0005        |
| O(4)  | 0.3668  | 0.6271 | 0.3994  | 0.0014        | 0.0013        | 0.0005        |
| O(5)  | 0.3193  | 0.2487 | 0.4578  | 0.0014        | 0.0013        | 0.0005        |
| H(3a) | 0.571   | 0.403  | 0.152   |               |               |               |
| H(3b) | 0.406   | 0.230  | 0.258   |               |               |               |
| H(3c) | 0.567   | 0.562  | 0.254   |               |               |               |
| H(4a) | 0.260   | 0.228  | 0.032   |               |               |               |
| H(4b) | 0.032   | 0.281  | 0.037   |               |               |               |
| H(4c) | 0.070   | 0.057  | 0.129   |               |               |               |
| H(7a) | -0.056  | -0.091 | 0.394   |               |               |               |
| H(7b) | 0.117   | -0.011 | 0.292   |               |               |               |
| H(7c) | -0.154  | -0.059 | 0.265   |               |               |               |
| H(9a) | -0.144  | 0.208  | 0.446   |               |               |               |
| H(9b) | -0.247  | 0.273  | 0.322   |               |               |               |
| H(9c) | -0.035  | 0.523  | 0.386   |               |               |               |
| H(10) | 0.606   | 0.081  | 0.127   |               |               |               |
| H(11) | 0.505   | 0.782  | 0.434   |               |               |               |

Table 2. Final temperature parameters

Temperature factors are given in the form  $\exp[-\frac{1}{4}(a^2B_{11}h^2 + b^2B_{22}k^2 + c^2B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$

|      | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ | $\sigma(B_{11})$ | $\sigma(B_{22})$ | $\sigma(B_{33})$ | $\sigma(B_{12})$ | $\sigma(B_{13})$ | $\sigma(B_{23})$ |
|------|----------|----------|----------|----------|----------|----------|------------------|------------------|------------------|------------------|------------------|------------------|
| C(1) | 3.5      | 3.9      | 3.1      | 2.1      | -0.1     | -0.2     | 0.5              | 0.5              | 0.4              | 0.5              | 0.4              | 0.4              |
| C(2) | 4.3      | 3.2      | 2.5      | 2.3      | -0.1     | -0.3     | 0.5              | 0.4              | 0.3              | 0.5              | 0.4              | 0.3              |
| C(3) | 4.6      | 3.4      | 3.9      | 2.4      | 0.3      | 0.1      | 0.6              | 0.5              | 0.5              | 0.5              | 0.4              | 0.4              |
| C(4) | 6.2      | 3.6      | 3.5      | 2.2      | 0.1      | -0.1     | 0.7              | 0.5              | 0.4              | 0.6              | 0.5              | 0.4              |
| C(5) | 5.3      | 3.4      | 2.9      | 2.5      | -0.5     | -0.1     | 0.6              | 0.5              | 0.4              | 0.5              | 0.4              | 0.3              |
| C(6) | 3.9      | 2.0      | 3.3      | 1.0      | 0.2      | 0.9      | 0.5              | 0.4              | 0.4              | 0.4              | 0.4              | 0.3              |
| C(7) | 5.9      | 2.4      | 4.0      | 1.5      | -0.4     | 0.2      | 0.7              | 0.4              | 0.5              | 0.5              | 0.5              | 0.4              |
| C(8) | 6.2      | 2.5      | 2.9      | 1.6      | 1.1      | 1.2      | 0.7              | 0.4              | 0.4              | 0.5              | 0.4              | 0.3              |
| C(9) | 6.7      | 5.7      | 4.6      | 4.3      | 1.3      | 0.7      | 0.8              | 0.7              | 0.5              | 0.7              | 0.5              | 0.5              |
| O(1) | 6.7      | 3.1      | 2.3      | 1.8      | 0.3      | 0.3      | 0.5              | 0.3              | 0.3              | 0.4              | 0.3              | 0.2              |
| O(2) | 6.9      | 2.9      | 3.3      | 1.8      | -1.0     | -0.3     | 0.5              | 0.3              | 0.3              | 0.4              | 0.3              | 0.3              |
| O(3) | 7.5      | 4.8      | 3.8      | 4.6      | 0.5      | 0.8      | 0.6              | 0.4              | 0.3              | 0.5              | 0.3              | 0.3              |
| O(4) | 5.2      | 2.3      | 4.2      | 1.5      | -0.7     | 0.0      | 0.4              | 0.3              | 0.3              | 0.3              | 0.3              | 0.2              |
| O(5) | 6.2      | 2.3      | 3.6      | 1.5      | -0.7     | 0.7      | 0.5              | 0.3              | 0.3              | 0.3              | 0.3              | 0.2              |

owing to the negligible value of  $\mu$ . The structure factors were converted to an absolute scale by Wilson's statistics (Wilson, 1942). An average temperature factor  $B=2.80 \text{ \AA}^2$  was determined in this way.

### Structural analysis

It is reasonable to assume that the molecules of TMKGA are associated in rows through hydrogen bonds formed about crystallographic inversion centres, as found in the structures of most dicarboxylic acids. In these cases the task of finding a starting structural model can be accomplished by use of the close-packing principle (Corradini, Diana, Ganis & Pedone, 1966; Corradini, Avitabile, Ganis & Martuscelli, 1967; Ganis, Pedone & Temussi, 1964). Such a procedure however requires the knowledge of reliable conformational parameters in order to build a molecular model, whereas as mentioned previously, some of these parameters were not available in our case. Accordingly we chose to solve the structure by means of direct methods. The structure factors were converted into normalized factors,  $E$ , by the formula

$$E_{hkl}^2 = \frac{F_{hkl}^2}{\exp[-2B(\sin\theta)^2/\lambda^2] \sum_{i=1}^N f_{i,\theta}^2}$$

$N$  is the number of atoms in the unit cell and  $f_{i,\theta}$  is the atomic factor of the  $i$ th atom relative to the reflexion angle  $\theta$ .

Among 208 reflexions with the higher  $E$ 's (that is, with  $E \geq 0.91$ ) all the triplets  $E_1, E_2, E_3$  were found that verify the condition of Sayre (1952), Cochran (1952) and Zachariasen (1952):

$$\begin{aligned} h_1 + h_2 &= h_3 \\ k_1 + k_2 &= k_3 \\ l_1 + l_2 &= l_3 \end{aligned}$$

For each condition the sign relation holds,

$$s_1 \times s_2 \times s_3 \simeq +1.$$

The numerical value of the probability that the product of the signs is  $+1$  was calculated by the formula

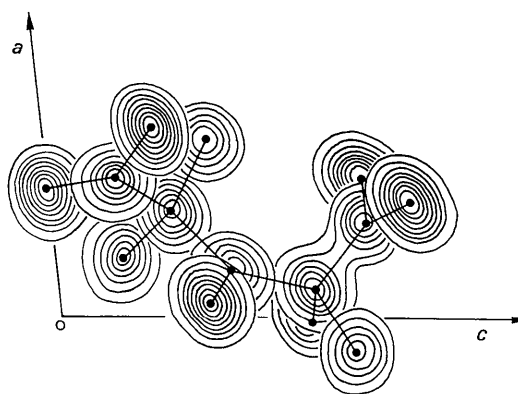


Fig. 1. Composite drawing of the final Fourier synthesis viewed along the  $b$  axis. Contours are at intervals of  $1 \text{ e. \AA}^{-3}$  starting with  $1 \text{ e. \AA}^{-3}$ .

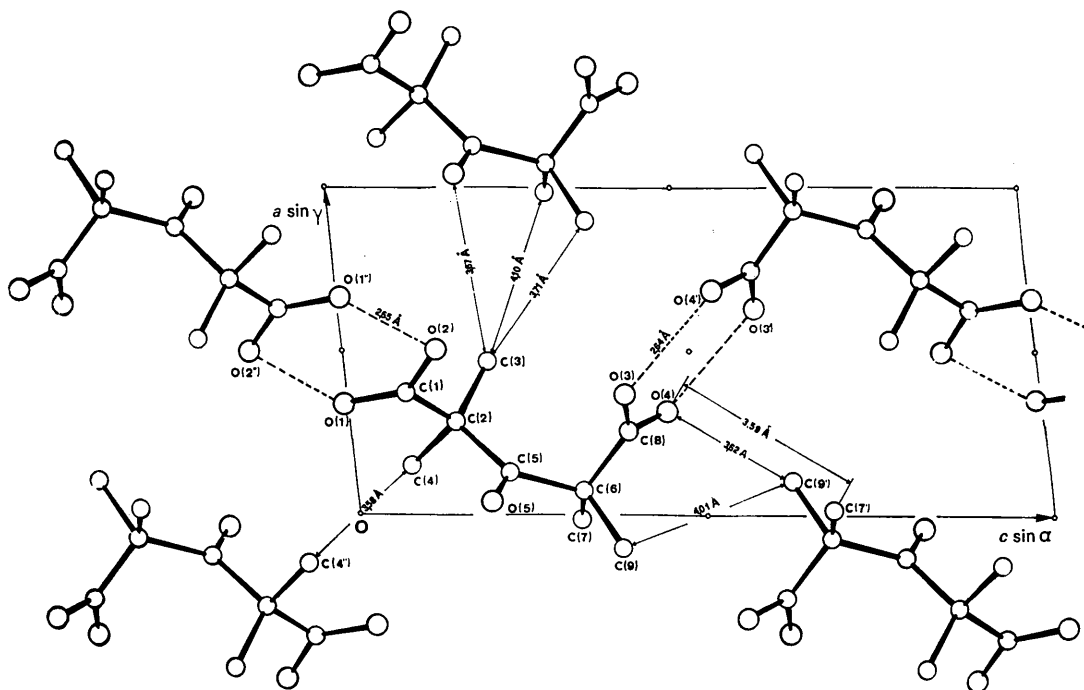


Fig. 2. Projection of the TMKGA structure on the (010) plane.



of Cochran & Woolfson (1955):

$$p = \frac{1}{2} \left( 1 + \operatorname{tgh} \frac{E_1 \times E_2 \times E_3}{\sqrt{N}} \right).$$

From an examination of these triplets, the signs of 145 reflexions were determined.

A Fourier synthesis was performed with the 145 normalized factors as coefficients and a molecular model was obtained by placing the O and C atoms of the structural unit on the 14 highest maxima of this first synthesis.

Table 4. Intramolecular distances and angles with standard deviations

| Distances                              |         |         |
|--|---------|---------|
| O(1)-C(1)                              | 1.197 Å | 0.012 Å |
| O(2)-C(1)                              | 1.309   | 0.016   |
| C(1)-C(2)                              | 1.517   | 0.017   |
| C(2)-C(3)                              | 1.516   | 0.017   |
| C(2)-C(4)                              | 1.542   | 0.018   |
| C(2)-C(5)                              | 1.536   | 0.016   |
| C(5)-O(5)                              | 1.225   | 0.017   |
| C(5)-C(6)                              | 1.526   | 0.015   |
| C(6)-C(7)                              | 1.575   | 0.018   |
| C(6)-C(9)                              | 1.551   | 0.019   |
| C(6)-C(8)                              | 1.458   | 0.017   |
| C(8)-O(3)                              | 1.349   | 0.016   |
| C(8)-O(4)                              | 1.215   | 0.016   |
| C(3)-C(7)                              | 3.456   | 0.018   |
| C(3)-C(8)                              | 3.042   | 0.016   |
| C(3)-C(9)                              | 4.617   | 0.019   |
| C(4)-C(7)                              | 3.345   | 0.016   |
| C(4)-C(8)                              | 4.342   | 0.015   |
| C(4)-C(9)                              | 4.664   | 0.018   |
| Angles                                 |         |         |
| O(1)-C(1)-O(2)                         | 121.3°  | 0.4°    |
| O(2)-C(1)-C(2)                         | 112.7   | 0.4     |
| O(1)-C(1)-C(2)                         | 125.9   | 0.4     |
| C(1)-C(2)-C(5)                         | 106.3   | 0.4     |
| C(1)-C(2)-C(3)                         | 109.2   | 0.5     |
| C(1)-C(2)-C(4)                         | 106.5   | 0.5     |
| C(3)-C(2)-C(4)                         | 111.1   | 0.5     |
| C(3)-C(2)-C(5)                         | 115.1   | 0.5     |
| C(4)-C(2)-C(5)                         | 108.0   | 0.5     |
| C(2)-C(5)-O(5)                         | 118.7   | 0.5     |
| C(2)-C(5)-C(6)                         | 123.0   | 0.5     |
| O(5)-C(5)-C(6)                         | 118.2   | 0.5     |
| C(5)-C(6)-C(8)                         | 112.6   | 0.5     |
| C(5)-C(6)-C(7)                         | 111.7   | 0.4     |
| C(5)-C(6)-C(9)                         | 111.2   | 0.5     |
| C(7)-C(6)-C(9)                         | 107.2   | 0.5     |
| C(7)-C(6)-C(8)                         | 107.7   | 0.5     |
| C(9)-C(6)-C(8)                         | 106.0   | 0.5     |
| C(6)-C(8)-O(4)                         | 128.6   | 0.6     |
| C(6)-C(8)-O(3)                         | 112.5   | 0.5     |
| O(3)-C(8)-O(4)                         | 118.9   | 0.5     |
| Dihedral angles                        |         |         |
| C(1)-C(2)-C(5) $\wedge$ C(2)-C(5)-C(6) | -155.1° |         |
| O(1)-C(1)-C(2) $\wedge$ C(1)-C(2)-C(5) | 113.3   |         |
| C(2)-C(5)-C(6) $\wedge$ C(5)-C(6)-C(8) | 66.4    |         |
| C(5)-C(6)-C(8) $\wedge$ C(6)-C(8)-O(4) | 134.7   |         |

From considerations of bond distances and angles it was clear that the position of only one C atom was incorrect; its position was therefore determined stereo-

chemically. A structure factor calculation for this model yielded a discrepancy index

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.35.$$

### Refinement

Beyond this stage the structure was refined by Fourier methods down to  $R=0.24$ . The subsequent refinement was performed by a block-diagonalized matrix least-squares method with a program written for an IBM 360/40 computer. The function minimized was:

$$R_w = \sum_{hkl} w(hkl) \left[ F_o(hkl) - \frac{1}{k} F_c(hkl) \right]^2$$

with unit value given to all the weighting factors,  $w(hkl)$ . All the reflexions with  $F_o < 0.5e$  were excluded from the refinement, because they are supposed to be affected by large errors.

In the first stage only C and O atoms were considered, with isotropic thermal factors, down to  $R=0.18$ ; beyond this stage anisotropic vibrational parameters were introduced and hydrogen atoms were placed in their stereochemically calculated positions and included in the calculations, with the same isotropic vibrational parameter,  $B=3.5 \text{ \AA}^2$  (that is, an average of the temperature factors of the carbon atoms to which they are bonded). The refinement converged to  $R=0.130$ .

The bridge hydrogen atoms supposedly bonded to O(2) and O(3) (the bond lengths C(1)-O(2) and C(8)-O(3) are the longer bonds of the carboxylic acid groups,

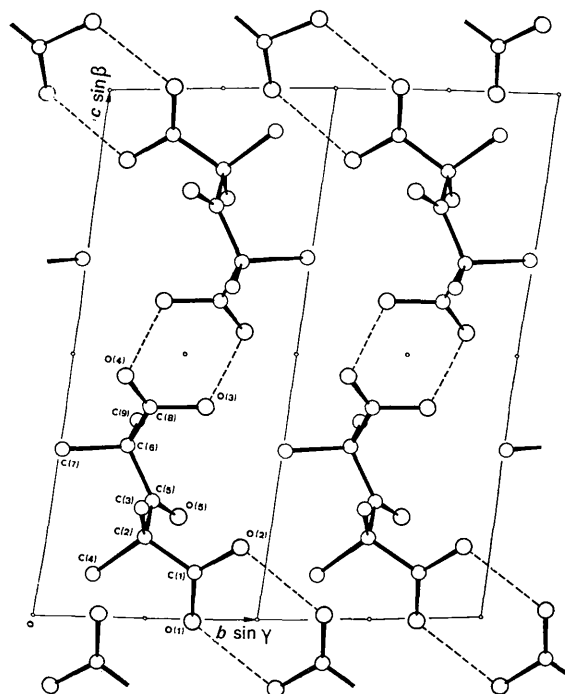


Fig. 3. Projection of the TMKGA structure on the (100) plane.

see Fig. 5) were introduced at this point, 1.10 Å being assumed for the O-H bond lengths. The *R* index did not change appreciably.

The scattering factors of Berghuis, Haanappel, Poters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen atoms, and of McWeeny (1951) for hydrogen, were used. The final atomic coordinates together with the corresponding standard deviations (Cruickshank, 1949) are reported in Table 1.

Table 2 shows the coefficients,  $B_{ij}$ , of the temperature factors of the form:

$$\exp \left[ -\frac{1}{4} (h^2 a^*{}^2 B_{11} + k^2 b^*{}^2 B_{22} + l^2 c^*{}^2 B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23}) \right]$$

with the corresponding standard deviations. In Table 3 observed and calculated structure factors are listed. The standard deviation of the electronic density is 0.2 e.Å<sup>-3</sup>. Fig. 1 shows a composite electron density map projected along *b*.

### Description of the structure

The projection of the structure on to the (010) plane is shown in Fig. 2. It can be seen that the packing is dominated essentially by the steric requirements of methyl groups of adjacent molecules. Intermolecular distances reveal a homogeneous filling of the available space; all C---C distances are larger than 3.60 Å, C---O distances are larger than 3.67 Å and O---O distances are larger than 3.60 Å.

The molecular rows are oriented along the crystallographic *b-c* direction as shown in the projection of the structure on to the (100) plane (Fig. 3).

### Molecular conformation

The conformation of the molecular skeleton is of type *GT* with torsion angles on the bonds adjacent to the central CO group of  $-155^\circ$  (*T*) and  $66^\circ$  (*G*). In Table 4

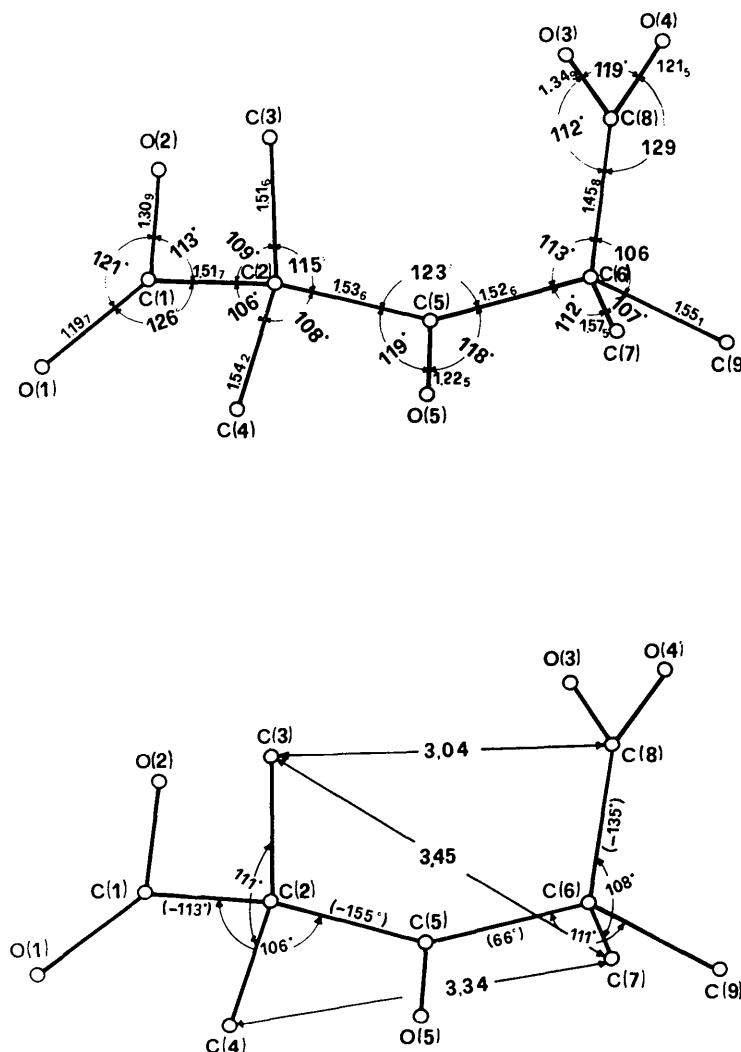
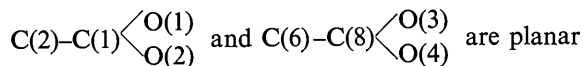


Fig. 4. Molecular model of the TMKGA molecule.

(see also Fig. 4) the most important conformational parameters of the TMKGA molecule are reported. Most of these parameters have normal values. Their standard deviations are about 0.015 Å for the bond lengths and about 0.5° for the valence angles.

The values of the bond lengths C(6)–C(7) (1.57 Å) and C(7)–C(8) (1.458 Å) are probably not real. The other C–C lengths are all in good agreement with the expected values. Their mean value is 1.531 Å, with a standard deviation of 0.011 Å, in very good agreement with the standard deviations of the single C–C bond lengths. On the other hand, the valence angles C(2)–C(5)–C(6), C(3)–C(2)–C(5) and C(5)–C(6)–C(8) are appreciably larger than the corresponding average values reported in the literature. This is certainly related to the fact that in this way the interaction between C(3) and C(8) (3.04 Å apart in the final structure) is relaxed. Also the carboxylic groups are in the expected conformation; the C(1)–O(1) bond is almost eclipsed by the C(2)–C(4) bond and C(8)–O(4) by the C(6)–C(7) bond, as in several analogous compounds. The atomic groups



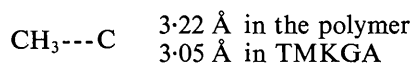
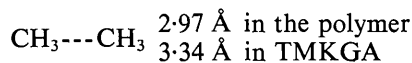
within the experimental error.

The contact distance C(3)---C(8) of 3.04 Å requires some comment. It is easy to verify that this interaction cannot be relaxed thorough rotation about the C(2)–C(5) and C(5)–C(6) bonds. In fact any other conformation attainable by rotation around these bonds is characterized by CH<sub>3</sub>---CH<sub>3</sub> distances shorter than those observed (3.3 to 3.5 Å). In this respect the observed conformation should be considered as a compromise resulting from the optimization of CH<sub>3</sub>---CH<sub>3</sub> distances and the least possible shortening of CH<sub>3</sub>---C distances. Such distances were never found in simple open chain compounds, only in some polymers [polydimethylketene (Bassi, Ganis & Temussi, 1967) and polyisobutylene (Liquori, 1955)]. The corresponding interactions must necessarily be competitive with the bending energies involved in the movement to increase the distance between C(3) and C(8). Indeed, one could obtain an energetically more favourable conformation by a greater enlargement of the valence angles C(2)–C(5)–C(6), C(3)–C(2)–C(5) and C(5)–C(6)–C(8). A deformation of 4 or 5° in each of these angles would be

sufficient to achieve C---C distances of at least 3.3–3.4 Å. The calculated energies for these angular deformations are not greater than 3–4 kcal.mole<sup>-1</sup> (Allinger, Hirsch, Miller, Tymisusky & van Coltedge, 1968).

The difference between the van der Waals energies associated with the C(3)---C(8) interaction, in going from say, 3.0 Å to 3.4 Å must be of the same order of magnitude. In fact, with different sets of potential functions (Mark, 1968) this difference of interaction energy between the two carbon atoms and the atoms bonded to them is calculated to be in the range 0 to 2 kcal.mole<sup>-1</sup>.

We can now actually compare the conformational parameters of TMKGA with those assigned to the corresponding group in polydimethylketene. In Table 5 some of the conformational parameters of the acid and of the polymer are reported. The resemblance between their conformations is obvious. Intramolecular contact distances are very short in both compounds; CH<sub>3</sub>---C<sub>3</sub> distances are slightly shorter and CH<sub>3</sub>---C slightly larger in the polymer:



We wish to point out that the previously quoted conformational analysis of the polymer (Ganis & Temussi, 1966) led to values of conformational parameters almost identical with those found in the structural analysis of the acid (Table 5, II). This result is a further indication that the conformation of the acid corresponds to an internal energy minimum. *i.e.* it is not influenced to a large extent by crystal field forces. On the contrary, as described in the paper quoted (Ganis & Temussi, 1966) the molecular structure of the polymer is modified by long range inter- and intramolecular interactions in the crystal.

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Table 5. Comparison between some conformational parameters of TMKGA and polydimethylketene

Conformation (I) was obtained from the X-ray structural analysis of the polymer (Bassi, Ganis & Temussi, 1967). Conformation (II) was obtained from the conformational analysis of the polymer (Ganis & Temussi, 1966).

| Parameters                             | Polydimethylketene |      | TMKGA       |
|--|--------------------|------|-------------|
|  | (I)                | (II) |             |
| <b>Angles</b>                          |                    |      |             |
| C(2)–C(5)–C(6)                         | 123° ± 4°          | 123° | 123° ± 0.5° |
| C(1)–C(2)–C(5)                         | 114° ± 4°          | 114° | 113° ± 0.4° |
| <b>Dihedral angles</b>                 |                    |      |             |
| C(1)–C(2)–C(5) $\wedge$ C(2)–C(5)–C(6) | 168° ± 10°         | 195° | 205° ± 3    |
| C(2)–C(5)–C(6) $\wedge$ C(5)–C(6)–C(8) | 70° ± 10°          | 75°  | 66° ± 3     |

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## The Crystal Structure of 4-Acetyl-3'-bromobiphenyl

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The crystal structure of 4-acetyl-3'-bromobiphenyl,  $C_{14}H_{11}OBr$ , has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic, space group  $P2_1/c$ , with unit-cell dimensions  $a = 3.91$ ,  $b = 9.06$ ,  $c = 32.76$  Å,  $\beta = 98.1^\circ$ . The structure was refined by block-diagonal least-squares with anisotropic thermal parameters to a residual of 9% for the 936 observed structure factors. The angle between the two phenyl rings and the angle between the acetyl group and the phenyl ring to which it is attached were found to be  $38.6^\circ$  and  $2.9^\circ$  respectively. All the intermolecular contacts correspond to normal van der Waals interactions.

### Introduction

Recent studies of the liquid crystalline properties of biphenyl derivatives (Branch, Byron, Gray, Ibbotson & Worrall, 1964) have created an interest in the interplanar angles of biphenyl nuclei in the liquid crystalline states. Whereas the molecule of biphenyl is planar in the solid phase (Dhar, 1932; Trotter, 1961; Hargreaves & Rizvi, 1962), several simple derivatives with 2 and 2' halogen substitutions have interplanar angles of around  $48^\circ$  (Young, Tollin & Sutherland, 1968; Sutherland & Hoy, 1968, 1969; Sutherland, 1969). Angles of this order are expected from a simple treatment of overcrowding (Branch *et al.*, 1964) and it was of interest to study a derivative with a 3' substituted halogen. Here details of the crystal and molecular structure of 4-acetyl-3'-bromobiphenyl are given, the fifth in a series of related compounds being investigated.

### Experimental

4-Acetyl-3'-bromobiphenyl was crystallized from methanol. The lattice constants have been refined from provisional photographic estimates made with a Hilger and Watts linear diffractometer.

### Crystal data

$C_{14}H_{11}OBr$ ,  $M = 275.16$ . Monoclinic,  $a = 3.91 \pm 0.1$ ,  $b = 9.06 \pm 0.1$ ,  $c = 32.76 \pm 0.3$  Å,  $\beta = 98.1 \pm 0.1^\circ$ ,  $U = 1149$  Å<sup>3</sup>,  $D_m = 1.59$  g.cm<sup>-3</sup>,  $D_c = 1.59$  g.cm<sup>-3</sup>.  $Z = 4$ ,  $F(000) = 552$ ,  $Cu K\alpha$  ( $\lambda = 1.5418$  Å).  $Mo K\alpha$  ( $\lambda = 0.7107$  Å).

Absent spectra:  $0k0$  when  $k$  odd and  $h0l$  when  $l$  odd. Space group  $P2_1/c$  (No. 14).

The crystals were colourless needles, the needle axis corresponding to the  $a$  axis of the unit cell. A suitable crystal of cross section  $0.03 \times 0.1$  cm perpendicular to the needle axis was selected for intensity data collection about the  $a$  axis. Data for the  $0kl$ ,  $1kl$ ,  $2kl$ ,  $3kl$  levels of reciprocal space were collected by the multiple-film equi-inclination Weissenberg technique with  $Cu K\alpha$  radiation. The  $h0l$  intensity data were collected from a crystal cut to  $0.15 \times 0.03 \times 0.02$  cm. Packs of six films of Ilford Industrial B were used throughout.

Intensities of the spots were measured on a Joyce-Loebl Flying Spot Densitometer; no correction for absorption was applied as variations of less than 5% were predicted from the range of  $\mu R$  values (0.08–0.15). The data were brought to the same arbitrary scale and final-