A Model Compound for Polyisobutene. The Crystal Structure of 2,2,4,4-Tetramethyladipic Acid[1a]

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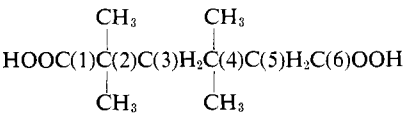
ABSTRACT: The chemical structure of the aliphatic portion of 2,2,4,4-tetramethyladipic acid is identical with that of a sequence of two monomer units in polyisobutene. The acid crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 12.34$, $b = 7.12$, $c = 7.28$ Å; $\alpha = 109.7°$, $\beta = 100.6°$, $\gamma = 98.9°$, and two molecules per unit cell. The crystal structure has been determined by the symbolic addition procedure with the aid of the Sayre's relations to a final R factor of 0.076 for 2005 independent reflections measured by countertechniques (Cu Kα radiation). The molecular conformation is characterized by an arrangement of the skeletal carbon atoms closely resembling a uniform helix ($\psi_{av} = 68.5°$, taking the *cis* conformation at 0°). The $(H_3C)_2C-CH_2-(CH_3)_2$ angle has the unusual value of 122.6° so that all the intramolecular C···C distances between atoms separated by four or more bonds are greater than 3.0 Å. The observed conformation of the molecule is discussed and compared with the three conformations proposed for crystalline polyisobutene.

The crystal structure of properly chosen dicarboxylic acids provides useful information for the description of the possible chain conformations of crystalline polymers.[2-6] In particular, these studies may give accurate values for bond lengths and bond angles to be transferred to the polymer chains, and they may also obtain useful information about the most probable rotational states around the chain single bonds.

In the molecule of 2,2,4,4-tetramethyladipic acid (TMADA) the sequence comprised between C(1)



and C(6) provides a possible model for the chain conformation of polyisobutene, whose crystal structure is still a subject of discussion.[7-10] Furthermore, since comparatively little is known hitherto on the detailed geometry of overcrowded aliphatic sequences, we have undertaken the structural investigation of TMADA in order to understand how the intramolecular strain is minimized in these types of molecules.

(1) (a) This paper has been presented in part before the Polymer Section of the VIII IUC Congress, Stony Brook, N. Y., Aug 1969; *Acta Cryst.*, **A25**, Part S3, S136 (1969). (b) Università di Napoli, Istituto Chimico, 80134, Napoli, Italy. (c) On sabbatical leave from the Istituto di Chimica Industriale del Politecnico di Milano, 20133 Milano, Italy.

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TABLE I

UNIT CELL DIMENSIONS

2,2,4,4-Tetramethyladipic acid, $C_{10}H_{18}O_4$, mol wt 202.25
Triclinic, space group $P\bar{1}$, $Z = 2$, $F(000) = 220$

$a = 12.345 \pm 0.004$ Å	$\alpha = 109° 43' \pm 15'$
$b = 7.120 \pm 0.002$ Å	$\beta = 100° 38' \pm 15'$
$c = 7.277 \pm 0.002$ Å	$\gamma = 98° 57' \pm 15'$

$d_{calcd} = 1.17$ g/cm³

Experimental Section

TMADA was prepared according to the procedure reported in literature[11] by oxidation with HNO_3 of 3,3,5,5-tetramethylcyclohexanone. Single crystals of TMADA suitable for X-ray diffraction analysis were grown by slow evaporation of cyclohexane solutions. A small irregularly shaped crystal (0.2 × 0.4 × 0.6 mm) was selected for investigation. On the basis of preliminary Weissenberg photographs taken with Cu Kα radiation, the crystal was found to belong to the triclinic system (space group P1 or $P\bar{1}$). The crystal was carefully centered on a Picker four-circle automated diffractometer equipped with a PDP-8 digital computer. The cell dimensions were determined from a least square treatment of the setting angles of 12 reflections with $2\theta > 80°$. The parameters obtained are reported in Table I. The density calculated on the basis of the molecular weight ($d_{x-r} = 1.17$ g/cm³) and assuming two molecules per unit cell agreed reasonably with the experimental value ($d_{exp} = 1.15$ g/cm³) obtained by flotation method.

Integrated intensities were measured by the θ–2θ scan mode using Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) and pulse height analysis to reduce unwanted background. A scan range of 1.67° was found to be sufficient for all the reflections over the range of 2θ examined (0–130°) with a scan speed of 1°/min. The take-off angle of the tube was 3.0° and a counteraperture, 4.0 × 4.0 mm, was placed 30 cm from the crystal. Two stationary crystal–stationary counterbackground counts of 10 sec were taken at each end of each scan. A total of 2005 independent reflections

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TABLE II

FINAL ATOMIC PARAMETERS

A. Positional Parameters

Atom	x	y	z	Atom	x	y	z
C(1)	0.0966 (2)	0.1568 (4)	−0.1035 (4)	H(3)CH_3(1)	0.122	0.026	−0.480
C(2)	0.1750 (2)	0.2781 (4)	−0.1826 (4)	H(1)CH_3(2)	0.096	0.536	−0.128
C(3)	0.2917 (2)	0.3859 (4)	−0.0279 (4)	H(2)CH_3(2)	0.034	0.337	−0.366
C(4)	0.3062 (2)	0.5620 (4)	0.1762 (4)	H(3)CH_3(2)	0.166	0.503	−0.322
C(5)	0.2936 (3)	0.7677 (5)	0.1599 (5)	H(1)CH_3(3)	0.490	0.625	0.220
C(6)	0.3829 (3)	0.8671 (5)	0.0872 (5)	H(2)CH_3(3)	0.437	0.449	0.323
CH_3(1)	0.1994 (3)	0.1180 (6)	−0.3666 (5)	H(3)CH_3(3)	0.447	0.713	0.446
CH_3(2)	0.1142 (3)	0.4227 (5)	−0.2545 (5)	H(1)CH_3(4)	0.135	0.493	0.203
CH_3(3)	0.4273 (3)	0.5899 (6)	0.2997 (6)	H(2)CH_3(4)	0.236	0.635	0.436
CH_3(4)	0.2206 (4)	0.5118 (6)	0.2900 (5)	H(3)CH_3(4)	0.227	0.371	0.312
O(1)	0.1401 (2)	0.0343 (4)	−0.0312 (4)	H(1)C(3)	0.325	0.265	0.008
O(2)	−0.0025 (2)	0.1700 (3)	−0.1122 (4)	H(2)C(3)	0.347	0.445	−0.106
O(3)	0.3879 (2)	0.7935 (4)	−0.0947 (4)	H(1)C(5)	0.211	0.741	0.057
O(4)	0.4542 (3)	1.0254 (4)	0.2120 (4)	H(2)C(5)	0.293	0.875	−0.309
H(1)CH_3(1)	0.244	0.014	−0.318	H(1)O(1)	0.092	−0.051	0.024
H(2)CH_3(1)	0.254	0.193	−0.435	H(1)O(3)	0.465	0.882	−0.159

B. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	4.3 (1)	4.7 (1)	4.9 (1)	0.8 (1)	1.0 (1)	2.0 (1)
C(2)	4.5 (1)	4.7 (1)	4.1 (1)	0.6 (1)	1.3 (1)	1.8 (1)
C(3)	4.0 (1)	4.4 (1)	4.5 (1)	0.8 (1)	1.5 (1)	1.9 (1)
C(4)	5.2 (1)	4.7 (1)	3.9 (1)	0.5 (1)	1.3 (1)	1.7 (1)
C(5)	6.6 (2)	4.3 (1)	6.1 (1)	1.2 (1)	2.7 (1)	1.8 (1)
C(6)	7.4 (2)	4.3 (1)	5.1 (1)	0.6 (1)	1.8 (1)	1.8 (1)
CH_3(1)	7.6 (2)	6.2 (2)	5.0 (1)	0.5 (1)	2.2 (1)	0.4 (1)
CH_3(2)	5.4 (1)	7.0 (2)	6.2 (2)	0.9 (1)	0.8 (1)	4.2 (1)
CH_3(3)	6.8 (2)	7.6 (2)	6.0 (2)	0.9 (2)	−0.6 (1)	2.3 (1)
CH_3(4)	9.6 (2)	6.8 (2)	5.1 (1)	−0.1 (1)	3.9 (2)	1.8 (1)
O(1)	5.1 (1)	6.7 (1)	10.2 (1)	1.9 (1)	2.8 (1)	5.6 (1)
O(2)	4.2 (1)	6.5 (1)	8.3 (1)	1.3 (1)	1.8 (1)	4.4 (1)
O(3)	10.1 (1)	6.3 (1)	5.1 (1)	−1.3 (1)	2.6 (1)	1.4 (1)
O(4)	12.0 (2)	6.5 (1)	5.5 (1)	−3.1 (1)	2.4 (1)	0.9 (1)

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

were collected. Two standard reflections were measured every 25 reflections (*i.e.*, every hour) during data collection to check the electronic stability of the instrument and any deterioration of the crystal. The fluctuations in the intensities of the standard reflections were within 3%. The integrated intensities from which the background counts were subtracted were then corrected for Lorentz and polarization effect in the usual way.

Structural Resolution and Refinement. The structure has been solved through application of direct methods. Assuming as probable the $P\bar{1}$ space group, the signs of most of the structure factors with $|E| > 1.8$ have been determined with the aid of the symbolic addition procedure.[12] The set of signs appearing to be the most consistent with the Sayre relations have been used to generate as many signs as possible for the structure factors with $1.3 < |E| < 1.8$. The three dimensional Fourier synthesis was then evaluated with about 200 structure factors, from a total amount of 2005 independently observed reflections. The 14 strongest peaks could be connected with each other by vectors not exceeding the range 1.0–1.7 Å, and the resulting molecular shape was reasonable; furthermore, each carboxylic group was oriented toward a center of symmetry, very much in the way expected to give rise to infinite chains of hydrogen bonded molecules.

(12) I. L. Karle and J. Karle, *Acta Cryst.*, **17**, 1356 (1964).

The structure has then been refined by nine cycles of full-matrix least squares; anisotropic thermal factors were assigned to all nonhydrogen atoms only after the R ($= \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) factor dropped below 0.18. As to the hydrogen atoms, they were introduced in the sterically expected positions ($d_{C-H} = 1.08$ Å, $d_{O-H} = 1.00$ Å, H–C–H $= 109.5°$, C–O–H $= 120°$) before the last cycle, and were held fixed with an isotropic thermal factor approximately equal to the average of the B_{ii} of the carbon atom to which they are bonded. At the end of the refinement the R factor is 0.076 for the 2005 measured reflections; the maximum shifts for either the positional or thermal coordinates were smaller than one-third of the corresponding standard deviation. The weighing scheme adopted corresponds to that suggested by Cruickshank [$w(hkl) = 1/(a\,F_o^2(hkl) + bF_o(hkl) + c)$; $a = 0.1111$, $b = 1/18 \times F_o(\max)$, $c = 2b \times F_o(\min)$].[13a] A list of the observed and calculated structure factors has been deposited as Document No. NAPS-00533 with the American Society for Information Science.[13b] In Table II the fractional coordinates and thermal factors are

(13) (a) D. W. J. Cruickshank and D. E. Pilling, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, Ltd., London, 1961, p 32. (b) A copy may be secured by citing the document number and by remitting $1.00 for microfilm or $3.00 for photocopies to ASIS National Auxiliary Publication Service, c/o CCM Information Science Inc., 22 W. 34th St., New York, N. Y. 10001.

TABLE III

INTERNAL ROTATION ANGLES[a]

	Angle, deg
C(1)–C(2)–C(3)–C(4)	66.9
C(2)–C(3)–C(4)–C(5)	72.7
C(3)–C(4)–C(5)–C(6)	66.0
CH_3(2)–C(2)–C(3)–C(4)	−58.2
CH_3(1)–C(2)–C(3)–C(4)	−178.1
CH_3(3)–C(4)–C(3)–C(2)	−167.6
CH_3(4)–C(4)–C(3)–C(2)	−48.4
CH_3(3)–C(4)–C(5)–C(6)	−51.7
CH_3(4)–C(4)–C(5)–C(6)	−169.5
O(1)–C(1)–C(2)–C(3)	49.8
O(2)–C(1)–C(2)–C(3)	−132.0
O(1)–C(1)–C(2)–CH_3(2)	177.5
O(1)–C(1)–C(2)–CH_3(1)	−65.0
C(2)–C(1)–C(2)–CH_3(1)	113.2
O(2)–C(1)–C(2)–CH_3(2)	−4.2
O(3)–C(6)–C(5)–C(4)	−72.7
O(4)–C(6)–C(5)–C(4)	108.3

[a] *trans* conformation = 180°.

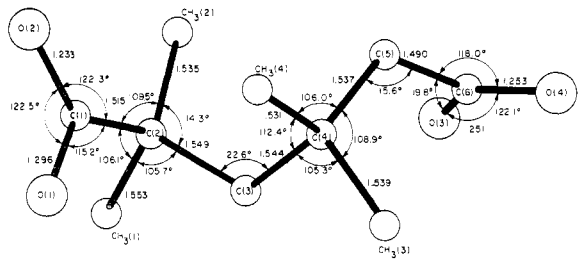


Figure 1. Molecular model of TMADA. Bond lengths (in ångströms) and bond angles (in degrees) are indicated except for C(1)–C(2)–C(3), C(3)–C(4)–C(5), CH_3(1)–C(2)–CH_3(2), and CH_3(3)–C(4)–CH_3(4), which are 111.8, 114.5, 109.0, and 109.6°, respectively. The average standard deviation of bond lengths is 0.005 Å, of angles 0.2°.

reported, together with the corresponding standard deviations, while Figure 1 shows the resulting molecular geometry, in terms of bond lengths and angles; the internal rotation angles are reported in Table III.

Discussion of the Structure

a. Molecular Conformation. Remarkable features of the molecular geometry are as follows (see Figure 1 and Table III).

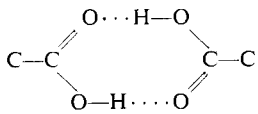
(1) The value of the C(2)–C(3)–C(4) bond angle (122.6 ± 0.1°) is about 13° greater than the tetrahedral angle. This is certainly due to repulsive interactions between the methyl groups linked to C(2) and to (C4), respectively. To the best of our knowledge, this is the maximum value accurately determined so far for a C–CH_2–C bond angle, and we believe that this result strongly suggests the importance of allowing for bond angle deformation in conformational analysis. This is particularly true for crowded molecules, but it can probably play an important role in substantially reducing the internal potential energy of otherwise unfavored conformations of other kinds of molecules. The average value of the C–C–C angles of the chain backbone (116.1° on four independent determinations, which reduces to 114.0° if the abnormal value of 122.6° is neglected) is larger than the average CH_3–C–CH_3 angle (109.3° on two determinations), which in turn seems to be slightly larger than the C(non-methyl)–C–CH_3 average angle (108.5° on eight determinations).

(2) The conformation of the molecular backbone (C(1) through C(6)) is regular and can be closely described as a fragment of a helix having the same value of the internal rotational angles on all the chain bonds: the C(1)–C(6) sequence is in fact characterized by three ψ values comprised in a range of only 5° (av +68.5°).

(3) The probable disorder in the orientation in space of the C(6)O(3)O(4) carboxylic group consists of the statistical substitution between the carbonylic and hydroxylic oxygen atoms (see Figure 1). This is indicated by three distinct observed effects: (i) the identical values found for the two C–O bond lengths; (ii) the small difference between the two C–C–O angles, much smaller than the difference usually quoted for nonstatistical carboxylic groups;[14,15] (iii) the high average values of the B_{ii} thermal parameters which characterize O(3) and O(4), actually the highest values found in the whole molecule. Neither of the two possible orientations of the C=O bond corresponds to the usual *syn*-planar arrangement of the C_β—C_α—C=O sequence,[15] probably because of the rather short distance that would exist between the oxygen and the carbon atom of the CH_3(3) methyl group (~2.7 Å), separated by four bonds, instead of the observed distances O(3)–CH_3(3) (3.62), O(4)–CH_3(3) (3.35 Å).

(4) On the other hand, an orientation close to that expected is found for the carboxylic group centered on C(1). The C=O bond is substantially *syn*-planar with the CH_3(2)–C(2) bond (ψ = 4 ± 1°).[15] It is to be remarked that at variance with the case of the other carboxylic group, no close (O···C) contact with carbon atoms separated by four (or more) bonds may arise in this case.

Both the crystallographically independent



groups are very close to planarity (m.s. distances from the m.s. planes being 0.013 and 0.008 Å for the carboxyl groups containing C(1) and C(6), respectively). The corresponding equations of the two m.s. planes, referred to the triclinic x, y, z fractional coordinates, are for the carboxyl group containing C(1), $0.016x + 0.427y + 0.654z = 0$; for the carboxyl group containing C(6), $0.672x - 0.805y + 0.334z + 1.582 = 0$. The above equations have been derived giving unit weights to all the eight nonhydrogen atoms belonging to the planes. The two nonequivalent O···O hydrogen bond distances are close to the values reported in the literature (2.645 and 2.637 Å, respectively, *cf.* Figure 2).

b. Molecular Packing. The crystal structure results from the packing of infinitely extended rows of hydrogen bonded molecules; the row axis is parallel to $(1/2\ \vec{a} + \vec{b})$. Since the molecular conformation is

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(15) J. D. Dunitz and P. Strickler, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, p 595.

asymmetric, and two consecutive molecules are related by a crystallographic center of inversion, the symmetry of the molecular rows is *ti*,[16] and the full repeat distance along the rows is 17.3 Å, corresponding to two molecules. In Figure 2 the mode of packing of TMADA is reported, together with the shortest intermolecular distances and also the intramolecular distances between atoms separated by four or more bonds. As for the intermolecular contacts, all C···C distances are larger than 4.0 Å, with the only exception of those connecting atoms belonging to facing carboxyl groups (3.89 Å): the shortest O···O distances are 2.64 and 3.72 Å for hydrogen-bonded and nonbonded atoms, respectively.

c. Comparison with Polyisobutylene. The geometrical parameters found for 2,2,4,4-tetramethyladipic acid (Figure 1 and Table III) suggest, as a possible conformation for polyisobutene (PIB), an almost uniform helix with $\psi = 68.5°$, $C\text{–}CH_2\text{–}C = 122.6°$, and $CH_2\text{–}C(CH_3)_2\text{–}CH_2 = 113°$. The ratio K (number of monomer units)/(number of turns) corresponding to such polymer would be very close to 2 Å (1.98), while the chain repeat per monomer unit is 2.06 Å. At the present, to the best of our knowledge, three conformational models have been proposed for crystalline PIB, on the basis of the X-ray diffraction data: (1) an 8/5 uniform helix, with all skeletal C–C–C angles equal to 114°, and $\psi = 97°$;[7] (2) an 8/5 helix with $C\text{–}CH_2\text{–}C = 126°$, $C\text{–}C(CH_3)_2\text{–}C = 107°$, and two different rotation angles, $\psi_1 = 129°$ and $\psi_2 = 77.5°$, per each monomer unit;[8] (3) an 8/3 helix with sketelal C–C–C angles of 120° and $\psi_1 = 180°$, $\psi_2 = 48°$.[10] In any case, it seems impossible to escape the conclusion that the chain conformation corresponds either to an 8/5 or to an 8/3 helix, and that the chain repeat per monomer unit is 2.33 Å. This rules out any possibility that the conformation found in the present investigation may be transferred to the polymer in the crystalline state. However, it may be of interest considering that, on the basis of the internal potential energy plot proposed by De Santis, *et al.*,[9] the conformation found by us is close to the minimum with $\psi_1 = \psi_2 \simeq 80°$. In spite of the fact that the above plot has been obtained under the assumption of C–C–C skeletal angles all equal to 114°, it is remarkable that, in the molecular conformation found by us for TMADA, all C···C intramolecular distances between atoms separated by four bonds are larger than 3.0 Å.

The disagreement still existing among the different conformational models proposed for polyisobutene both in the crystalline state[7,8,10] and in solution,[17,18] together with the unusual parameters found in the present investigation, have prompted us to undertake a new conformational analysis for polyisobutene, in which allowance is made for the variation of the bond angles along the chain. Preliminary results[19] indicate that several competing conformations of similar energy, including that corresponding to the one found for TMADA, are indeed available to the monomer units, thus imparting a relatively high flexibility to the macromolecules in solution.[20]

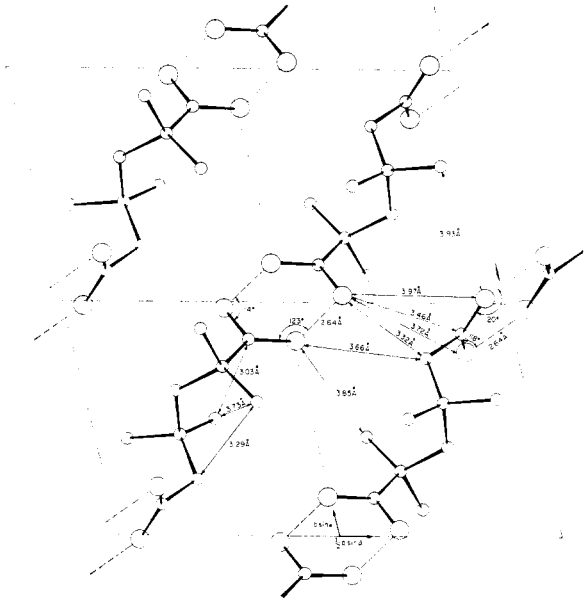

Figure 2. Mode of packing of TMADA along [001]. The intramolecular and intermolecular shortest distances are indicated together with the relevant parameters of the hydrogen bonding.

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