

The C form of *n*-hexadecanoic acidEvelyn Moreno,^a Raquel Cordobilla,^a Teresa Calvet,^{a*}
Fernando J. Lahoz^b and Ana I. Balana^b^aDepartament de Cristal·lografia, Universitat de Barcelona, Martí i Franquès, sn, E-08028 Barcelona, Spain, and ^bDepartamento de Química Inorgánica – ICMA, Facultad de Ciencias, Universidad de Zaragoza–CSIC, E-50009 Zaragoza, Spain
Correspondence e-mail: mtcalvet@ub.edu

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In the crystal structure of the title compound, C₁₆H₃₂O₂, the molecules are arranged into dimers through O—H···O hydrogen bonds. These dimers are packed in bilayers with terminal methyl groups at both external faces, and these layers are parallel to the crystallographic (100) plane. All C—C bonds of the alkyl chain show an antiperiplanar (*trans*) conformation, with slight deviations from the ideal value in the C—C bonds close to the intermolecular hydrogen bonds. The similarity between the carboxyl C—O bond distances is consistent with the existence of *cis*–*trans* tautomerism.

Comment

Carboxylic or fatty acids represent a very common type of natural compound used in different industrial fields (pharmaceutical, food and cosmetic industries). A new application for unbranched saturated carboxylic acids C_{*n*}H_{2*n*}O₂ (abbreviated C_{*n*}) lies in the field of energy storage and thermal protection, due to their high melting enthalpy (162–232 kJ g^{−1} for *n* in the range 10–20) and other related properties, such as their stability during thermal cycling. Against this background, our group, integrated in REALM (Réseau Européen sur les Alliages Moléculaires, or European Network on Molecular Alloys), has been studying the polymorphism and solid-state miscibility of this family of substances.

Normal saturated acids show a complex polymorphic behaviour, only partially characterized to date due to the difficulty of obtaining suitable single crystals for X-ray analysis: problems arise involving crystallization processes, several crystalline habits and forms, and crystallization conditions. In general, different forms, or a mixture of them, are usually observed after a crystallization process. Their occurrence depends on several variables, such as the number of C atoms in the chain, the temperature, the solvent and precipitant used, the grinding (after crystallization) of the sample and the crystallization rate (Kaneko *et al.*, 1998; Sato *et al.*, 1991; Moreno *et al.*, 2006). Typically, the forms are named *A*, *B*, *C*, *D* and *E* for fatty acids with an even number of

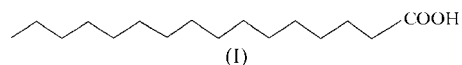
C atoms, and *A'*, *B'*, *C'*, *D'* and *E'* for those with an odd number. Some of these forms have been characterized for specific members of the family.

In general, the structure of these forms consists of molecules packed in bilayers containing two molecules, with the saturated carbon chains in the all-*trans* conformation (except for *B* and some triclinic forms, where the molecules adopt a *gauche* conformation), and with their carboxyl groups forming dimers through a typical R₂²(8) hydrogen-bond system (Bernstein *et al.*, 1995). These dimers are arranged so as to exhibit monolayers of terminal methyl and carboxyl groups, except for some triclinic forms, *viz.* A_{super} and A₁, where both terminal groups co-exist in the same monolayer face.

The *A'* (von Sydow, 1954*a*, 1955*b*; Goto & Asada, 1980) and *B'* forms (von Sydow, 1954*b*; Goto & Asada, 1984) are triclinic, P $\bar{1}$, with *Z* = 2 and 4, respectively. Different triclinic *A* forms (also P $\bar{1}$) have been observed for C₁₂: an A_{super} form (Goto & Asada, 1978*a*) and an A₁ form (Lomer, 1963), with *Z* = 6 and 2, respectively. A different triclinic A₂ form was found for C₁₆ (Kobayashi *et al.*, 1984). Two different polytypes have been distinguished for the *B* and *E* forms, one monoclinic, P2₁/*a*, with *Z* = 4 (Goto & Asada, 1978*b*; Kaneko *et al.*, 1990), and the other orthorhombic, P*bca*, with *Z* = 8 (Kaneko *et al.*, 1994*a,b*). On raising the temperature, all these forms transform to a monoclinic *C* form for even acids (Vand *et al.*, 1951; Malta *et al.*, 1971) and to *C'* for odd acids (von Sydow, 1955*a*). In the case of even acids, the transition is irreversible and the *C* form is always obtained from quenching the melt.

Bond (2004) has recently determined, from single-crystal *in situ* crystallization, the high-temperature phases of the fatty acids with chain lengths from *n* = 6 to *n* = 15, *i.e.* the *C* form, P2₁/*c*, with *Z* = 4 for the even acids, and the *C'* form, P2₁/*c*, with *Z* = 4 for the odd acids C₇, C₉ and C₁₁, and he has also pointed out the existence of a new monoclinic form *C''*, C2/*c*, with *Z* = 8 for the C₁₃ and C₁₅ acids. By means of a geometrical approach based on structural data, Bond has shown the existence of a clear correlation between the alternating melting points for even and odd carboxylic acids and their crystal density; a different orientation adopted by the terminal C—C bonds with respect to the methyl-group interface explains the observed alternation in crystal density (the methyl groups approach each other less closely in the odd acids compared with the even acids). In a recent study, Gbabode (2005) has characterized the lower- and high-temperature forms for C₁₁ to C₂₃ odd acids from high-quality powder diffraction patterns, combining Rietveld refinements with force-field minimization methods.

This paper deals with the structure of the *C* form of *n*-hexadecanoic acid, (I). This structure determination has been accomplished in order to obtain a molecular model for longer even carboxylic acids that could be used in the structural Rietveld refinement from X-ray powder diffraction data.



A general view of the molecule is shown in Fig. 1. Selected bond distances and angles are presented in Table 1 and

geometric details of the hydrogen-bonding scheme are given in Table 2. It is apparent from Table 2, and also from Fig. 2, which shows a representation of the structure in the *ac* plane, that molecules are linked into centrosymmetric dimers *via* O—H...O hydrogen bonds. These dimers are arranged into bilayers parallel to the crystallographic *bc* plane. The long axis of the molecules is tilted over this *bc* plane by an angle of 54.7 (1)°. It should be noted that the intermolecular contact [3.050 (4) Å] between atom O1 and atom C1(−*x* + 1, *y* − ½, −*z* − ½) of an adjacent molecule in the same layer indicates a stronger interchain interaction than that attributed only to van der Waals forces.

The average C—C bond length in the aliphatic carbon chain (atoms C3–C16) is 1.508 (2) Å and the mean C—C—C bond angle (atoms C2–C15) is 114.6 (1)°. All C—C bonds show an antiperiplanar (*trans*) Conformation [mean absolute C—C—C—C torsion angle = 178.6 (1)°]. The C2—C3—C4—C5 [−175.2 (3)°], C1—C2—C3—C4 [−178.1 (3)°] and O1—C1—

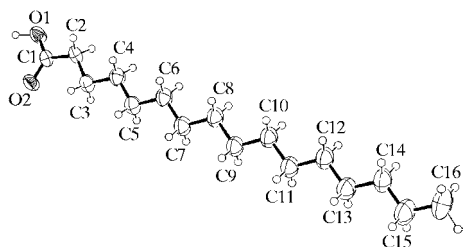


Figure 1
A view of the *n*-hexadecanoic acid molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

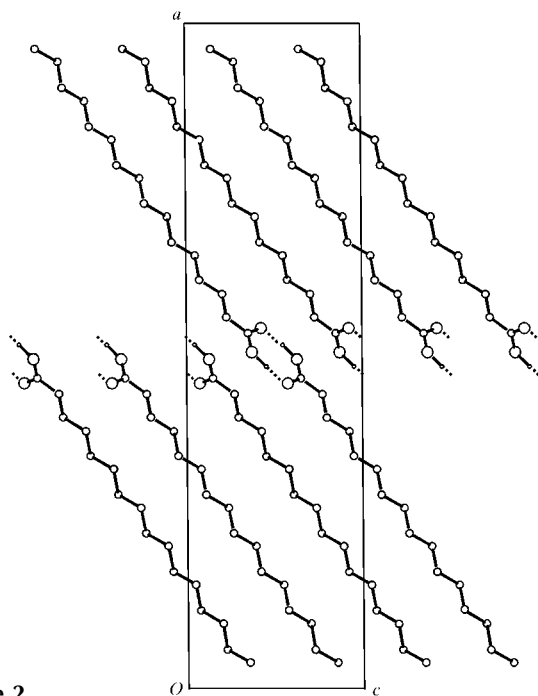


Figure 2
A view of the packing of (I) in the *ac* plane, showing the intermolecular hydrogen bonds (dashed lines) and the bilayer disposition with respect to the unit cell. H atoms not involved in hydrogen bonding have been omitted for clarity.

C2—C3 [−177.4 (3)°] torsion angles deviate significantly from the ideal value of 180°. This could be explained by the steric hindrance produced by the hydrogen bonds. The carboxyl group is nearly coplanar with the skeletal plane of the hydrocarbon chain [dihedral angle = 6.0 (2)°].

The C1—O1 and C1—O2 bond distances are very similar [1.269 (4) and 1.247 (4) Å, respectively], showing the involvement of both O atoms in the intermolecular hydrogen bonds that create the dimer aggregate; the O1...O2 hydrogen-bond distance is 2.621 (3) Å and the O1—H1...O2 angle is 173 (5)°. This similarity of both C—O bond lengths within the carboxyl functional group was also observed by Bond (2004) for the *C* form of even carboxylic acids with 6 to 14 C atoms.

These results are also in agreement with the study of Hayashi *et al.* (1975) on the solid-state IR spectra of these *C* forms measured in the range from room to liquid-helium temperature. They observed, in the regions of the characteristic frequencies of the carboxyl group and in the region of the CH₂ wagging modes, that many bands decrease in intensity with decreasing temperature and others near the latter bands increase in intensity. Their results suggest that the carboxyl group and the C2—C3 bond can adopt two relative configurations (*cis* and *trans*) around the C1—C2 bond at room temperature, concluding that the *trans* configuration is more stable at low temperatures for even acids. They pointed out that the transition between the two configurations involves a simple prototropic exchange between the two carboxylic acid groups forming the dimer. This *cis*–*trans* disordering was confirmed by Kanters *et al.* (1975) by X-ray crystallographic measurements for crystalline fluoromalonic acid, observing a splitting in the H-atom electron density of the carboxyl group at room temperature which disappears at liquid nitrogen temperature.

The similarity observed between the two C—O bond distances, in our case at room temperature, and the short O1...O2 distance, suitable for H-atom transfer, agree with the existence of this configurational disorder in hexadecanoic acid, as was previously observed for the *C* form of other related even carboxylic acids.

Experimental

n-Hexadecanoic acid (palmitic acid) was purchased from Fluka with a purity greater than 99.5% (as determined by GC–MS). Tests with several solvents were carried out at different temperatures but it was not possible to obtain single crystals of suitable quality. Although with some indications of being slightly twinned, eventually a thin plate grown for 15 d at 298 K from a saturated solution of toluene was selected.

Crystal data

C₁₆H₃₂O₂
M_r = 256.42
 Monoclinic, *P*2₁/*c*
a = 35.620 (11) Å
b = 4.9487 (16) Å
c = 9.406 (3) Å
 β = 90.447 (5)°
V = 1658.0 (9) Å³
Z = 4

D_x = 1.027 Mg m^{−3}
 Mo Kα radiation
 Cell parameters from 2055 reflections
 θ = 2.3–23.1°
 μ = 0.07 mm^{−1}
T = 298 (2) K
 Plate, colourless
 0.48 × 0.46 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω rotation scans with narrow frames
 Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 2001)
 $T_{\min} = 0.956$, $T_{\max} = 0.991$
 14859 measured reflections

2912 independent reflections
 1918 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = -42 \rightarrow 42$
 $k = -5 \rightarrow 5$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.092$
 $wR(F^2) = 0.263$
 $S = 1.13$
 2910 reflections
 215 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1015P)^2 + 1.0414P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.006$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.269 (4)	C2—C3	1.506 (4)
O2—C1	1.247 (4)	C14—C15	1.510 (6)
C1—C2	1.488 (4)	C15—C16	1.502 (6)
O2—C1—O1	122.9 (3)	C1—C2—C3	116.7 (3)
O2—C1—C2	121.1 (3)	C2—C3—C4	111.6 (3)
O1—C1—C2	116.0 (3)	C3—C4—C5	115.5 (3)
O1—C1—C2—C3	-177.4 (3)	C2—C3—C4—C5	-175.2 (3)
O2—C1—C2—C3	3.6 (4)	C3—C4—C5—C6	179.2 (3)
C1—C2—C3—C4	-178.1 (3)	C4—C5—C6—C7	-177.0 (3)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O2 ⁱ	1.12 (6)	1.51 (6)	2.621 (3)	173 (5)

Symmetry code: (i) $-x + 1, -y + 1, -z - 1$.

All C-bound H atoms were included in calculated positions and refined with free isotropic displacement parameters using a riding model with variable C—H bond distances [0.93–1.12(3) \AA]. The H atom of the carboxyl function was included in the refinement in an observed position and was refined as a free isotropic atom.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to

solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b) and PLATON (Spek, 2003); software used to prepare material for publication: PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3001). Services for accessing these data are described at the back of the journal.

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