Conformational Polymorphism of Unsaturated Dicarboxylic Acids

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WE report some preliminary results of a calorimetric and an *X*-ray study of the polymorphic behaviour of some unsaturated dicarboxylic acids. The compounds we have examined are:

(1) Deca-*trans*-3-*trans*-7-diene-1,10-dioic acid (DECA-T-T) $HO_2C{\cdot}CH_2{\cdot}CH:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH:CH{\cdot}CH_2{\cdot}CO_2H$.

(2) Octa-*trans*-2-*trans*-6-diene-1,8-dioic acid (OCTA-T-T) $HO_2C{\cdot}CH:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH:CH{\cdot}CO_2H$.

(3) Octa-*trans*-2-*cis*-6-diene-1,8-dioic acid (OCTA-T-C) $HO_2C{\cdot}CH:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH:CH{\cdot}CO_2H$.

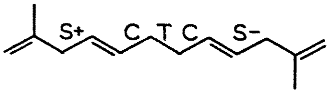
The differential thermal analysis (d.t.a.) data are reported in Table 1

TABLE 1

Differential thermal analysis data.

	Crystal–crystal transition			Crystal–melt transition		
Compound	T(°K)	ΔH(cal./g.)	ΔS(cal./g.deg.)	T(°K)	ΔH(cal./g.)	ΔS(cal./g.deg.)
DECA-T-T	366	7·9±0·5	0·022	394	48±1	0·12
OCTA-T-T	439	15·5±1	0·035	541	39±3	0·072
OCTA-T,C	—	—	—	380	32±3	0·085

The crystal structure of the low-temperature form of DECA-T-T has already been studied by one of us.[1] In this molecule (see Figure 1B) the eight central atoms of the backbone are essentially coplanar. Its conformation corresponds to the following succession of internal rotation angles:



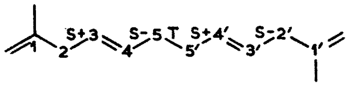
where the symbols T, C, S+ and S− refer respectively to the *trans*, the *cis*(eclipsed), and the two enantiomorphous skew conformations of a C·C·C·C chain.[2,3]

In the absence of strong repulsive nonbonded interactions, *cis* and skew conformations of a single bond adjacent to a *trans* double bond are almost isoenergetic and correspond to minima of the torsional potential.[4,5]

This led us to associate the polymorphic behaviour of DECA-T-T with different, almost isoenergetic, molecular conformations in the solid state. The unit cell of the high-temperature form of DECA-T-T is as follows:

$$a = 11{\cdot}11 \pm 0{\cdot}02; b = 4{\cdot}66 \pm 0{\cdot}01; c = 10{\cdot}45 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 97°12' \pm 30';\ Z = 2,\ \text{Space group } P2_1/c.$$

These data were taken at room temperature, where this form is metastable. The specific volume is 5% higher than that of the low-temperature modification. The molecules form hydrogen-bonded rows in the crystalline state parallel to [101]; Fourier projection of the structure along [010] is shown in Figure 1A. As expected, the molecular conformation of the high-temperature form of DECA-T-T differs from that of the low-temperature modification and may be shown as:



The molecule is more extended, but this time atoms C-2, C-3, C-4, C-5 and C-2′, C-3′, C-4′, C-5′ form two distinct planes and the molecule is kinked around bond

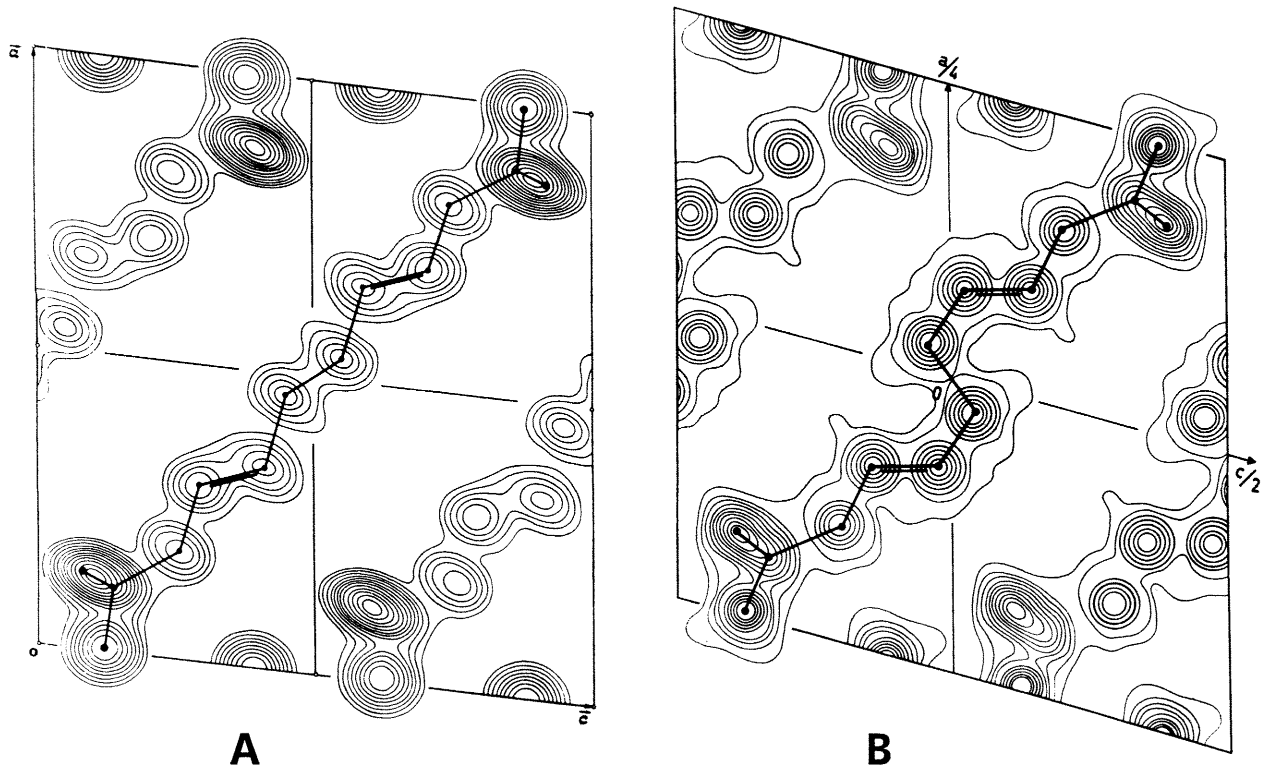


FIGURE. *Projection of electron density on the* (010) *plane for* (A) *the high-temperature form, and* (B) *the low-temperature form, of DECA-T-T.*

C-5–C-5 . Some dihedral angles of the molecule in the two polymorphs are compared in Table 2.

The refinement of the structure will be published elsewhere.[6] We are currently studying the crystal structure of OCTA-T-C and of the low-temperature form of OCTA-T-T. Unit-cell constants and the nature of the internal rotation angles characterizing the respective molecular geometries are reported in Table 3.

In the high-temperature form of OCTA-T-T, we believe that the molecules may have the conformation (*trans*) (S+) (T)(S−)(*trans*) by analogy with the corresponding molecules of DECA-T-T. Polymorphism phenomena are very frequent in the case of long-chain molecules, such as aliphatic mono- and di-carboxylic acids, paraffins, and polymers.

TABLE 2

Some relevant conformational parameters of DECA-T-T in the two forms. The values refer to the backbone chain of the molecule: C-1–C-2–C-3–C-4–C-5–C5′–C-4′–C-3′–C-2′–C-1′.

Dihedral angles		Low-temp. form	High-temp. form
C-1 (C-2–C-3)C-4	..	−126° (S−)	−135° (S−)
C-2 (C-3–C-4)C-5	..	180° (*trans*)	178° (*trans*)
C-3 (C-4–C-5)C-5′	..	−2° (C)	+123° (S+)
C-4 (C-5–C-5′)C-4′	..	180° (T)	180° (T)

TABLE 3

Unit-cell parameters and some relevant conformational parameters of OCTA-T-C and OCTA-T-T in the low-temperature form

	Unit-cell parameters	Conformation of the backbone
OCTA-T-C	$a = 7{\cdot}75 \pm 0{\cdot}02$ Å $b = 17{\cdot}34 \pm 0{\cdot}03$ Å $c = 10{\cdot}10 \pm 0{\cdot}02$ Å $\beta = 138°52' \pm 30'$ $Z = 4$ $P2_1/c$	 S − = − 97° T = 180° S + = 127° T
OCTA-T-T	$a = 12{\cdot}00 \pm 0{\cdot}02$ Å $b = 3{\cdot}94 \pm 0{\cdot}01$ Å $c = 7{\cdot}72 \pm 0{\cdot}02$ Å $\alpha = 121°21' \pm 30'$ $\beta = 139°24' \pm 30'$ $\gamma = 70°03' \pm 30'$ $Z = 1$ $P\bar{1}$	 C = 0° $\underbrace{\text{T = 180°}}_{\text{by symmetry}}$

In general, we can distinguish two main types of polymorphism:

(1) Polymorphism due to different modes of packing of chains having essentially the same conformation. Aliphatic mono- and di-carboxylic acids,[7,8] paraffins,[9] and some polymers such as isotactic polypropene[10] and polypentadiene[11] show this type of polymorphism.

(2) Polymorphism due to different chain conformations. This type is very common in the case of polymers, (1,4-*trans*-polybutadiene,[12] poly-α-butene,[13] syndiotactic polypropene,[10] 1,4-*trans*-polyisoprene[14]). The different chain conformations may correspond to the same, or different, energy minima of the multidimensional potential-energy surface as a function of the internal rotation angles. This latter type of polymorphism may be called "conformational polymorphism".

There are not many observations in the literature of this type of polymorphism for low-molecular-weight compounds. In fact the only case previously studied in detail was DL-methionine.[15] We may expect cases of conformational polymorphism whenever two different nonequivalent conformers of the same molecule are almost isoenergetic.

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