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Partial ordering of tripivaloylmethane at 110 K

Vladimir Stilinović and Branko Kaitner*

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102 A, HR-10000 Zagreb, Croatia
Correspondence e-mail: kaitner@chem.pmf.hr

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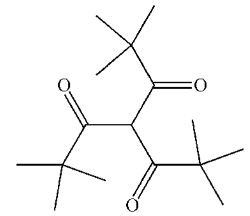
Tripivaloylmethane [systematic name: 4-(2,2-dimethylpropanoyl)-2,2,6,6-tetramethylheptane-3,5-dione], $C_{16}H_{28}O_3$, is known to crystallize at room temperature in the space group *R*3*m* with three molecules in the unit cell. The molecules are conformationally chiral and pack so that each molecular site is occupied with equal probability by the two enantiomers. Upon cooling to 110 K, the structure partially orders; two molecules in the unit cell order into two different conformations of opposite chirality, while the third remains disordered. The symmetry of the resulting crystal is *P*3, with each of the molecules lying about a different threefold rotation axis. This paper describes an unusual case of order–disorder phase transition in which the structure partially orders by changes of molecular conformation in the single crystals. Such behaviour is of interest in the study of phase transitions and molecular motion in the solid state.

Comment

Triacylmethanes are a group of acyclic 1,3,3′-triketones which can be obtained by reaction of *β*-diketones (Lim *et al.*, 2001), their salts (Rogers & Smith, 1955) and their transition metal complexes (Murdoch & Nonhebel, 1962; Collman *et al.*, 1963) with acyl halogenides and acid anhydrides. Although such compounds have been known since the late nineteenth century (Fischer & Bülow, 1885; Claisen, 1893), they have not received much attention to date. However, cyclic 1,3,3′-triketones have attracted some interest as a result of their application as herbicides (Lee *et al.*, 1998, and references therein).

In a previous publication (Kaitner & Stilinović, 2007) we reported the structure of tripivaloylmethane, (I), at room temperature. The three carbonyl groups of the triketo group define a helix, rendering the molecular conformation chiral. The compound has been found to crystallize in the space group *R*3*m* with a conformational enantiomeric disorder. The molecules are in the 3(*a*) special positions of the space group, so that each molecular site is occupied with equal probability by the two (*M* and *P*) enantiomers. It remained unclear whether the equal occupancy by the two enantiomers of the average molecular site is caused by spatial or temporal disorder or perhaps a combination of the two.



(I)

Recently, we have redetermined the crystal structure of tripivaloylmethane at 110 K. Although the molecular symmetry remains as *C*3, the space-group symmetry is reduced from *R*3*m* at ambient temperature to *P*3. The unit cell of tripivaloylmethane at 110 K contains three independent molecules (Fig. 1) in the 1(*a*), 1(*b*) and 1(*c*) positions of the space group, *i.e.* all lying about threefold rotation axes. Two molecules are ordered, one as an *M* and the other as a *P* conformational enantiomer. In addition to the difference in the absolute sense of the triketo group twist, the two molecules also differ somewhat in the torsion of the *tert*-butyl groups to the respective carbonyl groups (the O11—C12—C13—C14 torsion angle is *ca* 44.22° and the O21—C22—C23—C24 angle is *ca* −38.41°). The third molecule remains disordered with *M* and *P* conformers occupying the same molecular sites. The occupancies of the two conformers were refined to 50% within experimental error. The relative positions of all three molecules remain almost entirely unchanged from those in the room-temperature structure (Fig. 2).

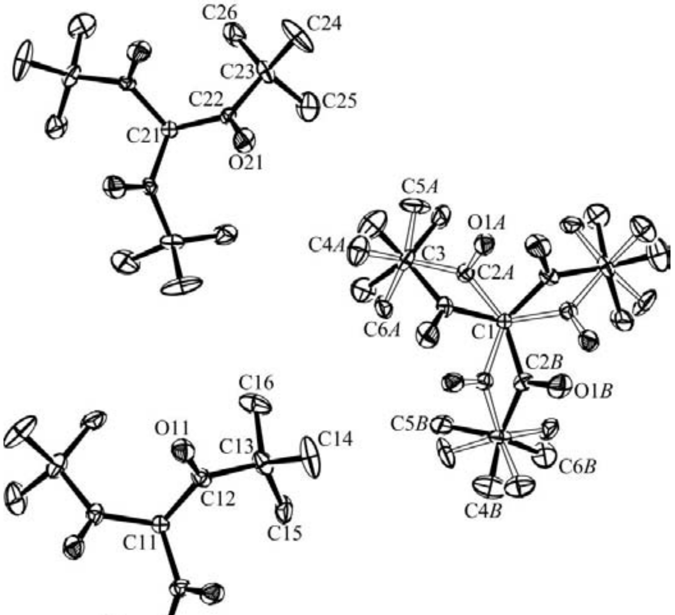


Figure 1
The molecular structures and the atom-numbering schemes of the three independent molecules of tripivaloylmethane at 110 K. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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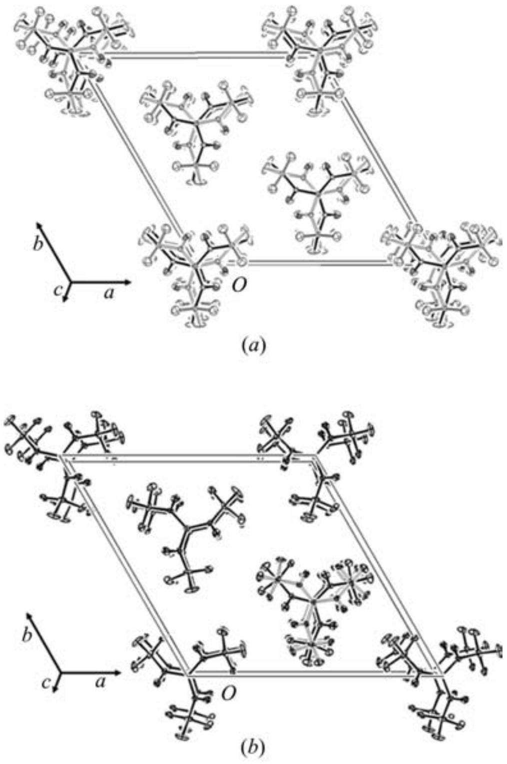

(a)

(b)

Figure 2
Packing diagrams for the two polymorphs of tripivaloylmethane, viewed along the *c* axis, showing (*a*) the room-temperature polymorph and (*b*) the low-temperature polymorph. The *M* conformers of the disordered molecules are shown with open and the *P* conformers with full bonds.

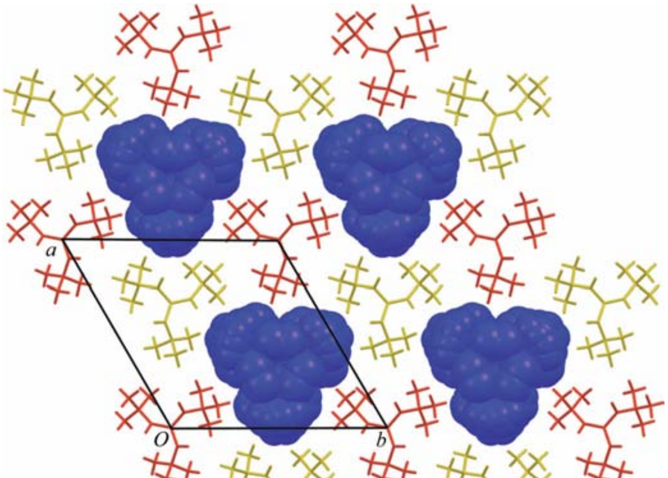

Figure 3
A representation of the stacking of the molecular columns for the low-temperature polymorph, viewed along the *c* axis. The *P* conformers are shown in dark grey (red in the electronic version of the paper), the *M* conformers in pale grey (yellow) and the disordered molecules as CPK models.

The ordered molecules stack to form homochiral columns along the [001] direction. Each column is adjacent to three columns of the opposite chirality and to three columns of disordered molecules. The structure could be viewed as a quasi-hexagonal packing of homochiral columns with the columns of disordered molecules in the voids (Fig. 3). The question remains whether the disordered molecules are placed at random within the columns themselves, or the 'disordered' columns are in fact homochiral, but placed stochastically throughout the structure. However, since the intermolecular distances are the same for all three types of columns it would be surprising that only two out of three molecules are ordered, so we are inclined toward the latter structural model.

Comparing the packing diagrams of the room-temperature structure with that of the 110 K structure, it is obvious that the ordering, *i.e.* the formation of the homochiral columns, has to include flipping of the triketo groups in (at least) one-third of the overall number of molecules. The flipping must include passing through a transition conformation of C_{3v} symmetry, which is more elongated along the threefold axis than the equilibrium C_3 conformation; the C1$\cdots$centroid(O1/O2/O3) distance is *ca* 1.75 Å for the putative C_{3v} conformation, compared with an average of *ca* 1.50 Å for the C_3 conformations.

Experimental

The preparation and crystallization of (I) were described in a previous publication (Kaitner & Stilinović, 2007).

Crystal data

$C_{16}H_{28}O_3$
$M_r = 268.38$
Trigonal, $P3$
$a = 15.5892\ (5)$ Å
$c = 5.6424\ (3)$ Å
$V = 1187.52\ (8)$ Å^3
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 110\ (1)$ K
0.65 × 0.29 × 0.22 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
9435 measured reflections
1725 independent reflections
1597 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.133$
$S = 1.11$
1725 reflections
220 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.34$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

In the absence of significant resonant scattering, the Flack (1983) parameter was indeterminate; hence, the Friedel equivalent reflections were averaged. No restraints were used for modelling the structural disorder. Methyl H atoms were placed in calculated positions and treated as riding atoms [C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)]. The methine H atoms of the ordered molecules were also treated as riding atoms [C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The methine H atom of the disordered molecule was located in a difference map and refined isotropically, giving a C—H distance of 1.04 (9) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997);

software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3228). Services for accessing these data are described at the back of the journal.

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