Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Conformational enantiomeric disorder in tripivaloylmethane

Branko Kaitner* and Vladimir Stilinović

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

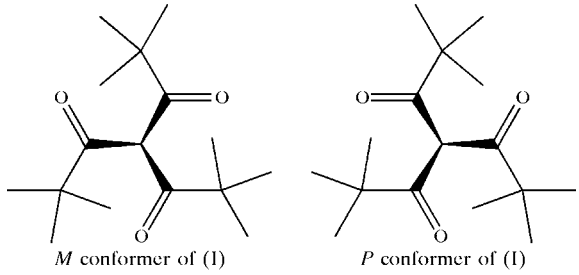
Received 12 March 2007
Accepted 16 March 2007
Online 11 May 2007

Tripivaloylmethane [systematic name: 4-(2,2-dimethylpropanoyl)-2,2,6,6-tetramethylheptane-3,5-dione], $C_{16}H_{28}O_3$, is a 1,3,3′-triketone with C_3 molecular symmetry, prepared by α-acylation of 2,2,6,6-tetramethylheptane-3,5-dione with 2,2-dimethylpropanoyl anhydride in the presence of barium metal. The molecules are conformationally chiral and pack so that each molecular site is occupied with equal probability by the two enantiomers. The carbonyl groups of the two superimposed enantiomeric molecules are at an angle of 75.4 (16)°.

Comment

1,3,3′-Triketones can be obtained by acylation, using acyl halides or acid anhydrides, of β-diketones (Lim *et al.*, 2001), their salts (Rogers & Smith, 1955) or their transition metal complexes (Murdoch & Nonhebel, 1962; Collman *et al.*, 1963). Alkylation and acylation in the α-position of β-diketones, especially with bulkier groups, affects the keto–enol equilibrium in favour of the keto form. Cyclic 1,3,3′-triketones have attracted some interest because of their application as herbicides, since it has been shown that their derivatives inhibit *p*-hydroxyphenylpyruvate dioxygenase (Lee *et al.*, 1998, and references therein). 1,3,3′-Triketones have also been studied as chelating ligands with group 2 and lanthanide cations (Ismail *et al.*, 1969). Although the crystal structures of many α-substituted β-diketones are known, only one crystal structure of an acyclic 1,3,3′-triketone [Cambridge Structural Database (CSD; Allen, 2002) refcode OCIQOG (Lim *et al.*, 2001)] and one transition metal complex with an acyclical 1,3,3′-triketonate ligand (CSD refcode IGAGUS; Carano *et al.*, 2002) have been reported to date.

The title compound, (I) (Fig. 1), is a potential tridentate monoanionic and neutral ligand for coordination to transition metal ions. Compound (I) crystallizes in the trigonal system, in space group *R*3*m*, with $Z = 3$. The molecules of (I) are in the 3(*a*) special position of the space group, with the methine C—H bond along the threefold axis. The molecule is a triketo tautomer with a C2═O1 distance of 1.221 (6) Å and a C1—C2═O1 angle of 117.6 (4)°. The molecule has C_3 molecular symmetry and is conformationally chiral. The space group accommodates equal numbers of *M* and *P* enantiomers, so that each molecular site is occupied with equal probability by the two enantiomers (Fig. 2). Atoms C1, C3 and C5 and the corresponding H atoms were assigned common sites in both enantiomers. The angle between the C1/C2/O1/C3 planes of the two enantiomers is 75.4 (16)°.



M conformer of (I) *P* conformer of (I)

The nature of the disorder raises the question of whether the structure might actually be ordered in space group *R*3. Refinement of such a model, both with the same unit-cell parameters and with a doubled *c*, however, led to *R* values above 0.25, with large and extremely anisotropic U_{ij} ellipsoids. The shapes of the ellipsoids of atoms C2 and O1, as well as the difference map, indicated that these atoms should be split in two. After splitting the atoms and further refinement, the refinements either became unstable or led to a structure where the carbonyl groups were disordered over two positions with occupancies of 0.5. This model was almost identical to the *R*3*m* model but had a much higher *R* value (0.13). For these reasons, both the ordered and the disordered *R*3 models were rejected in favour of the disordered *R*3*m* model. The question also arose whether the separate pivaloyl groups rather than the entire molecule are disordered. This was easily shown not to be the case, since the inversion of only one pivaloyl group (reducing the symmetry of the molecule to *C*1) would create a conformer with an unreasonably short nonbonded contact of 1.156 Å between two carbonyl O atoms.

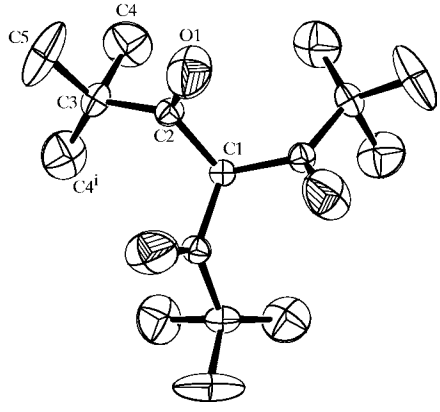


Figure 1
A view of the *M* enantiomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $x, y - x, z$.]

 DOI: 10.1107/S0108270107012474

Equal occupancy by the two enantiomers of the average molecular site may be caused by either spatial or temporal disorder, as well as a combination of both; however, from the available data, it is not possible to distinguish between the two. The disorder may be a result of a random displacement of the two enantiomers, since it is unlikely that, in a crystal that consists of domains containing only one enantiomer, the occupancies of both enantiomers would be identical. The placement of enantiomers may be random in all directions, or it could be ordered in some. There are no significant intermolecular interactions in the [100] and [010] directions. The shortest intermolecular distance is a C—H···O^{i} contact of 3.478 (9) Å [symmetry code: (i) x, y, $1 + z$] involving a methyl C—H bond. Such contacts are of identical length and arrangement for all combinations of enantiomers. These observations support the interpretation that there is no spacial correlation of the site occupancies by the two enantiomers.

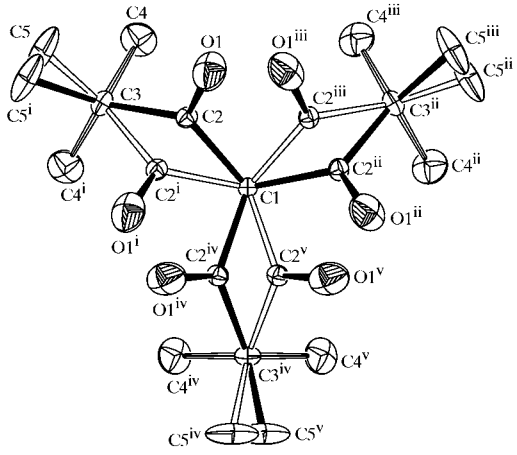


Figure 2
The contents of a single molecular site in (I), showing the relative orientations of the two enantiomers. The bonds of the *M* enantiomer are shown as full bonds, those of the *P* enantiomer as open bonds and the bonds common to both enantiomers as open bonds filled with one line. Displacement ellipsoids are drawn at the 10% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $x, x - y, z$; (ii) $-y, x - y, z$; (iii) $-y, -x, z$; (iv) $-x + y, y, z$; (v) $-x + y, -x, z$.]

Experimental

Compound (I) was prepared by a method similar to that described by Lim *et al.* (2001). 2,2,6,6-Tetramethylheptane-3,5-dione (1.0 mmol) was dissolved in cyclohexane (30 ml); powdered barium metal (0.5 mmol) was added and the mixture was heated under reflux for 45 min. 2,2-Dimethylpropanoyl anhydride (2.0 mmol) was added to the resulting solution, which was then heated under reflux for a further 6 h. The resulting precipitate of barium pivaloate was removed by filtration and the solution was then left to cool to ambient temperature, at which point white needles of (I) (0.3 mmol) crystallized from the mother liquor. NMR ($CDCl_3$): δ(H) 5.92 (*s*, 1H, –CH), 1.18 (*s*, 27H, –CH_3); δ(C) 27.5 (C4, C5, C6), 45.2 (C3), 64.6 (C1), 207.1 (C2). The compound crystallized as elongated colourless prisms by slow isothermal evaporation of a solution in dimethyl sulfoxide.

Crystal data

$C_{16}H_{28}O_3$	$Z = 3$
$M_r = 268.38$	Mo $K\alpha$ radiation
Trigonal, *R*3*m*	$\mu = 0.07$ mm^{-1}
$a = 15.711$ (7) Å	$T = 298$ (2) K
$c = 5.792$ (2) Å	0.65 × 0.29 × 0.22 mm
$V = 1238.1$ (9) Å^3	

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	518 independent reflections
3386 measured reflections	433 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.075$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.234$	$\Delta\rho_{max} = 0.12$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.13$ e Å^{-3}
518 reflections	
50 parameters	
2 restraints	

Crystals of compound (I) are trigonal. Initially, space group *R*3 was selected, but during the refinement it was found that the symmetry is higher as a result of the disorder and the space group was assigned as *R*3*m*, which was confirmed by the successful structure analysis. Since the space group is achiral, the Friedel equivalents were averaged. Methyl H atoms were placed in calculated positions and treated as riding, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C). The methine H atom was located in a difference map and refined isotropically with x and y coordinates restrained to 0.

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST97* (Nardelli, 1995).

The authors thank the Ministry of Science, Education and Sport, Republic of Croatia, for financial support of this work through grant No. 119–1193079-3069.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3098). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Carano, M., Cicogna, F., Houben, J. L., Ingrosso, G., Marchetti, F., Mottier, L., Paolucci, F., Pinzino, C. & Roffia, S. (2002). *Inorg. Chem.* **41**, 3396–3409.
Collman, J. P., Marshall, R. L., Young, W. L. & Sears, C. T. (1963). *J. Org. Chem.* **28**, 1449–1455.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Ismail, M., Lyle, S. J. & Newberry, J. E. (1969). *J. Inorg. Nucl. Chem.* **31**, 2091–2093.
Lee, D. L., Knudsen, C. G., Michaely, W. J., Chin, H.-L., Nguyen, N. H., Carter, C. G., Cromartie, T. H. & Lake, B. H. (1998). *J. Pestic. Sci.* **54**, 377–384.
Lim, S., Min, Y., Choi, B., Yoon, I., Lee, S. S. & Lee, I.-M. (2001). *Tetrahedron Lett.* **42**, 7645–7649.
Murdoch, H. D. & Nonhebel, D. C. (1962). *J. Chem. Soc.* pp. 2153–2162.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.170. Oxford Diffraction Ltd, Wrocław, Poland.
Rogers, N. A. J. & Smith, H. (1955). *J. Chem. Soc.* pp. 341–346.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.