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An orthorhombic polymorph of 3-oxapentane-1,5-diyl bis(*p*-toluenesulfonate)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.068
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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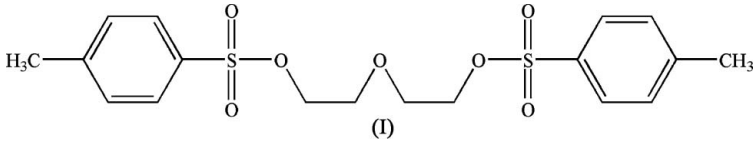
An orthorhombic (space group *Pbcn*) polymorph of the title compound, $C_{18}H_{22}O_7S_2$, was obtained from a methanol solution to complement the known monoclinic (space group *C*2/*c*) phase. No phase transition has been found between the two systems in the temperature range 120–296 K. The central O atom of the molecule has site symmetry 2.

Comment

In the course of our studies of materials containing the tosyl group for biological applications we investigated the crystal structure of 3-oxapentane-1,5-diyl bis(*p*-toluenesulfonate), (I). The material was reported previously by Groth (1985) at 153 K (LT), and later the structure was reinvestigated by Ferchaux *et al.* (1990) at room temperature (RT). Both authors crystallized their material from dichloroethane to yield a monoclinic product (space group *C*2/*c* with *Z* = 4).



(I)

We have now obtained an orthorhombic modification of (I) by crystallization from methanol solution and we describe its low-temperature (120 K) crystal structure here. The complete molecule in both the orthorhombic and monoclinic forms of (I) is generated from the asymmetric unit by twofold symmetry, with the central O atom lying on the rotation axis (Fig. 1). The tosylate unit has normal geometrical parameters. The only significant difference in the two modifications is the value of the C—O—C bond angle at the central ether O atom, which is 111.35 (15)° [112.3 (2)° at 298 K] here compared with 114.07 (2)° (Groth, 1985) and 114.02 (5)° (Ferchaux *et al.*, 1990) in the monoclinic modification. The central fragment

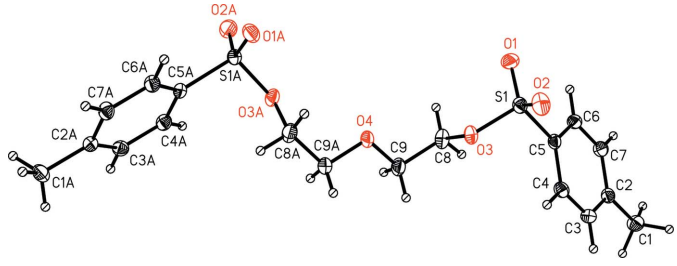


Figure 1
A view of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (A) $1-x, y, \frac{1}{2}-z$.]

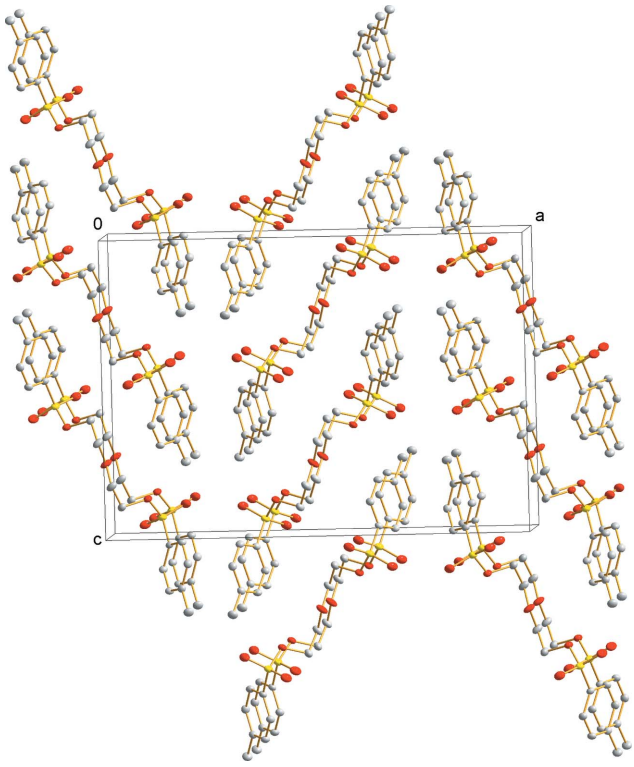


Figure 2
The packing in (I), viewed down [010] (50% probability displacement ellipsoids; H atoms omitted for clarity).

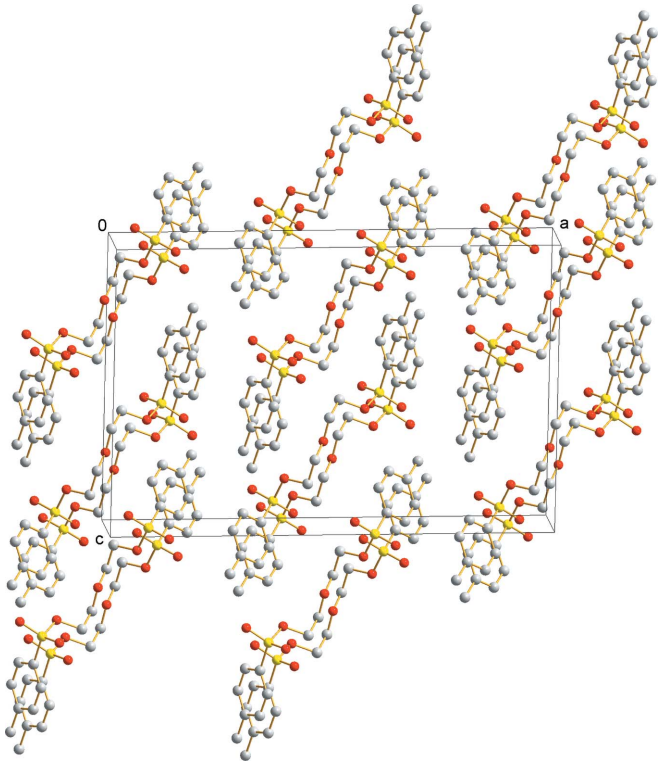


Figure 3
The packing in the monoclinic modification of (I), viewed down [010]. Redrawn from Groth (1985) (30% probability displacement spheres; H atoms omitted for clarity).

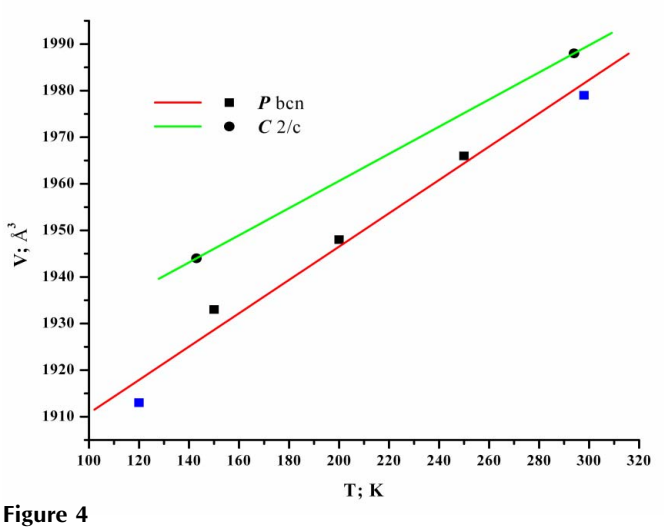


Figure 4
Variation of the unit-cell volumes in the *Pbcn* (squares) and *C*2/*c* (circles) modifications of (I) as a function of temperature. The blue squares represent the unit cells of the full structures of (I) obtained at 120 and 298 K.

connecting the tosylate groups has the conformation *trans–gauche–trans–trans–gauche– trans* (*tgttgt*) (Table 1).

Polymorphism in crystalline materials may occur as a result of crystallization from different solvents, crystallization in the presence of small-molecule or macromolecular additives, phase transitions *etc.* (Bernstein, 2002). Here, although the unit-cell parameters for the two modifications are qualitatively similar, the molecular packing motifs are quite different (Figs. 2 and 3). In the monoclinic form, all the molecules point in the same direction, while in the orthorhombic form, a herringbone arrangement occurs. In the orthorhombic phase, a C—H$\cdots\pi$(arene) contact of 2.94 Å occurs, which is not present in the monoclinic modification.

A plot of the variation of the unit-cell volumes of the two polymorphs as a function of temperature is presented in Fig. 4. It is clear that the unit cell volume of the monoclinic polymorph is somewhat higher than that found for the orthorhombic form of (I) at all temperatures. Therefore, the calculated densities of the monoclinic form [1.416 Mg m^{-3} (LT) and 1.385 Mg m^{-3} (RT)] are somewhat lower than for the orthorhombic polymorph [1.438 Mg m^{-3} (LT) and 1.391 Mg m^{-3} (RT)]. This suggests that the orthorhombic form of (I) is thermodynamically more stable (Burger & Ramberger, 1979). This graph suggests also that there is no phase transition between the two forms in the temperature interval from 120 K to room temperature, which is perhaps not surprising given their different packing arrangements. We speculate that the major factor in obtaining these two polymorphs is the different solvents from which the crystals were grown.

Experimental

A commercial sample of (I) (Aldrich) was recrystallized from a methanol solution at ambient temperature.

Crystal data

$C_{18}H_{22}O_7S_2$
M_r = 414.48
Orthorhombic, *Pbcn*
a = 21.914 (2) Å
b = 5.6447 (6) Å
c = 15.4723 (15) Å
V = 1913.9 (3) Å^3
Z = 4
D_x = 1.438 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 120 (2) K
Prism, colorless
0.50 × 0.30 × 0.30 mm

Data collection

Bruker SMART APEX-II CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.786, T_{max} = 0.911
17461 measured reflections
2621 independent reflections
2462 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 29.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.068
S = 1.00
2621 reflections
156 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 2.05P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected torsion angles (°).

O2—S1—O3—C8	176.42 (9)	C3—C4—C5—S1	−178.97 (9)
C5—S1—O3—C8	−68.50 (10)	O2—S1—C5—C4	58.77 (11)
C1—C2—C3—C4	179.21 (12)	O3—C8—C9—O4	69.63 (13)

The aromatic and methylene H atoms were placed in idealized locations, then their positional and U_{iso}(H) values were freely refined. The methyl H atoms were positioned geometrically (C—H = 0.98 Å) and refined as riding with U_{iso}(H) = 1.5U_{eq}(C). The structure of (I) was also investigated at 298 K. There are no significant differences, apart from the expected expansion of the unit-cell parameters. These data have been deposited (CCDC-607626).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL-NT* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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