

Cal Y. Meyers,^a William Roper,^b
Floyd Klavetter,^b Toyokazu
Horii,^b Paul B. Sandrock^a and
Paul D. Robinson^{c*}

^aMeyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry and Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA, ^bDepartment of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA, and ^cDepartment of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA

Correspondence e-mail: robinson@geo.siu.edu

Key indicators

Single-crystal X-ray study

$T = 296\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.036

wR factor = 0.120

Data-to-parameter ratio = 15.4

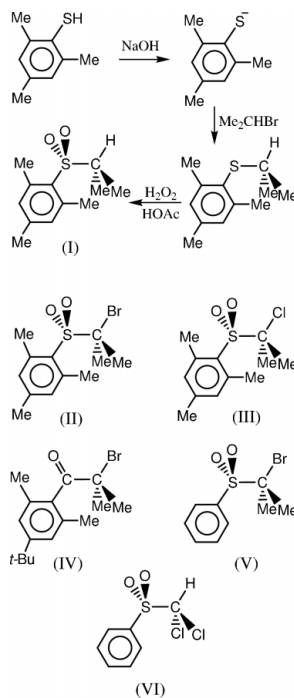
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-Propyl mesityl sulfone

2-Propyl mesityl sulfone, $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$, (I), is entirely devoid of the rotational disorder displayed in the corresponding 2-bromo- and 2-chloro-2-propyl mesityl sulfones. Each molecule of (I) hydrogen bonds with four other molecules, each utilizing the acidic α -H atom of its 2-propyl group and a p -methyl-H atom as donors, and its two sulfonyl-O atoms as acceptors, resulting in a structure consisting of two-dimensional layers of hydrogen-bonded molecules.

Comment

We have reported that crystalline 2-bromo-2-propyl mesityl sulfone, (II) (Chan-Yu-King *et al.*, 2001), 2-chloro-2-propyl mesityl sulfone, (III) (Meyers *et al.*, 2001), and a related ketone, 2-bromo-2-propyl 2-(5-*tert*-butyl-1,3-xylyl) ketone, (IV) (Robinson, Sandrock *et al.*, 2001), all exhibit rotational disorder, while 2-bromo-2-propyl phenyl sulfone, (V) (Robinson, Parady *et al.*, 2001), and dichloromethyl phenyl sulfone, (VI) (Chan-Yu-King *et al.*, 2002), do not. To learn more about the relationship between structure and rotational disorder, we have now examined crystalline 2-propyl mesityl sulfone, (I), the only 2-propyl mesityl structure in this series possessing an α -H atom.



The structure of (I), prepared as illustrated (see Scheme), is shown with its atom numbering in Fig. 1. An important aspect

Received 23 September 2002

Accepted 25 September 2002

Online 30 September 2002

This paper is dedicated to Dr James W. Neckers on the occasion, of his 100th birthday.

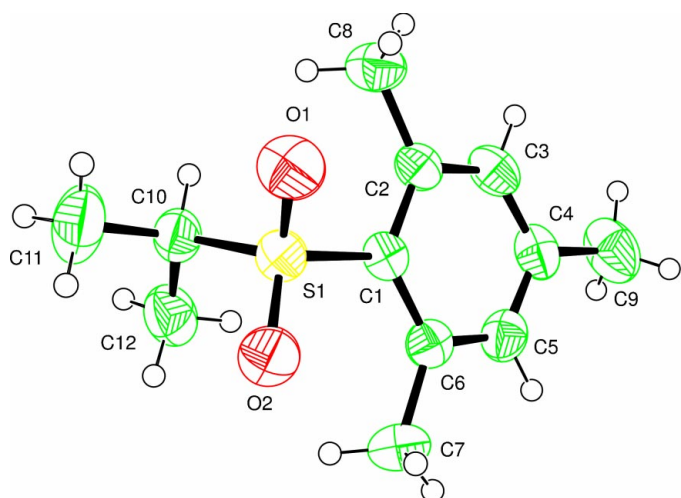


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids at the 50% probability level.

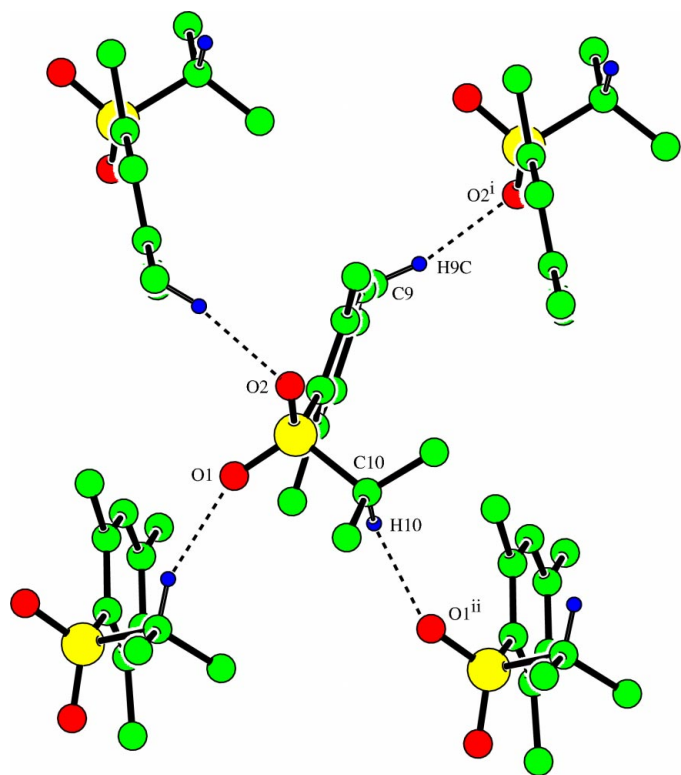


Figure 2
The hydrogen bonding in (I). Symmetry codes are as given in Table 1.

of this structure resides in its extensive hydrogen bonding, shown in Fig. 2. Each molecule hydrogen bonds with four other molecules, each utilizing the acidic α -H atom of its 2-propyl group and a *p*-methyl-H atom as donors, and its two sulfonyl-O atoms as acceptors. Hydrogen-bond geometry is given in Table 1. As a consequence, the molecular packing consists of two-dimensional layers of hydrogen-bonded molecules. Four such layers, parallel to (100), are shown in Fig. 3.

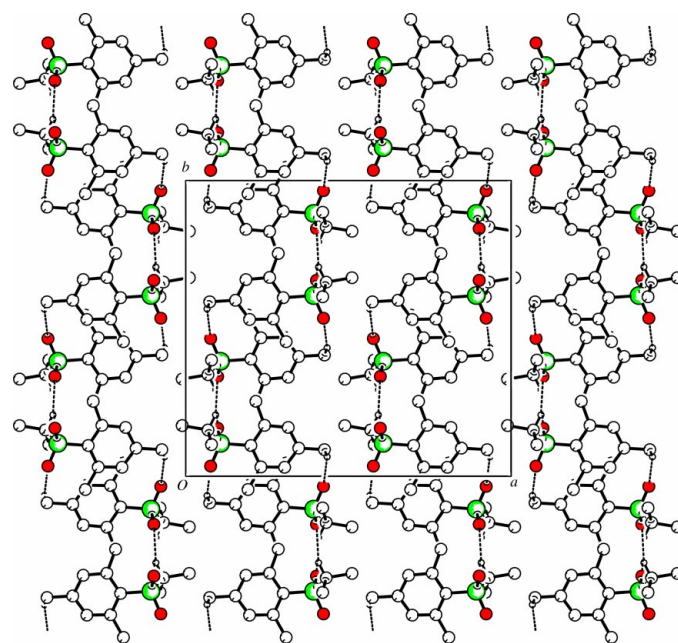


Figure 3
The molecular packing in (I), viewed down [001]. An edge view of four discrete two-dimensional molecular layers can be seen parallel to (100). H atoms not involved in hydrogen bonding have been omitted for clarity.

This information suggests that rotational disorder in crystalline mesityl 2-propyl sulfones and ketones, *e.g.* (II), (III) and (IV), is associated with a combination of the steric effect of the mesityl group and absence of intermolecular hydrogen bonding involving an acidic α -H atom. In such a situation, crystallization would provide a packing structure of molecules without a common conformation of their 2-propyl group. This reasoning would account for the absence of rotational disorder in (I) (possessing a mesityl group and an acidic α -H atom providing extensive intermolecular hydrogen bonding with the sulfonyl group), (V) (possessing neither a mesityl group nor an α -H atom) and (VI) (possessing an α -H atom but no mesityl group).

The effect of intermolecular hydrogen bonding in increasing intermolecular proximity and thus reducing rotational disorder in the packing structure is illustrated by the following example. In compound (II), which exhibits extensive rotational disorder (Chan-Yu-King *et al.*, 2001), the intermolecular distance between atoms O1 and Br1 is 0.13 Å greater than the sum of their van der Waals radii. However, in compound (I), which shows no rotational disorder, the intermolecular distance between the corresponding, but ostensibly hydrogen-bonded atoms O1 and H10 is 0.21 Å less than the sum of their van der Waals radii, and even the O1...C10 distance is only 0.17 Å greater than the sum of the van der Waals radii.

Experimental

Compound (I) was prepared from mesitylenethiol and 2-bromopropane; m.p. 347.5–349.0 K (literature: m.p. 353 K; Shostakovskii &

Bobrov, 1969), ^1H NMR (CDCl_3 , p.p.m.): δ 1.33, (*d*, $J = 7$ Hz, 6H), 2.27 (*s*, 3H), 2.68 (*s*, 6H), 3.28 (*hep*, $J = 7$ Hz, 1H), 6.98 (*s*, 2H).

Crystal data

$\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$
 $M_r = 226.32$
 Orthorhombic, *Pbca*
 $a = 18.728$ (2) Å
 $b = 17.0310$ (16) Å
 $c = 7.758$ (3) Å
 $V = 2474.5$ (9) Å³
 $Z = 8$
 $D_x = 1.215$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 16.6$ – 17.8°
 $\mu = 0.24$ mm⁻¹
 $T = 296$ K
 Prism, colorless
 $0.50 \times 0.30 \times 0.21$ mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: none
 2878 measured reflections
 2189 independent reflections
 1386 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 22$
 $k = 0 \rightarrow 20$
 $l = -9 \rightarrow 2$
 3 standard reflections
 every 100 reflections
 intensity decay: 2.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.120$
 $S = 1.02$
 2189 reflections
 142 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 0.5143P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0046 (8)

Table 1
 Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C9}-\text{H9C}\cdots\text{O2}^{\text{i}}$	0.96	2.50	3.403 (4)	158
$\text{C10}-\text{H10}\cdots\text{O1}^{\text{ii}}$	0.98	2.51	3.395 (4)	150

Symmetry codes: (i) $\frac{3}{2} - x, -y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

The rotational orientations of the methyl groups were determined by the circular Fourier synthesis method available in *SHELXL97* (Sheldrick, 1997). All H atoms were treated as riding, with C–H distances in the range 0.93–0.98 Å. All methyl groups were allowed to rotate but not to tip.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN*, *SHELXL97*, and *PLATON* (Spek, 2000).

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
 Chan-Yu-King, R., Anil, J., Meyers, C. Y. & Robinson, P. D. (2002). *Acta Cryst.* **E58**, o592–o595.
 Chan-Yu-King, R., Hou, Y., Sandrock, P. B., Meyers, C. Y. & Robinson, P. D. (2001). *Acta Cryst.* **E57**, o449–o450.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Meyers, C. Y., Hua, D. H., Hou, Y. & Robinson, P. D. (2001). *Acta Cryst.* **E57**, o587–o589.
 Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. (Present address: 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.)
 Molecular Structure Corporation (1997). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. (Present address: 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.)
 Robinson, P. D., Parady, T. E., Hou, Y. & Meyers, C. Y. (2001). *Acta Cryst.* **E57**, o584–o586.
 Robinson, P. D., Sandrock, P. B., Xie, Songwen & Meyers, C. Y. (2001). *Acta Cryst.* **E57**, o555–o557.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Shostakovskii, S. M. & Bobrov, A. V. (1969). *Zh. Org. Khim.* **5**, 908–913; *J. Org. Chem. USSR*, **5**, 896–900.
 Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.