organic papers

Isopropyl 2,4,6-triisopropylphenyl sulfone: an aryl sulfone with unusual atom deviations from the aromatic least-squares plane

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Isopropyl 2,4,6-triisopropylphenyl sulfone, $C_{18}H_{30}O_2S$, (I), has been synthesized for the first time. In spite of the bulky isopropyl substituents on both *ortho* positions, crystalline (I) does not exhibit rotational disorder of the isopropyl group bonded to the sulfonyl. In contrast, the corresponding bromo- and chloroisopropyl groups of crystalline aryl sulfones possessing much smaller di-*ortho*-methyl substituents display striking rotational disorder. While the aryl rings of the latter compounds are essentially planar, considerable atom deviation from the aromatic least-squares plane of (I) was observed. None of the intra- or intermolecular distances between the methyl C atoms of the sulfonylisopropyl group and those of the two *ortho*-isopropyl groups of (I) is shorter than the sum of their van der Waals radii, making it unlikely that they would interfere with the rotation of the α-isopropyl group prior to crystallization.

Comment

Highly hindered isopropyl 2,4,6-triisopropylphenyl sulfone, (I), which resisted preparation by some of the common synthetic routes to sulfones, has been prepared and unequivocally characterized for the first time, *via* the reactions 2,4,6-triisopropylbenzenesulfonyl chloride (II) $\rightarrow$ 2,4,6-triisopropylbenzenethiol $\rightarrow$ isopropyl 2,4,6-triisopropylphenyl sulfide $\rightarrow$ (I), as illustrated in the scheme. Compound (I) was prepared to compare its crystal structure (shown with atom numbering in Fig. 1) with those of the corresponding isopropyl 2,4,6-trimethylphenyl sulfone (Meyers *et al.*, 2002) and related
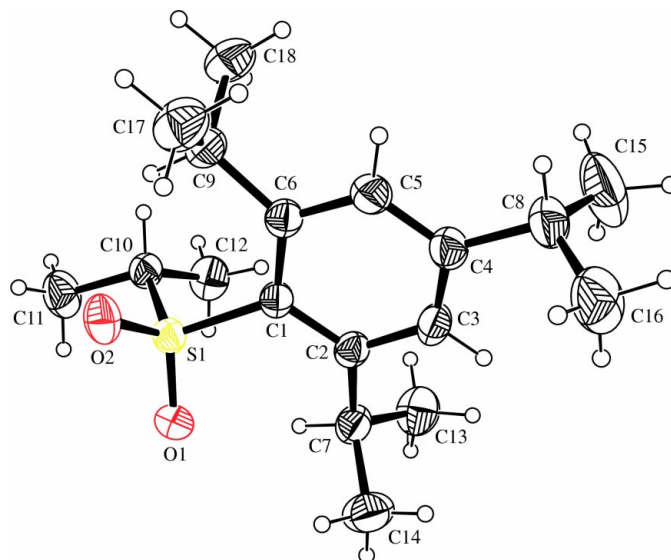

Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probablilty level.
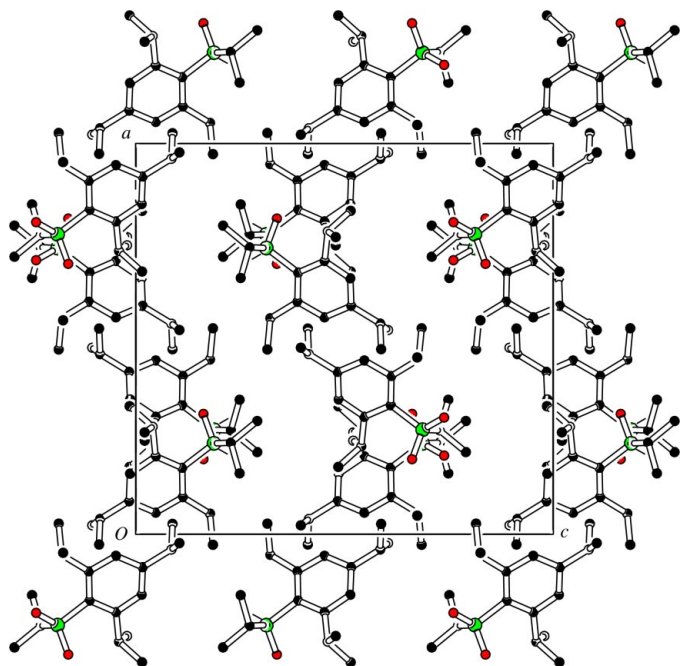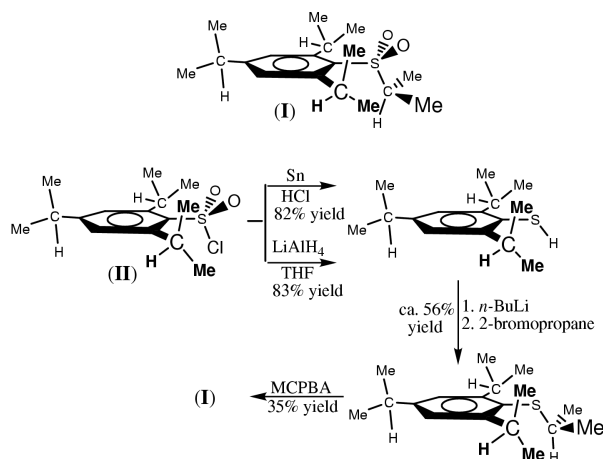
Figure 2
The molecular packing in (I), viewed down the *b* axis.

Figure 3
Edge view of (I), showing the aromatic ring and its directly attached atoms. Note the significant deviation from planarity.

might possess a similarly interactive combination to promote rotational disorder.

While such a structure is provided by (I), it exhibits no rotational disorder. The absence of such disorder parallels the fact that crystalline (I) possesses no intermolecular distances between the atoms in question (*viz.* C10, C11 and C12), nor intramolecular distances between the atoms in question (*viz.* C11 or C12 and C13, C14, C17 or C18), within the sum of their van der Waals radii. The molecular packing is shown in Fig. 2.

Considerable deviation from benzene-ring planarity in (I) is observed (Fig. 3 and Table 2). The χ^2 value, as calculated by *PLATON* (Spek, 2003), is extremely high (647.3) compared with values (18.2–168) for the previously studied related compounds noted above (lower values correlate with increasing approximation to planarity). This poor ring planarity is accompanied by an unusually wide variation in the ring-atom geometric parameters (Table 1). In particular, the C1—C2 and C1—C6 distances are quite large compared with the other ring distances. A possible explanation for these distortions can be found in the short intramolecular O1···C7 and O2···C9 distances, which are, respectively, 0.38 and 0.28 Å less than the sum of their van der Waals radii. The congestion caused by these two close approaches probably explains the abnormal lengthening of the benzene C1—C2 and C1—C6 bonds, the generally poor ring planarity, and the fact that atom S1 and the two C substituents *ortho* to it (C7 and C9) are substantially farther out of the benzene least-squares plane than the *para*-C substituent (C8; Table 2).

This congestion would also explain the dynamic ^{1}H NMR results. In solution at 298 K, (I) exhibits a single sharp resonance for the two methyl groups of the sulfonyl isopropyl group and a single sharp resonance for the four methyl groups of the two *ortho*-isopropyl groups, indicating rapid rotation of these isopropyl groups. The steric hindrance to rotation becomes apparent at reduced temperatures. At 183 K, the relative half width of these resonances is increased by a factor of approximately nine, indicating that lowering the temperature reduces the rate of rotation sufficiently relative to NMR acquisition time to allow the two methyl groups in each isopropyl group to begin to exhibit separate NMR resonances.

α-haloisopropyl sulfones, *viz.* α-bromoisopropyl 2,4,6-trimethylphenyl sulfone (Chan-Yu-King *et al.*, 2001), α-chloroisopropyl 2,4,6-trimethylphenyl sulfone (Meyers *et al.*, 2001), α-bromoisopropyl phenyl sulfone (Robinson, Sandrock *et al.*, 2001) and the ketone, α-bromoisopropyl 2,6-dimethyl-4-*tert*-butylphenyl ketone (Robinson, Parady *et al.*, 2001).

Of these previously reported crystalline aryl isopropyl sulfones and ketones, only those possessing a combination of di-*ortho*-methyl and α-chloro or -bromo substitution exhibited rotational disorder. It was reasoned, therefore, that an interaction between the di-*ortho*-methyl groups and the α-haloisopropyl group might be responsible. On this basis, it was suggested that a related sulfone bearing, on one side, a benzene ring possessing much more hindering di-*ortho*-isopropyl groups, and a simple isopropyl group on the other side,
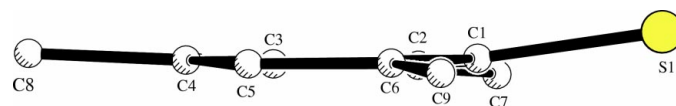
Experimental

Compound (I) was synthesized in three steps starting from commercially available 2,4,6-triisopropylbenzenesulfonyl chloride (II) (kindly donated by Professor Duy H. Hua, Kansas State University). (i) Treatment with tin–HCl produced the thiol in 82% yield; with LiAlH$_4$, the yield was 83%. (ii) The thiol, treated with *n*-BuLi followed by 2-bromopropane, was converted into 2,4,6-triisopropylphenyl isopropyl sulfide (77% yield of crude product), which was purified by vacuum distillation to yield a colorless oil (56%

yield). (iii) Oxidation of the sulfide with MCPBA (*meta*-chloroperbenzoic acid) produced the desired sulfone, (I), which was purified by radial chromatography (35% yield) and recrystallization (hexanes); fine white needles, m.p. 393–395 K. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.26 (*d*, *J* = 7.2 Hz, 12H), 1.27 (*d*, *J* = 6.9 Hz, 6H), 1.39 (*d*, *J* = 6.9 Hz, 6H), 2.91 (sept, 1H), 3.24 (sept, 1H), 4.13 (sept, 2H), 7.19 (*s*, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 15.1, 23.5, 25.1, 29.8, 34.2, 56.2, 124.2, 151.7, 153.4, 154.7. After many trials with a variety of solvents and mixed solvents, the crystals grown very slowly from isooctane–ethyl acetate proved to be amenable to X-ray analysis and were used in this study.

Crystal data

C$_{18}$H$_{30}$O$_2$S	Mo $K\alpha$ radiation
M_r = 310.49	Cell parameters from 7039
Orthorhombic, *Pbca*	reflections
a = 17.4705 (6) Å	θ = 2.4–25.1°
b = 11.5964 (4) Å	μ = 0.17 mm^{-1}
c = 18.6412 (7) Å	*T* = 295 (2) K
V = 3776.6 (2) Å^3	Rectangular plate, colorless
Z = 8	0.44 × 0.31 × 0.10 mm
D_x = 1.092 Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	2530 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.048
Absorption correction: none	θ_{max} = 25.0°
47 817 measured reflections	$h = -20 \rightarrow 20$
3319 independent reflections	$k = -13 \rightarrow 13$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.047	$+ 1.2339P]$
$wR(F^2)$ = 0.134	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max} < 0.001$
3319 reflections	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
198 parameters	$\Delta\rho_{min}$ = -0.22 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.415 (3)	C3—C4	1.385 (3)
C1—C6	1.417 (3)	C4—C5	1.373 (3)
C2—C3	1.392 (3)	C5—C6	1.383 (3)
C2—C1—C6	120.47 (19)	C5—C4—C3	117.0 (2)
C3—C2—C1	117.0 (2)	C4—C5—C6	123.6 (2)
C4—C3—C2	123.8 (2)	C5—C6—C1	117.88 (19)

Table 2
Deviation of atoms from benzene ring least-squares plane (Å).

Atom	Deviation
C1	0.035 (2)
C2	−0.024 (2)
C3	−0.007 (2)
C4	0.027 (2)
C5	−0.017 (2)
C6	−0.014 (2)
S1†	0.281 (1)
C7†	−0.108 (2)
C8†	0.096 (3)
C9†	−0.120 (2)

† These atoms were not used in the least-squares-plane calculation.

The rotational orientations of the methyl groups were refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997). All H atoms were treated as riding with C—H distances ranging from 0.93 to 0.98 Å, and U_{iso}(H) values equal to 1.5 (methyl H atoms) or 1.2 (all other H atoms) times U_{eq} of the parent atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON*.

References

Bruker (2001). *SMART* (Version 5.4) and *SAINT* (Version 6.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Burla, M. C., Carmalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Chan-Yu-King, R., Hou, Y., Sandrock, P. B., Meyers, C. Y. & Robinson, P. D. (2001). *Acta Cryst.* E**57**, 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.* E**57**, o587–o589.
Meyers, C. Y., Roper, W., Klavetter, F., Horii, T., Sandrock, P. B. & Robinson, P. D. (2002). *Acta Cryst.* E**58**, o1166–o1168.
Molecular Structure Corporation (1997). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Robinson, P. D., Parady, T. E., Hou, Y. & Meyers, C. Y. (2001). *Acta Cryst.* E**57**, o584–o586.
Robinson, P. D., Sandrock, P. B., Xie, S. & Meyers, C. Y. (2001). *Acta Cryst.* E**57**, o555–o55.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.