Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(*tert*-butylsulfonyl)ethyne and 1-*tert*-butylsulfinyl-2-*tert*-butylsulfonylethyne

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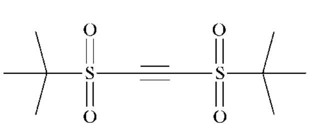
Received 10 October 2006
Accepted 10 November 2006
Online 12 December 2006

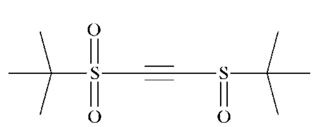
The title compounds are electron-poor ethynes. The structure determination of bis(*tert*-butylsulfonyl)ethyne, $C_{10}H_{18}O_4S_2$, (I), is the first of a bis-sulfonyl-substituted ethyne. The molecule is situated on a crystallographic inversion centre. The S—C*sp* bond [1.737 (2) Å] is the longest of this type reported to date. 1-*tert*-Butylsulfinyl-2-*tert*-butylsulfonylethyne, $C_{10}H_{18}O_3S_2$, (II), which is basically the same as (I) minus one O atom, crystallizes isomorphous with (I). This results in a nearly equal distribution of the three O atoms over the four possible positions.

Comment

The high reactivity of bis(*tert*-butylsulfonyl)ethyne, (I), as a dienophile in Diels–Alder reactions has been demonstrated in several reports (Riera *et al.*, 1990; Virgili *et al.*, 1991; Gleiter & Ohlbach, 1994; Gleiter *et al.*, 1996). Compound (I) is the only known stable ethyne substituted by two sulfonyl groups, whereas bis(arylsulfonyl)ethynes are reported as unstable at room temperature (Pasquato *et al.*, 1991).



(I)



(II)

Compound (I) (Fig. 1) forms colourless polyhedral crystals and crystallizes in the monoclinic space group $P2_1/n$. Crystallographically imposed inversion symmetry was found in the structure of (I). Thus, there is only half a molecule in the asymmetric unit. This structure determination is the first to be reported of an uncomplexed bis-sulfonyl-substituted ethyne. Structures of mono-sulfonyl-substituted ethynes are also very rare (Hu *et al.*, 2004; Tykwinski *et al.*, 1993), so there is very little knowledge of the geometric parameters of such compounds. The C≡C triple bond is rather short (1.194 Å), whereas the sulfonyl SO_2—C*sp* bond is the longest of this type reported to date.

It is interesting to note that all sulfonyl SO_2—C*sp* bonds known in the literature [1.707 (Hu *et al.*, 2004), 1.711 (Tykwinski *et al.*, 1993) and 1.737 Å (present work)] are significantly longer than reported sulfide S—C*sp* bonds [mean 1.681 Å, standard error (SE) = 0.001, standard deviation = 0.013; Cambridge Structural Database, Version 5.27; Allen, 2002]. This observation was confirmed by the determination and investigation of the structure of a mixed sulfonyl–thio compound, *tert*-butylsulfonyl-*tert*-butylthioethyne, (III) (Werz *et al.*, 2006), which continues the series of (I) and (II), with another O atom absent at the same site. In that compound, the SO_2—C*sp* bond is also longer than the S—C*sp* bond [1.697 (2) and 1.684 (3) Å, respectively]. In the case of saturated Csp^3 atoms, this is not the case; in contrast, the sulfonyl SO_2—Csp^3 bonds have a mean length of 1.788 Å (SE = 0.001, standard deviation = 0.024), which is significantly shorter than the sulfide S—Csp^3 bonds, with a mean length of 1.812 Å (SE = 0.001, standard deviation = 0.024) (Allen, 2002).

The bond angles at the S atom of (I) are as expected. The smallest angle is Csp^3—S—C*sp* [103.22 (8)°] and the largest is O═S═O [118.90 (8)°]. The O═S—C angles are within this range, with the O═S—C*sp* angles being smaller than the O═S—Csp^3 angles.

Due to the symmetry of the molecule of (I), the *tert*-butyl—SO_2—SO_2—*tert*-butyl torsion angle is exactly 180°. In contrast, in the mixed compound (III) (Werz *et al.*, 2006), the *tert*-butyl—SO_2—S—*tert*-butyl torsion angle is nearly perfectly orthogonal (91.5°). We assume electronic rather than steric reasons. Further examinations are in progress.

The sulfonyl–sulfinyl compound 1-*tert*-butylsulfinyl-2-*tert*-butylsulfonylethyne, (II), with its three O atoms, is in the middle of the series between compounds (I) and (III). It crystallizes isomorphous with (I), which results in a nearly equal distribution of the three O atoms over the four possible positions. This disorder also occurs in all lower symmetry space groups, so that $P2_1/n$ is the correct choice to describe the

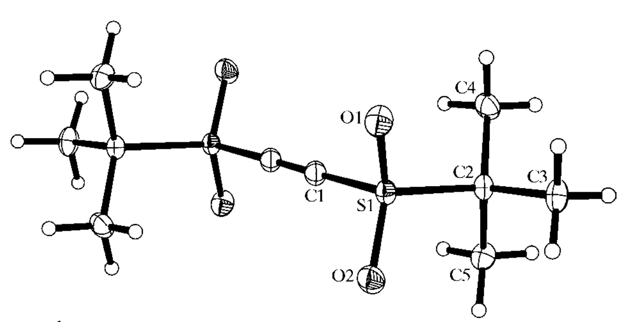


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x + 1, -y + 1, -z)$.

 DOI: 10.1107/S0108270106047834

structure. From an analytical point of view (chromatography, NMR, FAB mass spectrometry; see *Experimental*), it is already inherently clear that there can only be three O atoms, and the pure crystallographic results also lead quite reliably to this interpretation. If the O-atom positions are refined with full occupancies, the displacement parameters of the O atoms become about twice as large as those of other atoms. Liberation of the occupation factors leads to reasonable displacement parameters and the freely refined occupancies nearly add exactly to 1.5, the value to which the occupancy was restrained in the final refinement. In doing so, the R values drop from 0.210 to 0.147 (R_2) and from 0.072 to 0.062 (R_1) compared with the results obtained with fully occupied O-atom positions. The observed disorder of the O atoms leads to a somewhat restricted quality of the structure compared with (I) and thus prevents a detailed quantitative discussion of the results. However, we can confidently state that, due to the observed symmetry, the torsion angle *tert*-butyl—SO_2—SO—*tert*-butyl is 180°, and thus compound (II) is much more similar to (I) than to (III) (Werz *et al.*, 2006).

Experimental

Compound (I) was obtained from bis(*tert*-butylsulfanyl)ethyne by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA; Riera *et al.*, 1990); it was recrystallized from chloroform. For the preparation of (II), *tert*-butylsulfonyl-*tert*-butylsulfanylethyne, (III) (Werz *et al.*, 2006) (1.0 equivalent) was dissolved in chloroform and petroleum ether (4:1 *v*/*v*). The mixture was cooled to 273 K and a solution of *m*-CPBA (0.9 equivalents) in chloroform was added slowly. The mixture was stirred for 2 d while warming to room temperature. After 2 d, the mixture was cooled to 273 K and filtered. The filtrate was washed three times with $Na_2S_2O_3$ solution and then three times with $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4 and concentrated. Silica-gel column chromatography yielded the desired compound in pure form as the major product (64%), with compound (I) as a by-product. The two compounds could be easily distinguished by thin-layer chromatography. The structure of (II) was assigned unequivocally by NMR and mass spectrometric analyses. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (*s*, 9H), 1.49 (*s*, 9H); ^{13}C NMR (125 MHz, $CHCl_3$): δ 22.9 (CH_3), 23.3 (CH_3), 60.9 (C), 61.9 (C), 89.2 (C*sp*), 92.1 (C*sp*); MS (FAB+), calculated: 250.3781; found: 250.3785.

Compound (I)

Crystal data

$C_{10}H_{18}O_4S_2$
M_r = 266.36
Monoclinic, $P2_1/n$
a = 5.7037 (7) Å
b = 10.7251 (14) Å
c = 10.5678 (14) Å
β = 90.267 (2)°
V = 646.45 (14) Å^3
Z = 2
D_x = 1.368 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 100 (2) K
Polyhedron, colourless
0.39 × 0.21 × 0.09 mm

Data collection

Bruker APEX diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.854, T_{max} = 0.960
6615 measured reflections
1599 independent reflections
1559 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 28.3°
115 standard reflections every 1740 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.084
S = 1.28
1599 reflections
109 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0158P)^2 + 0.7261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

S1—O1	1.4321 (14)	S1—C2	1.8044 (17)
S1—O2	1.4351 (13)	C1—C1^i	1.195 (4)
S1—C1	1.7374 (18)		
O1—S1—O2	118.90 (8)	O2—S1—C2	109.63 (8)
O1—S1—C1	106.66 (8)	C1—S1—C2	103.22 (8)
O2—S1—C1	106.82 (8)	C1^i—C1—S1	178.9 (2)
O1—S1—C2	110.35 (8)		

Symmetry code: (i) $-x+1, -y+1, -z$.

Compound (II)

Crystal data

$C_{10}H_{18}O_3S_2$
M_r = 250.36
Monoclinic, $P2_1/n$
a = 5.7463 (4) Å
b = 10.7328 (8) Å
c = 10.5299 (7) Å
β = 92.1090 (10)°
V = 648.98 (8) Å^3
Z = 2
D_x = 1.281 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 200 (2) K
Polyhedron, colourless
0.56 × 0.10 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.73, T_{max} = 0.97
4914 measured reflections
1326 independent reflections
1014 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 26.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.147
S = 1.05
1326 reflections
78 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 1.6512P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}

For compound (I), all H atoms could be located in a difference Fourier map and were refined isotropically; the resulting C—H distances range from 0.91 (3) to 0.99 (2) Å. For compound (II), the H atoms were taken into account using appropriate riding models, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The occupancies of the two disordered O atoms were restrained using the SUMP command (*SHELXL97*; Sheldrick, 1977) to sum to 1.5.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3049). Services for accessing these data are described at the back of the journal.

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