[Sulfonylbis(bromomethylene)]dibenzene

Peter W. R. Corfield*

Department of Chemistry, Fordham University, 441 East Fordham Road, Bronx, NY 10458, USA. *Correspondence e-mail: pcorfield@fordham.edu

The title compound, C_{14}H_{12}Br_{2}O_{2}S, crystallizes as the meso isomer of a diastereoisomeric pair. This structure determination was key to determining that the 1,3 elimination of bromine by triphenylphosphine occurs with inversion of the configuration at each of the two chiral carbon atoms. In the crystal, the molecules are linked by weak C—H···O and C—H···Br hydrogen bonds.

Structure description

This structure determination was undertaken because of the high interest in the stereochemistry of 1,3 elimination reactions, particularly in the formation of α-sulfonyl carbanions (Cram et al., 1966; Bordwell et al., 1968a). Two diastereoisomers, 1 and 2, of PhCHBrSO_{2}-CHBrPh (Fig. 1) react stereospecifically with triphenylphosphine leading to 1,3 elimination of bromine followed by loss of sulfur dioxide to give stilbene, PhCH=CHPh, with 1 giving almost exclusively trans stilbene and 2 giving cis stilbene. Determination that the title compound 2 was the meso isomer was key to showing that the elimination occurred with double inversion of chirality at the C atoms (Bordwell et al., 1968b).

Figure 1

The two diastereoisomers, 1 and 2, of PhCHBrSO_{2}-CHBrPh.
data reports

Bond lengths and angles in the molecular structure of 2 appear normal. As can be seen in Fig. 2, the chirality at C1 is R while that at C9 is S, indicating that this compound is the meso isomer. All molecules in this centrosymmetric crystal will be the same meso isomer, although of course half will have opposite chiralities at C1 and C9. The C1—Br1 entity is gauche with respect to S—C2, whereas C2—Br2 is trans to S—C1, with conformational angles of −58.3 (5) and 171.3 (4)°, respectively.

The packing diagram (Fig. 3) shows the sulfone O atoms and the Br atoms projecting into hydrophobic areas of the crystal. A number of putative C—H···O and C—H···Br intermolecular hydrogen-bonding contacts are given in Table 1. The C···O distances range from 3.46 (2) to 3.55 (2) Å while angles at the H atom are in the general range of 120–130°. The three C···Br distances listed are longer, with a range of 3.74 (2) to 3.79 (2) Å and there is more variation in the angles at the H atoms. Intermolecular H···H contacts are all greater than 2.5 Å except for H6···H10(x−1/2, y, z, which is 2.36 Å.

Synthesis and crystallization

Details of the synthesis of the title compound are not given in the Bordwell papers, but details of two methods of preparing the compound are given in Carpino et al. (1971).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

In 1967, when this dataset was collected, mechanical failures were frequent enough that minimum redundancy was sought. This accounts for the low resolution of the data and the lack of symmetry-equivalents. An empirical absorption correction involving a 24-parameter fit was made with XABS2 (Parkin et al., 1995), which led to a much smoother difference-Fourier map. The H atoms attached to chiral C1 and C2 atoms were located as the two highest peaks on a difference map calculated without their contributions.

In the final refinements, the phenyl ring carbon atoms were refined as rigid groups in order to keep a reasonable ratio of observations to refined parameters. The C—C distance in the phenyl rings was set at 1.372 Å to minimize the weighted R factor. Although this distance is a little less than the average 1.39 Å usually found, a number of well-refined sulfone structures in the Cambridge Structural Database (Groom et al., 2016) have C—C distances less than 1.39 Å, see: TUXFIC02 (Eccles et al., 2011), BECRAE (Malwal & Chakrapani, 2015), GIPQON (Periasamy et al., 2013), HEXLOO (Matsumoto et al., 2018). The phenyl and H atoms attached to chiral C atoms all were constrained to lie in their expected positions, with C—H distances of 0.93 and 0.98 Å respectively, and displacement parameters set at 1.2U(eq) for the adjoining carbon atoms.

![Figure 2](image-url) View of the title molecule showing the atomic numbering and displacement ellipsoids at the 50% probability level.

![Figure 3](image-url) Projection of the crystal structure of 2 down the b axis. An arbitrary sphere size is given for C and H atoms, and a 50% probability level for the displacement ellipsoids of Br, S and O atoms. The reference molecule has Br and S atoms identified.

| Table 1 | Hydrogen-bond geometry (Å, °). |
|---------|--------------------------------|
|         | D—H···A                        | D—H | H···A | D···A | D—H···A |
| C6—H6···O1i | 0.93 | 2.92 | 3.523 (14) | 123 |
| C7—H7···O1i | 0.93 | 2.80 | 3.462 (13) | 129 |
| C11—H11···O1ii | 0.93 | 2.92 | 3.486 (14) | 120 |
| C12—H12···O2ii | 0.93 | 2.89 | 3.545 (15) | 128 |
| C14—H14···O1iii | 0.93 | 2.86 | 3.539 (17) | 131 |
| C14—H14···O2ii | 0.93 | 2.86 | 3.548 (14) | 132 |
| C7—H7···Br1iv | 0.93 | 3.18 | 3.777 (14) | 124 |
| C8—H8···Br2iv | 0.93 | 2.88 | 3.789 (15) | 166 |
| C13—H13···Br2iv | 0.93 | 3.12 | 3.741 (19) | 126 |

Symmetry codes: (i) −x+1, y−1/2, −z+1; (ii) −x+1/2, y+1/2, z−1; (iii) −x+1/2, −y+1, z−1; (iv) x, −y+1/2, z−1/2; (v) −x+1, −y+1, −z+1.
Table 2
Experimental details.

| Crystal data                                      |            |
|---------------------------------------------------|------------|
| Chemical formula                                  | C₁₄H₁₂Br₂O₂S |
| Molecular weight (Da)                             | 404.12     |
| Crystal system, space group                       | Orthorombic, Pbc a |
| Temperature (K)                                   | 295        |
| a, b, c (Å)                                       | 16.53 (10), 12.81 (5), 13.46 (7) |
| V (Å³)                                            | 2850 (25)  |
| Z                                                 | 8          |
| Radiation type                                    | Mo Kα      |
| μ (mm⁻¹)                                          | 5.83       |
| Crystal size (mm)                                 | 0.60 × 0.50 × 0.40 |

Data collection

| Diffractometer                                    | Picker, punched card control |
|---------------------------------------------------|-----------------------------|
| Absorption correction                             | Empirical (using intensity measurements) four-dimensional tensor analysis (Parkin et al., 1995) |

| Tmin, Tmax                                        | 0.148, 0.226               |
|---------------------------------------------------|-----------------------------|
| No. of measured, independent and observed [I > 2σ(I)] reflections | 1334, 1334, 1059 |
| Rint                                             | 0                          |
| θmax (°)                                          | 20.0                       |
| (sin θ/λ)max (Å⁻¹)                               | 0.482                      |

Refinement

| R[F² > 2σ(F²)], wR(F²), S                         | 0.046, 0.105, 1.10         |
|---------------------------------------------------|-----------------------------|
| No. of reflections                                | 1334                        |
| No. of parameters                                 | 148                         |
| H-atom treatment                                  | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³)                             | 0.33, −0.42                 |

Computer programs: PICK (local program by J. A. Ibers), PICKOUT (local program by R. J. Doedens), FORDAP (local version), SHELXL (Sheldrick, 2015), ORTEP-III (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 2012), and publCIF (Westrip, 2010).

Acknowledgements

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full crystallographic data

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Crystal data
C_{14}H_{12}Br_{2}O_{2}S  
$M_r = 404.12$
Orthorhombic, $Pbca$
$a = 16.53$ (10) Å  
$b = 12.81$ (5) Å  
$c = 13.46$ (7) Å  
$V = 2850$ (25) Å$^3$
$Z = 8$

$F(000) = 1584$

Data collection
Picker, punched card control
diffractometer
Radiation source: sealed X-ray tube
$\theta/2\theta$ scans
Absorption correction: empirical (using intensity measurements) 
  four-dimensional tensor analysis (Parkin et al., 1995)

$T_{\text{min}} = 0.148$, $T_{\text{max}} = 0.226$
1334 measured reflections

Refinement
Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.105$
$S = 1.10$
1334 reflections
148 parameters
0 restraints
Primary atom site location: heavy-atom method
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained

$w = 1/\sigma^2(F_c)$

$\Delta\rho_{\text{max}} = 0.33$ e Å$^{-3}$
$\Delta\rho_{\text{min}} = -0.42$ e Å$^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. After the empirical absorption correction with XABS2, a difference map based upon all of the atoms except H1 and H2 clearly revealed H1 and H2 as the two highest peaks.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x   | y   | z   | Uiso*/Ueq |
|----|-----|-----|-----|-----------|
| Br1| 0.53460 (5) | 0.75393 (8) | 0.42515 (7) | 0.0479 (4) |
| Br2| 0.81089 (6) | 0.86936 (8) | 0.53831 (8) | 0.0592 (4) |
| S  | 0.66395 (13) | 0.74518 (19) | 0.58854 (17) | 0.0397 (7) |
| O1 | 0.6327 (4) | 0.8427 (5) | 0.6245 (5) | 0.0514 (18) |
| O2 | 0.7024 (4) | 0.6746 (5) | 0.6565 (4) | 0.0522 (18) |
| C1 | 0.5828 (5) | 0.6707 (6) | 0.5315 (6) | 0.035 (2) |
| H1 | 0.605758 | 0.607183 | 0.502400 | 0.042* |
| C2 | 0.7319 (5) | 0.7715 (6) | 0.4857 (6) | 0.039 (2) |
| H2 | 0.701115 | 0.807103 | 0.433486 | 0.047* |
| C3 | 0.5219 (3) | 0.6398 (5) | 0.6091 (4) | 0.034 (2) |
| C4 | 0.4714 (4) | 0.7116 (4) | 0.6524 (5) | 0.046 (3) |
| H4 | 0.474013 | 0.781339 | 0.63357 | 0.055* |
| C5 | 0.4171 (4) | 0.6804 (6) | 0.7235 (5) | 0.055 (3) |
| H5 | 0.382825 | 0.729053 | 0.752842 | 0.066* |
| C6 | 0.4132 (3) | 0.5774 (7) | 0.7513 (4) | 0.062 (3) |
| H6 | 0.376382 | 0.556327 | 0.799451 | 0.074* |
| C7 | 0.4637 (4) | 0.5057 (4) | 0.7079 (5) | 0.062 (3) |
| H7 | 0.461127 | 0.435885 | 0.726776 | 0.075* |
| C8 | 0.5181 (4) | 0.5368 (5) | 0.6369 (5) | 0.048 (3) |
| H8 | 0.552316 | 0.488169 | 0.607490 | 0.058* |
| C9 | 0.7698 (4) | 0.6757 (4) | 0.4412 (5) | 0.044 (3) |
| H10| 0.8307 (4) | 0.6217 (5) | 0.4877 (4) | 0.041 (2) |
| H11| 0.849895 | 0.643029 | 0.549794 | 0.050* |
| C11| 0.8646 (3) | 0.5363 (5) | 0.4425 (6) | 0.059 (3) |
| H12| 0.905920 | 0.499671 | 0.473964 | 0.071* |
| C12| 0.8377 (4) | 0.5049 (4) | 0.3508 (6) | 0.057 (3) |
| H13| 0.860697 | 0.446934 | 0.320211 | 0.069* |
| C14| 0.7768 (4) | 0.5589 (6) | 0.3044 (4) | 0.054 (3) |
| C15| 0.758539 | 0.537555 | 0.242287 | 0.064* |
| C16| 0.7429 (3) | 0.6443 (5) | 0.3496 (5) | 0.043 (3) |
| C17| 0.701603 | 0.680914 | 0.318116 | 0.052* |

Atomic displacement parameters (Å²)

|    | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|----|-----|-----|-----|-----|-----|-----|
| Br1| 0.0465 (6) | 0.0488 (7) | 0.0482 (6) | −0.0038 (5) | −0.0090 (5) | 0.0088 (5) |
| Br2| 0.0507 (7) | 0.0452 (7) | 0.0817 (8) | −0.0152 (5) | −0.0008 (6) | −0.00116 (6) |
| S  | 0.0405 (14) | 0.0389 (15) | 0.0397 (15) | −0.0038 (13) | −0.0045 (12) | −0.0029 (13) |
| O1 | 0.056 (4) | 0.043 (4) | 0.055 (4) | 0.001 (3) | 0.000 (3) | −0.018 (4) |
| O2 | 0.049 (4) | 0.066 (4) | 0.042 (4) | 0.005 (4) | −0.010 (3) | 0.014 (4) |
| C1 | 0.032 (5) | 0.027 (5) | 0.046 (6) | 0.002 (4) | 0.005 (5) | −0.001 (5) |
| C2 | 0.040 (6) | 0.042 (7) | 0.035 (5) | −0.009 (5) | −0.007 (5) | 0.011 (5) |
| Atom | U(11)  | U(22)  | U(33)  | U(12)  | U(13)  | U(23)  |
|------|--------|--------|--------|--------|--------|--------|
| C3   | 0.040  | 0.024  | 0.038  | 0.000  | −0.004 | −0.005 |
| C4   | 0.047  | 0.050  | 0.041  | 0.006  | −0.001 | 0.006  |
| C5   | 0.049  | 0.057  | 0.058  | 0.010  | 0.001  | −0.016 |
| C6   | 0.056  | 0.086  | 0.043  | −0.019 | 0.004  | −0.014 |
| C7   | 0.080  | 0.037  | 0.070  | −0.015 | 0.011  | 0.006  |
| C8   | 0.058  | 0.035  | 0.052  | 0.000  | 0.014  | −0.011 |
| C9   | 0.043  | 0.031  | 0.056  | −0.005 | 0.003  | 0.015  |
| C10  | 0.049  | 0.039  | 0.036  | 0.003  | 0.007  | 0.006  |
| C11  | 0.067  | 0.037  | 0.073  | 0.004  | −0.004 | 0.002  |
| C12  | 0.068  | 0.034  | 0.069  | −0.007 | 0.027  | −0.005 |
| C13  | 0.063  | 0.053  | 0.046  | −0.011 | 0.006  | −0.004 |
| C14  | 0.049  | 0.034  | 0.047  | −0.002 | −0.009 | 0.008  |

**Geometric parameters (Å, †)**

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| Br1—C1                | 1.954        |
| Br2—C2                | 1.943        |
| S—O2                  | 1.435        |
| S—O1                  | 1.436        |
| S—C1                  | 1.817        |
| S—C2                  | 1.815        |
| C1—C3                 | 1.503        |
| C1—H1                 | 0.980        |
| C2—C9                 | 1.502        |
| C2—H2                 | 0.980        |
| C3—C4                 | 1.3720       |
| C3—C8                 | 1.3720       |
| C4—C5                 | 1.3720       |
| C4—H4                 | 0.9300       |
| C5—C6                 | 1.3720       |
| O2—S—O1               | 119.5        |
| O2—S—C1               | 105.4        |
| O1—S—C1               | 109.5        |
| O2—S—C2               | 109.2        |
| O1—S—C2               | 108.5        |
| C1—S—C2               | 103.4        |
| C3—C1—Br1             | 112.4        |
| S—C1—Br1              | 108.9        |
| C3—C1—H1              | 108.6        |
| S—C1—H1               | 108.6        |
| Br1—C1—H1             | 108.6        |
| C9—C2—S               | 114.2        |
| C9—C2—Br2             | 113.1        |
| S—C2—Br2              | 104.9        |
| C9—C2—H2              | 108.1        |

IUCrData (2022). 7, x211351
S—C2—H2  108.1  C10—C11—H11  120.0
Br2—C2—H2  108.1  C12—C11—H11  120.0
C4—C3—C8  120.0  C13—C12—C11  120.0
C4—C3—C1  121.7 (6)  C13—C12—H12  120.0
C8—C3—C1  118.3 (6)  C11—C12—H12  120.0
C5—C4—C3  120.0  C12—C13—C14  120.0
C5—C4—H4  120.0  C12—C13—H13  120.0
C3—C4—H4  120.0  C14—C13—H13  120.0
C4—C5—C6  120.0  C13—C14—C9  120.0
C4—C5—H5  120.0  C13—C14—H14  120.0
C6—C5—H5  120.0  C9—C14—H14  120.0

O2—S—C1—C3  63.6 (6)  C3—C4—C5—C6  0.0
O1—S—C1—C3 −66.2 (6)  C4—C5—C6—C7  0.0
C2—S—C1—C3  178.3 (5)  C5—C6—C7—C8  0.0
O2—S—C1—Br1 −172.9 (4)  C6—C7—C8—C3  0.0
O1—S—C1—Br1  57.3 (5)  C4—C3—C8—C7  0.0
C2—S—C1—Br1 −58.3 (5)  C1—C3—C8—C7  179.5 (6)
O2—S—C2—C9  47.6 (7)  S—C2—C9—C10 −74.4 (7)
O1—S—C2—C9 −179.5 (6)  Br2—C2—C9—C10 −45.5 (7)
C1—S—C2—C9  −64.3 (7)  S—C2—C9—C14  107.3 (6)
O2—S—C2—Br2 −76.8 (6)  Br2—C2—C9—C14 −132.8 (4)
O1—S—C2—Br2  55.1 (5)  C14—C9—C10—C11  0.0
C1—S—C2—Br2  171.3 (4)  C2—C9—C10—C11 −178.2 (6)
S—C1—C3—C4  71.0 (6)  C9—C10—C11—C12  0.0
Br1—C1—C3—C4 −50.4 (7)  C10—C11—C12—C13  0.0
S—C1—C3—C8 −108.5 (5)  C11—C12—C13—C14  0.0
Br1—C1—C3—C8  130.1 (4)  C12—C13—C14—C9  0.0
C8—C3—C4—C5  0.0  C10—C9—C14—C13  0.0
C1—C3—C4—C5 −179.5 (6)  C2—C9—C14—C13  178.3 (5)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C6—H6···O1i | 0.93 | 2.92 | 3.523 (14) | 123 |
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Symmetry codes: (i) −x+1, y−1/2, −z+3/2; (ii) −x+3/2, y−1/2, z; (iii) −x+3/2, −y+1, z−1/2; (iv) x−y+3/2, z−1/2; (v) −x+1, −y+1, −z+1.