Structure of *cis* and *trans*-4-Bromophenylstyrylsulfones

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The title compounds ($C_{14}H_{11}O_2SBr$) are *cis* and *trans*-isomers of 4-bromophenylstyrylsulfone. These compounds crystallize in monoclinic space groups $C2/c$ and $P2_1/c$, respectively. The cell parameters for *cis* are: $a = 14.866(2)\text{\AA}$, $b = 14.133(3)\text{\AA}$, $c = 12.830(2)\text{\AA}$, $\beta = 90.58(1)^\circ$, $Z = 8$, $V = 2657.88(4)\text{\AA}^3$ and $D_{\text{calc}} = 1.615\text{ Mg m}^{-3}$; *trans* are: $a = 6.964(1)\text{\AA}$, $b = 10.840(1)\text{\AA}$, $c = 17.583(10)\text{\AA}$, $\beta = 94.09(2)^\circ$, $Z = 4$, $V = 1324.1(10)\text{\AA}^3$ and $D_{\text{calc}} = 1.621\text{ Mg m}^{-3}$. The geometries of both molecules were compared. In the *cis*-isomer, the groups at C(7) and C(8) are *cis* oriented, as the torsion angle is $3.9(1)^\circ$, whereas in the *trans*-isomer the angle is $175.2(3)^\circ$, indicating that, the orientation is *trans*. The *cis*-isomer molecule exhibits a folded structure compared to the *trans*-isomer. In the molecular packing, two adjacent molecules form square-shaped structures in the crystal. This is one of the important facets of the molecular packing.

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Natural and synthetic zeolites form a variety of beautiful framework structures. These structures contain cages or cavities as well as channels. Access to these channels, cages or cavities is through a pore or window, which can be of the same size or smaller than their sizes. In cation-exchanged faujasite zeolites, the cage sizes always depend on the cation size. The geometrical isomerization of 4-bromophenyl styryl sulfone has been studied in solution media as well as in the presence of various cation-exchanged Y-type faujasite zeolites.¹ In these zeolites, the cage free volume decreases as the cation size increases, resulting in an increase in the proportion of the *cis*-isomer. Moreover, it is observed that while stirring as a hexane slurry, the *cis*-isomer **1** readily goes into the zeolite cage while the *trans*-isomer **2** remains in the hexane. This suggests that the molecular dimension of the *trans*-isomer is incompatible for its facile entry through the cage window. This interesting observation prompted us to grow single crystals of compounds **1** and **2** to gain more insight into their molecular structures, geometrical conformations and intermolecular interactions.

The *cis* and *trans* forms of 4-bromophenyl styryl sulfone compounds were synthesized as per reported methods.^{2,3} The final products of **1** and **2** were crystallized by a slow-evaporation method using the solvent isooctane. Initially, both structures were confirmed by the H-NMR and C-NMR spectra.

The selected geometrical parameters of both molecules [**1** & **2**] are given in Table 2. The hydrogen bonding interactions of **1** and **2** are presented in Table 3.

Fig. 1 Chemical structure of *cis* and *trans*-4-bromophenyl styryl sulfones.

Figures 2(a) and 2(b) show the molecular structures of **1** & **2** with thermal ellipsoid atoms. In **1** & **2**, the S-C(9) bond lengths are 1.762(8) and 1.758(4) $\text{\AA}$, respectively; an average, this dimension is slightly longer compared with S-C(8) [1.372(9)

Table 1 Crystal data and refinement details of *cis* and *trans* isomers of 4-bromophenyl styryl sulfones

	1	2
CCDC deposit no.	CCDC-617773	CCDC-617772
Colour/Shape	colorless/block	colorless/needle
Empirical formula	$C_{14}H_{11}SO_2Br$	$C_{14}H_{11}SO_2Br$
Formula weight	323.2	323.2
Temperature, K	293(2)	293(2)
Wavelength	0.70930 $\text{\AA}$	0.71069 $\text{\AA}$
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions	$a = 14.866(2)\text{\AA}$ $b = 14.133(3)\text{\AA}$ $c = 12.830(2)\text{\AA}$ $\beta = 90.58(1)^\circ$	$a = 6.964(1)\text{\AA}$ $b = 10.840(4)\text{\AA}$ $c = 17.583(10)\text{\AA}$ $\beta = 94.09(2)^\circ$
Density (calculated)	1.615 Mg/m^3	1.621 Mg/m^3
μ	3.240 mm^{-1}	3.252 mm^{-1}
$F(0\ 0\ 0)$	1296	648
Crystal size	0.35 $\times$ 0.32 $\times$ 0.20 mm	0.30 $\times$ 0.25 $\times$ 0.25 mm
θ range for data collection	2.00 to 24.97 $^\circ$	2.20 to 24.90 $^\circ$
Data/Parameters	2339/163	2232/207
Goodness-of-fit (F^2)	0.921	0.961
Final R_1/wR_2 indices [$I > 2\sigma(I)$]	0.082/0.191	0.033/0.081
Final R_1/wR_2 indices (for all)	0.167/0.225	0.087/0.094
$(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}}$	1.13/−0.80 $\text{e.\AA}^{-3}$	0.23/−0.31 $\text{e.\AA}^{-3}$
Measurement	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Program System	SHELXS97, SHELXL97	
Structure determination	direct methods	direct methods
Refinement	full-matrix	full-matrix

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Fig. 2 The molecular structure of (a) **1** and (b) **2** showing atom labeling scheme with 50% probability displacement ellipsoids.

Table 2 Selected bond lengths (Å) and angles (°) of **1** and **2**

	1	2
Bond lengths, (Å)		
Br—C(12)	1.905(9)	1.893(4)
C(8)—S	1.732(9)	1.741(4)
S—C(9)	1.762(8)	1.758(4)
S—O(2)	1.433(7)	1.436(3)
S—O(1)	1.440(6)	1.441(3)
Bond angles, (°)		
C(14)—C(9)—C(10)	120.5(7)	119.7(4)
C(13)—C(12)—Br	118.0(8)	118.6(3)
C(11)—C(12)—Br	119.1(7)	119.9(3)
C(2)—C(7)—C(8)	131.8(9)	126.4(4)
C(7)—C(8)—S	129.6(8)	121.1(3)
C(8)—S—C(9)	100.6(4)	103.4(2)
S—C(9)—C(10)	120.4(7)	120.1(3)
C(14)—C(9)—S	119.1(6)	120.2(3)
O(2)—S—O(1)	118.6(4)	118.6(2)
O(2)—S—C(8)	108.5(4)	109.5(2)
O(1)—S—C(8)	110.9(4)	107.5(2)
O(2)—S—C(9)	108.3(4)	109.4(2)
O(1)—S—C(9)	108.4(4)	107.5(2)

and 1.741(4) Å]. This may be due to the effect of a π -cloud of the adjacent aryl ring, and these values are close to the reported structure.⁴ Between **1** & **2**, the angles subtended at the C(7), C(8) and S atoms show significant differences in their angles as 5.7, 8.5, 2.8°, respectively. This may be attributed to the different orientations of H-atoms attached to C(7) and C(8).

The geometries of both structures were compared. Importantly, in **2** the relative orientation of the groups at C(7) and C(8) bearing the torsion angle [C(2)—C(7)—C(8)—S] 175.2(3)° confirms that the orientation is *trans*, but in structure **1** this angle is 3.9(1)°, explicitly indicating that the orientation is *cis*. In compound **2**, the dihedral angle between the phenyl ring and the aryl ring having a bromine atom is 72.1°. Notably, this angle is much larger compared to that of structure **1** [64.5°]. However, the above-mentioned twist angles of **1** & **2** of the backbone C(2)—C(7)—C(8)—S allow us to differentiate the extent of folding of molecules. Figures 2(a) & (b) show the nature of the

Fig. 3 Molecular packing of **1** showing how the two adjacent molecules forming square shaped structures in the unit cell.

Table 3 C—H...O bonding interactions of **1** and **2**

D—H...A	D—H(Å)	H...A(Å)	D...A(Å)	D—H...A(°)
1				
C(6)—H(6)...O(1) ⁱ	0.93(1)	2.975(7)	3.84(1)	155.6(7)
C(11)—H(11)...O(2) ⁱⁱ	0.93(1)	2.837(7)	3.53(1)	132.0(6)
2				
C(3)—H(3)...O(1) ⁱⁱⁱ	0.94(4)	2.72(4)	3.636(5)	165(3)
C(8)—H(8)...O(1) ⁱⁱⁱ	0.99(4)	2.25(4)	3.211(5)	164(3)
C(7)—H(7)...O(2) ^{iv}	0.92(4)	2.74(4)	3.469(5)	137(3)
C(13)—H(13)...O(2) ^v	0.89(3)	2.52(3)	3.130(5)	126(3)

Symmetry code: (i) $-x-1/2, -y+1/2+1, -z$ (ii) $-x-1/2, -y+1/2, -z$ (iii) $-x, -y-1, -z$ (iv) $-x-1, -y-1, -z$ (v) $x+1, y, z$.

structural folding of **1** & **2**. The molecular dimensions of **1** ($x = 11.595, y = 6.269, z = 4.594$ Å) and **2** ($x = 10.082, y = 8.366, z = 4.584$ Å) were measured; these values are approximately close to the reported predicted dimensions, in theoretical structures.¹ Precisely, the present finding indicates that the y and z dimensions are crucial, and play very significant roles for the passage of molecules through the pore. In structure **1**, since these values are relatively small, perhaps, these are the preferred dimensions for the molecules to pass through the pores of faujasite zeolite Y.¹

On the whole, the molecular packings in both crystals were stabilized by weak van der Waals C—H...O interactions. Interestingly, the rotation of the aromatic ring in the *cis* isomer facilitates two adjacent molecules [symmetry: (i) $1-x, y, 1/2-z$ & (ii) $1-x, 1+y, 1/2-z$] to form distorted square-shaped structures (Fig. 3) in the crystal, unlike structure **2**, which adopts different stacking modes. This is one of the important facets of the molecular packing of **1** in the crystal. Comparatively, the *trans* isomer has a greater number of intermolecular short contacts than does the *cis* isomer.

References

1. A. Lalitha, K. Pichumani, P. Kannan, and C. Srinivasan, *Tetrahedron*, **1998**, 54, 15667.
2. V. Baliah and M. Seshapathirao, *J. Org. Chem.*, **1959**, 24, 867.
3. W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **1956**, 78, 2756.
4. P. Kumaradhas and K. A. Nirmala, *Acta Cryst.*, **1997**, C53, 313.