Structure of (*E*)-3,4-dibromotetrahydrothiophene 1,1-dioxide, $C_4H_6Br_2SO_2$, as determined in the gas phase by electron diffraction, in the crystalline phase at 150 K by X-ray diffraction and by *ab initio* computations

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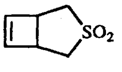
The structure of (*E*)-3,4-dibromotetrahydrothiophene 1,1-dioxide, $C_4H_6SO_2Br_2$, has been determined at 150 K by X-ray crystallography and in the gas phase by electron diffraction constrained using bond length and angle differences calculated *ab initio*. The results show that in both phases the ring adopts the half-twist conformation with C_2 symmetry. However, in the solid phase the bromine atoms occupy equatorial positions, whereas in the gas phase the optimum fit is for a mixture of axial and equatorial conformers. These are present in effectively equal amounts [proportion of axial conformer 47.2(23)%], as also predicted by *ab initio* calculations at the MP2/6-31G* level. Salient mean structural parameters (*r*/pm, angles/degrees) for the gas phase (r_a) and the solid phase, respectively, are: *r*(S=O) 142.5(1), 143.8(7); *r*(S–C) 179.0(3), 179.7(18); *r*(C–C) 152.9(4), 153.6(10); *r*(C–Br) 194.8(3), 194.7(10); OSO 117.9(10), 117.7(8); CSC 92.8(7), 96.4(6); CCCC 55.9(10), 57.7(15); BrCCBr (axial) −167.9(18) and (equatorial) −70.8(11), −64.3(20). These values are in good agreement with those obtained in an *ab initio* (MP2/6-31G* level) study of the molecular geometry.

Contrary to expectation, addition of molecular bromine to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (**1**) yielded substantial amounts of the *cis*-1,2-dibromide (1 : 1 mixture in dichloromethane of *cis* and *trans* isomers by NMR, confirmed by X-ray diffraction),[1] suggesting that the remote SO_2 group exerted an extraordinary directive influenced by means of a long-range coulomb interaction that stabilised an open carbocation intermediate at the expense of the usually favoured bridged bromonium ion.[2] This unprecedented loss of stereoselection in the bromination of a non-conjugated alkene, caused by a remote SO_2 group, prompted an investigation into the structural identity of the single isomers obtained in the corresponding bromination of 2,5-dihydrothiophene 1,1-dioxide (**2**).[3] We have carried out a structural study of 3,4-dibromotetrahydrothiophene 1,1-dioxide, $C_4H_6SO_2Br_2$ (**3**), in the solid phase by low-temperature single crystal X-ray diffraction and, for comparison, in the gas phase by electron diffraction. In the initial gas-phase structure determination of **3**, the OSO and CSC bond angles were poorly determined. Therefore, *ab initio* calculations were obtained at a reasonable level of theory (MP2/6-31G*) as an aid in the gas phase structure determination of **3**.



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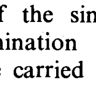

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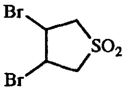

3

Experimental

X-Ray structure determination of $C_4H_6Br_2SO_2$

A colourless plate (0.8 × 0.4 × 0.2 mm) suitable for X-ray analysis was obtained by slow cooling of a saturated solution in ethyl acetate.

Crystal data

$C_4H_6SO_2Br_2$, M = 555.9, orthorhombic, space group $Pbc2_1$, a = 543.2(2), b = 1299.4(1), c = 2129.8(16) pm, U = 1.5033 nm^3 (from accurate 2θ values for 17 reflections with 2θ = 10–20°, λ = 71.073 pm), Z = 8, D_c = 2.456 Mg m^{-3}, T = 150 K, μ = 10.988 mm^{-1}, $F(000)$ = 1056.

Data collection and processing

Stoë Stadi-4 diffractometer equipped with an Oxford Cryosystems low temperature device,[4] Mo-Kα radiation, ω–2θ scans using on-line profile-fitting,[5] 1648 data collected ($2\theta_{max}$ 55°, h 0–7, k 0–16, l 0–22), of which 1370 had $|F^2| > 2\sigma(F^2)$. Three standard reflections were collected every 60 min; the maximum drift was 1%.

Electron diffraction (ED) measurements

Electron scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus operating at *ca.* 44.5 kV (electron wavelength *ca.* 5.7 pm).[6] Nozzle-to-plate distances were *ca.* 200 and 260 mm, yielding data in the s range 20–224 nm^{-1}; two usable plates were obtained at each distance. The sample and nozzle were held at *ca.* 453 and 469 K, respectively, during the exposure periods.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analysed in exactly the same way as those of the 3,4-dibromotetrahydrothiophene 1,1-dioxide so as to minimize systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors and electron wavelengths for the measurements are collected together in Table 1.

The electron scattering patterns were converted into digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with a scanning program described elsewhere.[7] The programs used for data reduction[7] and least-squares refinement[8] have been described previously; the complex scattering factors of Ross *et al.* were employed.[9]

Theoretical calculations

Ab initio computations were performed employing standard methods,[10] the GAUSSIAN92 program[11] and the following basis set: for S and Br, quasi-relativistic MEFIT[12] pseudopotentials (6 and 7 valence electrons, respectively),[13,14,15] together with a valence 2s2p1d basis set contracted from the 4s4p1d primitive sets[15,16] (d-exponents 0.65 and 0.348 for S and Br, respectively[17]); for C, O and H a standard 6-31G* basis set.[10] Five Cartesian d-functions were used throughout. This basis set is of split-valence double zeta plus polarization quality and is, for simplicity, referred to as 6-31G*.

Geometries were fully optimized at the SCF level in the given symmetry. Harmonic frequencies were computed numerically, followed by re-optimization at the electron-correlated MP2 level. Unless otherwise noted, energies are given at the MP2/6-31G* level (employing the MP2/6-31G* optimized geometries) including SCF/6-31G* zero point corrections (scaled by 0.89).[10]

Results

X-Ray structure solution and refinement

At first a data set collected at room temperature was used and was solved in the space group *Pbca* using SHELX-86.[18] However, extensive disorder was evident and for further work data collected at 150 K were used. The structure was solved by substitution of the coordinates of a bromine atom from the room temperature data. The bromine atoms were found in the first Fourier map and the remaining non-hydrogen atoms were found in subsequent Fourier maps; the structure was refined with SHELXL-93.[19] The low temperature data set is $Pbc2_1$, and not *Pbca*, as it has a significant number of weak reflections with *h* odd in the zone *h*0*l*, and an average $|E^2 - 1|$ of 0.83 for all the data. The coordinates of the two independent molecules (differentiated by prime and non-prime) possess pseudo-symmetry relating them to one another; this was broken by making shifts in the coordinates of one pair of bromine atoms as indicated by their anisotropic displacement parameters. Disorder was still observed in C(3) and C(4) of both molecules and two alternative positions with isotropic thermal parameters were included in the final model for each disordered atom. The relative site occupancy factors for the two disordered regions when refined converged to values of 0.66(3) and 0.79(3) for the non-prime and prime molecules, respectively. The bonds to C(3) and C(4) in both molecules were restrained to be equal with an effective standard deviation of 0.03 Å as their positions are poorly determined. Hydrogen atoms were included at calculated positions. At final convergence, $wR_2 = 0.128$ for all data, $R_1 = 0.044$ for the 1370 data with $|F^2| > 2\sigma(F^2)$, $S = 1.09$ for 159 parameters and the final ΔF synthesis showed no peak outside the range −952–972 e nm^{-3}. The major peaks and troughs in the final ΔF synthesis are all located near the bromine atoms. The weighting scheme $w^{-1} = \sigma^2(F_o^2) + 0.0794P + 4.46P$, where $P = [\text{maximum of } (F_o^2 \text{ or } 0) + 2F_c^2]/3$, gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max} = 0.004$. Tables of bond lengths and angles, fractional coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1. Selected bond lengths and angles are given in Table 2. Plots of the structure, including the atom numbering scheme, are shown in Fig. 1 and the molecular packing in the crystal is shown in Fig. 2.

Table 1 Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors and electron wavelengths used in the electron diffraction study

Nozzle-to-plate distance/mm	199.91	259.54
Weighting function/nm^{-1}		
Δs	4	2
s_{min}	40	20
sw_1	60	40
sw_2	192	134
s_{max}	224	158
Correlation parameter	0.360	0.342
Scale factor, k[a]	0.870(16)	1.250(18)
Electron wavelength/pm[b]	5.691	5.693

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapour.

ED Structural analysis: molecular model

Two models were used to generate atomic coordinates of $C_4H_6Br_2SO_2$: model A described a single conformer, as found in the solid phase and model B (which was suggested by *ab initio* calculations) described a mixture of two conformers with C_2 symmetry as optimized in the theoretical study. The parameters used in model B, subsequently found to provide the optimum fit, are given in Table 3. The atomic coordinates for both models were generated as follows. The heavy atoms were defined by the S–C distance (p_2), the mean C–C distance ($p_3 = \{2r[\text{C(2)–C(3)}] + r[\text{C(3)–C(4)}]\}/3$) and difference $\{r[\text{C(2)–C(3)}] - r[\text{C(3)–C(4)}]\}$, the CSC angle ($p_7$), the S=O distance ($p_1$), the OSO angle ($p_6$), the C–Br distance ($p_4$), the CCBr angle ($p_8$) and the torsion angle CCCBr (p_{13}). The hydrogen atoms were defined by a common C–H distance (p_5), the SCH and CCH angles, (p_9) and (p_{10}), and the torsion angles CSCH and CCCH,

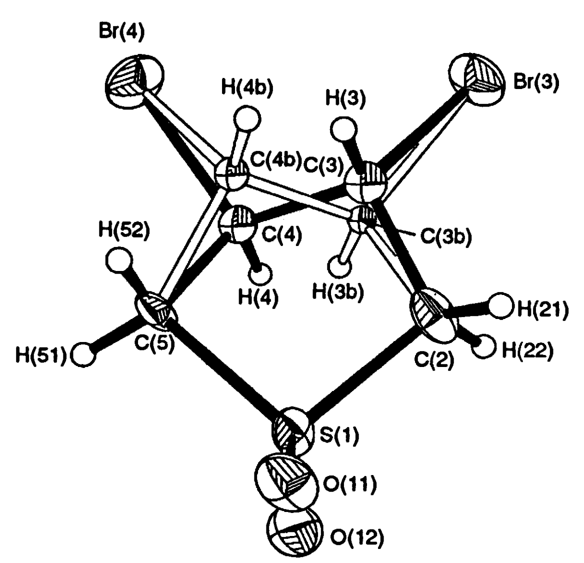

Fig. 1 Thermal ellipsoid plot of one of the crystallographically independent molecules of $C_4H_6SO_2Br_2$ showing the atom numbering scheme adopted and the additional atoms used to model the disorder about C(3) and C(4)

Table 2 Bond lengths (pm) and angles (°) determined by X-ray diffraction[a]

	Molecule 1	Molecule 2
S(1)–O(11)	144.4(12)	144.1(11)
S(1)–O(12)	143.8(14)	142.7(12)
S(1)–C(2)	180.4(14)	177.8(14)
S(1)–C(5)	182.3(13)	178.2(14)
C(2)–C(3)	153.8(16)	155.2(15)
C(3)–C(4)	152.5(16)	152.6(17)
C(4)–C(5)	155.4(16)	152.1(16)
C(3)–Br(3)	194.2(14)	194.5(14)
C(4)–Br(4)	196.4(13)	193.8(13)
O(11)–S(1)–O(12)	117.2(8)	118.1(7)
C(2)–S(1)–C(5)	96.1(6)	96.7(5)
O(11)–S(1)–C(2)	111.0(6)	111.8(7)
O(12)–S(1)–C(2)	110.3(8)	108.8(7)
O(11)–S(1)–C(5)	109.9(7)	110.5(6)
O(12)–S(1)–C(5)	110.3(6)	108.8(6)
S(1)–C(2)–C(3)	105.3(9)	104.1(7)
S(1)–C(5)–C(4)	99.1(8)	101.2(8)
C(2)–C(3)–C(4)	103.9(11)	104.0(11)
C(3)–C(4)–C(5)	104.1(11)	103.0(11)
C(2)–C(3)–Br(3)	111.7(10)	109.6(10)
C(4)–C(3)–Br(3)	114.0(11)	113.6(10)
C(3)–C(4)–Br(4)	112.3(10)	111.3(10)
C(5)–C(4)–Br(4)	109.2(9)	109.6(10)
S(1)–C(2)–C(3)–C(4)	−34.5(15)	−35.3(14)
S(1)–C(5)–C(4)–C(3)	−52.4(13)	−51.5(13)
C(2)–S(1)–C(5)–C(4)	27.8(11)	27.1(11)
C(5)–S(1)–C(2)–C(3)	3.2(12)	4.6(12)
C(2)–C(3)–C(4)–C(5)	58.0(15)	57.3(15)
S(1)–C(2)–C(3)–Br(3)	−157.8(9)	−157.1(8)
S(1)–C(5)–C(4)–Br(4)	−172.5(7)	−170.1(8)
C(2)–C(3)–C(4)–Br(4)	175.9(11)	174.7(11)
C(5)–C(4)–C(3)–Br(3)	179.7(11)	176.4(10)
Br(3)–C(3)–C(4)–Br(4)	−62.3(14)	−66.2(14)

[a] Molecular parameters for the major component of disordered structure only; figures in parentheses are estimated standard deviations.

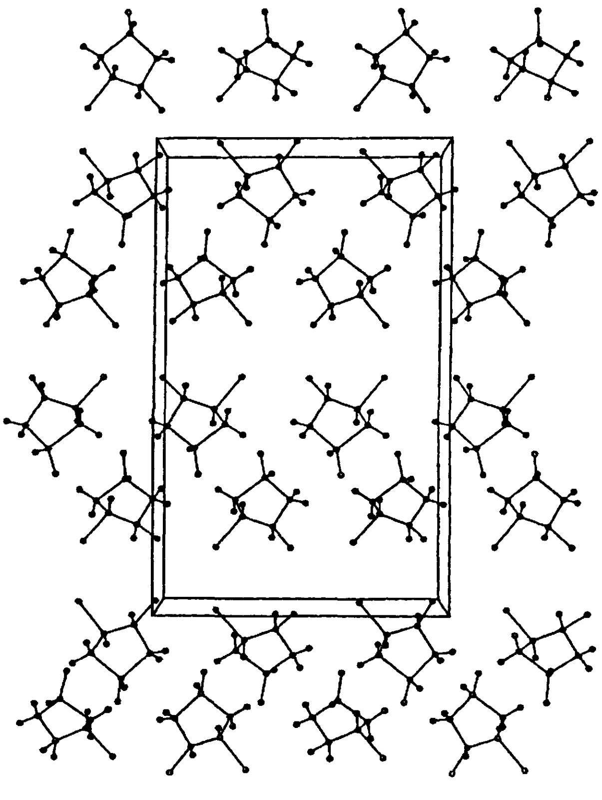

Fig. 2 Molecular packing in the crystal

Table 3 Bond lengths (pm) and angles (°) determined by electron diffraction[a]

p_1	r(S=O)(mean)	142.5(1)
p_2	r(S–C)(mean)	179.0(3)
p_3	r(C–C)(mean)	152.9(4)
p_4	r(C–Br)(mean)	194.8(3)
p_5	r(C–H)	112.0(rf)
p_6	OSO(mean)	117.9(10)
p_7	CSC(mean)	92.8(7)
p_8	CCBr(mean)	109.2(3)
p_9	SCH(mean)	107.8(f)
p_{10}	CCH(mean)	111.0(f)
p_{11}	Twist(mean)	32.6(9)
p_{12}	Twist(axial–equatorial)	5.4(f)
p_{13}	CCCBr(mean)	122.3(7)
p_{14}	CCCBr(axial–equatorial)	104.4(15)
p_{15}	CSCH(mean)	119.0(f)
p_{16}	CCCH(mean)	118.0(f)
p_{17}	% Axial	47.2(23)[b]

[a] For definition of parameters, see the text. Figures in parentheses are the estimated standard deviations. [b] esd from R-factor plot at 95% confidence level; f = fixed; rf = refined then fixed. 17 Additional differences were fixed at values calculated by *ab initio*.

(p_{15}) and (p_{16}). Model A allowed for both a twist and a tilt in the ring; the twist angle was defined by the torsion C(2)–M(1)–M(2)–C(3), where M(1) is the mid-point of the C(2) ··· C(5) interatomic distance and M(2) is at the mid-point of the C(3)–C(4) bond. The tilt angle was defined as the angle S(1)–M(1)–M(2). Model B incorporated a different twist angle for each of the two conformers defined by a mean twist angle [$p_{11} = \frac{1}{2}$(axial twist) + $\frac{1}{2}$(equatorial twist)] and a difference between these angles [p_{12} = (axial twist) − (equatorial twist)]. A number of other small differences between bond distances, angles, *etc.* in the two conformers were incorporated into model B and were fixed at the values calculated *ab initio* throughout the structure refinement.

Refinement of the structure

The radial-distribution curve for $C_4H_6SO_2Br_2$ consists of five well defined peaks at *ca.* 150, 180, 270, 360 and 440 pm and a broad feature at *ca.* 510 pm (Fig. 3). The peak at *ca.* 150 pm corresponds to the scattering from the bonded S=O and C–C pairs with a shoulder at *ca.* 110 pm corresponding to the C–H bond distance and the peak at *ca.* 180 pm is due to the S–C and C–Br bonded distances. The peak at *ca.* 270 pm corresponds to two bond distances, the most significant contribution coming from the C ··· Br distances. The remaining features in the radial-distribution curve define the conformation of the molecule, the principal contributions arising from the S ··· Br and Br ··· Br distances. The peak at *ca.* 510 pm is mainly due to the O ··· Br distances.

The molecular parameters from the solid phase structure were used as the starting values for the refinement with the single conformer model A. With the OSO and CSC angles fixed at the mean solid phase values, refinement of the remaining parameters defining the heavy atom coordinates converged with an R_G factor of 0.189. Refinements including the OSO and CSC angles gave unrealistic values when compared with the solid state parameters {too high [127.0(15)°] and too low [88.4(6)°] respectively}, the R_G factor remaining relatively large for this refinement at 0.132.

The molecular parameters obtained from the theoretical axial and equatorial geometries and amplitudes of vibration obtained from their scaled *ab initio* force fields were used as the starting values for the refinement with model B. Initially, owing to the effects of correlation, it was necessary to define weighted mean and difference parameters for the S=O and C–C distances [weighted mean = $(2p_1 + 3p_3)/5$, difference = $p_1 - p_3$] and

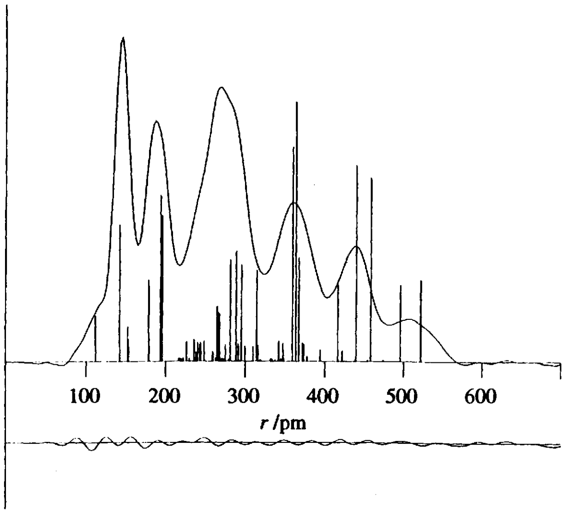

Fig. 3 Observed and final weighted difference radial-distribution curves for $C_4H_6SO_2Br_2$. Before Fourier inversion, the data were multiplied by $s \times \exp[(-0.000\,02s^2)/(Z_{Br} - f_{Br})(Z_C - f_C)]$.

for the S–C and C–Br distances [weighted mean = $(p_2 + p_4)/2$, difference = $p_2 - p_4$], unacceptable values being obtained for the freely refining distances. The differences in the bond lengths were set at the values calculated *ab initio*. It was also necessary to fix the OSO angle in the initial refinements, because the O ··· O distances contributed little to the peak at *ca.* 270 pm.

Ten of the parameters defining the molecular geometry could be refined simultaneously in the final analysis. The C–H bond distance was refined and subsequently fixed at a value which gave a lower R_G factor than that obtained with the theoretical value. The remaining parameters (those defining the bond and torsion angles to the hydrogen atoms and the difference twist angle) were fixed at values identical to the theoretical values. In addition, it was also possible to refine seven amplitudes of vibration. The vibrational amplitudes for bonded distances were refined then fixed subsequently, the remaining amplitudes were set at the theoretical values. Ratios used to constrain the amplitudes refining in groups were set at the theoretical values. A series of refinements was carried out with the proportion of the axial conformer (p_{15}) fixed at various values over the range 35–55%. {The CSC angle (p_7), the CCCBr difference angle (p_{14}) and the amplitudes *u*[S(1) ··· Br(8)] and *u*[O(2) ··· Br(9)] were removed from these refinements as they had high esds and were therefore rather unstable.} A third-order polynomial was fitted to a plot of R_G *vs.* p_{15}, the minimum occurring with the proportion of axial conformer being 47.2(23)%, the error of this value being given at the 95% confidence level.[20] Subsequently, p_{15} was fixed at this value. The refinement converged with $R_G = 0.072$. An estimate of the error in the twist angle difference (p_{13}) was obtained by including it in one cycle of least squares with a very low partial shift, giving a value of 5.4(21)°. For this optimum refinement, the structural details and vibrational amplitudes are listed in Tables 3 and 4, respectively, and the most significant part of the least-squares correlation matrix is shown in Table 5. Fig. 4 shows the experimental and difference molecular scattering intensity curves.

Discussion

The disorder present in the single-crystal X-ray structure is consistent with (*E*)-3,4-dibromotetrahydrothiophene 1,1-dioxide with equatorial bromine atoms. A disordered *cis*-dibromide isomer was discounted as the distances between the two components of the disorder within a given molecule are too short to be C–C single bonds [*e.g.* C(3)–C(4b) = 131.6(32), C(3b)–C(4) = 126.5(32), C(3′)–C(4′b) = 126.6(36) and (C3′b)–C(4′) = 125.5(38) pm]. The electron diffraction model used consists of a mixture of the axial and equatorial conformers of the *trans*-dibromide and provided a good fit to the diffraction pattern. Thus, from the analyses of both the single-crystal X-ray and electron diffraction patterns it is concluded that the addition of molecular bromine to 2,5-dihydrothiophene 1,1-dioxide yields the *trans*-dibromide.

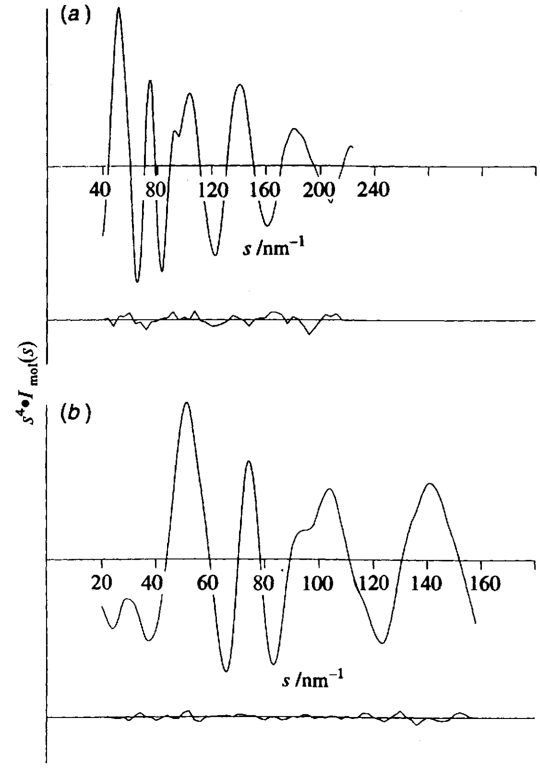

Fig. 4 Observed and final weighted difference molecular scattering intensity curves for $C_4H_6SO_2Br_2$. Nozzle-to-plate distances were (*a*) 199.9 and (*b*) 259.5 mm.

After the first, unsatisfactory refinements of model A, a more detailed conformational study of the title compound was undertaken *ab initio* which led to the definition of model B. Of the two C_2 symmetry minima located, the axial conformer was found to be 2.9 kJ mol^{-1} higher in energy at the SCF level than the equatorial one. However, inclusion of electron correlation and zero-point correction afforded essentially the same energy for both conformers, the axial form being slightly favoured by 0.1 kJ mol^{-1}.

In both minima, the five-membered ring adopts a twist conformation (see Fig. 5). No minimum corresponding to an envelope conformation could be located; starting from a structure with S(1) displaced from an otherwise planar C(2)C(3)C(4)C(5) framework (no symmetry constraints imposed), the SCF optimization led back to the equatorial twist form. (However, an envelope-like transition structure was found; see below.)

The MP2/6-31G* optimized structural parameters of the axial and equatorial conformers (Table 6) are in good agreement with those refined from the electron diffraction data and also with those of the equatorial conformer in the crystalline phase (Table 7). Only the mean S=O and S–C bond lengths are somewhat overestimated at the MP2/6-31G* level (146.3 and 181.7 pm, respectively), compared with the values obtained experimentally [GED: 142.5(1) and 179.0(3) pm, respectively]. The computations predicted that the axial and equatorial conformers should be practically isoenergetic and that they should

Table 4 Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm) for the gas phase structure[a]

r_1	C–H	112.0(f)	8.6(rf)
Axial conformer			
r_2	C(3A)–C(4A)	153.7(4)	5.9(rf)
r_3	C(2A)–C(3A)	152.5(4)	5.8(rf)
r_4	S(1A)–C(2A)	179.2(3)	5.9(rf)
r_5	S(1A)–O(11A)	142.5(2)	4.1(rf)
r_6	C(3A)–Br(3A)	195.9(3)	6.7(rf)
r_7	S(1A) ··· C(3A)	268.0(5)	13.5 (tied to u_{12})
r_8	O(11A) ··· O(12A)	243.7(13)	6.4(f)
r_9	O(11A) ··· C(2A)	265.7(3)	7.1 (tied to u_{10})
r_{10}	C(2A) ··· Br(3A)	295.2(10)	7.3(8)
r_{11}	C(4A) ··· Br(3A)	281.3(4)	7.4 (tied to u_{10})
r_{12}	C(2A) ··· C(4A)	240.5(13)	13.5(11)
r_{13}	C(2A) ··· C(5A)	259.8(18)	7.2(f)
r_{14}	S(1A) ··· Br(3A)	359.0(19)	19.9(4)
r_{15}	O(11A) ··· C(3A)	347.4(8)	16.3(f)
r_{16}	O(11A) ··· C(4A)	373.3(5)	11.5(f)
r_{17}	C(2A) ··· Br(4A)	313.6(34)	17.0 (tied to u_{14})
r_{18}	Br(3A) ··· Br(4A)	458.1(6)	19.4(20)
r_{19}	O(11A) ··· Br(3A)	366.6(33)	25.0(rf)
r_{20}	O(11A) ··· Br(4A)	495.6(19)	27.0(48)
Equatorial conformer			
r_{21}	C(3E)–C(4E)	153.1(4)	5.8(rf)
r_{22}	C(2E)–C(3E)	152.9(4)	6.0(rf)
r_{23}	S(1E)–C(2E)	178.9(3)	6.5(rf)
r_{24}	S(1E)–O(11E)	142.6(2)	4.1(rf)
r_{25}	C(3E)–Br(3E)	193.7(3)	6.4(rf)
r_{26}	S(1E) ··· C(3E)	265.0(5)	7.8 (tied to u_{10})
r_{27}	O(11E) ··· O(12E)	244.6(13)	13.5 (tied to u_{12})
r_{28}	O(11E) ··· C(2E)	265.4(4)	8.9(f)
r_{29}	C(2E) ··· Br(3E)	416.2(12)	16.9 (tied to u_{18})
r_{30}	C(4E) ··· Br(3E)	288.3(4)	7.3 (tied to u_{10})
r_{31}	C(2E) ··· C(4E)	236.0(14)	13.5 (tied to u_{12})
r_{32}	C(2E) ··· C(5E)	258.7(18)	13.5 (tied to u_{12})
r_{33}	S(1E) ··· Br(3E)	439.5(4)	12.1(7)
r_{34}	O(11E) ··· C(3E)	372.2(5)	23.0(f)
r_{35}	O(11E) ··· C(4E)	341.9(9)	43.5(f)
r_{36}	C(2E) ··· Br(4E)	416.2(12)	16.9 (tied to u_{18})
r_{37}	Br(3E) ··· Br(4E)	363.3(13)	17.1 (tied to u_{18})
r_{38}	O(11E) ··· Br(3E)	522.0(8)	24.4(10)
r_{39}	O(11E) ··· Br(4E)	521.4(14)	24.4 (tied to u_{38})

[a] Other Br ··· H, S ··· H, O ··· H and C ··· H distances were included in the refinement (a total of 66), but are not listed here. Estimated standard deviations are given in parentheses; f = fixed at values calculated from the *ab initio* force field; rf = refined then fixed.

Table 5 Least-squares correlation matrix (× 100) for the optimum experimental refinement of the gas-phase structure of $C_4H_6SO_2Br_2$[a]

	p_2	p_3	p_4	p_6	p_8	p_{11}	p_{13}	p_{14}	u_{14}	k_1
p_4		64								
p_6		−52								
p_7		62	−82							
p_8		−62								
p_{11}			62	−80						
p_{13}			−52	64	−72					
p_{14}			56	−74	96	72				
u_{12}	−58							52		
u_{14}				62						
u_{20}				−56	69	−55	69		69	
u_{33}									76	
k_2			58							53

[a] Only absolute elements ≥50 are included; k_1 and k_2 are scale factors.

be present in roughly equal amounts. This has indeed been found in the gas phase where the proportion of the axial form was refined to 47.2(23)%. In the solid state, only the equatorial conformer is present, presumably due to packing effects which preclude the crystallization of the axial form.

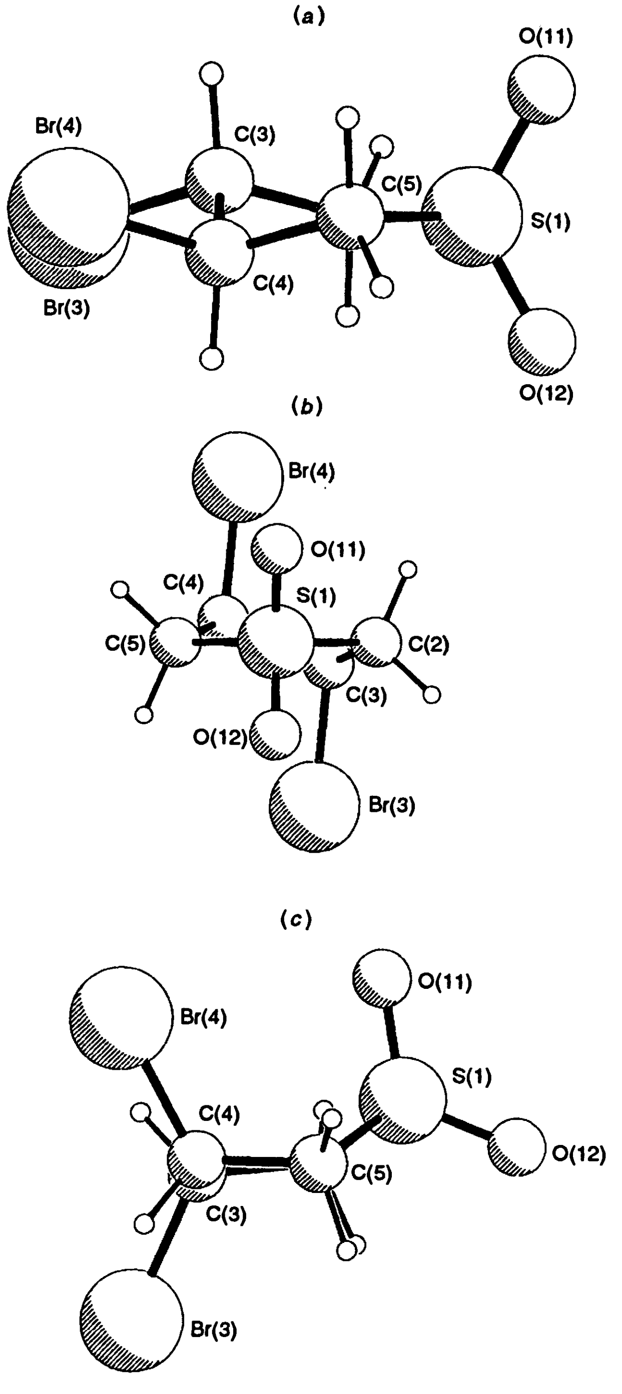

Fig. 5 Views of the *ab initio* optimized geometries for (*a*) the equatorial conformer (C_2), (*b*) the axial conformer (C_2) and (*c*) the transition state (C_1) between the two minima

If the two conformers are present in solution, their interconversion is expected to be quite rapid, at least on the NMR timescale, as found generally for the dynamical behaviour of five-membered rings.[21] In order to estimate the magnitude of the interconversion barrier for 3, the transition structure (TS) between the axial and equatorial conformers was located. A first TS optimization imposing C_2 symmetry afforded a stationary point with an essentially planar SC_4 framework. This, however, showed two imaginary frequencies indicating a 'hilltop' rather than a saddle-point on the potential energy surface. The true TS (one imaginary frequency) was found to possess C_1 symmetry, a slightly twisted C(2)C(3)C(4)C(5) moiety (*ca.* 11°), and an overall envelope conformation {*cf.* the two CCSC dihedral angles of −38° and +32° [Fig. 5(*c*)]}. The computed barrier is relatively large at the SCF/6-31G* level, *ca.* 32 kJ mol^{-1}, but is lowered substantially to *ca.* 17 kJ mol^{-1} by inclusion of electron correlation and zero point corrections. Thus, dynamic methods of NMR spectroscopy can probably not be applied to **3** in solution.[22]

The packing of the (*E*)-3,4-dibromotetrahydrothiophene 1,1-dioxide molecules in the crystal is shown in Fig. 2. The molecules are stacked up the short *a*-axis direction and ordered with the bromine of adjacent columns close to one another [the closest intermolecular Br • • • Br distances are 373.8(3) pm].

Table 6 Theoretical bond lengths (pm) and angles (°)[a]

	Axial	Equatorial
S=O	146.3	146.4
S–C	181.8	181.5
C(2)–C(3)	152.1	152.5
C(3)–C(4)	153.3	152.8
C–Br	197.2	195.0
C–H	109.2	109.3
OSO	121.9	122.5
CSC	95.6	95.3
OSC	109.0	108.9
SCC	106.2	104.9
CCC	108.0	105.7
C(2)–C(3)–Br(3)	111.3	110.7
C(4)–C(3)–Br(3)	107.7	113.2
SCCC	−33.0	39.6
CSCC	−12.1	14.4
CCCC	−43.5	52.2
CCCBr	−76.7	−173.4
SCCBr	85.0	162.4
BrCCBr	163.0	65.3

[a] r_e geometries optimized at the MP2/6-31G* level.

Table 8 shows structural parameters for some tetrahydrothiophene 1,1-dioxides. Although care must be exercised in comparing the results for structures with different substituents and determined by different methods, it would appear that the bond lengths and angles for $C_4H_6Br_2SO_2$ are typical of the values found for other tetrahydrothiophene 1,1-dioxides.

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Table 7 Comparison of the principal structural parameters obtained from the X-ray, electron diffraction (ED) and *ab initio* analyses[a]

		ED[b]		*Ab initio*[c]	
	X-ray	axial	equatorial	axial	equatorial
S=O	143.8(7)	142.5(2)	142.6(2)	146.3	146.4
S–C	179.7(18)	179.2(3)	178.9(3)	181.8	181.5
C(2)–C(3)	154.1(13)[d]	152.5(4)	152.9(4)	152.1	152.5
C(3)–C(4)	152.5(17)	153.7(4)	153.1(4)	153.3	152.7
C–Br	194.7(10)	195.9(3)	193.7(3)	197.2	195.0
OSO	117.7(8)	117.6(8)	118.2(8)	121.9	122.5
CSC	96.4(6)	92.9(10)	92.6(10)	95.6	95.3
CCCC	57.7(15)	−51.9(10)	59.8(9)	43.5	−52.5
BrCCBr	−64.3(20)	−167.9(18)	−70.8(11)	163.0	65.3

[a] Figures in parentheses are the estimated standard deviations. [b] Distances are r_a. [c] r_e geometry optimized at the MP2/6-31G* level. [d] Mean value = $\frac{1}{2}r$[C(2)–C(3)] + $\frac{1}{2}r$[C(4)–C(5)].

Table 8 Mean structural parameters [distances (pm), angles (°)] for some tetrahydrothiophene 1,1-dioxides[a]

Compound	$C_4H_6Ph_2SO_2$	$C_4H_6Ph_2Cl_2$ SO_2	$C_3H_6N_6O_6$, $C_4H_8SO_2$	$C_4H_6Br_2SO_2$	$C_4H_6Br_2SO_2$
S=O	144.1(2)	142.8(1)	143.5(2)	143.8(7)	142.5(1)
S–C	179.7(3)	188.6(1)	177.7(3)	179.7(18)	179.0(3)
C(2)–C(3)	152.5(4)	152.8(2)	150.5(4)	154.5(16)	152.7(4)
C(3)–C(4)	152.5(4)	153.1(2)	151.4(5)	152.5(17)	153.4(4)
C(4)–C(5)	153.7(4)	152.8(2)	151.0(5)	153.8(16)	152.7(10)
OSO	117.2(1)	118.8(1)	116.8(1)	117.7(8)	117.9(10)
CSC	94.5(1)	96.1(1)	96.8(1)	96.4(6)	92.8(7)
Method[b]	XRD[c]	XRD[d]	XRD[e]	XRD[f]	GED[f]

[a] Figures in parentheses are the estimated standard deviations. [b] XRD = X-ray diffraction of a single crystal, GED = gas-phase electron diffraction. [c] Ref. 23: *cis*-2,5-diphenyltetrahydrothiophene 1,1-dioxide. [d] Ref. 23: *trans*-2,5-dichloro-2,5-diphenyltetrahydrothiophene 1,1-dioxide. [e] Ref. 24: 1,3,5-trinitrohexahydrotriazine-sulfolane complex. [f] This work.

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