



# The X-ray Structures of 2- and 3-Sulfolene and Two Halogenated Derivatives

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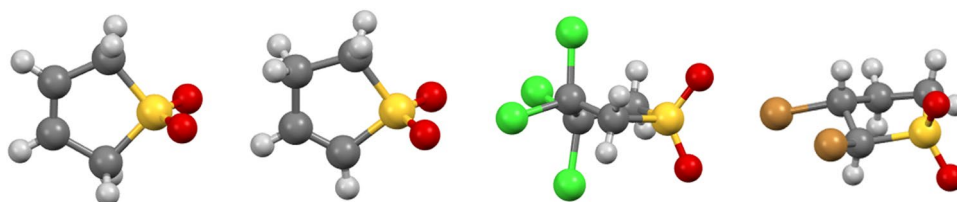
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## Abstract

The structures of the isomeric 2,5-dihydrothiophene 1,1-dioxide [orthorhombic,  $a = 11.340(2)$ ,  $b = 7.0887(15)$ ,  $c = 6.2811(13)$  Å, space group  $Pnma$ ] and 2,3-dihydrothiophene 1,1-dioxide [orthorhombic,  $a = 6.3903(13)$ ,  $b = 7.2783(16)$ ,  $c = 11.075(2)$  Å, space group  $Pnma$ ] have been determined and show perfectly planar rings with the expected bond lengths and angles. In contrast, the halogenated derivatives 3,3,4,4-tetrachlorotetrahydrothiophene 1,1-dioxide [monoclinic,  $a = 11.8716(8)$ ,  $b = 6.5579(4)$ ,  $c = 11.4802(8)$  Å,  $\beta = 97.705(17)$ , space group  $P2_1/c$ ] and 2,3-dibromotetrahydrothiophene 1,1-dioxide [orthorhombic,  $a = 5.2502(3)$ ,  $b = 11.3561(6)$ ,  $c = 24.9802(17)$  Å, space group  $Pbca$ ] both show twisted conformations. The degree of planarity is compared with that in the structures of comparable 5-membered ring cyclic sulfones and C–H...O hydrogen bonding patterns are discussed for all four structures.

## Graphical Abstract

The two isomeric sulfolenes are perfectly planar while tetrachloro- and dibromo-derivatives adopt twisted structures.



**Keywords** Cyclic sulfones · X-ray structure · Conformation

## Introduction

Some time ago we described the X-ray structures of a range of ten symmetrical and unsymmetrical sulfones [1]. Although these included diaryl, aryl alkyl and dialkyl sulfones they were all acyclic. In studies related to the thermal extrusion of SO<sub>2</sub> from cyclic sulfones, we and others have recently reported structures for various cyclic sulfones (Fig. 1) [2–5]. A survey of the structural data for simple cyclic sulfones, particularly those containing a five-membered ring, led to the realisation that the structures of several

key compounds have not yet been determined. In this paper we report the crystal and molecular structures for 2,5-dihydrothiophene 1,1-dioxide (butadiene sulfone, 3-sulfolene) **1**, its isomer 2,3-dihydrothiophene 1,1-dioxide (2-sulfolene) **2** and the halogenated derivatives 3,3,4,4-tetrachlorotetrahydrothiophene 1,1-dioxide **3** and 2,3-dibromotetrahydrothiophene 1,1-dioxide **4** (Scheme 1).

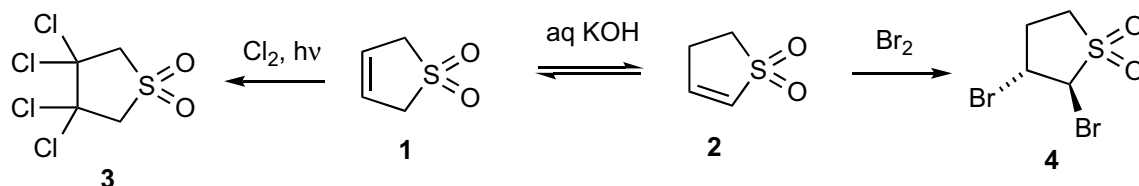
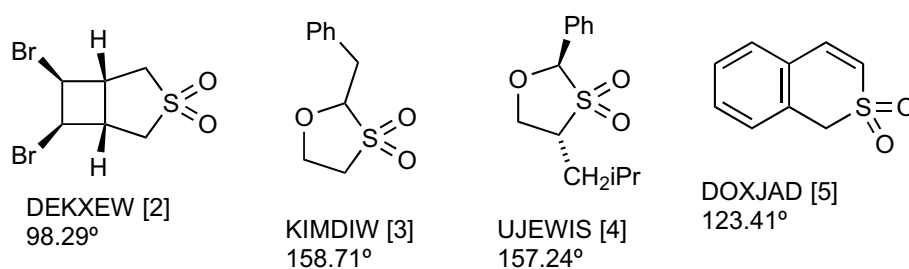
## Experimental

Compound **1** was obtained commercially and converted into the isomer **2** by base-induced isomerisation using the published method [6]. Photochemical chlorination of **1** gave **3** [7, 8] while addition of bromine to **2** gave the *trans*-dibromide **4**

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**Fig. 1** Some recently determined cyclic sulfone structures with CCDC Ref Codes, literature references and sum of in-ring torsion angles



**Scheme 1** Structures and synthetic routes for compounds 1–4

[9, 10]. All four compounds had melting points and spectroscopic data in agreement with published values.

Data were collected on Rigaku XtaLAB P200 (1,2,4) or Rigaku SCX Mini (3) diffractometers using graphite monochromated Mo K $\alpha$  radiation  $\lambda = 0.71075$  Å and are summarised in Table 1. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>. The structures were solved by direct methods and refined by full-matrix least-squares against  $F^2$  (SHELXL, Version 2018/3 [11]).

## Results and Discussion

The structures of 3-sulfolene **1** and 2-sulfolene **2** are shown in Fig. 2 and both are perfectly planar with equivalent oxygen atoms located equidistant above and below the plane containing the ring atoms. The bond lengths and angles (Table 2) are as expected and in good agreement with those observed for acyclic sulfones [1] and the average bond lengths of 1.786 Å for C–S and 1.436 Å for S=O for sulfones in general [12]. The structure of **1** was in fact investigated at a very early stage (Ref Code ZZZGBM) [13], but the methods of that time only allowed some rough information on the unit cell dimensions to be obtained. There is a more recent structure determination, which for some reason is not included in the CSD, that gives a very similar result to ours (space group  $Pnma$ ,  $a = 11.484$ ,  $b = 7.262$ ,  $c = 6.316$  Å) [14]. Whilst wishing to give full credit to this earlier determination, we feel it is important

to finally document the structure of this fundamental compound in the CSD.

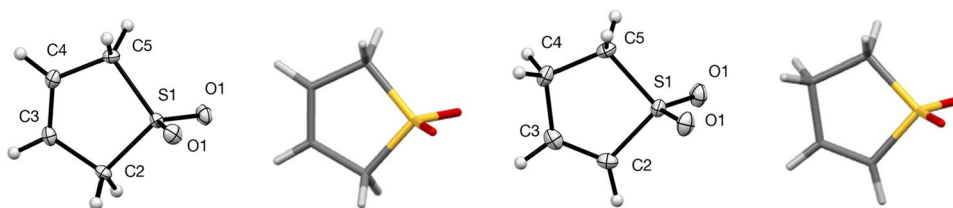
For comparison a range of simple analogues of **1** (Fig. 3) [15–22] and **2** (Fig. 4) [15, 23–26] that have been crystallographically characterised are shown with CSD reference codes, literature references and, as a measure of planarity, the sum of the five in-ring torsion angles. As compared to the structures of **1** and **2** which have all torsion angles zero, we can see that introducing a substituent has a range of effects on the degree of planarity from no effect (IPRNSO) to small (GAMKEK), moderate (BAHQEG, MIXYUN, XOJFUX, WASBOI) and fairly large (BAHQIK, VUFKIS, XUTVUF, VAGXAC). However the presence of a ring double bond in all these compounds limits the possible degree of non-planarity. As might be expected, coordination of the oxygen of **1** to MoCl<sub>5</sub> results in significant lengthening of that S–O bond and movement of sulfur out of the plane of the ring carbons [22].

The structures of both **1** and **2** show a range of weak C–H...O hydrogen bonds and these are listed in Table 3. As shown in Fig. 5, the different position of the double bond between **1** and **2** leads to different higher level motifs with **1** forming  $R^2_2(8)$  dimers while **2** displays  $R^2_1(4)$  interactions.

The structures of halogenated derivatives **3** and **4** are shown in Fig. 6 and, in contrast to those of **1** and **2**, these are significantly twisted with C(3) 0.432 Å above and C(4) 0.261 Å below the plane defined by S(1), C(2) and C(5) in **3**. In the case of **4** there is again a twisted conformation with C(3) 0.489 Å above and C(4) 0.249 Å below the plane defined by S(1), C(2) and C(5), although

**Table 1** Summary of crystallographic data obtained for compounds **1–4**

Compound	1	2	3	4
CCDC deposit no.	2225717	2225718	2225722	2225720
Empirical formula	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> S	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> S	C <sub>4</sub> H <sub>4</sub> Cl <sub>4</sub> O <sub>2</sub> S	C <sub>4</sub> H <sub>6</sub> Br <sub>2</sub> O <sub>2</sub> S
Formula weight	118.15	118.15	257.95	277.96
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pnma</i> (No. 62)	<i>Pnma</i> (No. 62)	<i>P2<sub>1</sub>/c</i> (No. 14)	<i>Pbca</i> (No. 61)
Temperature (K)	93	93	173	93
Crystal form	Colourless prism	Colourless prism	Colourless prism	Colourless prism
Size (mm)	0.10 · 0.05 · 0.05	0.10 · 0.05 · 0.05	0.25 · 0.10 · 0.07	0.12 · 0.03 · 0.03
Unit cell Dimensions (Å, °)	<i>a</i> = 11.340(2) <i>b</i> = 7.0887(15) <i>c</i> = 6.2811(13)	<i>a</i> = 6.3903(13) <i>b</i> = 7.2783(16) <i>c</i> = 11.075(2)	<i>a</i> = 11.8716(8) <i>b</i> = 6.5579(4) <i>c</i> = 11.4802(8) <i>β</i> = 97.705(17)	<i>a</i> = 5.2502(3) <i>b</i> = 11.3561(6) <i>c</i> = 24.9802(17)
Volume (Å <sup>3</sup> )	504.91(17)	515.19(18)	885.70(11)	1489.36(15)
<i>Z</i>	4	4	4	8
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.554	1.523	1.934	2.479
Absorption coefficient	0.512 mm <sup>-1</sup>	0.502 mm <sup>-1</sup>	1.514 mm <sup>-1</sup>	11.122 mm <sup>-1</sup>
<i>F</i> <sub>(000)</sub>	248.00	248.00	512.00	1056.00
<i>θ</i> range	3.593–25.315°	3.349–25.310°	1.731–27.522°	1.630–28.708°
Limiting indices	−13 ≤ <i>h</i> ≤ 13, −8 ≤ <i>k</i> ≤ 8, −7 ≤ <i>l</i> ≤ 7	−7 ≤ <i>h</i> ≤ 7, −8 ≤ <i>k</i> ≤ 8, −13 ≤ <i>l</i> ≤ 13	−15 ≤ <i>h</i> ≤ 15, −8 ≤ <i>k</i> ≤ 8, −14 ≤ <i>l</i> ≤ 14	−6 ≤ <i>h</i> ≤ 7, −14 ≤ <i>k</i> ≤ 14, −30 ≤ <i>l</i> ≤ 32
Refins collected/unique	6856/503	6958/506	8449/2026	21054/1784
<i>R</i> <sub>int</sub>	0.0252	0.0409	0.0818	0.0552
Data/restraints/parameters	503/0/41	506/1/41	2026/0/100	1784/0/82
Data with <i>I</i> > 2 <i>s</i> ( <i>I</i> )	500	490	1459	1529
Goodness of fit on <i>F</i> <sup>2</sup>	0.932	1.068	0.988	1.089
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (data <i>I</i> > 2 <i>s</i> ( <i>I</i> ))	0.0245, 0.0774	0.0260, 0.0776	0.0420, 0.1015	0.0313, 0.0853
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0246, 0.0776	0.0265, 0.0780	0.0664, 0.1111	0.0382, 0.0890
Largest diff. peak/hole (e Å <sup>-2</sup> )	0.394 and −0.341	0.286 and −0.437	0.574 and −0.432	1.079 and −0.662

**Fig. 2** The molecular structure of compounds **1** and **2** showing numbering system used

in this case there is a small torsion angle of  $-9.6(2)$  for C(2)–S(1)–C(5)–C(4) and it is perhaps more accurate to describe it as an envelope conformation with C(3) at the flap. With no double bond present, the deviation from planarity can be much larger and the sum of in-ring torsion angles is  $149.07^\circ$  for **3** and  $160.96^\circ$  for **4**. These values can be compared to the four values between  $172^\circ$

and  $190^\circ$  that occur in the structure of ZUFWIG (Fig. 7), the isomer of **4**.

The parent tetrahydrothiophene dioxide (Ref. Code BUGHOA), although solid at room temperature, forms a plastic phase with disorder from which no detailed information on the conformation can be gained [27], however the isomeric *trans*-3,4-dibromodihydrothiophene dioxide (Ref Code ZUFWIG) obtained by reaction of **1** with

**Table 2** Bond lengths, angle and in ring torsions for **1–4**

Bond Å/angle °	1	2	3	4
S(1)–O(1)	1.4496(10)	1.4499(11)	1.431(2)	1.442(2)
S(1)–O(1/2)	1.4496(10)	1.4499(11)	1.430(3)	1.441(2)
S(1)–C(2)	1.801(2)	1.744(2)	1.800(3)	1.833(3)
C(2)–C(3)	1.500(3)	1.325(3)	1.531(4)	1.524(4)
C(3)–C(4)	1.328(3)	1.502(3)	1.557(4)	1.527(4)
C(4)–C(5)	1.506(2)	1.536(3)	1.518(4)	1.540(4)
C(5)–S(1)	1.7960(18)	1.794(2)	1.816(3)	1.794(3)
C(3)–Cl(1)	–	–	1.766(3)	–
C(3)–Cl(2)	–	–	1.777(3)	–
C(4)–Cl(3)	–	–	1.779(3)	–
C(4)–Cl(4)	–	–	1.772(3)	–
C(2)–Br(2)	–	–	–	1.923(3)
C(3)–Br(3)	–	–	–	1.943(3)
C(5)–S(1)–C(2)	97.81(9)	95.62(10)	96.39(14)	96.14(13)
S(1)–C(2)–C(3)	103.87(13)	111.33(16)	104.97(19)	102.89(18)
C(2)–C(3)–C(4)	117.15(18)	117.85(19)	105.9(2)	105.8(2)
C(3)–C(4)–C(5)	117.61(18)	108.40(16)	106.7(2)	105.7(2)
C(4)–C(5)–S(1)	103.56(13)	106.80(15)	105.6(2)	105.21(19)
O(1)–S(1)–O(1/2)	116.94(8)	115.66(9)	118.83(16)	117.54(13)
C(2)–S(1)–O(1)	110.02(5)	110.73(6)	109.27(14)	109.07(13)
C(2)–S(1)–O(1/2)	110.02(5)	110.73(6)	110.09(16)	110.42(13)
C(5)–S(1)–O(1)	110.19(5)	111.18(6)	110.87(16)	112.01(14)
C(5)–S(1)–O(1/2)	110.19(5)	111.18(6)	109.08(15)	109.59(14)
C(3)–C(4)–C(5)–S(1)	0.0	0.0	34.4(3)	36.2(2)
C(2)–C(3)–C(4)–C(5)	0.0	0.0	–48.4(3)	–52.7(3)
S(1)–C(2)–C(3)–C(4)	0.0	0.0	39.0(2)	43.2(2)
C(5)–S(1)–C(2)–C(3)	0.0	0.0	–17.0(2)	–19.2(2)
C(4)–C(5)–S(1)–C(2)	0.0	0.0	–10.3(2)	–9.6(2)

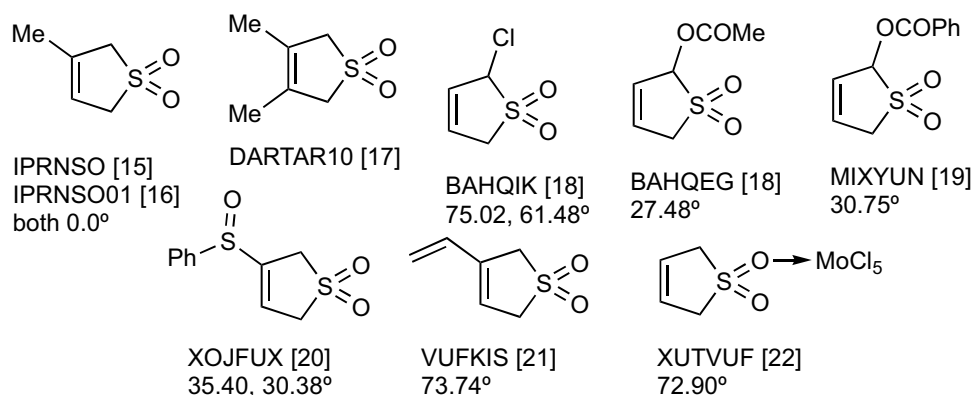
bromine has been found to exhibit an unusual form of disorder in the crystal with the large bromine atoms and the  $\text{CH}_2\text{SO}_2\text{CH}_2$  group remaining relatively fixed but the two  $\text{CH}(\text{Br})$  centres occupying positions above and below the mean molecular plane to give two alternative forms which pack at random (Fig. 7) [28]. No such problems occur in the less symmetrical isomer **4**.

The structures of **3** and **4** also contain a series of weak hydrogen bonding interactions (Fig. 8; Table 3). In **3** the molecules form symmetrical  $R^2_2(8)$  dimers through H(2B) and O(2) which are then linked by a further unsymmetrical  $R^2_2(8)$  interaction involving H(2A)–O(1) and H(5B)–O(1) interactions. In this case there is also a Cl(2)–Cl(4) interaction with a Cl–Cl distance of 3.397 Å. The structure of **4** shows five separate hydrogen bonding interactions with an  $R^2_2(7)$  motif involving H(5A)–O(1) and H(4A)–O(2), an  $R^2_1(6)$  motif involving H(2), H(4B) and O(2), and a further interaction between H(5B) and O(2).

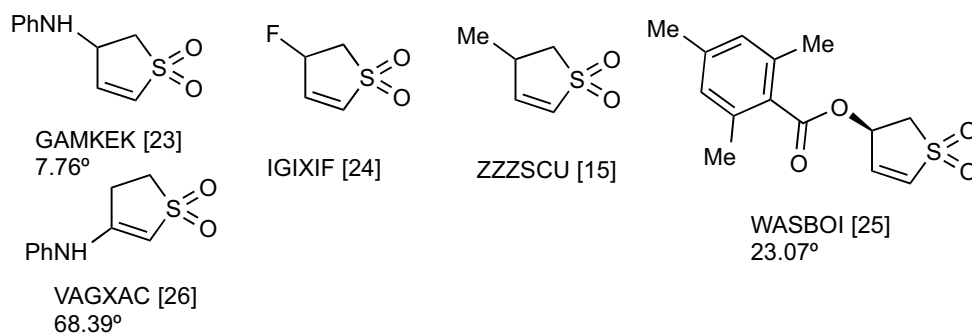
## Conclusion

The crystal and molecular structures of the isomeric 2,5- and 2,3-dihydrothiophene 1,1-dioxides **1** and **2** have been fully documented for the first time and show similar perfectly planar rings with the expected bond lengths and angles. In contrast the 3,3,4,4-tetrachloro- and 2,3-dibromotetrahydrothiophene 1,1-dioxides **3** and **4** are distinctly non-planar with no sign of the disorder that occurs in the previously determined structure of the 3,4-dibromo isomer of **4**.

**Fig. 3** Simple substituted derivatives of **1** with CSD Ref Codes, literature references and sum of in-ring torsion angles



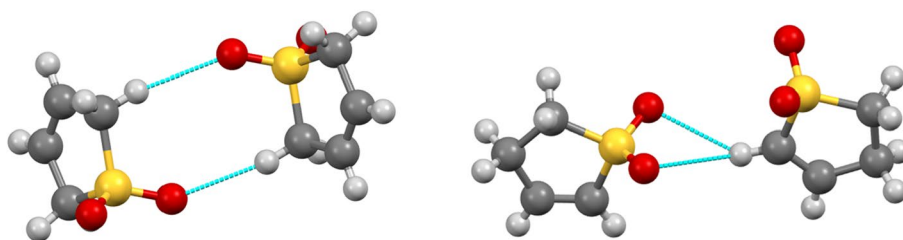
**Fig. 4** Simple substituted derivatives of **2** with CSD Ref Codes, literature references and sum of in-ring torsion angles



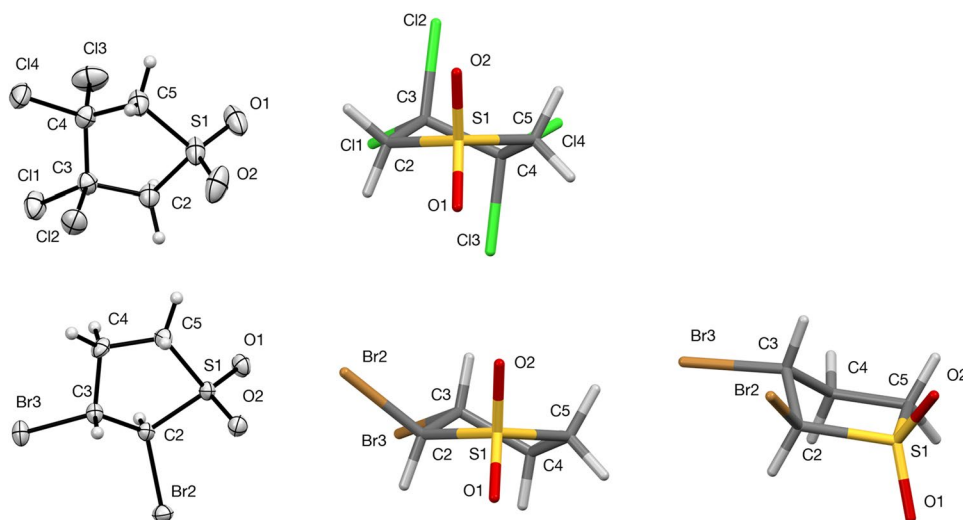
**Table 3** Hydrogen bonding parameters (Å, °)

Compound	D–H...A	D–A	D–H	H...A	Angle DHA
<b>1</b>	C(2)–H(2 A)...O(1)	3.440	0.990	2.510	156.3
	C(5)–H(5 A)...O(1)	3.364	0.990	2.403	163.4
<b>2</b>	C(2)–H(2)...O(1)	3.465	0.950	2.656	143.4
	C(4)–H(4 A)...O(1)	3.563	0.990	2.651	153.2
<b>3</b>	C(5)–H(5 A)...O(1)	3.402	0.990	2.446	162.0
	C(2)–H(2 A)...O(1)	3.274(3)	0.990	2.324	133.9
<b>4</b>	C(5)–H(5B)...O(1)	3.099(4)	0.990	2.521	117.0
	C(2)–H(2B)...O(2)	3.112(4)	0.990	2.531	117.3
	C(5)–H(5 A)...O(1)	3.481(3)	0.990	2.623	145.0
	C(4)–H(4 A)...O(2)	3.411(3)	0.989	2.451	163.6
	C(4)–H(4B)...O(2)	3.360(3)	0.990	2.509	144.0
	C(2)–H(2)...O(2)	3.338(4)	1.000	2.511	139.8
	C(5)–H(B)...O(2)	3.522(3)	0.990	2.605	154.1

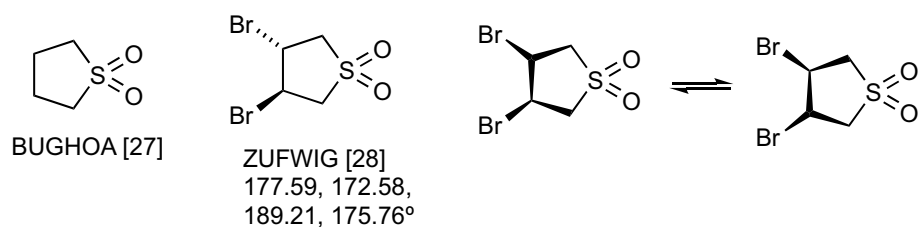
**Fig. 5** Hydrogen bonding motifs in the structures of **1** and **2**



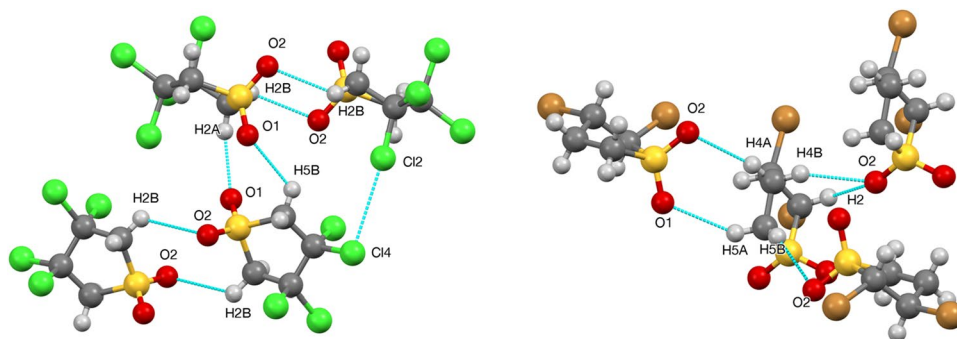
**Fig. 6** The molecular structure of compounds **3** and **4** showing numbering system used



**Fig. 7** Structures of sulfolane and the dibromide isomeric with **4** with CSD Ref Codes, literature references and sum of in-ring torsion angles



**Fig. 8** Hydrogen bonding motif in the structures of **3** and **4**



**Author Contributions** DKS prepared the compounds, collected the diffraction data and came to preliminary structure solutions; AMZ supervised the crystallography and produced the final structure solutions; RAA conceived the study, provided overall supervision and wrote the manuscript. All authors have reviewed and approved the final manuscript.

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**Data Availability** The crystallographic data CIF files have been deposited at the Cambridge Crystallographic Data Centre with deposit numbers as noted in Table 1. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

## Declarations

**Conflict of interest** The authors declare no conflict of interest.

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