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Bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)pentasulfane: an occupancy modulated structure

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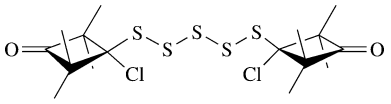
The title compound crystallizes in the space group $P2_1/n$ and may be described by a partial ordering of a 1:1 disordered $P2_1/a$ parent structure with the **c** axis halved. The pentasulfane chain completes a full turn of a helix, which gives molecules containing left- or right-handed helices similar spatial requirements and allows them to be interchanged. The structure can be redescribed as containing 0.732 (1) of an ordered $P2_1/n$ structure and 0.268 (1) of a 1:1 disordered $P2_1/a$ structure, implying that 0.134 (1) of the molecule sites contain molecules of the opposite hand to that predicted by an ordered $P2_1/n$ structure. It is found that the average molecular position in the asymmetric unit is not the same for each component and that these structural differences must be recognized to obtain a satisfactory refinement.

1. Introduction

During the routine crystal structure analyses of a series of bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)oligosulfanes containing 2–6 S atoms (Linden *et al.*, 2002), the structure of the pentasulfane (IV) proved to be troublesome. Although the structure init2ially also appeared to be routine, albeit disordered, unusual bond lengths were detected which could not be corrected by a standard restrained refinement. Constrained refinement imposed by implementing a simple stacking fault mechanism to scale *l* odd reflections differently to *l* even reflections was still not fully satisfactory. The procedures used to complete the model and successfully refine the structure are described here, along with an analysis of the molecular conformation itself.



(IV)

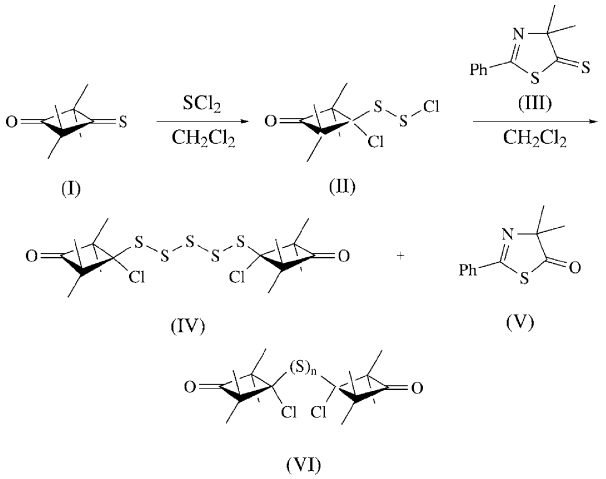
1.1. Chemical background

Recently, we reported the convenient syntheses of the stable 3-chloro-3-(chlorosulfanyl)-2,2,4,4-tetramethylcyclobutan-1-one and 3-chloro-3-(chlorodisulfanyl)-2,2,4,4-tetramethylcyclobutan-1-one (II) compounds, which were prepared by the treatment of 2,2,4,4-tetramethyl-3-thioxocyclobutan-1-one (I) in dichloromethane or tetrachloromethane with a chlorinating reagent such as chlorine (Koch *et al.*, 1999; which can be replaced by phosphorus pentachloride or sulfuryl chloride; Mloston *et al.*, 2002) and sulfur dichloride (Mloston *et al.*, 2002), respectively. It has also

been shown that these compounds undergo smooth reactions with C=S functionalized compounds (Mloston *et al.*, 2002; Majchrzak *et al.*, 2003) to give di- and trisulfanes, respectively. For example, the reaction with (I) yielded the symmetric bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)di- and trisulfane. Similarly, treatment of (I) with disulfur dichloride led to the homologous tetrasulfane, with (1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)trisulfanyl chloride being a likely intermediate (Mloston *et al.*, 2002). Unexpectedly, the reaction of 3-chloro-3-(chlorosulfanyl)-2,2,4,4-tetramethylcyclobutane-1-one with tetrabutylammonium hexasulfane in tetrahydrofurane gave a symmetrical hexasulfane bearing a 2,2,4,4-tetramethyl-3-oxocyclobutyl residue at each terminus (Linden *et al.*, 2002).

An unexpected result was also obtained when (II) was reacted with 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (III) in dichloromethane. Instead of the likely unsymmetrical trisulfane, bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)pentasulfane (IV) and 4,4-dimethyl-2-phenyl-1,3-thiazol-5(4*H*)-one (V) were obtained in equal yields of *ca* 78% (Majchrzak *et al.*, 2003). Apparently, (III) acts as a sulfur transfer reagent (for discussions of sulfur transfer reactions see *e.g.* Senning, 1979; Steudel & Kustos, 1994; Mloston & Heimgartner, 1995; Mloston *et al.*, 1996; Huisgen & Rapp, 1997; Huisgen *et al.*, 1997; Hawata *et al.*, 2000, and references therein) and a reaction mechanism has been proposed (Majchrzak *et al.*, 2003).

Recently, we published the crystal structures of four bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)oligosulfanes (VI) with n = 2, 3, 4 and 6 (Linden *et al.*, 2002). It was found that the polysulfane chain in each structure has a helical conformation, with each additional S atom in the chain adding approximately one quarter of a turn to the helix. The crystal structure of the missing pentasulfane (IV) [= (VI), n = 5] is the subject of the current discourse.



2. Experimental

2.1. Synthesis and characterization

The synthesis of (IV) has been reported by Majchrzak *et al.* (2003) and single crystals of the compound were obtained by slow evaporation from its hexane solution. The spectroscopic data of (IV) and its homologues (VI), n = 2, 3, 4 and 6, are almost identical and do not allow any distinction to be made between them.

2.2. Data collection, structure solution and refinement

Diffraction data were collected at 160 (1) K using a Nonius KappaCCD area-detector diffractometer and graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Data reduction was performed without any special treatment with *HKL Denzo* and *Scalepack* (Otwinowski & Minor, 1997). The intensities were corrected for Lorentz and polarization effects and an absorption correction based on the multi-scan method was applied (Blessing, 1995). The structure was solved by direct methods using *SIR*92 (Altomare *et al.*, 1994). Details of the unit cell, data collection and refinement parameters are given in Table 1, together with details of the software employed.[1] The first column in Table 1 lists the results obtained when the model was developed and refined using standard procedures under the (false) assumption that this was a routine structure. The second column contains the results of the refinement when the structure was treated as an occupancy modulated structure. The initial 'standard' refinement was conducted with all data on F^2. The non-H atoms were refined anisotropically. The methyl H atoms were constrained to an ideal geometry (C—H 0.98 Å), with U_{iso}(H) = 1.5U_{eq}(C), but were allowed to rotate freely about the C—C bonds. The S atoms of the pentasulfane chain and the Cl atoms are disordered over two orientations. Two positions were defined for each of these atoms and refinement of the site occupation factors yielded a value of 0.853 (1) for the major conformer. No correction for secondary extinction was applied. Two reflections, 012 and 101, were suspected of being partially obscured by the beam stop and were omitted from the final refinement.

The refinement of the occupancy modulated model was conducted on F using only the $I > 3\sigma(I)$ reflections. This procedure is described in detail in §3.2. Details of the molecular geometry obtained from each refinement strategy are listed in Tables 2 and 3. The diagrams were produced with the aid of *PLATON* (Spek, 2003).

3. Results and discussion

3.1. The problem

Initially, the structure determination and refinement for compound (IV) appeared to be quite routine. The crystal quality was good, with a mean reflection mosaicity of 0.440 (1)° after data reduction by *DENZO* (Otwinowski & Minor, 1997). The structure solution and refinement were straightforward with the only noteworthy feature being that the S atoms of the pentasulfane chain and the Cl atoms are disordered over two orientations, which can be generated by

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: CK5003). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	Disordered standard model	Occupancy modulated model
Crystal data		
Chemical formula	$C_{16}H_{24}Cl_2O_2S_5$	$C_{16}H_{24}Cl_2O_2S_5$
M_r	479.57	479.57
Cell setting	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, b, c (Å)	11.6666 (1), 8.1343 (1), 23.8366 (2)	11.6666 (1), 8.1343 (1), 23.8366 (2)
β (°)	99.6985 (6)	99.6985 (6)
V (Å^3)	2229.75 (4)	2229.75 (4)
Z	4	4
D_x (Mg m^{-3})	1.428	1.428
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	39 932	39 932
θ range (°)	2.0–30.0	2.0–30.0
μ (mm^{-1})	0.77	0.77
Temperature (K)	160 (1)	160 (1)
Crystal form, colour	Prism, colourless	Prism, colourless
Crystal size (mm)	0.25 × 0.22 × 0.17	0.25 × 0.22 × 0.17
Data collection		
Diffractometer	Nonius KappaCCD area detector	Nonius KappaCCD area detector
Data collection method	ω scans with κ offsets	ω scans with κ offsets
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.811	0.811
T_{max}	0.880	0.880
No. of measured, independent and observed reflections	53 514, 6525, 4992	53 514, 6525, 4992
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	0.053	0.053
θ_{max} (°)	30.0	30.0
Range of h, k, l	$-16 \Rightarrow h \Rightarrow 16$ $-11 \Rightarrow k \Rightarrow 11$ $-33 \Rightarrow l \Rightarrow 33$	$-16 \Rightarrow h \Rightarrow 16$ $-11 \Rightarrow k \Rightarrow 11$ $-33 \Rightarrow l \Rightarrow 33$
Refinement		
Refinement on	F^2	F
R, wR, S	0.033 [$F^2 > 2\sigma(F^2)$], 0.086 (F^2), 1.03	0.039 [$F^2 > 3\sigma(F^2)$], 0.059 (F), 1.42
No. of reflections	6523	4595
No. of parameters	298	188
H-atom treatment	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.5412P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o) + (0.03F_o)^2]$
$(\Delta/\sigma)_{max}$	0.001	0.05
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.31, −0.29	0.51, −0.78

Computer programs used: *COLLECT* (Nonius, 2000), *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997), *SIR*92 (Altomare *et al.*, 1994), *SHELXL*97 (Sheldrick, 1997), *RAELS*00 (Rae, 2000), *PLATON* (Spek, 2003).

swapping the positions of the S and Cl substituents on each cyclobutanyl ring and inverting the screw direction of the helix formed by the pentasulfane chain. However, the disorder could be treated routinely without restraints (see §2.2) and it was found by refinement of the site occupation factors of the disordered atoms that the major conformer is present in approximately 85% of the molecules. After the model refinement was completed, all the usual structure quality indicators (Tables 1 and 2), such as R factors, residual electron density, the precision of the atomic and geometric parameters, and the atomic displacement parameters, were excellent. The resulting model for the molecule is depicted in Fig. 1, which, to the eye, appears to be quite normal.

Examination of the bond lengths, however, revealed some startling features. For the minor conformer, the C—Cl bonds were far too long at around 1.97 Å, while the C—S bond lengths were quite short and in the range 1.67–1.71 Å (Table 2). Even for the major conformer, the C—Cl and C—S bonds were slightly longer and shorter, respectively, than their counterparts in the structures of the n = 2, 3, 4 and 6 oligo-

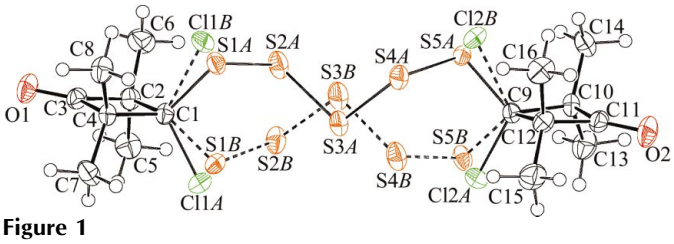


Figure 1
View of the molecule of (IV) after refinement of the initial disordered and inadequate model by standard procedures. The atom labelling scheme and both of the disordered conformations are shown and the view does not reveal any obvious disquieting features. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii.

Table 2
Selected geometric parameters (Å, °) in the initial disordered model.

Cl1*A*—C1	1.8204 (14)	Cl1*B*—C1	1.983 (4)
Cl2*A*—C9	1.8188 (14)	Cl2*B*—C9	1.966 (4)
S1*A*—C1	1.7946 (14)	S1*B*—C1	1.660 (4)
S5*A*—C9	1.7914 (15)	S5*B*—C9	1.707 (4)
S1*A*—S2*A*	2.0361 (7)	S5*B*—S4*B*	2.033 (4)
S2*A*—S3*A*	2.0623 (8)	S4*B*—S3*B*	2.070 (5)
S3*A*—S4*A*	2.0589 (8)	S3*B*—S2*B*	2.054 (5)
S4*A*—S5*A*	2.0370 (8)	S2*B*—S1*B*	2.044 (4)
C1—S1*A*—S2*A*	102.95 (5)	C1—S1*B*—S2*B*	105.5 (2)
S1*A*—S2*A*—S3*A*	106.86 (3)	S1*B*—S2*B*—S3*B*	107.46 (19)
S2*A*—S3*A*—S4*A*	105.56 (3)	S2*B*—S3*B*—S4*B*	105.9 (2)
S3*A*—S4*A*—S5*A*	107.35 (3)	S3*B*—S4*B*—S5*B*	107.85 (19)
S4*A*—S5*A*—C9	102.02 (5)	S4*B*—S5*B*—C9	103.56 (19)
S1*A*—C1—Cl1*A*	107.79 (7)	S5*A*—C9—Cl2*A*	108.06 (7)
S1*B*—C1—Cl1*B*	106.02 (17)	S5*B*—C9—Cl2*B*	105.24 (18)

sulfanes (Linden *et al.*, 2002), where the C—Cl and C—S bond lengths are in the ranges 1.78–1.81 and 1.81–1.85 Å, respectively. One might conclude that suitable restraints need only be applied to the model, particularly to the atoms of the minor conformer, in order to obtain appropriate geometric parameters. However, attempts to do this yielded unsatisfactory results. Firstly, very strong restraints were required to correct the recalcitrant bond lengths. This led to a significant elevation of the *R* factors, significant peaks of residual electron density, particularly in the vicinity of the unrestrained positions for the Cl atoms, and quite unreasonable atomic displacement parameters for the restrained Cl and S atoms.

A second observation was that data validation (Spek, 2003) run on the unrestrained model suggested that there was overlooked symmetry, which could be accounted for by halving the length of the unit-cell **c** axis and changing the space group from $P2_1/n$ to $P2_1/a$. However, the molecule would then lie on a crystallographic centre of inversion, imposing a 1:1 disorder in the smaller unit cell. An attempt at refining the model in the smaller unit cell, with its imposed 1:1 disorder, produced refinement results of a quality similar to those from the refinement in the larger unit cell, but did not remove the inconsistencies in the lengths of the C—Cl and C—S bonds.

The findings suggest that the observed geometry in the unrestrained model is not simply a result of instability in the refinement, caused by the disorder and pseudo-symmetry, but has its origin in the physical make-up of the crystal structure itself, which cannot be readily described by the above models. The derivation of the correct model for the description of this crystal structure is the subject of the remaining discussion.

The Fourier transform of the *l* even relections of a $P2_1/n$ structure necessarily has $P2_1/a$ symmetry for the cell $\mathbf{a}_p = \mathbf{a}$, $\mathbf{b}_p = \mathbf{b}$, $\mathbf{c}_p = \mathbf{c}/2$. Any symmetry operator $(\mathbf{R},\mathbf{t}_1\mathbf{a} + \mathbf{t}_2\mathbf{b} + \mathbf{t}_3\mathbf{c})$ of $P2_1/n$ becomes the symmetry operator $(\mathbf{R},\mathbf{t}_1\mathbf{a}_p + \mathbf{t}_2\mathbf{b}_p + 2\mathbf{t}_3\mathbf{c}_p)$ of $P2_1/a$. There is then an exact 1:1 disorder imposed by the true inversion centre of $P2_1/a$ at the $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ site which corresponds to the inversion-related sites $\frac{1}{2},\frac{1}{2},\frac{1}{4}$ and $\frac{1}{2},\frac{1}{2},\frac{3}{4}$ of $P2_1/n$, since $z_p\mathbf{c}_p = 2z\mathbf{c}_p = z\mathbf{c}$. The structure has pseudo-centrosymmetric molecules at these sites and their equivalents and a choice of handedness at each site is laid down at the time of crystallization. These choices produce mistakes and molecules of the wrong handedness for an ordered $P2_1/n$ structure occur at $\sim 1/8$ th of the sites.

Table 3
Selected geometric parameters (Å, °) in the occupancy modulated model.

Cl1—C1	1.797 (2)	S3—S4	2.059 (1)
Cl2—C9	1.799 (2)	S4—S5	2.040 (1)
S1—C1	1.817 (2)	S11—S21	2.038 (1)
S5—C9	1.811 (2)	S21—S31	2.061 (1)
S1—S2	2.038 (1)	S31—S41	2.059 (1)
S2—S3	2.061 (1)	S41—S51	2.040 (1)
Cl1—C1—S1	108.0 (1)	S4—S5—C9	101.5 (1)
Cl2—C9—S5	108.2 (1)	C011—S11—S21	105.3 (1)
C1—S1—S2	102.7 (1)	S11—S21—S31	105.9 (2)
S1—S2—S3	107.1 (1)	S31—S41—S51	107.8 (2)
S2—S3—S4	105.5 (1)	S21—S31—S41	105.8 (2)
S3—S4—S5	107.4 (1)	C091—S51—S41	99.5 (1)
C1—S1—S2—S3	−92.6 (1)	C011—S11—S21—S31	−91.1 (2)
S1—S2—S3—S4	−91.9 (1)	S11—S21—S31—S41	−98.4 (2)
S2—S3—S4—S5	−94.1 (1)	S21—S31—S41—S51	−88.1 (2)
S3—S4—S5—C9	−91.8 (1)	S31—S41—S51—C091	−93.6 (2)
Cl1—C1—S1—S2	61.6 (1)	Cl11—C011—S11—S21	59.8 (1)
Cl2—C9—S5—S4	63.3 (1)	Cl21—C091—S51—S41	65.8 (1)

Table 4
Final refinement statistics for the occupancy modulated model.

Reflection class	Number of reflections	$R(F)$	$R(F^2)$	$wR(F)$	*GoF*
l even, $I_o(\mathbf{h}) \geq 3\sigma[I_o(\mathbf{h})]$	2386	0.036	0.048	0.058	1.44
l odd, $I_o(\mathbf{h}) \geq 3\sigma[I_o(\mathbf{h})]$	2209	0.043	0.063	0.060	1.40
All with $I_o(\mathbf{h}) \geq 3\sigma[I_o(\mathbf{h})]$	4595	0.039	0.052	0.059	1.42
All with $I_o(\mathbf{h}) < 3\sigma[I_o(\mathbf{h})]$†	1929	0.345	0.527	0.398	1.28

† Reflections not included in the refinement.

Additional data sets were collected using another crystal obtained from a second recrystallization of the material. Both the temperature used for the original data collection (160 K) and room temperature were employed. The resulting structural models had the same features. Therefore, the unusual structure is probably representative of the bulk crystalline material, rather than being a one-off chance selection of a rogue crystal.

It is worth mentioning that, at 160 K, the monoclinic unit-cell dimensions for this second crystal were $a = 11.7019\ (2)$, $b = 8.1514\ (2)$, $c = 23.8499\ (4)$ Å, $\beta = 99.9046\ (10)^\circ$, while at room temperature they were $a = 11.7905\ (2)$, $b = 8.1926\ (2)$, $c = 24.0312\ (5)$ Å, $\beta = 100.3711\ (11)^\circ$. The differences between the unit-cell parameters for the two determinations at 160 K (*cf.* Table 1) demonstrate the severe underestimation of the standard uncertainties of these parameters that are frequently being derived by the least-squares techniques currently incorporated into much of the modern diffractometer software.

3.2. Refinement as an occupancy modulated structure

As indicated in Table 1, the observed monoclinic unit cell has $a = 11.6666\ (1)$, $b = 8.1343\ (1)$, $c = 23.8366\ (2)$ Å, $\beta =$

99.6985 (6)° with $Z = 4$ and the systematic absences correspond with the space group $P2_1/n$.

The crystal structure can be regarded as an occupancy modulation of an idealized 1:1 disordered $Z = 2$ parent structure in the space group $P2_1/a$ ($\mathbf{a}_p = \mathbf{a}$, $\mathbf{b}_p = \mathbf{b}$, $\mathbf{c}_p = \mathbf{c}/2$). Pseudo-centrosymmetric molecules lie on inversion centres in this structure. There are a number of possible orderings modulo the observed cell ($\mathbf{a} = \mathbf{a}_p$, $\mathbf{b} = \mathbf{b}_p$, $\mathbf{c} = 2\mathbf{c}_p$) of this disordered parent structure with scattering density $\rho_1(\mathbf{r})$. The four equivalent positions of $P2_1/a$ modulo the parent cell become eight equivalent positions modulo the observed cell. Partial ordering requires a statistical distribution between inversion-related molecules at each of four sites per cell. Irreducible representation theory indicates that the generalized partial ordering requiring eight population parameters P_m can be described using eight symmetrized components p_n.

Equivalent position	Population
x, y, z	$P_1 = p_1 + p_2 + p_3 + p_4 + p_5 + p_6 + p_7 + p_8$
$-x, -y, -z$	$P_2 = p_1 + p_2 - p_3 - p_4 + p_5 + p_6 - p_7 - p_8$
$-x + \frac{1}{2}, y + \frac{1}{2}, -z$	$P_3 = p_1 - p_2 + p_3 - p_4 + p_5 - p_6 + p_7 - p_8$
$x + \frac{1}{2}, -y + \frac{1}{2}, z$	$P_4 = p_1 - p_2 - p_3 + p_4 + p_5 - p_6 - p_7 + p_8$
$x, y, z + \frac{1}{2}$	$P_5 = p_1 + p_2 + p_3 + p_4 - p_5 - p_6 - p_7 - p_8$
$-x, -y, -z + \frac{1}{2}$	$P_6 = p_1 + p_2 - p_3 - p_4 - p_5 - p_6 + p_7 + p_8$
$-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$	$P_7 = p_1 - p_2 + p_3 - p_4 - p_5 + p_6 - p_7 + p_8$
$x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$	$P_8 = p_1 - p_2 - p_3 + p_4 - p_5 + p_6 + p_7 - p_8$

In other words, $P_m = \Sigma_n \chi_{mn} p_n$, where χ_{mn} is a coefficient, in this instance ± 1, associated with the mth symmetry operator $(\mathbf{R}_m, \mathbf{t}_m)$. The inverse relationship is $p_n = (1/8)\Sigma_m \chi^*_{mn} P_m$. The scattering density can be described as $\rho(\mathbf{r}) = \Sigma_n p_n \rho_n(\mathbf{r})$, where $p_n\rho_n(\mathbf{r})$ is the scattering density obtained by putting $p_{n'} = 0$ for $n' \neq n$ when evaluating the populations P_m.

The first four components $p_n\rho_n(\mathbf{r})$ corresponding to p_1, p_2, p_3, p_4 have different symmetries modulo the parent cell $\mathbf{a}_p$, $\mathbf{b}_p$, $\mathbf{c}_p$, *viz.* $P2_1/a$, $P\bar{1}$, $P2_1$, Pa, while the second four components have symmetries modulo the observed cell $\mathbf{a}_p$, $\mathbf{b}_p$, $2\mathbf{c}_p$, *viz.* $P2_1/a$, $P2_1/n$, $P2_1/n$, $P2_1/a$. The components $p_n\rho_n(\mathbf{r})$ are antisymmetric with respect to the remaining symmetry elements of $P2_1/a$ modulo $\mathbf{a}_p$, $\mathbf{b}_p$, $\mathbf{c}_p$ not implied by the above labels. For a disordered molecule pair at $\frac{1}{2},\frac{1}{2},\frac{1}{4}$ and its equivalents, it is necessary that $P_1 + P_6 = P_2 + P_5 = P_3 + P_8 = P_4 + P_7 = 1.0$. It then follows that $p_1 = \frac{1}{2}$ and $p_2 = p_7 = p_8 = 0$ and since $0 \leq P_i \leq 1$ for $i = 1$ to 8, it follows that $|p_3| + |p_4| + |p_5| + |p_6| \leq \frac{1}{2}$. If one of p_3, p_4, p_5 or p_6 is $\pm\frac{1}{2}$, then the remainder are 0 and we obtain a perfectly ordered structure. The sign selects between inversion equivalents (p_3 and p_4) or origins $\frac{1}{2}\mathbf{c} = \mathbf{c}_p$ apart (p_5 and p_6).

It is thus reasonable to consider the structure as having five possible symmetrized components. One is the disordered parent structure and the other four are perfectly ordered structures (allowing for the atomic displacement parameters U^{ij} to describe Gaussian variations in positions) in the proportions $[1 - 2(|p_3| + |p_4| + |p_7| + |p_8|)]{:}2|p_3|{:}2|p_4|{:}2|p_5|{:}2|p_6|$. *It is not necessarily reasonable* to impose the extra condition that the average molecule in the reference equivalent position is in the same orientation or location with the same atomic displacement parameters for all five components, although this is a good initial model for constrained refinement. This realisation was a necessary precursor to the eventual successful refinement

Let us now consider the structure factors which we can describe as $F(\mathbf{H}) = \Sigma_n F_n(\mathbf{H})$, where $F_n(\mathbf{H})$ is the structure factor corresponding to the symmetrized component $p_n\rho_n(\mathbf{r})$ (see above), now created by taking the true electron density $\rho(\mathbf{r})$ and creating the components $\rho_n(\mathbf{r}) = (1/8)\Sigma_m \chi^*_{mn} \rho(\mathbf{R}_m\mathbf{r} + \mathbf{t}_m)$. Thus, $F_n(\mathbf{H}) = (1/8)\Sigma_m \chi^*_{mn} \exp(2\pi i \mathbf{H}\cdot\mathbf{t}_m) F(\mathbf{R}_m^{-1}\mathbf{H})$ and $F(\mathbf{R}_m^{-1}\mathbf{H}) = \exp(-2\pi i \mathbf{H}\cdot\mathbf{t}_m)\Sigma_n \chi_{mn} F_n(\mathbf{H})$, *i.e.*

$$
\begin{aligned}
F_1(\mathbf{H}) &= (1/8)[1 + (-1)^l][[F(\mathbf{H}) + F(-\mathbf{H})] \\
&\quad + (-1)^{h+k}[F(2\mathbf{H}) + F(\mathbf{mH})]] \\
F_2(\mathbf{H}) &= (1/8)[1 + (-1)^l][[F(\mathbf{H}) + F(-\mathbf{H})] \\
&\quad - (-1)^{h+k}[F(2\mathbf{H}) + F(\mathbf{mH})]] \\
F_3(\mathbf{H}) &= (1/8)[1 + (-1)^l][[F(\mathbf{H}) - F(-\mathbf{H})] \\
&\quad + (-1)^{h+k}[F(2\mathbf{H}) - F(\mathbf{mH})]] \\
F_4(\mathbf{H}) &= (1/8)[1 + (-1)^l][[F(\mathbf{H}) - F(-\mathbf{H})] \\
&\quad - (-1)^{h+k}[F(2\mathbf{H}) - F(\mathbf{mH})]] \\
F_5(\mathbf{H}) &= (1/8)[1 - (-1)^l][[F(\mathbf{H}) + F(-\mathbf{H})] \\
&\quad + (-1)^{h+k}[F(2\mathbf{H}) + F(\mathbf{mH})]] \\
F_6(\mathbf{H}) &= (1/8)[1 - (-1)^l][[F(\mathbf{H}) + F(-\mathbf{H})] \\
&\quad - (-1)^{h+k}[F(2\mathbf{H}) + F(\mathbf{mH})]] \\
F_7(\mathbf{H}) &= (1/8)[1 - (-1)^l][[F(\mathbf{H}) - F(-\mathbf{H})] \\
&\quad + (-1)^{h+k}[F(2\mathbf{H}) - F(\mathbf{mH})]] \\
F_8(\mathbf{H}) &= (1/8)[1 - (-1)^l][[F(\mathbf{H}) - F(-\mathbf{H})] \\
&\quad - (-1)^{h+k}[F(2\mathbf{H}) - F(\mathbf{mH})]].
\end{aligned}
$$

Note that $\Sigma_n |F_n(\mathbf{H})|^2 = (1/4)[|F(\mathbf{H})|^2 + |F(-\mathbf{H})|^2 + |F(2\mathbf{H})|^2 + |F(\mathbf{mH})|^2]$ and a perfectly twinned crystal sees intensities which are the uncorrelated addition of intensity contributions from the symmetrized components. This concept may be generalized for any space group. To a first approximation, $\langle |F_n(\mathbf{H})|^2 \rangle$ varies as $|p_n|^2$ making $F_2(\mathbf{H}) = F_7(\mathbf{H}) = F_8(\mathbf{H}) = 0$.

The crystal of (IV) had $2/m$ diffraction symmetry for both l even and l odd reflections. The n glide absence condition implied that $F_3(\mathbf{H}) = 0$ and $F_5(\mathbf{H}) = 0$ so that $F_6(\mathbf{H})$ is the only non-zero contributor to the l odd reflections and $F_1(\mathbf{H})$ and possibly $F_4(\mathbf{H})$ are the only non-zero contributors to the l even reflections. These reflections then have monoclinic diffraction symmetry without twinning. Our first refinement model was therefore to assume the same reference molecule applied to all equivalent positions of all component structures and that only $F_1(\mathbf{H})$ and $F_6(\mathbf{H})$ are non-zero. This model corresponds to a fully correlated coexistence of $(1 - 2p_6)$ of a 1:1 disordered $P2_1/a$ structure modulo the parent cell, and $2p_6$ of a perfectly ordered $P2_1/n$ structure with inversion centres coincident at the origin and the reference molecule centred about $\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$ with respect to the cell $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. The parameter $p_1 = \frac{1}{2}$ necessarily, see above. If $p_6 = \frac{1}{2}$, then we have a perfectly ordered $P2_1/n$ structure, $F_1(\mathbf{H})$ is the Fourier transform of the scattering

density $[\rho(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{c}/2)]/2$ which has $P2_1/a$ symmetry and is only non-zero for the l even reflections, while $F_6(\mathbf{H})$ is the *Fourier* transform of the scattering density $[\rho(\mathbf{r}) - \rho(\mathbf{r} + \mathbf{c}/2)]/2$ and is only non-zero for the l odd reflections. Changing the value of p_6 simply changes the scale of $F_6(\mathbf{H})$ by $2p_6 \leq 1$ and corresponds to a simple stacking fault, *i.e.* some of the unit cells are translated by $\mathbf{c}/2$.

The reflection data with l odd were given a different scale constant from those reflections with l even and the structure refined as a perfectly ordered $P2_1/n$ structure. A value of $2p_6 = 0.762$ (3) was obtained. Although reasonable molecular geometry was obtained, thereby correcting the anomalous C—Cl and C—S bond lengths produced by the standard refinement (see §3.1), the data fit was not as good as hoped for: $R(F) = 0.063$ for the 2386 l even reflections with $I > 3\sigma(I)$ and 0.071 for the 2209 l odd reflections with $I > 3\sigma(I)$; the values for the goodness-of-fit were 2.36 and 2.47, respectively. An uncorrelated 3% error in F was included in evaluating weights, $w = 1/[\sigma^2(F) + (0.03\ F)^2]$, where the $\sigma^2(F)$ values were obtained from counting statistics and data merging. In this refinement, pseudo-inversion-related C atoms were constrained to have the same anisotropic atomic displacement parameters. The subsequent difference-Fourier map showed large residual electron density near the positions corresponding to $\frac{1}{2}\mathbf{c}$ translations of the S atom positions in the ordered model. In the 'average structure', *viz.* $[\rho(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{c}/2)]/2$, pseudo-inversion-related atoms of the reference molecule can overlap because of the imposed symmetry element $(1 - x,\ 1 - y,\ 1/2 - z)$. Only the S and Cl atoms are not strongly overlapped. Even then, atom S1 is close to atom Cl2′ (′ implies pseudo-inversion-related), atom S5 is close to atom Cl1′, and atom S3 is close to atom S3′, leaving only atoms S2 and S4 clearly resolved. The largest peaks in the difference-Fourier map corresponded to atoms S2′ and S4′, but not in an exact relationship.

Thus, despite using two scale constants to avoid the refinement problems associated with overlapping atoms, one is forced to contemplate a refinement where the average molecule associated with the different components, $F_n(\mathbf{H})$, changes with the value of n. In other words, when a mistake is made in the dominantly $P2_1/n$ structure by including a molecule in a position that is pseudo-inversion-related to that predicted by $P2_1/n$, the operation $(-x, -y, \frac{1}{2} - z)$ modulo the observed cell is not a sufficiently accurate description of reality. It is to be noted that in the absence of anomalous dispersion the observed intensities can be written as $|F_1(\mathbf{H})|^2 + |F_4(\mathbf{H})|^2$ for l even and $|F_6(\mathbf{H})|^2$ for l odd. The existence of $F_4(\mathbf{H})$ could induce an $F_7(\mathbf{H})$ component, as allowed by Pn symmetry, so that the observed intensity for l odd becomes $|F_6(\mathbf{H})|^2 + |F_7(\mathbf{H})|^2$. The generation of such a component would be by atom displacement, not by changing populations. The lack of correlation between the $F_n(\mathbf{H})$ components implies they would make independent assessments of the reference molecule should these components be refinable in isolation. Problems with data partitioning and scaling usually make refinement using a single component $|F_n(\mathbf{H})|^2$ impractical.

A partially ordered Pn structure model was then refined using the program *RAELS*00 (Rae, 2000). The program allows molecules to be described using refinable local orthonormal coordinates relative to refinable axial systems (Rae, 1975) or multiple axial systems (Haller *et al.*, 1995; Rae & Willis, 2003), which is a strategy that cannot readily be emulated by the current more commonly used structure refinement programs. This allowed the use of four molecules in the asymmetric unit. Molecules 1 and 4 had equal occupancy and were related by an exact inversion centre so that on their own $P2_1/n$ symmetry resulted and these molecules do not contribute to $F_4(\mathbf{H})$ or $F_7(\mathbf{H})$. Molecules 2 and 3 had equal occupancies and were related by an exact translation of $\mathbf{c}/2$, so that on their own an exact Pa symmetry, modulo the parent cell, resulted and these molecules do not contribute to $F_6(\mathbf{H})$ or $F_7(\mathbf{H})$. All molecules contribute to $F_1(\mathbf{H})$. The first and second molecules were coincident to start with, but after that their axial systems were refined independently. The same local coordinates for the C atoms and the attached S and Cl atoms were used for all molecules. The S2, S3 and S4 atoms were allowed to vary independently for both molecules 1 and 2, but weak restraints were applied to make any differences in the corresponding S—S distances approach zero. Two scale constants were used to permit an extra degree of freedom to allow for a disordered $P2_1/a$ component. This model allows some rudimentary investigation of polytypic behaviour, *i.e.* ordered domains of different symmetries, $P2_1/a$, Pa and $P2_1/n$, as has been observed by Rae & Willis (2003). In such a description of our just described model, the $P2_1/a$ domain is a stacking fault disordering of the $P2_1/n$ domain. Twinning was ignored as its consequences would be undetectable because of the minimal anomalous scattering with Mo $K\alpha$ radiation.

All atoms related by pseudo-translation or pseudo-inversion were constrained to have the same anisotropic atomic displacement parameters. The H atoms were relocated in geometrically sensible positions after each refinement cycle (C—H 1.00 Å). Standard deviations were calculated using the inverse of the least-squares matrix and assume the correctness of the various constraints and restraints described above. This refinement behaved and caused some improvement in agreement parameters. There were no significant peaks on the final difference-Fourier map.

However, on changing the space group from Pn to $P2_1/n$ by imposing an exact centre of inversion at the origin, a totally satisfactory refinement (Table 4) was obtained using a single scale constant for all reflections. This model then consists of $F_1(\mathbf{H})$ and $F_6(\mathbf{H})$ only and is composed of 0.732 (1) of a $P2_1/n$ structure and 0.268 (1) of a $P2_1/a$ structure. Molecule 4 can then be removed and the site occupation factors adjusted appropriately. This is the final result presented in Tables 1 and 3, and Fig. 2. Both component structures contribute to the l even reflections, but only the major component contributes to the l odd reflections. The reference molecules for the two components have their midpoints of the C1···C9 axis 0.016 (1) Å apart and their reference frames differ by a rotation of 1.71 (3)°. The rotation is roughly about the C1···C9 direction, these directions being 0.12 (3)° apart.

The proportions of the $P2_1/n$ and $P2_1/a$ structures in the crystal are consistent with the ratio of disordered conformers found in the original refinement described in §3.1, *i.e.* by using a disordered model solely in $P2_1/n$. This is because molecule 1 from the $P2_1/n$ component and molecule 2 from the $P2_1/a$ component closely overlap (Fig. 3), so would have been indistinguishable in the original model and would have a site occupation therein of $0.732 + \frac{1}{2}(0.268) = 0.866$, which agrees exceptionally well with the site occupation factor of 0.853 (1) found for the major conformer in the original standard model. The inversion of molecule 3 also places it coincident with the positions of molecules 1 and 2 (Fig. 4), with the exception that the inversion reverses the helicity of the pentasulfane chain, thereby leading to the observed disorder of the S and Cl atoms in the original model. The site occupation factor for molecule 3 of 0.134 (1) also consequently agrees with that found for the minor conformer in the original model [0.147 (1)].

We have described the structure as the sum of two components, 0.732 of an ordered $P2_1/n$ structure (reference molecule $M1'$) and 0.268 of a 1:1 disordered $P2_1/a$ structure (reference molecule $M2'$), so as to isolate one component of the reflection data (l odd reflections) with the major component. Features of this component were then used to constrain the description of the minor component using the program *RAELS*00 (Rae, 2000). Equivalently, the structure could be described as a $P2_1/n$ structure with a 0.866:0.134 disorder modulo the unit cell between different handed molecules ($M1$ and $M2$) at the general position $\frac{1}{2},\frac{1}{2},\frac{1}{4}$. The l even reflections would then see 0.866 of the major component plus 0.134 of the minor component, whereas the l odd reflections see 0.866 of the major component minus 0.134 of the minor component.

A linear algebra description is appropriate, implying $0.732M1' + 0.268M2' = 0.866M1 + 0.134M2$ and $0.732M1' = 0.866M1 - 0.134M2$ so that $M2 = M2'$ and $M1 = (0.732M1' + 0.134M2')/0.866$ supplies a recipe for obtaining the coordinates of $M1$ and $M2$ from those of $M1'$ and $M2'$. A stacking fault model would say $M1$ and $M2$ are identical and, although simplifying the refinement, does not produce as good a refinement. When mistakes are made in the structure, an exact operation $1-x, 1-y, \frac{1}{2}-z$ to describe the minor component at the refence molecule position is not sufficiently accurate.

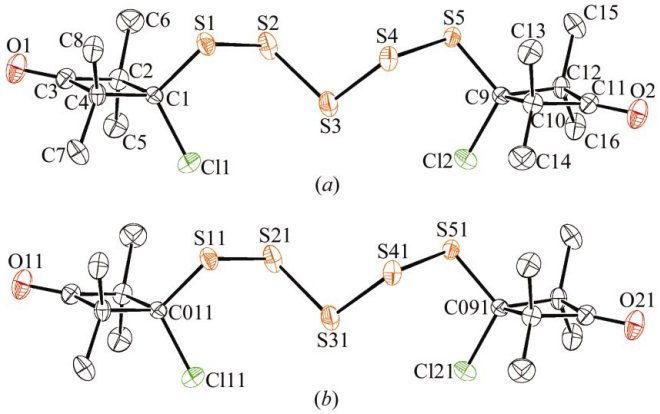


Figure 2
Views of (*a*) molecule 1 and (*b*) molecule 2 in the occupancy modulated model. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Molecule 3 was constrained to be identical with molecule 2, except for a translation of **c**/2, so is not depicted.

3.3. The molecular conformation

This discussion is based on the results from the final refinement of the occupancy modulated model. All bond lengths and angles within each of the three molecules used in the model are now in complete agreement with their counterparts in the structures of the corresponding oligosulfanes with 2, 3, 4 and 6 S atoms (Linden *et al.*, 2002). Table 3 lists selected non-redundant geometric parameters and it should be borne in mind that, with the exception of atoms S21, S31 and S41 in molecule 2, the three 'independent' molecules were constrained to have the same geometry.

Linden *et al.* (2002) remarked that the polysulfane chain in the corresponding oligosulfanes with 2, 3, 4 and 6 S atoms always has a helical conformation. The magnitudes of the torsion angles about the S—S bonds were found to be fairly constant and lie between 83 and 101°, while in any one structure, successive torsion angles along the chain have the same sign. Thus, the compounds with 2, 3, 4 and 6 S atoms display approximately 0.25, 0.5, 0.75 and 1.25 full turns of the helix, respectively. The pentasulfane (IV) was expected to display one complete turn and the current results confirm this with the relevant torsion angles in any one of the three defined molecules having the same sign and their magnitudes all being very close to 90° (Table 3). An analysis of the Cambridge Structural Database (April 2002 release; Allen, 2002) indicates that a helical conformation of this type with torsion

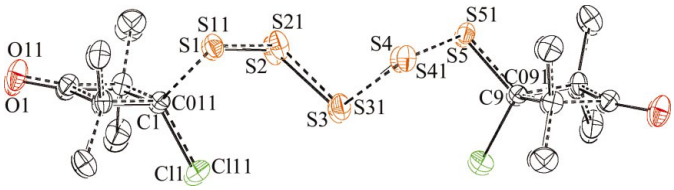


Figure 3
The superposition of the defined positions for molecules 1 and 2. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

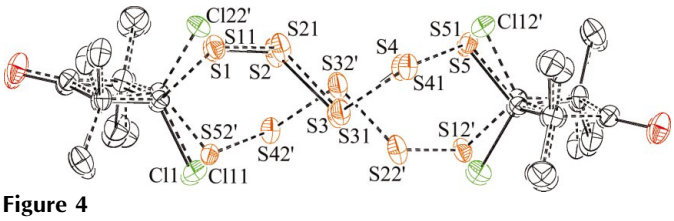


Figure 4
The superposition of the defined positions for molecules 1 and 2 and the position of molecule 3 after applying the centre of inversion showing the close similarity with the disordered standard model depicted in Fig. 1. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. A prime (′) denotes atoms transformed through the operation $(1-x, 1-y, 1-z)$.

angles about the S—S bond in the 70–110° range is quite normal for polysulfane chains.

It is probable that the exact full turn of the polysulfane chain in (IV) is what allows it to partially disorder. When a full turn is present, it makes little difference to the spatial requirements of the molecule whether the polysulfane chain is a left- or right-handed helix, because the cyclobutanyl groups have roughly the same orientation and position either way. Therefore, adjacent molecules of either hand may fit together quite well, but not so well that complete randomization occurs and detectable differences between molecules defined by different symmetrized components of the reflection data could not be found. For the corresponding oligosulfanes with 2, 3, 4 and 6 S atoms, the polysulfane moiety makes a fractional or incomplete helical turn, which apparently does not allow a randomization of the packing of molecules with left- and right-handed helices.

The cyclobutanyl ring at one end of the molecule (defined by atoms C1, C2, C3 and C4 in molecule 1 and the corresponding atoms in molecules 2 and 3) is quite planar, while the other cyclobutanyl ring is slightly distorted towards a flattened tetrahedron. The magnitudes of the folds about the C10···C12 and C9···C11 ring diagonals are 11.1 (3) and 10.4 (2)°, respectively. The fold about the C10···C12 axis is such that it places atom Cl2 above the concave side of the ring, or in a pseudo-axial position. A similar analysis of the corresponding oligosulfanes with 2, 3, 4 and 6 S atoms by Linden *et al.* (2002) found that small tetrahedral distortions of the cyclobutanyl ring planes were normally present and that a completely planar variant was observed in only one ring in one structure. The distribution of the Cl atoms between a pseudo-axial or a pseudo-equatorial (lies above the convex side of ring) arrangement does not appear to favour any one particular conformation.

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