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Four bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)oligosulfanes

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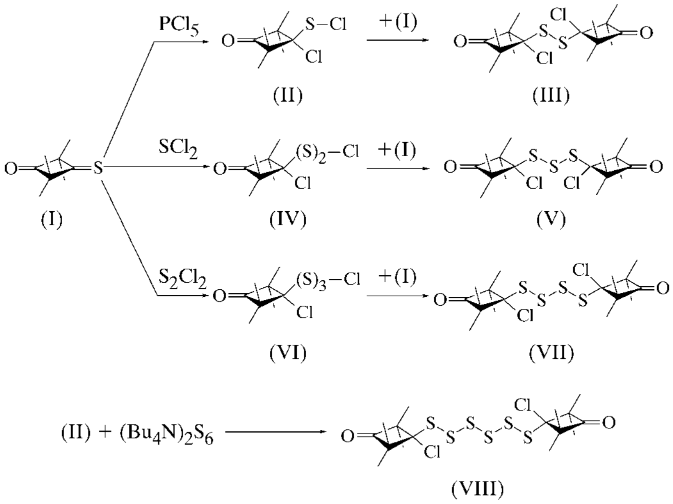
The four oligosulfanes, bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)disulfane, $C_{16}H_{24}Cl_2O_2S_2$, (III), 1,3-bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)trisulfane, $C_{16}H_{24}Cl_2O_2S_3$, (V), 1,4-bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)tetrasulfane, $C_{16}H_{24}Cl_2O_2S_4$, (VII), and 1,6-bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl)hexasulfane, $C_{16}H_{24}Cl_2O_2S_6$, (VIII), all have similar geometric parameters, with the C—C bond lengths involving the chloro-substituted cyclobutanyl C atom being elongated to about 1.59 Å. There are two molecules in the asymmetric units of the tri- and tetrasulfanes, and the molecules in the latter compound have local C_2 symmetry. The molecule of the hexasulfane has crystallographic C_2 symmetry. Most of the cyclobutanyl rings are not perfectly planar and have slight but varying degrees of distortion towards a flattened tetrahedron. 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.

Comment

Although there are some classical methods for the synthesis of organic polysulfanes (Gunderman & Hümke, 1985; Steudel & Kustos, 1994), they often result in mixtures of homologous compounds which are difficult to separate. Therefore, in recent years, new protocols for the selective preparation of linear and cyclic polysulfanes have been elaborated (Steudel, Pridöhl *et al.*, 1995; Steudel, Westphal & Pickardt, 1995, and references therein). For example, titanocene pentasulfane has been shown to be a very useful sulfur-transfer reagent. It reacts with chloroalkanes to give dialkylpentasulfanes, and with alkylsulfenyl chlorides to give dialkylheptasulfanes (Steudel & Kustos, 1991; Westphal & Steudel, 1991; Kustos *et al.*, 1993). On the other hand, several reactions of thioketones have been described in which polysulfur compounds are formed in the absence of a sulfur-transfer reagent, for example, the formation of 1,2,4-trithiolanes on treatment with organic azides (Mloston & Heimgartner, 1995; Mloston *et al.*, 1995, 1996). In this case, an intermediate thiaziridine is believed to be responsible for the sulfur transfer, which leads to reactive thiocarbonyl *S*-sulfides. Similar sulfur-transfer reactions occur under mild conditions between thiiranes and thioketones (*e.g.* Huisgen & Rapp, 1997; Huisgen *et al.*, 1997), whereas the formation of reactive thiocarbonyl *S*-sulfides from thioketones and S_8 needs higher temperatures (*e.g.* Saito, Nagashima *et al.*, 1992; Saito, Shundo *et al.*, 1992; Okuma *et al.*, 1993) or the presence of sodium benzenethiolate as a catalyst (Huisgen *et al.*, 1997). In the case of adamantanethione, the corresponding 1,2,4-trithiolane was formed on treatment with silica gel in dichloromethane (Linden *et al.*, 2002).

As the intermediacy of thiocarbonyl *S*-sulfides and their isomeric dithiiranes has frequently been proposed to explain the formation of polysulfur heterocycles (Mloston & Heimgartner, 1995; Huisgen *et al.*, 1997; El-Essawy *et al.*, 1998; Fabian & Senning, 1998; Hegab *et al.*, 1999; Hawata *et al.*, 2000), many attempts have been undertaken to synthesize those compounds. Within the last few years, several stable dithiiranes have been prepared (Ishii *et al.*, 1994; Ishii & Nakayama, 1999, 2000; Shimada *et al.*, 1999), and the parent compound has been generated photolytically and isolated in a matrix at 10 K (Mloston *et al.*, 2001).

Recently, we reported the synthesis of α-chlorosulfenyl chloride (II) from thioketone (I) by using either chlorine (Koch *et al.*, 1999), phosphorus pentachloride or sulfuryl chloride (Mloston *et al.*, 2002) as the chlorinating agent (see *Scheme*). The reaction of (II) with thioketone (I) in dichloromethane at 298 K gave the disulfane (III). Treatment of (I) with sulfur dichloride in tetrachloromethane at 298 K led to a 1:1 mixture of α-chlorodisulfanyl chloride, (IV), and the trisulfane (V), which was separated by trituration with petroleum ether. The latter was formed in high yield when purified (IV) was reacted with (I) in dichloromethane. Tetrasulfane (VII) has been obtained from the reaction of (I) and disulfur dichloride in dichloromethane at 298 K, with α-chlorotrisulfanyl chloride, (VI), being a likely intermediate. Unexpectedly, the reaction of (II) with tetrabutylammonium hexasulfane in tetrahydrofuran gave the symmetrical hexa-



sulfane (VIII) as colourless crystals in low yield. As part of their full characterization, low-temperature X-ray crystal structure determinations of compounds (III), (V), (VII) and (VIII) were carried out and the results are presented here.

The molecules of compounds (III) and (V) do not possess any local or crystallographic symmetry (Figs. 1 and 2). The asymmetric units in compounds (V) and (VII) each contain two molecules which have very similar conformations and can be superimposed very closely; the r.m.s. fit between the non-H atoms of the symmetry-independent molecules is 0.59 Å for (V) and 0.23 Å for (VII). Both symmetry-independent molecules of (VII) display local C_2 symmetry about an axis passing through the middle of the central S—S bond, with the r.m.s. deviations of the C_2-related atoms being 0.08 and 0.11 Å for molecules *A* and *B*, respectively (Fig. 3). The molecule of (VIII) has crystallographic C_2 symmetry about an axis passing through the middle of the central S—S bond (Fig. 4).

The pattern of bond lengths and angles is consistent across all four structures and these parameters have normal values (Tables 1–4), although the S1—C1 bond in (III) is about 0.03 Å longer than any of the other S—C bonds in these structures [mean value 1.816 (2)°], including the chemically equivalent S2—C9 bond in (III). The C—C bond lengths involving the chloro-substituted cyclobutanyl C atom are longer than normal C—C single bonds, in the range 1.585 (2)–1.601 (2) Å. However, they are consistent with those previously found in a similar environment (Mloston *et al.*, 1999). This is evidently due to the electron-withdrawing properties of the S and Cl substituents. As a result, the cyclobutanyl rings are not perfect squares. While the C—C—C bond angle at the chloro-substituted C atom is always close to 90°, that at the oxo-substituted C atom is consistently about 96°, while those at the dimethyl-substituted C atoms hover around 86°.

With the exception of one planar ring in compound (VII), the cyclobutanyl rings in the four structures are not planar, but are slightly distorted towards a flattened tetrahedron. The magnitudes of the folds about the ring diagonals vary from structure to structure and from one end of a molecule to the next, with some rings being much flatter than others, as indicated in Table 5. The direction of the fold also varies from one ring to the next and is not necessarily the same for all rings in any one particular structure. The Cl substituent on the ring can be described as being in a pseudo-axial (ax) or a pseudo-equatorial (eq) position, depending on whether the fold about the $(\mathrm{Me_2})\mathrm{C}\cdots\mathrm{C}(\mathrm{Me_2})$ axis places the Cl atom above the concave or convex side, respectively, of the ring. The ax/eq assignments for each structure are also listed in Table 5.

The polysulfane chain in each structure always has a helical conformation. The magnitudes of the torsion angles about the S—S bonds are fairly constant and lie between 83 and 101°, while, in any one structure, successive torsion angles along the chain have the same sign. Thus, compounds (III), (V), (VII) and (VIII) display approximately 0.25, 0.5, 0.75 and 1.25 full turns, respectively. The one structure missing in this series is the pentasulfane, which should display one complete turn. We have actually determined the structure of this latter compound and it does display the expected full-turn conformation.

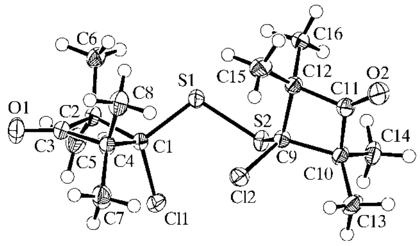


Figure 1
A view of the molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

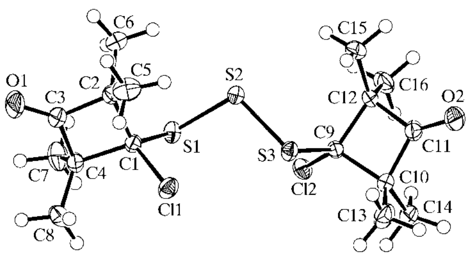


Figure 2
A view of one of the symmetry-independent molecules of (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

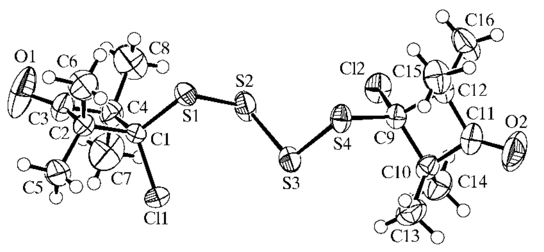


Figure 3
A view of one of the symmetry-independent molecules of (VII), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

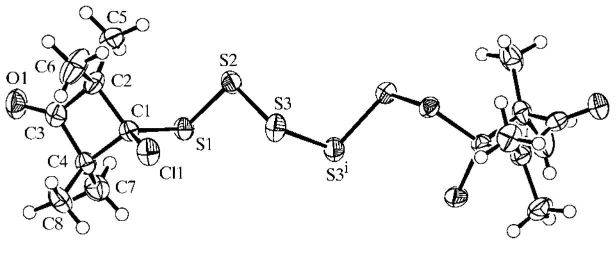


Figure 4
A view of the molecule of (VIII), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $y-1, 1+x, -z$.]

Acta Cryst. (2002). C**58**, o480–o484 Anthony Linden *et al.* • $\mathrm{C_{16}H_{24}Cl_2O_2S_2}$, $\mathrm{C_{16}H_{24}Cl_2O_2S_3}$, $\mathrm{C_{16}H_{24}Cl_2O_2S_4}$ and $\mathrm{C_{16}H_{24}Cl_2O_2S_6}$ **o481**

However, unexpected geometrical and crystallographic anomalies in this structure determination require further investigation and the structure of the pentasulfane will be published at a later date. An analysis of the Cambridge Structural Database (April 2002 Release; Allen & Kennard, 1993) indicates that a helical conformation of this type, with torsion angles about the S—S bond in the range 70–110°, is quite normal for polysulfane chains.

Experimental

The syntheses of (III), (V) and (VII) have been reported by Mloston *et al.* (2002), and single crystals of each compound were obtained by slow evaporation from their respective solutions in hexane–dichloromethane. For the preparation of (VIII), tetrabutylammonium hexasulfane (745 mg, 1.1 mmol) was added to a stirred solution of (II) (257 mg, 1.1 mmol) in tetrahydrofuran (5 ml) at 233 K. After stirring for 2 h at 233 K and for 24 h at 298 K, the solvent was evaporated and the residue dissolved in dichloromethane and filtered through silica gel. Evaporation of the solvent and recrystallization of the residue yielded 30 mg (10%) of (VIII) as colourless crystals (m.p. 402–404 K). The spectroscopic data for (III), (V) and (VII) have been reported by Mloston *et al.* (2002), and the corresponding data for (VIII) (see below) are virtually identical. These compounds cannot be distinguished by mass spectrometry, as they produce similar fragmentation patterns and the molecular ion does not appear in the spectra. Spectroscopic data for (VIII), ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 1.38 (*s*, 4 Me), 1.41 (*s*, 4 Me); ^{13}C NMR (CDCl$_3$, δ, p.p.m.): 22.7 (*q*, 4 Me), 23.4 (*q*, 4 Me), 69.2 (*s*, C2, C2′, C4, C4′), 87.4 (*s*, C1, C1′), 215.4 (*s*, 2 C═O); IR (KBr, ν, cm^{-1}): 1790 (*vs*, C═O), 1770 (*s*, C═O), 1461 (*s*), 1455 (*s*), 1443 (*s*), 1380 (*s*), 1365 (*s*), 1169 (*s*), 1134 (*s*), 1029 (*s*), 912 (*s*), 887 (*s*), 832 (*s*).

Compound (III)

Crystal data

$C_{16}H_{24}Cl_2O_2S_2$
M_r = 383.39
Monoclinic, $P2_1/n$
a = 6.7379 (1) Å
b = 26.7454 (4) Å
c = 10.6473 (2) Å
β = 105.4292 (6)°
V = 1849.58 (5) Å^3
Z = 4

D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 103 426 reflections
θ = 2.0–30.0°
μ = 0.58 mm^{-1}
T = 160 (1) K
Rod, colourless
0.32 × 0.12 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min}$ = 0.872, $T_{\max}$ = 0.961
40 268 measured reflections

5400 independent reflections
3839 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.069
$\theta_{\max}$ = 30°
$h = -9 \rightarrow 9$
$k = -37 \rightarrow 37$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.093
S = 1.06
5397 reflections
207 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.5066P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (III).

Cl1—C1	1.7786 (17)	C1—C2	1.595 (2)
Cl2—C9	1.7915 (17)	C1—C4	1.590 (2)
S1—C1	1.8462 (16)	C9—C10	1.601 (2)
S1—S2	2.0243 (6)	C9—C12	1.589 (2)
S2—C9	1.8146 (17)		
C1—S1—S2	109.71 (6)	C1—C4—C3	86.12 (12)
C9—S2—S1	106.17 (6)	C10—C9—C12	90.52 (12)
C2—C1—C4	90.28 (12)	C9—C10—C11	85.79 (12)
C1—C2—C3	86.26 (12)	C10—C11—C12	95.69 (13)
C2—C3—C4	95.53 (13)	C9—C12—C11	86.33 (12)
C1—S1—S2—C9	−97.90 (8)		

Compound (V)

Crystal data

$C_{16}H_{24}Cl_2O_2S_3$
M_r = 415.45
Monoclinic, $P2_1/c$
a = 13.0673 (1) Å
b = 25.7808 (2) Å
c = 13.1619 (1) Å
β = 114.6674 (3)°
V = 4029.43 (5) Å^3
Z = 8

D_x = 1.370 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 77 343 reflections
θ = 2.0–30.0°
μ = 0.64 mm^{-1}
T = 160 (1) K
Block, colourless
0.38 × 0.30 × 0.22 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.826, $T_{\max}$ = 0.890
93 177 measured reflections

11 777 independent reflections
9407 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.050
$\theta_{\max}$ = 30°
$h = -18 \rightarrow 18$
$k = -36 \rightarrow 36$
$l = -18 \rightarrow 18$

Table 2
Selected geometric parameters (Å, °) for (V).

Cl1—C1	1.7957 (14)	Cl21—C21	1.7934 (14)
Cl2—C9	1.7903 (14)	Cl22—C29	1.8070 (14)
S1—C1	1.8168 (14)	S21—C21	1.8181 (14)
S1—S2	2.0426 (5)	S21—S22	2.0417 (5)
S2—S3	2.0502 (5)	S22—S23	2.0513 (5)
S3—C9	1.8167 (14)	S23—C29	1.8110 (14)
C1—C2	1.593 (2)	C21—C22	1.591 (2)
C1—C4	1.592 (2)	C21—C24	1.589 (2)
C9—C10	1.593 (2)	C29—C30	1.594 (2)
C9—C12	1.5905 (19)	C29—C32	1.585 (2)
C1—S1—S2	101.82 (5)	C21—S21—S22	103.61 (5)
S1—S2—S3	107.65 (2)	S21—S22—S23	107.99 (2)
C9—S3—S2	103.63 (5)	C29—S23—S22	101.41 (5)
C2—C1—C4	90.69 (10)	C22—C21—C24	90.54 (11)
C1—C2—C3	86.49 (11)	C21—C22—C23	86.53 (11)
C2—C3—C4	95.95 (12)	C22—C23—C24	95.86 (12)
C1—C4—C3	86.51 (11)	C21—C24—C23	86.84 (11)
C10—C9—C12	90.49 (10)	C30—C29—C32	90.79 (10)
C9—C10—C11	85.97 (10)	C29—C30—C31	85.55 (10)
C10—C11—C12	95.65 (11)	C30—C31—C32	95.53 (11)
C9—C12—C11	85.92 (10)	C29—C32—C31	86.07 (10)
C1—S1—S2—S3	89.80 (5)	C21—S21—S22—S23	97.00 (5)
S1—S2—S3—C9	100.76 (5)	S21—S22—S23—C29	90.52 (5)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.086$
$S = 1.04$
11 772 reflections
431 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 1.605P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.72$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Compound (VII)

Crystal data

$C_{16}H_{24}Cl_2O_2S_4$
$M_r = 447.51$
Triclinic, $P\overline{1}$
$a = 11.1372$ (1) Å
$b = 13.0843$ (1) Å
$c = 16.3379$ (2) Å
$\alpha = 71.8478$ (5)°
$\beta = 89.8055$ (5)°
$\gamma = 73.5431$ (5)°
$V = 2160.20$ (4) Å^3

$Z = 4$
$D_x = 1.376$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 875 reflections
$\theta = 2.0$–30.0°
$\mu = 0.69$ mm^{-1}
$T = 253$ (1) K
Tablet, colourless
0.25 × 0.25 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.884$, $T_{\max} = 0.936$
61 153 measured reflections

12 599 independent reflections
9118 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 30°$
$h = -15 \rightarrow 15$
$k = -18 \rightarrow 18$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.114$
$S = 1.05$
12 596 reflections
450 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.5211P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL*97)
Extinction coefficient: 0.0049 (10)

Table 3
Selected geometric parameters (Å, °) for (VII).

Cl1—C1	1.7799 (16)	Cl21—C21	1.7796 (16)
Cl2—C9	1.7885 (16)	Cl22—C29	1.7863 (16)
S1—C1	1.8131 (16)	S21—C21	1.8176 (16)
S1—S2	2.0341 (7)	S21—S22	2.0361 (7)
S2—S3	2.0680 (7)	S22—S23	2.0681 (7)
S3—S4	2.0332 (7)	S23—S24	2.0336 (7)
S4—C9	1.8174 (16)	S24—C29	1.8172 (16)
C1—S1—S2	103.59 (6)	C21—S21—S22	103.93 (6)
S1—S2—S3	105.29 (3)	S21—S22—S23	105.30 (3)
S4—S3—S2	105.17 (3)	S24—S23—S22	105.29 (3)
C9—S4—S3	103.61 (6)	C29—S24—S23	103.69 (6)
C2—C1—C4	90.73 (13)	C22—C21—C24	90.73 (13)
C1—C2—C3	86.31 (14)	C21—C22—C23	86.14 (13)
C2—C3—C4	96.49 (14)	C22—C23—C24	96.00 (13)
C1—C4—C3	86.48 (14)	C21—C24—C23	86.43 (13)
C10—C9—C12	90.97 (13)	C30—C29—C32	90.69 (13)
C9—C10—C11	86.27 (14)	C29—C30—C31	86.44 (13)
C10—C11—C12	96.36 (14)	C30—C31—C32	96.12 (14)
C9—C12—C11	86.32 (14)	C29—C32—C31	86.63 (13)
C1—S1—S2—S3	−99.07 (6)	C21—S21—S22—S23	−98.25 (6)
S1—S2—S3—S4	−92.44 (3)	S21—S22—S23—S24	−94.27 (3)
S2—S3—S4—C9	−96.10 (6)	S22—S23—S24—C29	−96.40 (6)

Compound (VIII)

Crystal data

$C_{16}H_{24}Cl_2O_2S_6$
$M_r = 511.63$
Tetragonal, $P4_12_12$
$a = 7.1475$ (1) Å
$c = 46.3268$ (8) Å
$V = 2366.69$ (6) Å^3
$Z = 4$
$D_x = 1.436$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 40 968 reflections
$\theta = 2.0$–27.5°
$\mu = 0.81$ mm^{-1}
$T = 160$ (1) K
Plate, colourless
0.17 × 0.17 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.858$, $T_{\max} = 0.944$
25 607 measured reflections

2715 independent reflections
1837 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.114$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 8$
$k = -9 \rightarrow 8$
$l = -59 \rightarrow 59$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.085$
$S = 1.06$
2715 reflections
123 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2{\rm P}]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Absolute structure: Flack (1983), with 989 Friedel pairs
Flack parameter = 0.39 (13)

Table 4
Selected geometric parameters (Å, °) for (VIII).

Cl1—C1	1.783 (3)	S3—S3^{i}	2.0461 (18)
S1—C1	1.819 (3)	C1—C2	1.589 (4)
S1—S2	2.0402 (11)	C1—C4	1.595 (4)
S2—S3	2.0567 (12)		
C1—S1—S2	103.03 (10)	C1—C2—C3	87.0 (2)
S1—S2—S3	106.00 (5)	C2—C3—C4	95.7 (3)
S3^{i}—S3—S2	106.39 (5)	C1—C4—C3	86.4 (2)
C2—C1—C4	90.5 (2)		
C1—S1—S2—S3	92.90 (11)	S2—S3—S3^{i}—S2^{i}	83.73 (6)
S1—S2—S3—S3^{i}	86.24 (6)		

Symmetry code: (i) $y - 1, 1 + x, -z$.

Table 5
Angles (°) between the planes on each side of the diagonals of the cyclobutanyl rings.

	O═C···C axis	(Me$_2$)C···C(Me$_2$) axis	Position of Cl atom
(III)			
Ring 1†	13.9 (2)	14.8 (2)	ax
Ring 2	13.41 (17)	14.27 (17)	ax
(V)			
Molecule *A*, ring 1	6.15 (17)	6.54 (17)	ax
Molecule *A*, ring 2	14.51 (16)	15.45 (17)	eq
Molecule *B*, ring 1	4.91 (17)	5.20 (17)	ax
Molecule *B*, ring 2	14.81 (14)	15.80 (15)	ax
(VII)			
Molecule *A*, ring 1	0.1 (2)	0.1 (2)	–
Molecule *A*, ring 2	2.64 (19)	2.8 (2)	ax
Molecule *B*, ring 1	8.69 (19)	9.26 (19)	eq
Molecule *B*, ring 2	3.7 (2)	3.9 (2)	eq
(VIII)			
Ring 1	7.2 (3)	7.7 (3)	eq

† Ring 1 is defined by atoms C1–C4, ring 2 by C9–C12. For (V) and (VII), add 20 to the atom numbers to obtain the corresponding atoms in molecule *B*.

For each structure, the methyl H atoms were constrained to an ideal geometry (C—H = 0.96–0.98 Å), with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C), while the methyl groups were allowed to rotate freely about the C—C bonds. For (III), (V) and (VII), three, five and three low-angle reflections, respectively, were omitted from the final refinement because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop. The structures of (V) and (VII) have two molecules in the asymmetric unit. In each case, the possibility of the two molecules being related by additional symmetry was excluded by comparing their atomic coordinates using *PLATON* (Spek, 2002). Attempts to collect the data for (VII) at 160 K were unsuccessful, because the thermal shock of cooling destroyed the crystals, so the analysis for this compound was conducted at 253 K. For (VIII), even though the molecule is achiral, the compound crystallized in a polar space group. Refinement of the absolute structure parameter (Flack, 1983) yielded a value of 0.39 (13), which suggests that the crystal may be a merohedral twin, although the large standard uncertainty on this parameter means that a definitive conclusion regarding the absolute structure cannot be drawn (Flack & Bernardinelli, 2000). The absolute structure defined by the model and space group ($P4_12_12$) used in the refinement has therefore been assigned arbitrarily. The inverted structure and space group ($P4_32_12$) could be used equally well.

For all compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1503). Services for accessing these data are described at the back of the journal.

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