



IUCrData

ISSN 2414-3146

# Methyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate

Noudjoud Hamdouni,<sup>a\*</sup> Ali Boudjada,<sup>a</sup> Jean Meinel,<sup>b</sup> Abdelali Fiala,<sup>c</sup> Hayet Brahim Ladouani<sup>c</sup> and Salah Eddine Lemallem<sup>c</sup>

<sup>a</sup>Laboratoire de Cristallographie, Département de Physique, Université Mentouri-Constantine, 25000 Constantine, Algeria, <sup>b</sup>UMR 6226 CNRS–Université Rennes 1 ‘Sciences Chimiques de Rennes’, Equipe ‘Matière Condensée et Systèmes Electroactifs’, Bâtiment 10C, Campus de Beaulieu, 263 Avenue du Général Leclerc, F-35042 Rennes, France, and <sup>c</sup>Unité de Recherche de Chimie de l’Environnement et Moléculaire, Structurale CHEMS, Université des frères Mentouri Constantine, Constantine, Algeria. \*Correspondence e-mail: n\_hamdouni@yahoo.fr

Received 21 June 2017

Accepted 8 July 2017

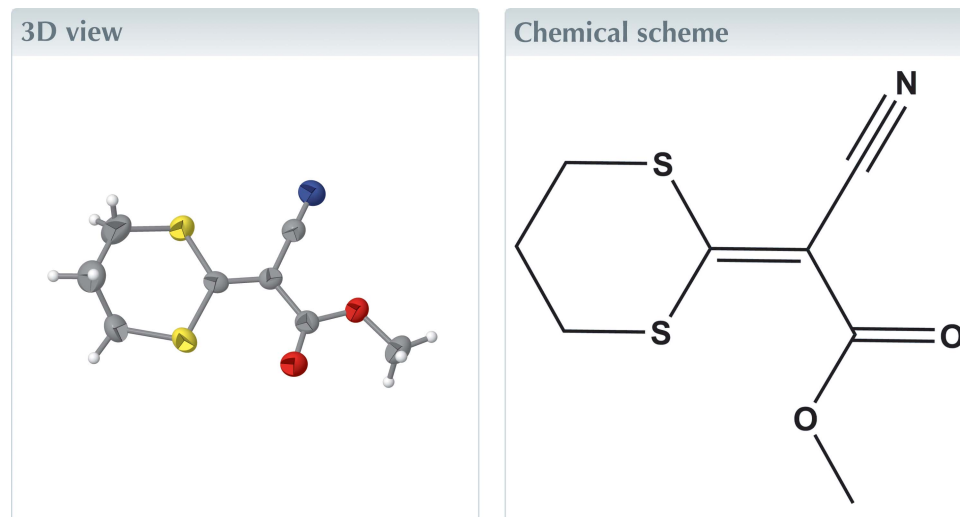
Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; 1,3-dithiane; cyano; ketene dithioacetals.

CCDC reference: 1561034

Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

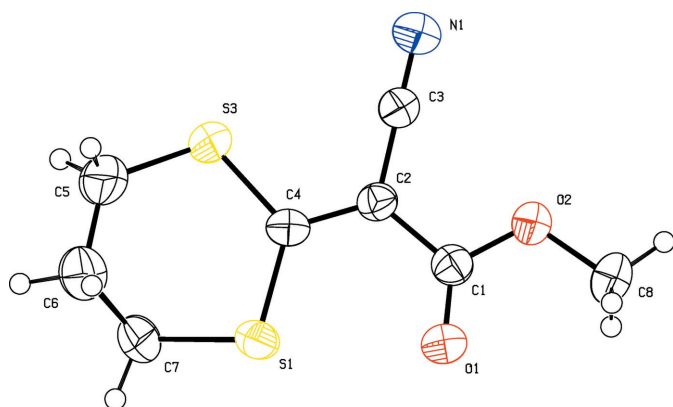
The title compound, C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>S<sub>2</sub>, contains a 1,3-dithiane ring which has a twist-boat conformation. In the crystal, there are no significant intermolecular interactions present. The dihedral angle between the planes of the acetate group and the dithiane ring is 177.1 (2)°



## Structure description

Ketene dithioacetals are useful intermediates in organic synthesis and have been used for the synthesis of heterocyclic compounds (Kolb, 1990; Ila *et al.*, 2001). The synthesis of trifluoromethyl ketene dithioacetals plays an important role in the field of pharmaceuticals and agrochemicals (Gouault-Bironneau *et al.*, 2012; Timoshenko & Portella, 2009). They have also been used to develop domino reactions owing to their ability to produce a wide range of substances of structural diversity and varied biological activities (Pan *et al.*, 2013; Samai *et al.*, 2012). The  $\alpha$ -C ketene dithioacetals are reactive towards electrophiles (Okuyama, 1986; Okuyama, 1984). They act as a precursors for C–C bond formation at the  $\alpha$ -C atom (Kouno *et al.*, 1998; Minami *et al.*, 1996). They have also been used for chlorination reactions to generate vinyl halides from  $\alpha$ -acetyl ketene dithioacetals; these dithioacetals are further transformed into the corresponding  $\alpha$ -ethynyl ketene dithioacetals (Liu *et al.*, 2003; Dong *et al.*, 2005). In the present study, we report the synthesis and crystal structure of the new title 1,3-dithian-2-ylidene derivative, which has a dipolar moment of the order of 6.8 Debye.

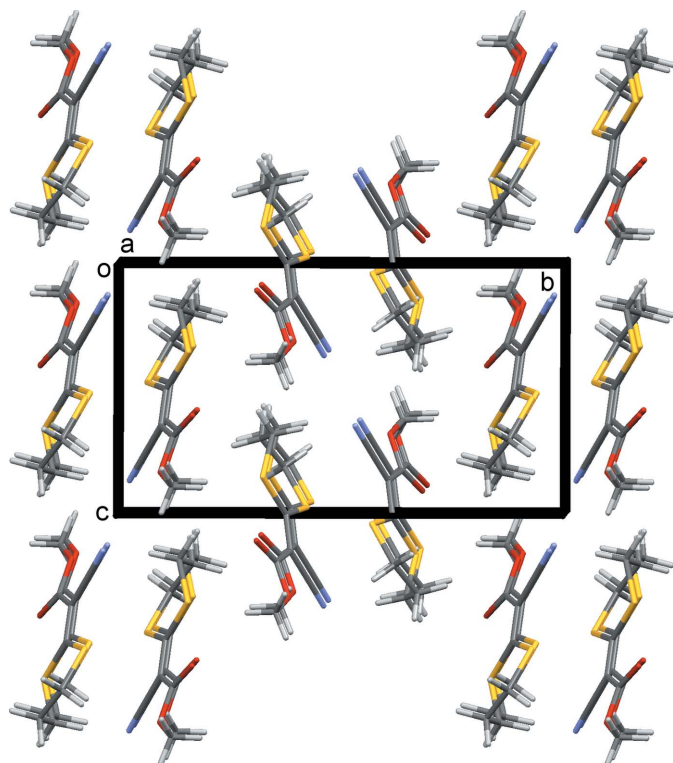
The molecular structure of the title compound is shown in Fig. 1. The 1,3-dithiane ring has a twist-boat conformation [puckering parameters: amplitude ( $Q$ ) = 0.632 (3) Å,  $\theta$  = 106.5 (3)° and  $\varphi$  = 114.3 (3)°]. In this ring, the two C–S bond lengths adjacent to the C4=C2 bond [1.381 (3) Å] are C4–S1 = 1.733 (2) Å and C4–S3 = 1.736 (2) Å. The



**Figure 1**  
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

geometric parameters and the deformation of the 1,3-dithiane ring are similar to those found for related structures. For example, in methyl 2-(diphenylmethyleneamino)-2-(1,3-dithian-2-ylidene)acetate (Dolling *et al.*, 1993) or (3*Z*,6*E*)-dimethyl 3,7-dichloro-2,8-bis(1,3-dithian-2-ylidene)-5-(4-nitrophenyl)nona-3,6-diene-1,9-dioate (Zhao *et al.*, 2007). In these two compounds, the C–S bond lengths vary from 1.736 to 1.758 Å and the C=C bond length varies from 1.349 to 1.366 Å. In both compounds, the 1,3-dithiane rings also have twist-boat conformations.

In the crystal of the title compound, there are no significant directional intermolecular interactions present (Fig. 2).



**Figure 2**  
A view along the *a* axis of the crystal packing of the title compound.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub> S <sub>2</sub>
<i>M<sub>r</sub></i>	215.28
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.4927 (6), 15.2501 (19), 8.5522 (9)
$\beta$ (°)	94.923 (9)
<i>V</i> (Å <sup>3</sup> )	973.61 (18)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.51
Crystal size (mm)	0.28 × 0.17 × 0.03
Data collection	
Diffractometer	Agilent Technologies Xcalibur Eos
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.842, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	6282, 3076, 1740
<i>R<sub>int</sub></i>	0.036
(sin $\theta$ /λ) <sub>max</sub> (Å <sup>-1</sup> )	0.754
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.058, 0.155, 1.00
No. of reflections	3076
No. of parameters	118
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.54, -0.40

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SIR92* (Altomare *et al.*, 1994), *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2012).

## Synthesis and crystallization

In a three-necked round-bottomed flask swept by a nitrogen current and equipped with a dropping funnel containing 1,3-dibromopropane, a suspension of K<sub>2</sub>CO<sub>3</sub> (42 g, 0.3 mol) mixed with the corresponding active methylene compound, NCCH<sub>2</sub>COOCH<sub>3</sub> (0.15 mol) in DMF (50 ml), was stirred with a magnetic stirrer. Carbon disulfide (9 ml, 0.15 mol) was added all at once, at room temperature. Stirring was continued for 10 min, after which 1,3-dibromopropane (0.12 mol) was added dropwise over a period of 20 min. After further stirring for 7 h at room temperature, ice-cold water (500 ml) was added to the reaction mixture. The precipitate that formed was filtered off, dried and then dissolved in ethanol, giving pale-yellow needle-like crystals on slow evaporation of the solvent.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

## Acknowledgements

We thank Mr F. Saidi, Engineer at the Laboratory of Crystallography, University Constantine 1, for assistance in collecting the X-ray data on the Xcalibur diffractometer.

## Funding information

Funding for this research was provided by: Laboratoire de Cristallographie, Département de Physique, Université Constantine 1, Algeria.

## References

- Agilent (2013). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Dolling, W., Frost, K., Heinemann, F. & Hartung, H. (1993). *Z. Naturforsch. Teil B*, **48**, 493–504.
- Dong, D., Liu, Y., Zhao, Y., Qi, Y., Wang, Z. & Liu, Q. (2005). *Synthesis*, pp. 85–91.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gouault-Bironneau, S., Timoshenko, V. M., Grellepois, F. & Portella, C. (2012). *J. Fluorine Chem.* **134**, 164–171.
- Ila, H., Junjappa, H. & Barun, O. (2001). *J. Organomet. Chem.* **624**, 34–40.
- Kolb, M. (1990). *Synthesis*, pp. 171–190.
- Kouno, R., Okauchi, T., Nakamura, M., Ichikawa, J. & Minami, T. (1998). *J. Org. Chem.* **63**, 6239–6246.
- Liu, Q., Che, G., Yu, H., Liu, Y., Zhang, J., Zhang, Q. & Dong, D. (2003). *J. Org. Chem.* **68**, 9148–9150.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Minami, T., Okauchi, T., Matsuki, H., Nakamura, M., Ichikawa, J. & Ishida, M. (1996). *J. Org. Chem.* **61**, 8132–8140.
- Okuyama, T. (1984). *J. Am. Chem. Soc.* **106**, 7134–7139.
- Okuyama, T. (1986). *Acc. Chem. Res.* **19**, 370–376.
- Pan, L., Bi, X. & Liu, Q. (2013). *Chem. Soc. Rev.* **42**, 1251–1286.
- Samai, S., Nandi, G. C. & Singh, M. S. (2012). *Tetrahedron*, **68**, 1247–1252.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Timoshenko, V. M. & Portella, C. (2009). *J. Fluorine Chem.* **130**, 586–590.
- Zhao, Y.-L., Chen, L., Liu, Q. & Li, D.-W. (2007). *Synlett*, pp. 37–42.

## full crystallographic data

*IUCrData* (2017). 2, x171018 [https://doi.org/10.1107/S2414314617010185]

## Methyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate

Noudjoud Hamdouni, Ali Boudjada, Jean Meinnel, Abdelali Fiala, Hayet Brahim Ladouani and Salah Eddine Lemallem

## Methyl 2-cyano-2-(1,3-dithian-2-ylidene)acetate

*Crystal data*

$C_8H_9NO_2S_2$

$M_r = 215.28$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.4927$  (6) Å

$b = 15.2501$  (19) Å

$c = 8.5522$  (9) Å

$\beta = 94.923$  (9)°

$V = 973.61$  (18) Å<sup>3</sup>

$Z = 4$

$F(000) = 448$

$D_x = 1.469$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å

Cell parameters from 1541 reflections

$\theta = 3.7$ – $28.9$ °

$\mu = 0.51$  mm<sup>-1</sup>

$T = 293$  K

Needle, pale yellow

$0.28 \times 0.17 \times 0.03$  mm

*Data collection*

Agilent Technologies Xcalibur Eos  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 8.02 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(CrysAlis PRO; Agilent, 2013)

$T_{\min} = 0.842$ ,  $T_{\max} = 1.000$

6282 measured reflections

3076 independent reflections

1740 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 32.4$ °,  $\theta_{\min} = 3.0$ °

$h = -6 \rightarrow 11$

$k = -10 \rightarrow 22$

$l = -12 \rightarrow 10$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.058$

$wR(F^2) = 0.155$

$S = 1.00$

3076 reflections

118 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.54$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.40$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.48769 (9)	0.16638 (5)	0.33331 (8)	0.0486 (2)
S3	0.82543 (9)	0.07137 (6)	0.46302 (9)	0.0594 (3)
O2	0.3383 (2)	0.10646 (12)	0.8114 (2)	0.0458 (4)
O1	0.2734 (2)	0.17772 (14)	0.5839 (2)	0.0537 (5)
C2	0.5515 (3)	0.10466 (16)	0.6310 (3)	0.0360 (5)
N1	0.7540 (3)	0.0327 (2)	0.8531 (3)	0.0665 (8)
C1	0.3739 (3)	0.13390 (17)	0.6686 (3)	0.0386 (6)
C4	0.6154 (3)	0.11524 (15)	0.4855 (3)	0.0357 (5)
C8	0.1685 (3)	0.1339 (2)	0.8649 (4)	0.0567 (8)
H8A	0.1569	0.1106	0.9678	0.085*
H8B	0.0723	0.1126	0.7937	0.085*
H8C	0.164	0.1968	0.8687	0.085*
C3	0.6647 (3)	0.06433 (18)	0.7544 (3)	0.0427 (6)
C7	0.6114 (4)	0.1453 (2)	0.1655 (3)	0.0561 (8)
H7A	0.6058	0.083	0.1425	0.067*
H7B	0.5534	0.1759	0.0755	0.067*
C6	0.8063 (4)	0.1728 (2)	0.1858 (4)	0.0711 (10)
H6A	0.8571	0.1671	0.0857	0.085*
H6B	0.8124	0.2343	0.2152	0.085*
C5	0.9137 (4)	0.1229 (3)	0.3017 (5)	0.0970 (15)
H5A	1.0079	0.1618	0.3448	0.116*
H5B	0.9718	0.0774	0.2453	0.116*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0506 (4)	0.0592 (4)	0.0353 (4)	0.0148 (3)	-0.0001 (3)	0.0032 (3)
S3	0.0458 (4)	0.0808 (6)	0.0529 (5)	0.0241 (4)	0.0109 (3)	0.0159 (4)
O2	0.0390 (9)	0.0551 (11)	0.0442 (10)	0.0026 (9)	0.0084 (8)	0.0065 (10)
O1	0.0442 (10)	0.0666 (13)	0.0500 (11)	0.0146 (9)	0.0036 (8)	0.0112 (11)
C2	0.0326 (11)	0.0367 (12)	0.0385 (13)	-0.0006 (10)	0.0013 (10)	0.0006 (11)
N1	0.0526 (14)	0.093 (2)	0.0536 (15)	0.0132 (14)	0.0026 (12)	0.0237 (16)
C1	0.0373 (12)	0.0397 (13)	0.0383 (13)	-0.0041 (11)	0.0010 (10)	-0.0008 (12)
C4	0.0370 (11)	0.0309 (11)	0.0382 (13)	0.0003 (10)	-0.0035 (10)	-0.0015 (11)
C8	0.0416 (14)	0.0693 (19)	0.0615 (18)	-0.0008 (15)	0.0172 (13)	0.0024 (18)
C3	0.0368 (12)	0.0495 (15)	0.0420 (15)	0.0028 (12)	0.0041 (11)	0.0057 (13)
C7	0.0578 (17)	0.076 (2)	0.0345 (14)	0.0023 (16)	0.0042 (12)	-0.0018 (16)
C6	0.0625 (19)	0.087 (2)	0.065 (2)	-0.0043 (19)	0.0135 (17)	0.020 (2)
C5	0.0493 (17)	0.153 (4)	0.091 (3)	0.012 (2)	0.0211 (18)	0.062 (3)

*Geometric parameters (Å, °)*

S1—C4	1.733 (2)	C8—H8A	0.96
S1—C7	1.803 (3)	C8—H8B	0.96
S3—C4	1.736 (2)	C8—H8C	0.96
S3—C5	1.765 (3)	C7—C6	1.515 (4)
O2—C1	1.339 (3)	C7—H7A	0.97
O2—C8	1.450 (3)	C7—H7B	0.97
O1—C1	1.202 (3)	C6—C5	1.440 (4)
C2—C4	1.381 (3)	C6—H6A	0.97
C2—C3	1.435 (3)	C6—H6B	0.97
C2—C1	1.465 (3)	C5—H5A	0.97
N1—C3	1.138 (3)	C5—H5B	0.97
C4—S1—C7	103.25 (13)	C6—C7—S1	114.6 (2)
C4—S3—C5	108.61 (15)	C6—C7—H7A	108.6
C1—O2—C8	116.5 (2)	S1—C7—H7A	108.6
C4—C2—C3	119.0 (2)	C6—C7—H7B	108.6
C4—C2—C1	123.6 (2)	S1—C7—H7B	108.6
C3—C2—C1	117.4 (2)	H7A—C7—H7B	107.6
O1—C1—O2	124.1 (2)	C5—C6—C7	114.1 (3)
O1—C1—C2	124.8 (2)	C5—C6—H6A	108.7
O2—C1—C2	111.1 (2)	C7—C6—H6A	108.7
C2—C4—S1	121.18 (18)	C5—C6—H6B	108.7
C2—C4—S3	116.27 (18)	C7—C6—H6B	108.7
S1—C4—S3	122.51 (15)	H6A—C6—H6B	107.6
O2—C8—H8A	109.5	C6—C5—S3	123.3 (2)
O2—C8—H8B	109.5	C6—C5—H5A	106.5
H8A—C8—H8B	109.5	S3—C5—H5A	106.5
O2—C8—H8C	109.5	C6—C5—H5B	106.5
H8A—C8—H8C	109.5	S3—C5—H5B	106.5
H8B—C8—H8C	109.5	H5A—C5—H5B	106.5
N1—C3—C2	179.5 (3)		
C8—O2—C1—O004	-1.3 (4)	C1—C2—C4—S3	-177.10 (18)
C8—O2—C1—C2	177.8 (2)	C7—S1—C4—C2	-169.9 (2)
C4—C2—C1—O1	-8.2 (4)	C7—S1—C4—S3	7.9 (2)
C3—C2—C1—O1	170.7 (3)	C5—S3—C4—C2	-159.8 (2)
C4—C2—C1—O2	172.7 (2)	C5—S3—C4—S1	22.4 (3)
C3—C2—C1—O2	-8.4 (3)	C4—S1—C7—C6	-53.9 (3)
C3—C2—C4—S1	-178.08 (18)	S1—C7—C6—C5	66.7 (4)
C1—C2—C4—S1	0.8 (4)	C7—C6—C5—S3	-26.9 (6)
C3—C2—C4—S3	4.0 (3)	C4—S3—C5—C6	-16.1 (5)