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2-[2-(4-Methylbenzoyl)-3,3-bis(methylsulfanyl)prop-2-enylidene]malononitrile

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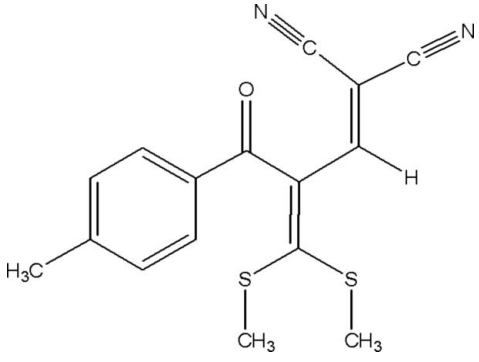
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.006 Å; R factor = 0.049; wR factor = 0.156; data-to-parameter ratio = 14.0.

The title compound, $C_{16}H_{14}N_2OS_2$, is an example of a push–pull butadiene in which the electron-releasing and electron-withdrawing attachments on either end of the butadiene chain enhance the conjugation in the system. The molecules are linked by intermolecular C—H···N interactions.

Related literature

For related literature, see: Anabha & Asokan (2006); Dahne (1978); Dastidar *et al.* (1993); Freier *et al.* (1999); Homrighausen & Krause Bauer (2004); Michalik *et al.* (2002).



Experimental

Crystal data

$C_{16}H_{14}N_2OS_2$
M_r = 314.41
Monoclinic, $C2$
a = 16.6050 (13) Å
b = 10.760 (2) Å
c = 9.905 (2) Å
β = 110.09 (2)°
V = 1662.0 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 295 (2) K
0.25 × 0.25 × 0.20 mm

Data collection

MacScience DIPLabo 32001 diffractometer
Absorption correction: none
4433 measured reflections
2717 independent reflections
2583 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.156
S = 1.11
2717 reflections
194 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983), with 1210 Friedel pairs
Flack parameter: 0.11 (12)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···N2^{i}	0.96	2.49	3.3871	155

Symmetry code: (i) $x-\frac{1}{2}, y-\frac{1}{2}, z-1$.

Data collection: *XPRESS* (MacScience, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2055).

References

Anabha, E. R. & Asokan, C. V. (2006). *Synthesis*, **1**, 151–155.
Dahne, S. (1978). *Science*, **199**, 1163–1167.
Dastidar, P., Guru Row, T. N. & Venkatesan, K. (1993). *Acta Cryst.* B**49**, 900–905.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Freier, T., Michalik, M. & Peseke, K. (1999). *J. Chem. Soc. Perkin Trans. 2*, pp. 1265–1271.
Homrighausen, C. L. & Krause Bauer, J. A. (2004). *Acta Cryst.* E**60**, o1828–o1829.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
MacScience (2002). *XPRESS*. MacScience Co. Ltd, Yokohama, Japan.
Michalik, M., Freier, T., Reinke, H. & Peseke, K. (2002). *J. Chem. Soc. Perkin Trans. 2*, pp. 114–119.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

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2-[2-(4-Methylbenzoyl)-3,3-bis(methylsulfanyl)prop-2-enylidene]malononitrile

Joseph Nirmala, N. V. Unnikrishnan, C. V. Asokan, E. R. Anabha and C. Sudarsanakumar

S1. Comment

Due to the presence of electron releasing alkyl sulfanyl groups and electron withdrawing nitrile groups on the terminal carbon atoms of butadiene moiety, these molecules are considered as push pull butadienes. The push pull substitution alters the polyene state of the unsubstituted butadiene with balanced pi-charge distribution to a polymethine structure with alternating charge densities at the carbon atoms (Dahne, 1978). The title compound, (I), was synthesized and its crystal structure determination was carried out in order to elucidate the molecular conformation to understand the influence of aroyl groups on the stereochemistry of the butadiene molecule in continuation of research in the synthesis of pyridine derivatives (Anabha & Asokan, 2006). A perspective view of (I) is shown in Fig. 1. The crystal structure of (I) shows that the double bonds in the aroyl substituted butadiene are arranged in a *transoid* manner. Bond lengths C9—C10 and C13—C14 indicate their double bond character while C8—C9 is a single bond. Moreover, the double bonds C9—C10 and C13—C14 and shortening of C10—S2 bond length shows the electronic effects on the push pull system. Crystal structures of other butadiene compounds reported also show similar geometric parameters (Dastidar *et al.*, 1993; Michalik *et al.*, 2002; Freier *et al.*, 1999; Homrighausen & Krause Bauer, 2004). The hydrogen-bond interactions of the type C—H···N stabilize the three dimensional structure along the *ac* plane (Fig. 2).

S2. Experimental

2-[3,3-Bis(methyl sulfanyl)-2-(4-methyl benzoyl)-2- propylidene] malononitrile was obtained by the Knoevenagel condensation reaction of 3,3-bis (methyl sulfanyl)-2-(4-methyl benzoyl)-acrylaldehyde (1.33 g., 5 mmol) with malononitrile (500 mg., 7.5 mmol) (Anabha *et al.*, 2006). Single crystals suitable for X-ray diffraction studies were grown by slow evaporation using solutions containing chloroform and hexane in the ratio 1:2. Pale yellow coloured crystals were obtained after two days.

S3. Refinement

The position of all H atoms were geometrically fixed and treated with riding atoms, with C—H distances of 0.93 or 0.96 A. Their isotropic displacement parameters were defined as U_{iso}= 1.5Ueq of the adjacent atom for the methyl H atoms and U_{iso} = 1.2Ueq for all other atoms. The 1210 Friedel opposites were not merged, and the choice of absolute structure was determined by the Flack parameter (Flack, 1983) of 0.11 (12). For the inverted structure the Flack parameter refined to 0.84 (12).

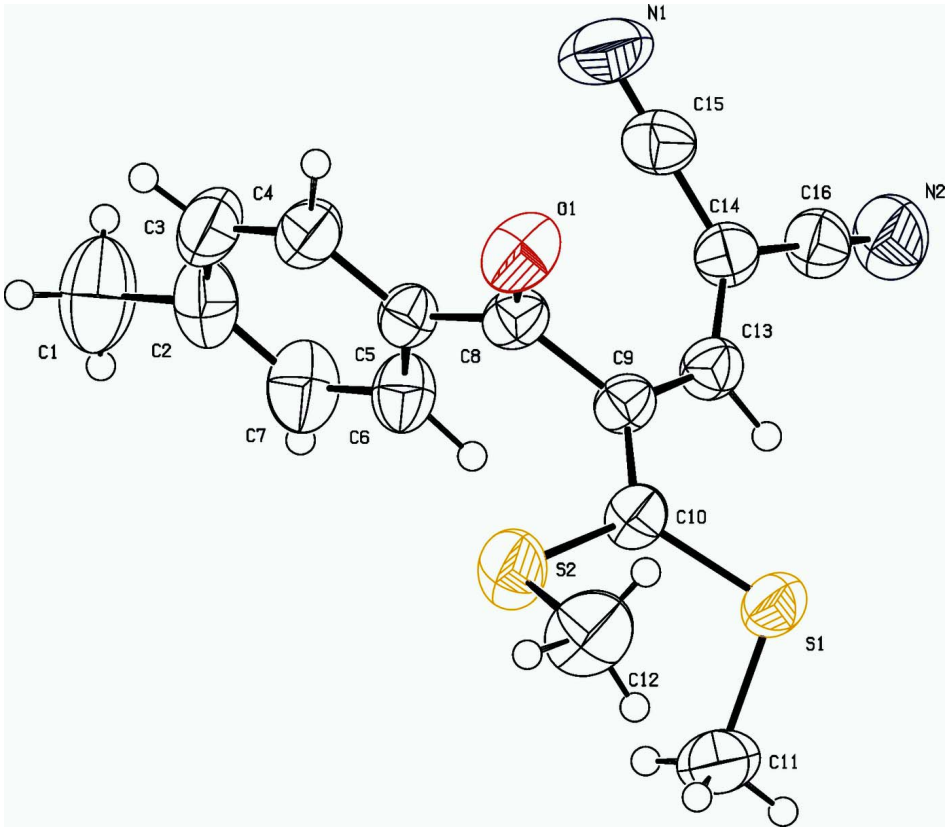

Figure 1

An *ORTEPII* (Johnson, 1976) view of (I) showing the atom-labeling scheme; displacement ellipsoids are drawn at 50% probability level.

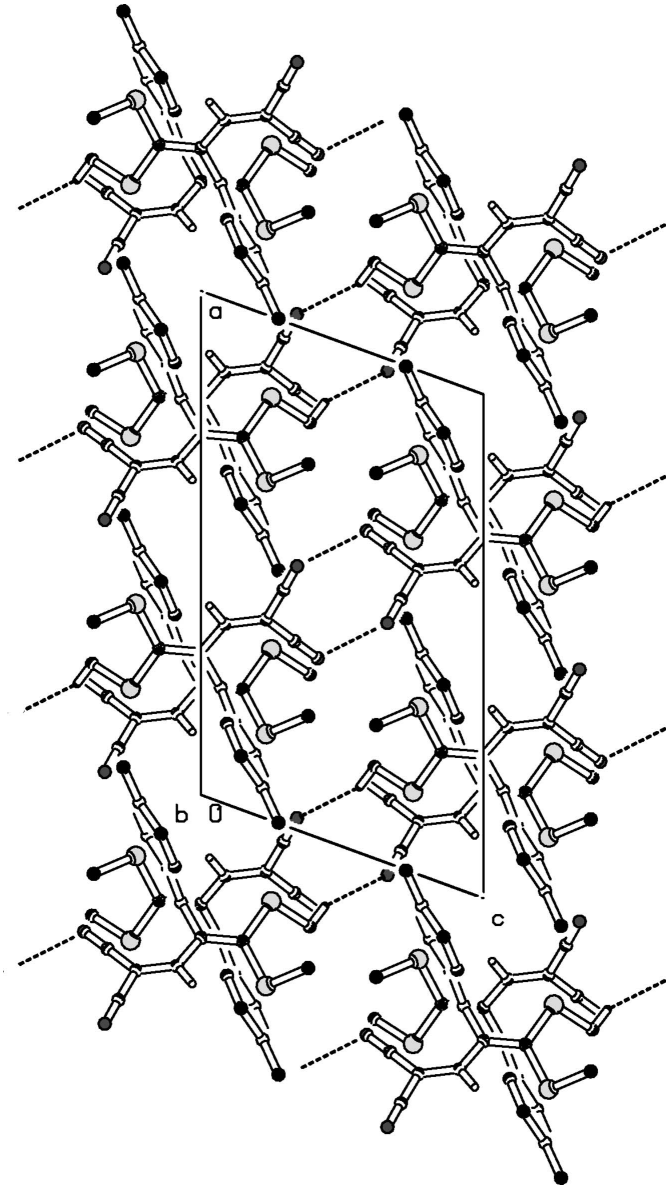

Figure 2

A view of the unit cell packing of (I) showing intermolecular interactions in the *ac* plane.

2-[2-(4-Methylbenzoyl)-3,3-bis(methylsulfanyl)prop-2-enylidene]malononitrile

Crystal data

$C_{16}H_{14}N_2OS_2$
$M_r = 314.41$
Monoclinic, *C*2
Hall symbol: C 2y
$a = 16.6050\ (13)$ Å
$b = 10.760\ (2)$ Å
$c = 9.905\ (2)$ Å
$\beta = 110.09\ (2)°$
$V = 1662.0\ (5)$ Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.257$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å
Cell parameters from 4224 reflections
$\theta = 3.5–25.5°$
$\mu = 0.32$ mm^{-1}
$T = 295$ K
Block, pale yellow
0.25 × 0.25 × 0.20 mm

Data collection

MacScience DIPLabo 32001 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm^{-1}
ω scans
4433 measured reflections
2717 independent reflections
2583 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.5°$, $\theta_{min} = 3.5°$
$h = -20 \rightarrow 20$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.156$
$S = 1.11$
2717 reflections
194 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.1066P)^2 + 0.5386P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.015 (3)
Absolute structure: Flack (1983)
Absolute structure parameter: 0.11 (12)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.33194 (6)	0.02065 (9)	0.76965 (9)	0.0543 (3)
S2	0.16024 (7)	−0.08895 (12)	0.75086 (11)	0.0689 (4)
C5	0.1681 (2)	−0.0204 (3)	1.1171 (4)	0.0458 (8)
C13	0.3562 (2)	0.0395 (4)	1.0845 (3)	0.0471 (7)
H13	0.3801	0.0925	1.0344	0.057*
C9	0.2833 (2)	−0.0289 (3)	0.9991 (3)	0.0430 (7)
C8	0.2276 (2)	−0.0956 (4)	1.0693 (3)	0.0471 (8)
C14	0.3959 (2)	0.0379 (4)	1.2301 (3)	0.0508 (8)
C10	0.2604 (2)	−0.0317 (3)	0.8523 (4)	0.0468 (7)
O1	0.2346 (2)	−0.2092 (3)	1.0871 (3)	0.0680 (8)
C4	0.1194 (3)	−0.0773 (4)	1.1895 (5)	0.0622 (10)
H4	0.1228	−0.1628	1.2041	0.075*
C6	0.1602 (3)	0.1060 (4)	1.0927 (5)	0.0592 (10)
H6	0.1916	0.1447	1.0428	0.071*
C16	0.4673 (2)	0.1193 (4)	1.2927 (4)	0.0553 (9)

C15	0.3732 (3)	−0.0373 (4)	1.3306 (4)	0.0588 (10)
C3	0.0660 (3)	−0.0065 (5)	1.2394 (5)	0.0716 (12)
H3	0.0341	−0.0452	1.2882	0.086*
C2	0.0592 (3)	0.1204 (6)	1.2184 (5)	0.0729 (13)
N1	0.3560 (3)	−0.0944 (5)	1.4132 (4)	0.0905 (14)
N2	0.5237 (3)	0.1858 (5)	1.3400 (5)	0.0795 (12)
C11	0.2658 (3)	0.1102 (5)	0.6206 (5)	0.0724 (12)
H11A	0.2391	0.0562	0.5405	0.109*
H11B	0.3003	0.1705	0.5942	0.109*
H11C	0.2223	0.1521	0.6470	0.109*
C12	0.1815 (4)	−0.1799 (6)	0.6150 (5)	0.0828 (15)
H12A	0.1970	−0.1258	0.5508	0.124*
H12B	0.1311	−0.2261	0.5620	0.124*
H12C	0.2278	−0.2364	0.6595	0.124*
C7	0.1061 (3)	0.1753 (5)	1.1419 (6)	0.0738 (13)
H7	0.1008	0.2602	1.1236	0.089*
C1	0.0013 (5)	0.2004 (8)	1.2746 (9)	0.105 (2)
H1A	−0.0539	0.1616	1.2510	0.157*
H1B	−0.0052	0.2812	1.2311	0.157*
H1C	0.0267	0.2085	1.3771	0.157*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0555 (5)	0.0664 (6)	0.0453 (5)	−0.0047 (4)	0.0227 (4)	−0.0002 (4)
S2	0.0532 (5)	0.0949 (9)	0.0551 (5)	−0.0188 (5)	0.0141 (4)	−0.0181 (5)
C5	0.0452 (17)	0.046 (2)	0.0481 (17)	−0.0059 (12)	0.0189 (14)	−0.0031 (13)
C13	0.0479 (16)	0.054 (2)	0.0413 (16)	−0.0045 (14)	0.0172 (13)	−0.0025 (13)
C9	0.0473 (17)	0.0434 (18)	0.0393 (15)	−0.0042 (12)	0.0162 (13)	−0.0027 (11)
C8	0.0526 (18)	0.049 (2)	0.0410 (16)	−0.0073 (14)	0.0176 (14)	−0.0026 (13)
C14	0.0494 (17)	0.063 (2)	0.0405 (15)	0.0010 (16)	0.0163 (13)	−0.0063 (15)
C10	0.0491 (18)	0.0487 (19)	0.0456 (17)	−0.0060 (13)	0.0202 (14)	−0.0053 (13)
O1	0.090 (2)	0.0475 (19)	0.081 (2)	−0.0027 (14)	0.0481 (17)	−0.0039 (13)
C4	0.062 (2)	0.062 (3)	0.072 (2)	0.0035 (18)	0.036 (2)	0.0115 (19)
C6	0.053 (2)	0.052 (3)	0.077 (3)	−0.0072 (15)	0.0284 (19)	−0.0051 (17)
C16	0.0472 (19)	0.071 (2)	0.0447 (18)	−0.0072 (17)	0.0118 (15)	−0.0098 (16)
C15	0.062 (2)	0.065 (3)	0.0454 (18)	−0.0017 (17)	0.0130 (16)	−0.0001 (17)
C3	0.069 (3)	0.076 (4)	0.085 (3)	0.0031 (19)	0.047 (2)	0.010 (2)
C2	0.052 (2)	0.090 (4)	0.079 (3)	−0.002 (2)	0.026 (2)	−0.024 (2)
N1	0.104 (3)	0.112 (4)	0.052 (2)	−0.021 (3)	0.023 (2)	0.015 (2)
N2	0.062 (2)	0.105 (4)	0.065 (2)	−0.020 (2)	0.0144 (19)	−0.016 (2)
C11	0.083 (3)	0.077 (3)	0.056 (2)	−0.003 (2)	0.024 (2)	0.016 (2)
C12	0.089 (3)	0.096 (4)	0.060 (3)	−0.033 (3)	0.022 (2)	−0.026 (2)
C7	0.071 (3)	0.052 (3)	0.107 (4)	−0.0002 (18)	0.041 (3)	−0.010 (2)
C1	0.090 (4)	0.104 (5)	0.140 (6)	−0.002 (3)	0.065 (4)	−0.036 (4)

Geometric parameters (Å, º)

S1—C10	1.751 (3)	C6—H6	0.9300
S1—C11	1.790 (5)	C16—N2	1.142 (6)
S2—C10	1.734 (3)	C15—N1	1.135 (6)
S2—C12	1.795 (5)	C3—C2	1.381 (8)
C5—C6	1.379 (6)	C3—H3	0.9300
C5—C4	1.393 (5)	C2—C7	1.390 (7)
C5—C8	1.475 (5)	C2—C1	1.531 (7)
C13—C14	1.364 (5)	C11—H11A	0.9600
C13—C9	1.421 (5)	C11—H11B	0.9600
C13—H13	0.9300	C11—H11C	0.9600
C9—C10	1.372 (5)	C12—H12A	0.9600
C9—C8	1.515 (4)	C12—H12B	0.9600
C8—O1	1.235 (5)	C12—H12C	0.9600
C14—C15	1.430 (6)	C7—H7	0.9300
C14—C16	1.433 (5)	C1—H1A	0.9600
C4—C3	1.383 (6)	C1—H1B	0.9600
C4—H4	0.9300	C1—H1C	0.9600
C6—C7	1.380 (6)		
C10—S1—C11	103.7 (2)	C2—C3—C4	121.4 (4)
C10—S2—C12	103.4 (2)	C2—C3—H3	119.3
C6—C5—C4	119.2 (4)	C4—C3—H3	119.3
C6—C5—C8	121.2 (3)	C3—C2—C7	118.0 (4)
C4—C5—C8	119.6 (3)	C3—C2—C1	122.0 (5)
C14—C13—C9	128.7 (3)	C7—C2—C1	119.9 (6)
C14—C13—H13	115.6	S1—C11—H11A	109.5
C9—C13—H13	115.6	S1—C11—H11B	109.5
C10—C9—C13	120.8 (3)	H11A—C11—H11B	109.5
C10—C9—C8	119.1 (3)	S1—C11—H11C	109.5
C13—C9—C8	120.1 (3)	H11A—C11—H11C	109.5
O1—C8—C5	122.6 (3)	H11B—C11—H11C	109.5
O1—C8—C9	119.4 (3)	S2—C12—H12A	109.5
C5—C8—C9	118.0 (3)	S2—C12—H12B	109.5
C13—C14—C15	126.6 (3)	H12A—C12—H12B	109.5
C13—C14—C16	118.5 (3)	S2—C12—H12C	109.5
C15—C14—C16	115.0 (3)	H12A—C12—H12C	109.5
C9—C10—S2	118.9 (3)	H12B—C12—H12C	109.5
C9—C10—S1	120.2 (3)	C6—C7—C2	121.2 (5)
S2—C10—S1	120.88 (19)	C6—C7—H7	119.4
C3—C4—C5	119.9 (4)	C2—C7—H7	119.4
C3—C4—H4	120.1	C2—C1—H1A	109.5
C5—C4—H4	120.1	C2—C1—H1B	109.5
C5—C6—C7	120.3 (4)	H1A—C1—H1B	109.5
C5—C6—H6	119.9	C2—C1—H1C	109.5
C7—C6—H6	119.9	H1A—C1—H1C	109.5
N2—C16—C14	178.5 (5)	H1B—C1—H1C	109.5

N1—C15—C14	178.0 (5)		
C14—C13—C9—C10	−169.0 (4)	C8—C9—C10—S1	−169.0 (3)
C14—C13—C9—C8	13.6 (6)	C12—S2—C10—C9	−138.8 (3)
C6—C5—C8—O1	−178.5 (4)	C12—S2—C10—S1	40.6 (3)
C4—C5—C8—O1	2.1 (6)	C11—S1—C10—C9	−136.9 (3)
C6—C5—C8—C9	3.1 (5)	C11—S1—C10—S2	43.7 (3)
C4—C5—C8—C9	−176.3 (3)	C6—C5—C4—C3	−1.9 (6)
C10—C9—C8—O1	80.2 (5)	C8—C5—C4—C3	177.5 (4)
C13—C9—C8—O1	−102.4 (4)	C4—C5—C6—C7	1.3 (7)
C10—C9—C8—C5	−101.3 (4)	C8—C5—C6—C7	−178.1 (4)
C13—C9—C8—C5	76.1 (4)	C5—C4—C3—C2	0.5 (7)
C9—C13—C14—C15	1.7 (6)	C4—C3—C2—C7	1.6 (8)
C9—C13—C14—C16	−177.8 (4)	C4—C3—C2—C1	−179.2 (5)
C13—C9—C10—S2	−167.0 (3)	C5—C6—C7—C2	0.9 (8)
C8—C9—C10—S2	10.4 (5)	C3—C2—C7—C6	−2.3 (8)
C13—C9—C10—S1	13.6 (5)	C1—C2—C7—C6	178.5 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*B*···N2^{i}	0.96	2.49	3.3871	155

Symmetry code: (i) *x*−1/2, *y*−1/2, *z*−1.