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2-(4-Chlorophenyl)-4,4-bis(methylsulfanyl)-1,3-butadiene-1,1-dicarbonitrile

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The title complex, $C_{14}H_{11}ClN_2S_2$, is an example of a push–pull butadiene. Typical π-electron delocalization along the butadiene moiety, influenced by the donor and acceptor groups, is observed.

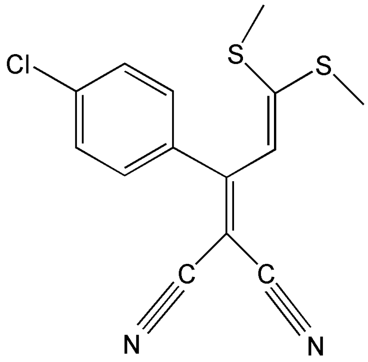
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.102
Data-to-parameter ratio = 20.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title complex, (I), belongs to a series of materials coined push–pull butadienes (Sandström, 1983; Sandström & Wennerbeck, 1978), due to their donor–acceptor characteristics. Push–pull butadienes have been under investigation for various reasons, one application being potential non-linear optical materials (Dastidar *et al.*, 1993; Tinant *et al.*, 1993; Wang *et al.*, 2001).



(I)

The molecular structure of (I) (Fig. 1) is similar to the related dimethylthio complexes, 4,4-bis(methylthio)-2-phenyl-1,3-butadiene-1,1-dicarbonitrile (Dastidar *et al.*, 1993), 2-cyano-3-(2-isopropylphenyl)-5,5-bis(methylthio)penta-2,4-dienenitrile (Michalik *et al.*, 2002), 2-cyano-3-(4-dimethylaminophenyl)-5,5-bis(methylthio)penta-2,4-dienenitrile and 2-cyano-3-(2-dimethylaminophenyl)-5,5-bis(methylthio)-penta-2,4-dienenitrile (Freier *et al.*, 1999). Compound (I) is also comparable to 2-cyano-5-(dimethylamino)-3-(2-isopropylphenyl)-5-(methylthio)penta-2,4-dienenitrile (Michalik *et al.*, 2002), 2-cyano-5-dimethylamino-3-(2-dimethylaminophenyl)-5-methylthiopenta-2,4-dienenitrile (Freier *et al.*, 1999) and 4-dimethylamino-4-methylthio-3-phenyl-1,3-butadiene-1,1-dicarbonitrile (Dastidar *et al.*, 1993).

Bond lengths of 1.376 (3) and 1.366 (3) Å for C7—C8 and C9—C12 in (I) indicate double-bond character, while the C7—C9 bond, with a length of 1.419 (3) Å, is single. In comparison, average distances obtained from the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002) and *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002) for these bonds in the above-

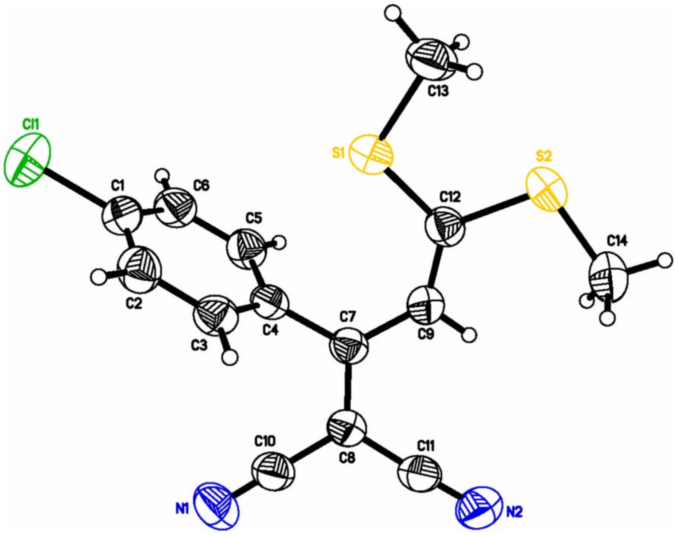


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering scheme.

mentioned complexes are 1.37, 1.38 and 1.42 Å, respectively. As Dastidar *et al.* (1993) and Freier *et al.* (1999) have pointed out, variations in the bond lengths for push–pull butadienes, as compared to 1,3-butadiene [1.337 (5) and 1.483 (1) Å; Almenningen *et al.*, 1958], arise from the π-electron delocalization along the butadiene chain, brought about by the nature of the acceptors and donors (*e.g.* nitrile groups and methylsulfanyl or methylamino groups).

The butadiene portion of (I) is planar, with torsion angles C9—C7—C8—C10, C8—C7—C9—C12 and C7—C9—C12—S1 in the range 0.4 (4)–13.0 (2)° (calculated so that $0 < \theta < 90°$). These angles are consistent with those observed in the related dimethylsulfanyl complexes mentioned above. The chlorophenyl substituent (plane defined by atoms Cl1/C1–C6) is twisted out of the butadiene plane defined by atoms C7/C8/C9; a dihedral angle of 69.2 (1)° is observed. The carbonitrile groups show typical bonding details; the C—C≡N angles are essentially linear and the nitrile C10—N1 and C11—N2 distances are indicative of triple-bond character.

Experimental

Crystals of (I) were obtained as plates and blocks by slow evaporation of methanol solutions maintained at room temperature.

Crystal data

$C_{14}H_{11}ClN_2S_2$
$M_r = 306.82$
Monoclinic, $P2_1/n$
$a = 9.1633\ (18)$ Å
$b = 11.836\ (2)$ Å
$c = 13.911\ (3)$ Å
$\beta = 98.40\ (3)°$
$V = 1492.6\ (5)$ Å^3
$Z = 4$
$D_x = 1.365$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
$\theta = 5.0$–$15.0°$
$\mu = 0.52$ mm^{-1}
$T = 296\ (2)$ K
Block, yellow
0.55 × 0.40 × 0.40 mm

Data collection

Siemens *P*3 diffractometer
θ–2θ scans
Absorption correction: none
3649 measured reflections
3442 independent reflections
2345 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 27.6°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 17$
3 standard reflections
every 300 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.102$
$S = 1.01$
3442 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.6836P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C12	1.737 (2)	C7—C8	1.376 (3)
S1—C13	1.790 (3)	C7—C9	1.419 (3)
N1—C10	1.136 (3)	C8—C11	1.427 (3)
N2—C11	1.140 (3)	C8—C10	1.429 (3)
C4—C7	1.485 (3)	C9—C12	1.366 (3)
N1—C10—C8	178.1 (3)	N2—C11—C8	177.7 (3)
C9—C7—C8—C10	4.2 (2)	C7—C9—C12—S1	0.4 (4)
C8—C7—C9—C12	13.0 (2)		

The positions of all H atoms were located directly and treated with a riding model (C—H = 0.93 or 0.96 Å). Their isotropic displacement parameters were defined as $U_{\rm iso} = 1.5U_{\rm eq}$ of the adjacent atom for the methyl H atoms and $U_{\rm iso} = 1.2U_{\rm eq}$ for all other H atoms.

Data collection: *P*3/*P*4-*PC* (Siemens, 1989); cell refinement: *P*3/*P*4-*PC*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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