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The 4-(3-chloro-4-methylphenyl)-1,2,3,5-dithiadiazol-3-yl radical

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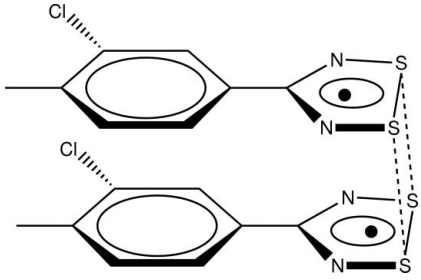
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.013 Å; R factor = 0.042; wR factor = 0.098; data-to-parameter ratio = 6.3.

The asymmetric unit of the title compound, $C_8H_6ClN_2S_2$, comprises two molecules forming a dimer *via* π–π stacking interactions [centroid–centroid distance = 3.634 (10) Å] and intradimer S···S contacts [3.012 (4) and 3.158 (4) Å] between the two molecules in a *cis*-antarafacial arrangement.

Related literature

For the properties of the 4-methylphenyl dithiadiazolyl radical, see: Boeré *et al.* (1992). For similar phenyl dithiadiazolyl radical structures, see: Allen *et al.* (2009); Clarke *et al.* (2010). For notes on the configurations adopted by phenyl dithiadiazolyl radicals in their crystal structures, see: Aherne *et al.* (1993).



Experimental

Crystal data

$C_8H_6ClN_2S_2$ M_r = 229.72
Monoclinic, $P2_1$
a = 5.937 (3) Å
b = 13.407 (3) Å
c = 11.573 (3) Å
β = 95.87 (4)°
V = 916.3 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.82 mm^{-1}
T = 150 K
0.25 × 0.18 × 0.15 mm

Data collection

Rigaku AFC-6S diffractometer
1655 measured reflections
1499 independent reflections
1054 reflections with $I > 2\sigma(I)$
R_{int} = 0.103
θ_{max} = 24.0°
3 standard reflections every 200 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.098
S = 1.09
1499 reflections
237 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Absolute structure: Flack (1983), 169 Friedel pairs
Flack parameter: −0.16 (19)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5594).

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S1. Comment

As observed in similar structures (Aherne *et al.* 1993; Allen *et al.* 2009 and Clarke *et al.* 2010), within the planar CS_2N_2 rings the C—N and S—N bonds distances exhibit intermediate values between those of standard single and double bonds indicating the delocalized nature of the radical about the N—C—N fragment. Though the S—S distance is unusually long it is comparable to similar phenyl dithiadiazolyl radical structures. Intradimer contacts include π-π stacking interactions between the aryl rings of the 3-chloro-4-methylphenyl dithiadiazolyl radicals with a centroid-to-centroid distance of 3.634 (10) Å, and two *cis*-antarafacial S···S contacts (S1···S3 = 3.012 (4) Å; S2···S4 = 3.158 (4) Å).

S2. Experimental

Lithium hexamethyldisilazane (1.67 g, 0.01 mol) was added to 3-chloro-4-methylbenzonitrile (1.51 g, 0.01 mol) in ethanol (40 ml) and stirred for 3 h. To the resulting yellow solution SCl_2 (1.27 ml, 0.02 mol) and diethyl ether (25 ml) was added producing a red solution containing the 3-chloro-4-methylphenyl dithiadiazolyl cation (yield: 91°). The radical was formed upon reduction of the cation (1.43 g, 5 mmol) with a Zn(Cu) couple (0.18 g, 2.8 mmol) as the reducing agent in THF (25 ml). Crystals suitable for X-ray crystallography were grown *via* sublimation of the product under vacuum at 373 K.

S3. Refinement

H atoms were positioned geometrically and refined as riding on their parent atoms, with C—H = 0.930 Å and *Uiso(H)* = 1.2*Ueq(C)*. Methyl hydrogen atoms were modeled in a similar fashion C—H = 0.960 Å and *Uiso(H)* = 1.5*Ueq(C)*. The most disagreeable reflections were omitted; six reflections exhibiting a $\Delta(F^2)$ value greater than 5 su were removed. The absolute structure was determined with a Flack (1983) parameter of -0.16 (19), using 169 reflections.

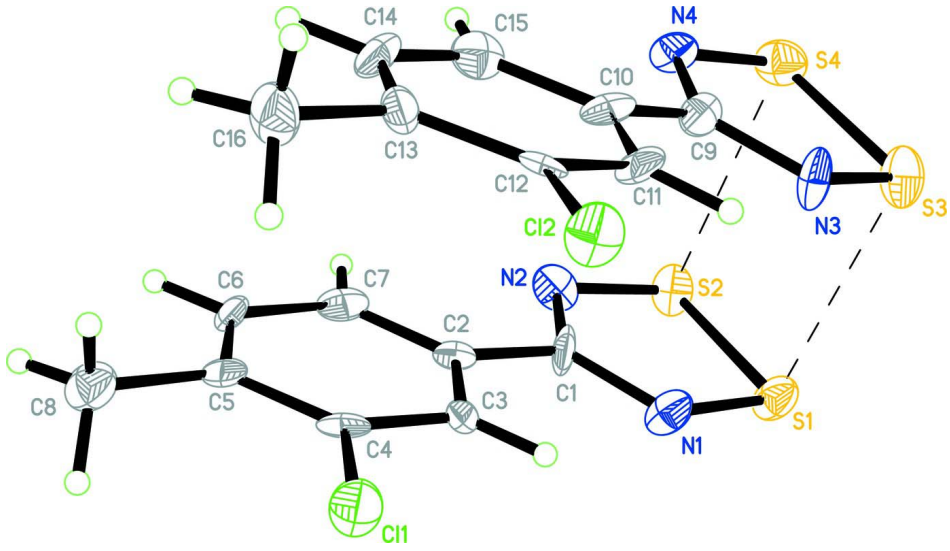

Figure 1

The structure of the title compound with displacement ellipsoids drawn at the 50% probability level showing S···S contacts (dashed lines).

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Crystal data

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$b = 13.407$ (3) Å
$c = 11.573$ (3) Å
$\beta = 95.87$ (4)°
$V = 916.3$ (6) Å^3
$Z = 4$
$F(000) = 468$
$D_x = 1.665$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 3.0$–$11.0°$
$\mu = 0.82$ mm^{-1}
$T = 150$ K
Prism, colourless
0.25 × 0.18 × 0.15 mm

Data collection

Rigaku AFC-6S diffractometer
Graphite monochromator
ω scans
1655 measured reflections
1499 independent reflections
1054 reflections with $I > 2\sigma(I)$
$R_{int} = 0.103$
$\theta_{max} = 24.0°$, $\theta_{min} = 3.5°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.098$
$S = 1.09$
1499 reflections
237 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
$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 2.2783P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Absolute structure: Flack (1983), 169 Friedel pairs
Absolute structure parameter: −0.16 (19)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
S2	0.5244 (5)	0.3269 (2)	−0.1014 (2)	0.0271 (7)
S1	0.2324 (4)	0.3359 (2)	−0.0142 (2)	0.0263 (7)
N2	0.6580 (15)	0.4154 (7)	−0.0244 (7)	0.025 (2)
N1	0.3323 (14)	0.4260 (6)	0.0724 (7)	0.024 (2)
C1	0.5430 (17)	0.4558 (8)	0.0533 (9)	0.024 (2)
C2	0.6477 (16)	0.5355 (8)	0.1287 (8)	0.017 (2)
C6	0.9463 (14)	0.6549 (7)	0.1743 (7)	0.019 (2)
H6	1.0823	0.6826	0.1567	0.023*
C7	0.8533 (15)	0.5770 (8)	0.1066 (8)	0.021 (2)
H7	0.9289	0.5524	0.046	0.025*
C3	0.5398 (15)	0.5719 (7)	0.2224 (8)	0.020 (2)
H3	0.4034	0.5447	0.2401	0.024*
C5	0.8434 (15)	0.6933 (8)	0.2681 (8)	0.021 (2)
C8	0.9427 (16)	0.7782 (8)	0.3392 (8)	0.026 (2)
H8A	1.061	0.8085	0.3007	0.039*
H8B	1.004	0.7542	0.414	0.039*
H8C	0.827	0.8267	0.3488	0.039*
C4	0.6413 (15)	0.6499 (7)	0.2885 (7)	0.018 (2)
Cl1	0.5049 (4)	0.6884 (2)	0.4074 (2)	0.0278 (7)
S3	0.3937 (5)	0.1726 (2)	0.1531 (2)	0.0302 (7)
S4	0.7080 (4)	0.1669 (2)	0.0853 (2)	0.0293 (7)
Cl2	0.5678 (4)	0.47502 (19)	0.6289 (2)	0.0259 (6)
N4	0.8253 (12)	0.2511 (6)	0.1763 (7)	0.0208 (19)
C10	0.7757 (15)	0.3556 (7)	0.3403 (7)	0.018 (2)
C15	0.9878 (16)	0.4033 (8)	0.3377 (8)	0.025 (2)
H15	1.079	0.3871	0.2797	0.031*
C9	0.6891 (16)	0.2851 (8)	0.2539 (8)	0.021 (2)
C12	0.7250 (15)	0.4511 (7)	0.5142 (7)	0.014 (2)
C11	0.6480 (15)	0.3831 (7)	0.4301 (8)	0.022 (2)
H11	0.506	0.3544	0.4332	0.027*
C14	1.0611 (14)	0.4740 (8)	0.4206 (7)	0.023 (2)
H14	1.2004	0.5047	0.4161	0.027*

C13	0.9336 (16)	0.5008 (7)	0.5106 (8)	0.020 (2)
C16	1.0139 (17)	0.5799 (8)	0.6005 (9)	0.029 (3)
H16A	0.8912	0.6245	0.6114	0.043*
H16B	1.1369	0.6169	0.5738	0.043*
H16C	1.0639	0.5482	0.673	0.043*
N3	0.4777 (14)	0.2515 (7)	0.2537 (7)	0.025 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0299 (17)	0.0296 (16)	0.0226 (14)	−0.0059 (15)	0.0067 (12)	−0.0050 (12)
S1	0.0193 (14)	0.0277 (15)	0.0311 (15)	−0.0007 (13)	−0.0007 (12)	−0.0104 (14)
N2	0.031 (5)	0.025 (5)	0.022 (4)	0.001 (4)	0.012 (4)	0.001 (4)
N1	0.019 (5)	0.026 (5)	0.026 (5)	0.000 (4)	0.001 (4)	−0.011 (4)
C1	0.018 (5)	0.022 (6)	0.031 (6)	−0.013 (5)	−0.005 (4)	0.006 (5)
C2	0.015 (5)	0.019 (6)	0.018 (5)	0.007 (4)	0.002 (4)	0.001 (4)
C6	0.008 (4)	0.025 (7)	0.023 (5)	−0.002 (4)	−0.001 (4)	0.004 (4)
C7	0.022 (6)	0.027 (6)	0.014 (5)	0.007 (5)	−0.002 (4)	0.007 (5)
C3	0.015 (5)	0.012 (5)	0.032 (6)	0.001 (4)	−0.005 (5)	0.007 (5)
C5	0.015 (5)	0.018 (6)	0.030 (5)	0.003 (5)	−0.007 (4)	0.008 (5)
C8	0.022 (5)	0.031 (6)	0.024 (5)	−0.001 (5)	−0.002 (5)	−0.004 (5)
C4	0.016 (5)	0.026 (7)	0.012 (5)	0.013 (5)	0.000 (4)	−0.003 (5)
Cl1	0.0259 (13)	0.0279 (17)	0.0310 (14)	−0.0008 (13)	0.0090 (10)	−0.0078 (13)
S3	0.0353 (15)	0.0314 (17)	0.0242 (13)	−0.0117 (14)	0.0047 (11)	−0.0063 (13)
S4	0.0318 (15)	0.0270 (17)	0.0287 (14)	0.0049 (14)	0.0005 (12)	−0.0049 (13)
Cl2	0.0266 (13)	0.0286 (16)	0.0240 (13)	−0.0004 (14)	0.0094 (10)	−0.0073 (13)
N4	0.019 (4)	0.019 (5)	0.025 (5)	0.005 (4)	0.003 (4)	−0.011 (4)
C10	0.015 (5)	0.031 (7)	0.008 (4)	0.008 (5)	−0.003 (4)	0.006 (4)
C15	0.028 (6)	0.028 (6)	0.022 (5)	0.005 (5)	0.010 (4)	0.008 (5)
C9	0.019 (5)	0.027 (6)	0.017 (5)	−0.003 (5)	0.001 (4)	0.010 (5)
C12	0.018 (5)	0.012 (5)	0.012 (5)	0.009 (4)	0.000 (4)	0.002 (4)
C11	0.013 (5)	0.026 (6)	0.026 (5)	0.001 (5)	−0.008 (4)	0.005 (5)
C14	0.012 (5)	0.034 (6)	0.022 (5)	−0.004 (5)	0.001 (4)	0.002 (5)
C13	0.023 (6)	0.013 (5)	0.024 (6)	−0.003 (4)	−0.003 (4)	0.002 (4)
C16	0.029 (6)	0.021 (6)	0.037 (6)	−0.005 (5)	0.008 (5)	−0.012 (5)
N3	0.023 (5)	0.030 (5)	0.024 (4)	−0.013 (4)	0.011 (4)	−0.008 (4)

Geometric parameters (Å, º)

S2—N2	1.639 (10)	S3—N3	1.613 (9)
S2—S1	2.096 (3)	S3—S4	2.098 (4)
S1—N1	1.641 (8)	S4—N4	1.648 (8)
N2—C1	1.302 (13)	Cl2—C12	1.728 (9)
N1—C1	1.352 (13)	N4—C9	1.348 (12)
C1—C2	1.476 (13)	C10—C11	1.398 (13)
C2—C7	1.388 (13)	C10—C15	1.415 (13)
C2—C3	1.403 (13)	C10—C9	1.432 (13)
C6—C7	1.387 (13)	C15—C14	1.387 (13)

C6—C5	1.397 (12)	C15—H15	0.93
C6—H6	0.93	C9—N3	1.333 (12)
C7—H7	0.93	C12—C11	1.377 (13)
C3—C4	1.395 (13)	C12—C13	1.411 (13)
C3—H3	0.93	C11—H11	0.93
C5—C4	1.375 (12)	C14—C13	1.396 (13)
C5—C8	1.491 (14)	C14—H14	0.93
C8—H8A	0.96	C13—C16	1.528 (13)
C8—H8B	0.96	C16—H16A	0.96
C8—H8C	0.96	C16—H16B	0.96
C4—Cl1	1.746 (8)	C16—H16C	0.96

N2—S2—S1	94.3 (3)	N3—S3—S4	94.2 (3)
N1—S1—S2	94.1 (3)	N4—S4—S3	94.0 (3)
C1—N2—S2	114.7 (7)	C9—N4—S4	114.5 (7)
C1—N1—S1	113.6 (7)	C11—C10—C15	116.6 (9)
N2—C1—N1	123.3 (10)	C11—C10—C9	120.6 (8)
N2—C1—C2	119.3 (9)	C15—C10—C9	122.7 (8)
N1—C1—C2	117.3 (9)	C14—C15—C10	120.7 (8)
C7—C2—C3	118.8 (9)	C14—C15—H15	119.6
C7—C2—C1	120.4 (9)	C10—C15—H15	119.6
C3—C2—C1	120.7 (9)	N3—C9—N4	120.9 (9)
C7—C6—C5	122.4 (9)	N3—C9—C10	119.7 (8)
C7—C6—H6	118.8	N4—C9—C10	119.4 (8)
C5—C6—H6	118.8	C11—C12—C13	121.4 (8)
C6—C7—C2	120.3 (9)	C11—C12—Cl2	119.9 (7)
C6—C7—H7	119.9	C13—C12—Cl2	118.7 (7)
C2—C7—H7	119.9	C12—C11—C10	122.3 (9)
C4—C3—C2	118.6 (9)	C12—C11—H11	118.9
C4—C3—H3	120.7	C10—C11—H11	118.9
C2—C3—H3	120.7	C15—C14—C13	122.4 (9)
C4—C5—C6	115.8 (9)	C15—C14—H14	118.8
C4—C5—C8	122.1 (9)	C13—C14—H14	118.8
C6—C5—C8	122.1 (9)	C14—C13—C12	116.5 (9)
C5—C8—H8A	109.5	C14—C13—C16	122.1 (9)
C5—C8—H8B	109.5	C12—C13—C16	121.4 (8)
H8A—C8—H8B	109.5	C13—C16—H16A	109.5
C5—C8—H8C	109.5	C13—C16—H16B	109.5
H8A—C8—H8C	109.5	H16A—C16—H16B	109.5
H8B—C8—H8C	109.5	C13—C16—H16C	109.5
C5—C4—C3	124.0 (8)	H16A—C16—H16C	109.5
C5—C4—Cl1	119.5 (7)	H16B—C16—H16C	109.5
C3—C4—Cl1	116.4 (7)	C9—N3—S3	116.4 (7)