Preparation and characterization of the disjoint diradical 4,4'-bis(1,2,3,5-dithiadiazolyl) [S2N2C-CN2S2] and its iodine charge transfer salt [S2N2C-CN2S2]

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Table S1 Crystal and refinement data

formula	$S_4N_4C_2I$
fw	335.19
crystal size, mm	0.03 x 0.08 x 0.54
crystal color	brown
crystal mount	on fiber by silicone rubber
a, Å	11.909(3)
b, Å	3.271(2)
c, Å	19.860(6)
V, Å^3	773.6(7)
cell detn, refls	25
cell detn, 2θ range, deg	16-29
d(calcd), g cm^{-3}	2.88
space group	Ccmm
Z	4
F_{000}	627.91
radiation	MoK_α, graphite monochromated
λ, Å	0.71073
temp, K	293
linear abs coeff, mm^{-1}	5.07
diffractometer	Enraf-Nonius CAD-4
scan technique	θ-2θ
scan speed, deg min^{-1}	4-16 (in omega)
scan width, deg	1.0 + 0.35tanθ
2θ range, deg	4-58
h,k,l ranges	-16,0; 0,4; -23,23
exposure time, hrs	13.0
std refl indices	0,2,0; -3,1,-2
drift of stds, %	1.6
absorption correction	empirical psi scans
absorption, range	0.78-1.00
refl meas	1177
unique refls	606
R for merge	0.044

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data with $I > 3\sigma(I)$	391
solution method	Direct Methods
parameters refined	42
$R(F)$, $R_w(F)$	0.059,0.078
GOF	1.60
p, $w^{-1}=[\sigma^2(I)+pI^2]/4F^2$	0.04
largest Δ/σ	0.000
extinction correction	83(35)[a]
final diff map, e $Å^{-3}$	-2.3(4) and +1.7(4)
programs	NRC386 (PC version of NRCVAX)[b]
scattering factors	International Tables for Crystallography Vol 4
I atom treatment	Occupancy factors were determined during isotropic refinement and locked at those values during subsequent anisotropic refinement.

[a]Larson, A.C., in *Crystallographic Computing*, edited by F.R.Ahmed, p. 293, 1970, Copenhagen, Munksgaard.

[b]NRCVAX - An Interactive Program System for Structure Analysis, E.J. Gabe, Y. LePage, J.P. Charland, F.L. Lee, and P.S. White, *J. Appl. Crystallogr.* **22**, 383 (1989).

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Table S2 Atomic parameters *x*, *y*, *z*, B_{eq} and occupancy factors for **[4]**[I]. ESDs refer to the last digit printed.

	x	*y*	*z*	B_{eq}	*Occupancy*
I1	0.6689 (24)	0	1/4	11.8 (27)	0.181
I2	0.67256(20)	0.0722 (21)	1/4	2.21(19)	0.409
S1	0.9216 (3)	0	0.15240(17)	2.23(13)	
S2	0.7806 (3)	0	0.08997(16)	2.18(13)	
N1	1.0118 (9)	0	0.0907 (6)	2.2 (4)	
N2	0.8536 (8)	0	0.0208 (5)	1.9 (4)	
C1	0.9636 (9)	0	0.0300 (6)	1.7 (4)	

B_{eq} is the mean of the principal axes of the thermal ellipsoid. Only those occupancy factors determined by least-squares refinement are included in this table.

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Table S3 Intramolecular distances (Å) and angles (deg) for [**4**][I]. ESDs refer to the last digit printed.

Distances

S(1)-S(2)	2.088(4)	
S(1)-N(1)	1.630(12)	
S(2)-N(2)	1.626(11)	
N(1)-C(1)	1.335(16)	
N(2)-C(1)	1.323(15)	
C(1)-C(1)	1.473(24)	at 2-x, -y, -z

Angles

S(2)-S(1)-N(1)	94.8(4)
S(1)-S(2)-N(2)	94.1(4)
S(1)-N(1)-C(1)	113.3(8)
S(2)-N(2)-C(1)	114.4(9)
N(1)-C(1)-N(2)	123.4(11)
N(1)-C(1)-C(1)	118.5(10)
N(2)-C(1)-C(1)	118.1(11)

Table S4 Intermolecular I...I, I...S, S...S, and S...N contacts (Å) for [**4**][I]. ESDs refer to the last digit printed.

I(1)-I(1)	3.271(2)	at x, y+1, z	[Unit cell repeat]
I(1)-I(2)	3.035(7)	at x, y-1, z	
I(2)-I(2)	2.799(14)	at x, 1-y, 0.5-z	
I(1)-S(1)	3.580(24)		
I(1)-S(2)	3.445(11)		
I(2)-S(1)	3.551(4)		
I(2)-S(2)	3.437(3)		
S(1)-S(1)	3.877(7)	at x, -y, 0.5-z	
S(2)-S(2)	3.997(6)	at 1.5-x, 0.5-y, -z	
S(2)-N(2)	3.172(9)	at 1.5-x, 0.5-y, -z	
S(2)-N(2)	3.172(9)	at 1.5-x, -0.5-y, -z	

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Table S5 Anisotropic temperature factors, u(i,j)*100, for [**4**][I]. ESDs refer to the last digit printed.

	u11	u22	u33	u12	u13	u23
I1	8.8 (19)	5.4 (16)	30.5 (53)	0.0	0.0	0.0
I2	2.52(10)	3.7 (4)	2.21(10)	0.39(10)	0.0	0.0
S1	2.54(15)	2.72(18)	3.22(17)	0.0	-0.19(12)	0.0
S2	2.00(14)	3.06(19)	3.24(17)	0.0	0.02(11)	0.0
N1	1.9 (4)	2.5 (6)	4.1 (6)	0.0	-0.4 (4)	0.0
N2	2.0 (5)	2.3 (6)	3.0 (5)	0.0	-0.2 (4)	0.0
C1	2.0 (5)	1.0 (5)	3.4 (6)	0.0	-0.2 (4)	0.0

Anisotropic temperature factors are of the form:

$$\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)].$$

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Table S6 Optimized geometries (subject to the symmetry constraints noted) of **4** and $[\mathbf{4}]_2$.[a]

	CEP-31G*	6-31G*	6-311G*
	planar diradical singlet (D_{2h}, τ = 0°)		
C-C	1.518	1.497	1.500
C-N	1.322	1.310	1.309
N-S	1.641	1.632	1.629
S-S	2.075	2.067	2.082
N-C-N	124.12	123.64	123.61
C-N-S	113.38	113.89	114.21
N-S-S	94.56	94.29	93.99
C-C-N	117.94	118.18	118.20
	planar triplet (D_{2h}, τ = 0°)		
C-C	1.520	1.499	1.502
C-N	1.322	1.311	1.309
N-S	1.641	1.632	1.628
S-S	2.075	2.067	2.081
N-C-N	124.21	123.73	123.71
C-N-S	113.33	113.85	114.15
N-S-S	94.56	94.29	93.99
C-C-N	117.90	118.14	118.15
	twisted diradical singlet (D_{2d}, τ = 90°)		
C-C	1.513	1.495	1.496
C-N	1.320	1.309	1.307
N-S	1.646	1.637	1.633
S-S	2.072	2.063	2.077
N-C-N	124.86	124.38	124.39
C-N-S	112.87	113.37	113.66
N-S-S	94.70	94.44	94.14
C-C-N	117.57	117.81	117.81

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	twisted triplet (D_{2d}, τ = 90°)		
C-C	1.515	1.497	1.498
C-N	1.320	1.309	1.307
N-S	1.646	1.636	1.633
S-S	2.071	2.062	2.077
N-C-N	124.94	124.47	124.49
C-N-S	112.84	113.33	113.62
N-S-S	94.69	94.46	94.14
C-C-N	117.53	117.77	117.76
	closed shell singlet dimer (D_{2h})		
S---S	3.129	3.099	3.096
C-C	1.517	1.499	1.501
C-N	1.323	1.312	1.310
N-S	1.635	1.624	1.621
S-S	2.061	2.054	2.065
N-C-N	124.48	124.06	124.05
C-N-S	112.83	113.31	113.55
N-S-S	94.93	94.65	94.42
C-C-N	117.76	117.97	117.98

[a]Distances are in Å and angles in degrees.

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Figure S1 ORTEP drawing of the asymmetric unit in [**4**][I], showing atom numbering.