University of Groningen

Molecular Conductors from Neutral-Radical Charge-Transfer Salts

Bryan, C.D.; Haddon, R.C.; Hicks, R.G.; Kennepohl, D.K.; MacKinnon, C.D.; Oakley, R.T.; Palstra, T.T.M.; Perel, A.S.; Scott, S.R.; Schneemeyer, L.F.

Published in:
Journal of the American Chemical Society

DOI:
[10.1021/ja00083a005](https://doi.org/10.1021/ja00083a005)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1994

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Bryan, C. D., Haddon, R. C., Hicks, R. G., Kennepohl, D. K., MacKinnon, C. D., Oakley, R. T., Palstra, T. T. M., Perel, A. S., Scott, S. R., Schneemeyer, L. F., Waszczak, J. V., & Cordes, A. W. (1994). Molecular Conductors from Neutral-Radical Charge-Transfer Salts: Preparation and Characterization of an Iodine-Doped Hexagonal Phase of 1,2,3,5-Dithiadiazolyl ([HCN₂S₂][•]). *Journal of the American Chemical Society*, 116(4). <https://doi.org/10.1021/ja00083a005>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

J-1210-m1

Table S1 Crystal and Refinement Data

formula	$S_4N_{4.16}C_2H_2$	$S_2N_2CHI_{0.18}$
fw	212.4	128.20
crystal size, mm	0.20 x 0.30 x 0.68	0.20 x 0.20 x 0.65
crystal color	black	black
crystal mount	in epoxy-filled capillary	in epoxy-filled capillary
a , Å	6.816(3)	14.132(16)
b , Å	13.940(2)	14.132(16)
c , Å	14.403(3)	3.352(5)
α , deg	116.830(14)	90
β , deg	98.64(3)	90
γ , deg	99.18(3)	120
V , Å ³	1166.5(6)	579.8(1)
cell detn, refls	25	25
cell detn, 2θ range, deg	13-25	16-18
d (calcd), g cm ⁻³	1.81	2.203
space group	$P\bar{1}$	$P6_1$
Z	6	6
F_{000}	645.1	376.39
radiation	MoK α , graphite monochromated	
λ , Å	0.71073	
temp, K	293	
diffractometer	Enraf-Nonius CAD-4	
scan technique	θ - 2θ	
linear abs coeff, mm ⁻¹	1.10	2.38
scan speed, deg min ⁻¹	4-16 (in omega)	4-16 (in omega)
scan width, deg	1.0 + 0.35tan θ	1.0 + 0.35tan θ
2θ range, deg	4-50	4-50
h , k , l ranges	-8,8; 0,19; 0,22	0,14; 0,14; 0,3
exposure time, hrs	53.4	15.6

© 1994 Am. Chem. Soc.
J. Am. Chem. Soc. v 116
p. 1205 Bryan

Supplementary material,
page 1

J-1210-m2

std refl indices	-2,1,-1; 0,0,5; 1,3,2	-4,2,-1; 5,0,0; 0,5,0
drift of stds, %	0.9	1.1
absorption correction	empirical psi-scans	empirical psi scans
absorption, range	0.80 - 1.00	0.517 - 0.999
refl meas	8176	2324
unique refls	4088	400
R for merge	0.04	0.091
data with $I > 3\sigma(I)$	1746	198
solution method	Direct Methods	SHELX
parameters refined	273	32
$R(F^2)$, $R_w(F^2)^a$	0.045,0.054	0.074,0.115
GOF	1.31	1.94
p , $w^{-1} = [\sigma^2(I) + pI_2]/4F^2$	0.03	0.05
largest Δ/σ	0.004	0.017
extinction correction	none	none
final diff map, $e \text{ \AA}^{-3}$	+0.50(9), -0.35(9)	-0.40(13) +0.51(13)
programs	NRC386 (PC version of NRCVAX) ^b	
scattering factors	Internat. Tables for Crystallography Vol 4	
H atom treatment	idealized positions (C-H = 0.95A)	

$$^a R = [\Sigma ||F_o| - |F_c||]/[\Sigma |F_o|]; R_w = \{[\Sigma w ||F_o| - |F_c||^2]/[\Sigma (w|F_o|^2)]\}^{1/2}$$

^bNRCVAX, an interactive program system for structure analysis; see E.J. Gabe, Y. LePage, J.P. Charland, F.L. Lee, and P.S. White, *J. Appl. Cryst.* 22, 383 (1989).

© 1994 Am. Chem. Soc.
J. Am. Chem. Soc. v 116
p. 1205 Bryan

Supplementary material,
page 2

J-1210-m3

Table S2 Interatomic distances (Å) and angles (deg) in $[\text{HCN}_2\text{S}_2]_2[\text{N}_2]_{0.08}$.

Distances

S(1)-S(2)	2.059(4)	S(11)-N(11)	1.636(9)
S(1)-N(1)	1.656(9)	S(12)-N(12)	1.637(9)
S(2)-N(2)	1.626(10)	N(1)-C(1)	1.333(16)
S(3)-S(4)	2.058(4)	N(2)-C(1)	1.328(16)
S(3)-N(3)	1.621(9)	N(3)-C(2)	1.335(16)
S(4)-N(4)	1.639(9)	N(4)-C(2)	1.311(16)
S(5)-S(6)	2.055(4)	N(5)-C(3)	1.334(15)
S(5)-N(5)	1.658(9)	N(6)-C(3)	1.334(16)
S(6)-N(6)	1.613(9)	N(7)-C(4)	1.335(16)
S(7)-S(8)	2.070(4)	N(8)-C(4)	1.308(15)
S(7)-N(7)	1.629(10)	N(9)-C(5)	1.330(15)
S(8)-N(8)	1.639(9)	N(10)-C(5)	1.323(14)
S(9)-S(10)	2.065(4)	N(11)-C(6)	1.338(14)
S(9)-N(9)	1.643(9)	N(12)-C(6)	1.301(15)
S(10)-N(10)	1.634(9)	N(98)-N(98) a	1.17
S(11)-S(12)	2.065(4)	N(98)-N(99)	1.13

Angles

S(2)-S(1)-N(1)	95.2(4)	S(5)-N(5)-C(3)	112.2(7)
S(1)-S(2)-N(2)	95.2(4)	S(6)-N(6)-C(3)	114.4(7)
S(4)-S(3)-N(3)	95.5(4)	S(7)-N(7)-C(4)	110.8(8)
S(3)-S(4)-N(4)	94.9(3)	S(8)-N(8)-C(4)	111.5(8)
S(6)-S(5)-N(5)	95.1(3)	S(9)-N(9)-C(5)	111.9(7)
S(5)-S(6)-N(6)	95.1(3)	S(10)-N(10)-C(5)	113.1(8)
S(8)-S(7)-N(7)	95.6(4)	S(11)-N(11)-C(6)	112.2(7)
S(7)-S(8)-N(8)	94.9(3)	S(12)-N(12)-C(6)	112.8(7)
S(10)-S(9)-N(9)	95.4(4)	N(1)-C(1)-N(2)	124.7(10)
S(9)-S(10)-N(10)	94.6(4)	N(3)-C(2)-N(4)	125.7(10)
S(12)-S(11)-N(11)	94.8(3)	N(5)-C(3)-N(6)	123.2(9)
S(11)-S(12)-N(12)	95.0(3)	N(7)-C(4)-N(8)	127.2(11)
S(1)-N(1)-C(1)	111.6(8)	N(9)-C(5)-N(10)	124.9(10)
S(2)-N(2)-C(1)	113.2(8)	N(11)-C(6)-N(12)	125.3(9)
S(3)-N(3)-C(2)	111.9(8)		
S(4)-N(4)-C(2)	112.0(8)		

© 1994 Am. Chem. Soc.
J. Am. Chem. Soc. v 116
p. 1205 Bryan

Supplementary material,
page 3

J-1210-m4

Table S3 Interatomic distances (Å) and angles (deg) in $[\text{HCN}_2\text{S}_2]_6[\text{I}_{1.1}]$.

Distances

S(1)-S(2) 2.051(11)
S(1)-N(1) 1.65(3)
S(2)-N(2) 1.654(24)
N(1)-C(1) 1.34(4)
N(2)-C(1) 1.31(4)

Angles

S(2)-S(1)-N(1) 95.4(10)
S(1)-S(2)-N(2) 95.3(8)
S(1)-N(1)-C(1) 111.2(19)
S(2)-N(2)-C(1) 112.1(20)
N(1)-C(1)-N(2) 125(3)

© 1994 Am. Chem. Soc.
J. Am. Chem. Soc. v 116
p. 1205 Bryan

Supplementary material,
page 4

J-1210-m5

Table S4 Table of $u(i,j)$ values (*100) for $[\text{HCN}_2\text{S}_2]_2[\text{N}_2]_{0.08}$. ESDs refer to the last digit printed.

	u11(U)	u22	u33	u12	u13	u23
S1	4.74(21)	3.73(18)	4.26(18)	-0.84(16)	0.58(16)	1.78(14)
S2	5.50(22)	3.62(19)	4.12(18)	0.36(17)	1.47(16)	1.56(14)
S3	6.58(24)	2.95(17)	4.62(19)	1.30(17)	1.64(18)	1.99(14)
S4	4.53(20)	3.62(18)	3.78(17)	0.74(16)	0.40(15)	1.70(14)
S5	4.27(20)	3.65(18)	4.54(18)	-0.05(16)	0.77(15)	2.08(14)
S6	5.12(20)	3.29(18)	4.24(18)	1.02(16)	0.95(16)	2.08(14)
S7	5.59(22)	3.68(19)	4.78(19)	1.00(17)	0.88(17)	2.04(15)
S8	4.64(20)	4.38(19)	3.22(16)	0.27(17)	0.94(15)	1.92(14)
S9	5.22(22)	4.08(21)	3.95(18)	0.74(19)	1.69(17)	1.89(15)
S10	4.16(20)	3.55(19)	3.95(18)	0.31(17)	0.44(15)	1.46(14)
S11	4.72(21)	3.73(19)	4.33(18)	0.74(18)	0.70(16)	2.12(15)
S12	4.62(20)	3.30(18)	3.38(17)	0.68(16)	1.14(15)	1.29(13)
N1	5.0 (7)	4.5 (7)	3.6 (6)	0.5 (6)	0.1 (5)	2.1 (5)
N2	4.4 (7)	4.4 (6)	5.3 (6)	1.3 (6)	1.7 (5)	2.2 (5)
N3	7.5 (8)	3.9 (6)	3.7 (6)	0.5 (6)	1.8 (6)	1.4 (5)
N4	5.7 (7)	3.6 (6)	4.6 (6)	0.4 (6)	1.1 (5)	2.1 (5)
N5	5.7 (7)	4.7 (7)	3.0 (6)	1.2 (6)	0.9 (5)	2.0 (5)
N6	8.1 (8)	2.9 (6)	3.3 (6)	0.8 (6)	1.3 (5)	1.0 (5)
N7	5.7 (7)	5.0 (7)	5.0 (6)	0.9 (6)	0.6 (5)	3.0 (5)
N8	4.4 (6)	4.6 (6)	3.8 (6)	0.1 (5)	0.9 (5)	1.9 (5)
N9	6.5 (8)	4.7 (7)	4.2 (6)	1.5 (6)	2.1 (6)	1.6 (5)
N10	4.9 (7)	3.5 (6)	6.6 (7)	1.1 (6)	1.2 (6)	3.0 (5)
N11	3.9 (6)	3.5 (6)	3.5 (6)	0.1 (5)	0.0 (5)	1.2 (5)
N12	6.8 (8)	4.3 (6)	2.6 (5)	1.4 (6)	1.8 (5)	1.7 (5)
C1	3.6 (7)	5.4 (8)	5.6 (8)	0.5 (7)	0.0 (6)	3.9 (7)
C2	7.4 (11)	4.6 (9)	4.4 (8)	1.3 (8)	2.8 (8)	2.4 (7)
C3	5.4 (9)	4.3 (8)	3.1 (7)	0.8 (7)	0.9 (6)	0.5 (6)
C4	4.9 (9)	6.2 (10)	3.7 (7)	0.6 (8)	0.0 (6)	2.5 (7)
C5	4.4 (8)	3.2 (7)	3.2 (7)	0.9 (6)	-0.4 (6)	0.2 (5)
C6	4.5 (8)	3.1 (7)	5.9 (8)	0.5 (6)	2.5 (7)	2.5 (6)

Table S5 Table of $u(i,j)$ values (*100) for $[\text{HCN}_2\text{S}_2]_6[\text{I}_{1.1}]$. ESDs refer to the last digit printed.

	u11(U)	u22	u33	u12	u13	u23
S1	8.1(5)	8.6(5)	7.5(7)	3.7(4)	-1.1(5)	1.1(5)
S2	8.6(6)	8.5(5)	9.7(8)	4.1(4)	-1.1(5)	2.3(6)

Anisotropic temperature factors are of the form:

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

J-1210-m6

Figure S1 ORTEP drawings of the three non-equivalent dimers in $[\text{HCN}_2\text{S}_2]_2[\text{N}_2]_{0.08}$, showing atom numbering.

© 1994 Am. Chem. Soc.
J. Am. Chem. Soc. v 116
p. 1205 Bryan

Supplementary material,
page 6

J-1210-m7

Figure S2 ORTEP drawings of the heterocyclic ring in $[\text{HCN}_2\text{S}_2]_6[\text{I}_{1.1}]$, showing atom numbering.

© 1994 Am. Chem. Soc.
J. Am. Chem. Soc. v 116
p. 1205 Bryan

Supplementary material,
page 7