Preparation and Solid State Characterization of 1,2,3,5-Diselenadiazolyl [HCN$_2$Se$_2$]$^+$

A. Wallace Cordes,a Sivert H. Glarum,b Robert C. Haddon,b Randal Hallford,a Robin G. Hicks,c Dietmar K. Kennepohl1,CRiehard T. Oakley,c Thomas T. M. Palstrab and Syrona R. Scotta

The reaction of N,N'-tris(trimethylsilyl)formamidine with SeC$_2$I affords 1,2,3,5-diselenadiazolium chloride, which can be reduced with triphenylantimony to the corresponding diselenadiazolyl radical [HCN$_2$Se$_2$]$^-$; the solid state structure and conductivity of the dimer [HCN$_2$Se$_2$I$_2$] are reported.

Interest in the design of molecular conductors based on neutral π-radicals has prompted the study of heterocyclic thiazyl and selenazyl radicals, in particular derivatives of 1,2,3,5-dithia- and diselena-diazolyl. Several systems with different substituents in the 4-position have been characterized in the solid state.3,4 Structure–conductivity correlations based on several selenium derivatives5–6 indicate that the size of the 4-substituent plays an important role in determining the number and magnitude of close intramolecular interactions, and hence band dispersion.7 In the belief that smaller organic substituents should lead to more densely-packed structures with narrower band gaps, we have prepared the prototypical diselenadiazolyl heterocycle 1, in which the organic group has been removed entirely. The solid state characterization of the dimer is also described.

Fig. 1 General view of the crystal structure of [HCN$_2$Se$_2$I$_2$], showing head-over-tail stacking of dimers. Intradimer distances (Å) are Se(1)...Se(2) 2.329(4); Se(3)...Se(4) 2.322(4); Se(1)...Se(3) 3.215(3); Se(2)...Se(4) 3.345(3); interdimer contacts (Å) are d$_1$, Se(4)...Se(2') 3.382(4); d$_2$, Se(4)...Se(4') 3.376(5); d$_3$, Se(1)...Se(4') 4.049(4); d$_4$, Se(1)...Se(1') 3.445(5); d$_5$, Se(2)...Se(4') 3.724(4); d$_6$, Se(1)...Se(3') 3.774(5).

The crystal structure of the dimer of 1 has been determined by X-ray diffraction.8 The structure consists of antiparallel arrays of cofacial dimers [HCN$_2$Se$_2$I$_2$]; Fig. 1 provides a general view of the structure, defines the interdimer contacts d$_1$–d$_6$, and illustrates the head-over-tail packing of dimers. All intramolecular bond lengths and angles are nominal, but the two interannular contacts Se(1)...Se(3) [3.215(3) Å] and Se(2)...Se(4) [3.345(3) Å] are notably different (cf. [PhC=NC$_2$Se$_2$]).9 The interdimer Se...Se contacts d$_5$ and d$_6$ are well within the van der Waals separation,10 and generate a strong network of lateral interactions. These lateral contacts help lace together interpenetrating spiral-like columns of dimers, one of which is shown in Fig. 2. Within these columns, which run parallel to z, there are many close Se...Se contacts. The interactions d$_1$, d$_2$ and d$_3$, which connect dimer units that approach one another in a side-slipped head-on manner, are all exceptionally short. The final contact d$_4$ runs almost parallel to z and connects (somewhat loosely) rings in a corner-to-corner fashion.

Our primary synthetic route to both 1,2,3,5-dithia- and diselena-diazolium cations has involved the condensation of persilylated amidines RCN(SiMe$_3$)$_2$NSiMe$_3$ with ECl$_3$ (E = S, Se). However, the method of preparation of the amidines, the addition of LiN(SiMe$_3$)$_2$ to a nitrile RCN, appears to be limited to aryl nitriles. We have now discovered that the parent compound N,N'-tris(trimethylsilyl)formamidine 2 can be conveniently generated by the reaction of LiN(SiMe)$_3$ with Me$_3$SiCl$_2$ (25.7 g, 237 mmol) in 200 ml toluene, followed by treatment of the intermediate lithiated amidine with Me$_3$SiCl (54.1 g, 224 mmol) with 1,3,5-triazine (6.2 g, 76 mmol) in 200 ml toluene, followed by treatment with triphenylantimony (0.96 g, 2.7 mmol) in acetone (140 ml) affords the diselenadiazolium chloride 3. Addition of 2 (6.38 g, 24 mmol) to selenium dichloride (3.60 g, 24 mmol, prepared in situ from Se and SeCl$_2$ in acetonitrile (140 ml) affords the diselenadiazolium cation 3 (E = Se) as a reddish-brown powder in virtually quantitative yield. Reduction of this crude salt (1.27 g, 5.4 mmol) with triphenylantimony (0.96 g, 2.7 mmol) in acetonitrile (20 ml) yields 1,2,3,5-diselenadiazolyl 1, which can be purified by sublimation at 50°C/10⁻³ Torr as lustrous grey-black needles (0.56 g, 52%); decom. > 100°C; MS (70 eV) m/z 201 (M⁺, 40%), 174 (Se$_2$N⁺, 95%), 160 (Se$_2$⁺, 100%), 107 (HCNSe⁺, 8%), 94 (SeN⁺, 20%), 80 (Se⁺, 50%). The ESR signal (in CH$_2$Cl$_2$, 295K) of 1 consists of a featureless singlet, with g = 2.041.

Fig. 1 General view of the crystal structure of [HCN$_2$Se$_2$I$_2$], showing head-over-tail stacking of dimers. Intradimer distances (Å) are Se(1)...Se(2) 2.329(4); Se(3)...Se(4) 2.322(4); Se(1)...Se(3) 3.215(3); Se(2)...Se(4) 3.345(3); interdimer contacts (Å) are d$_1$, Se(4)...Se(2') 3.382(4); d$_2$, Se(4)...Se(4') 3.376(5); d$_3$, Se(1)...Se(4') 4.049(4); d$_4$, Se(1)...Se(1') 3.445(5); d$_5$, Se(2)...Se(4') 3.724(4); d$_6$, Se(1)...Se(3') 3.774(5).

Crystal data for 1: Se$_2$N$_2$CH, M = 199.0, triclinic, $\overline{P}1$, a = 6.279(4) Å, b = 7.96(1) Å, c = 8.012(5) Å, α = 69.94(5)°, β = 88.98(5)°, γ = 84.63(6)°, V = 374.1(4) Å$^3$, Z = 4, D$_m$ = 3.53 g cm$^{-3}$, $\mu$ = 19.4 mm$^{-1}$. Data were collected with an Enraf-Nonius CAD-4 automated diffractometer, with graphite-monochromated Mo-Kα-radiation (λ = 0.71073 Å) using 0–2θ scans to a 2θ$_{max}$ = 50°. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares analysis which minimized Σw(E$^2$ - F$^2$). 81 Parameters were refined using 700 unique observed reflections $\Sigma$ > 2.5σ(F) to give R = 0.048 and R$_{w}$ = 0.050. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Notice to Authors, Issue No. 1.
In the solid state the dimer \([\text{HCN}_2\text{Se}_2\text{I}_2]\) is diamagnetic, with a residual spin density, estimated by ESR, of 0.01\%. The material exhibits a single crystal conductivity of \(7 \times 10^{-6}\) S cm\(^{-1}\), a value which is at least three orders of magnitude higher than that seen in other monofunctional selenium-based radical dimers.\(^4\) Collectively the interdimer Se····Se contacts, indicated above, generate a structure in which dispersion of the valence and conduction bands is more pronounced than in organo-substituted materials.

We thank the NSERC of Canada, the NSF and the State of Arkansas for financial support.

Received, 13th May 1992; Com. 202481K

References