

An unprecedented mode of association in diselenadiazolyl radicals: crystal structures and magnetic properties of $[p\text{-XC}_6\text{F}_4\text{CNSeSeN}]_2$ ($\text{X} = \text{Cl}, \text{Br}$)[†]

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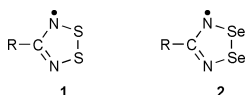
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Received (in Cambridge, UK) 13th June 2000, Accepted 1st November 2000

First published as an Advance Article on the web 27th November 2000

The two title compounds are isostructural with pairs of diselenadiazolyl radicals associating in an unprecedented manner *via* an orthogonal interaction between singly occupied molecular orbitals which renders them essentially diamagnetic in the solid state.

The 1,2,3,5-dithiadiazolyl radical **1** is an extremely persistent stable free radical.¹ Solution EPR studies on several derivatives



have established² that the dimerisation energy is substantial ($\Delta H_{\text{dim}} \approx 35 \text{ kJ mol}^{-1}$). In 1985, Mews and coworkers described³ the crystal structure of $[\text{CF}_3\text{CNSSN}]_2$ and predicted that association of dithiadiazolyl radicals could occur through a favourable π -bonding interaction between singly occupied molecular orbitals (SOMOs). The energy differences between *cisoid*, *transoid* and twisted conformations [Fig. 1(i)–(iii)] was estimated³ at $< 10 \text{ kJ mol}^{-1}$ and examples of all of these three modes of association have since been established by X-ray crystallography.¹ More recently a fourth, *trans*-cofacial motif has been observed [Fig. 1(iv)].⁴

The isoelectronic diselenadiazolyl radicals **2** have also been prepared⁵ and exhibit a greater tendency to dimerise in solution.⁶ Theoretical studies have estimated⁷ that ΔH_{dim} is higher [cf. **1** and **2** ($\text{R} = \text{H}$) with $\Delta H_{\text{dim}} = 33$ and 46 kJ mol^{-1} , respectively, using the same basis sets]. In the solid state, derivatives of **2** have invariably crystallised in the *cisoid* configuration observed for **1** [Fig. 1(i)]. Here we report the syntheses and characterisation of two diselenadiazolyl radicals **2a** and **2b** ($\text{R} = p\text{-ClC}_6\text{F}_4$ and $p\text{-BrC}_6\text{F}_4$, respectively), which associate in an unprecedented manner [Fig. 1(v)].

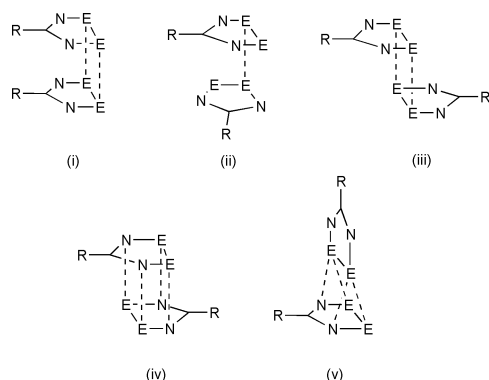


Fig. 1 Modes of association of dithiadiazolyl ($\text{E} = \text{S}$) and diselenadiazolyl ($\text{E} = \text{Se}$) radicals: (i) *cis*-cofacial, (ii) twisted, (iii) *trans*-antarafacial, (iv) *trans*-cofacial (v) orthogonal.

[†] Electronic supplementary information (ESI) available: analytical data for **2a** and **b**. See <http://www.rsc.org/suppdata/cc/b0/b004705h/>

Radicals **2a** and **2b** were prepared[†] from $p\text{-ClC}_6\text{F}_4\text{CN}$ and $p\text{-BrC}_6\text{F}_4\text{CN}$ using standard synthetic procedures,⁵ and purified by sublimations under static vacuum (100°C , 10^{-2} Torr). The crystal structures of **2a** and **2b** are isostructural, although not isomorphous.[‡] The structure of **2b** contains two molecules of conventional geometry⁸ in the asymmetric unit (Fig. 2). However, their mode of association is exceptional; The two heterocyclic rings in **2b** are inclined at 85° with respect to each other, with each of the selenium atoms of one ring situated approximately equidistant between an N and an Se atom of the second ring. This leads to a set of intermolecular $\text{Se}\cdots\text{N}$ and $\text{Se}\cdots\text{Se}$ contacts in the range $3.09\text{--}3.21 \text{ \AA}$. The $\text{Se}\cdots\text{Se}$ contact is similar to that observed in conventional *cisoid* diselenadiazolyls. Because of the anisotropy in the van der Waals radius of selenium (*ca.* 2.15 \AA perpendicular to the ring plane and *ca.* 1.7 \AA in the ring plane),⁹ the $\text{Se}\cdots\text{Se}$ interaction in this orthogonal arrangement (sum of van der Waals radii is 3.85 \AA)⁹ is likely to be weaker than that observed in the *cisoid* dimers (sum of the van der Waals radii perpendicular to the ring plane is *ca.* 4.3 \AA).⁹ A packing diagram of **2b** viewed in the *ac* plane (Fig. 3) shows how the dimer pairs pack in an antiparallel fashion along the crystallographic *c*-axis. The inter-dimer separation along the *c*-direction is longer, with the closest inter-dimer Se contacts in the range $3.6\text{--}3.7 \text{ \AA}$.

Previous magnetic studies on other derivatives of **2** have indicated that the $\pi^*\text{--}\pi^*$ interaction between cofacial radicals renders them diamagnetic. In order to establish the strength of the orthogonal interaction between radicals, variable temperature magnetic measurements were carried out on samples of both **2a** and **2b**.

Susceptibility measurements were made on a SQUID magnetometer with an applied field of 1 T in the range $1.8\text{--}300 \text{ K}$ and isothermal magnetisation curves were recorded at 1.8 and

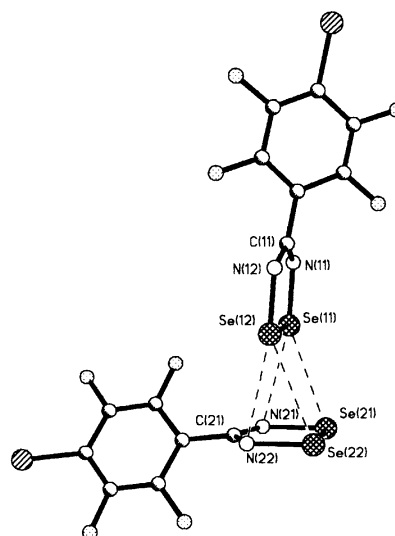


Fig. 2 Asymmetric unit of **2b**, with atom labelling scheme; the structural parameters of **2a** are the same as those for **2b**, within error.

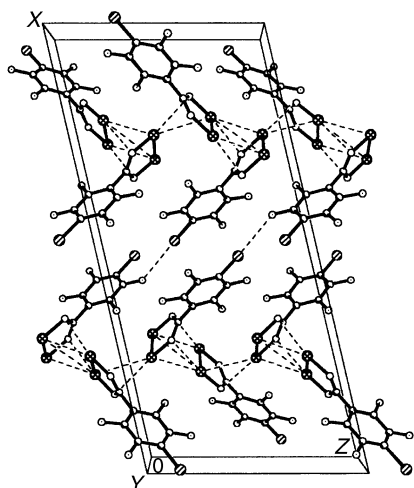


Fig. 3 Crystal structure of **2b** viewed in the *ac* plane. The closest inter-dimer contacts (illustrated) are Se...Se at 3.60 Å and Se...N at 3.46 Å.

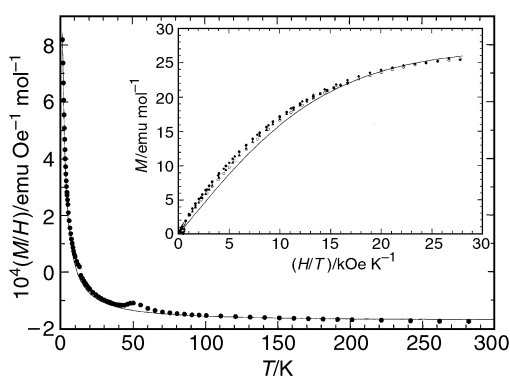


Fig. 4 Magnetic susceptibility as a function of temperature for **2b**. The solid line is the fit to the Curie–Weiss law and a diamagnetic contribution. Inset: Magnetisation behaviour of the unpaired spin moments of **2a** and **2b** as a function of the applied field. The solid line is the Brillouin function corresponding to $S = 1/2$ and a mol fraction of 0.0049 paramagnetic molecules. The data for **2a** has been scaled to the number of paramagnetic molecules found in **2b**.

3.0 K. A plot of susceptibility vs. temperature for both **2a** and **2b** are similar (that for **2b** is shown in Fig. 4) and shows that both **2a** and **2b** are essentially diamagnetic. A rapid increase in susceptibility at low temperatures is due to the presence of a small number of paramagnetic centres in the sample (a small spike can be observed at 50 K due to the antiferromagnetic transition of a minute amount of oxygen in the sample). A good fit to the Curie–Weiss law, including a diamagnetic contribution indicates that, for **2a**, the mol fraction of paramagnetic centres was 0.0045 and for **2b** 0.0054.

After a diamagnetic correction, the behaviour of the magnetisation as a function of the applied field in **2a** and **2b** closely follows a Brillouin function for $S = 1/2$ (Fig. 4, inset). A fit to the Brillouin function yielded mol fractions of paramagnetic centres as 0.0031 and 0.0049 for **2a** and **2b** respectively, in good agreement with the susceptibility results.

A preliminary examination of the interaction between SOMOs for this orthogonal mode of association indicates a symmetry-allowed bonding interaction (Fig. 5) which could give rise to a closed-shell singlet and thereby rationalise the observed diamagnetism. However, the poor orbital overlap anticipated from the perpendicular orientation of π^* orbitals could also be anticipated to favour an open shell ground state. The magnetic measurements clearly indicate a singlet ground state, although both closed-shell singlet (spin-paired dimer) and open-shell singlet (antiferromagnetically coupled radicals) are possible. In the latter case, the singlet–triplet separation would need to be extremely large to suppress the paramagnetism arising from the triplet state. However, very large exchange

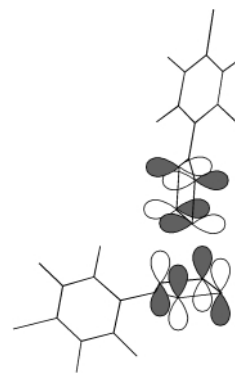


Fig. 5 The π^* – π^* bonding interaction between orthogonal π -systems on neighbouring diselenadiazolyl radicals.

interactions in group 15/16 radicals are not without precedent; Fujita and Awaga recently reported¹⁰ a dithiazolyl radical with an exchange interaction of -1300 K. Further theoretical and experimental studies are required to confirm the electronic ground state of **2**, viz-*a-viz* an open shell or closed shell singlet. These studies, and additional structural studies on closely related diselenadiazolyl radicals, will be the subject of a future report.

We thank the Royal Society for an equipment grant (J. M. R.) and the EPSRC for a studentship (R. J. L.). This work was also supported by the Materials Program of the Comision Interministerial de Ciencia y Tecnologia under grant MAT97-951.

Notes and references

‡ *Crystal data for 2b*: $C_7BrF_4N_2Se_2$, $M = 425.92$, monoclinic, space group $P2_1/c$, $a = 26.275(11)$, $b = 6.131(7)$, $c = 12.513(10)$ Å, $\beta = 102.85(6)^\circ$, $Z = 8$, $T = 180(2)$ K, $\mu(\text{Mo-K}\alpha) = 11.620$ mm⁻¹. Of a total of 2270 collected reflections, 2197 were unique ($R_{\text{int}} = 0.0321$) and used in all calculations. The final $wR_2 = 0.2821$ (all data), $R_1 [F > 2\sigma(F)] = 0.0971$. Significant residual electron-density (max: $+2.4$ e Å⁻³) was observed in the final difference map close to Se and Br atoms and anisotropic refinement of C and N atoms proved impossible. [The same structural motif was observed for **2a** which crystallises in the orthorhombic space group $Pca2_1$, $a = 12.454(3)$, $b = 6.1040(12)$, $c = 25.231(5)$ Å at $T = 150(2)$ K]. CCDC 182/1838. See <http://www.rsc.org/suppdata/b0/b004705h/> for crystallographic files in .cif format.

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