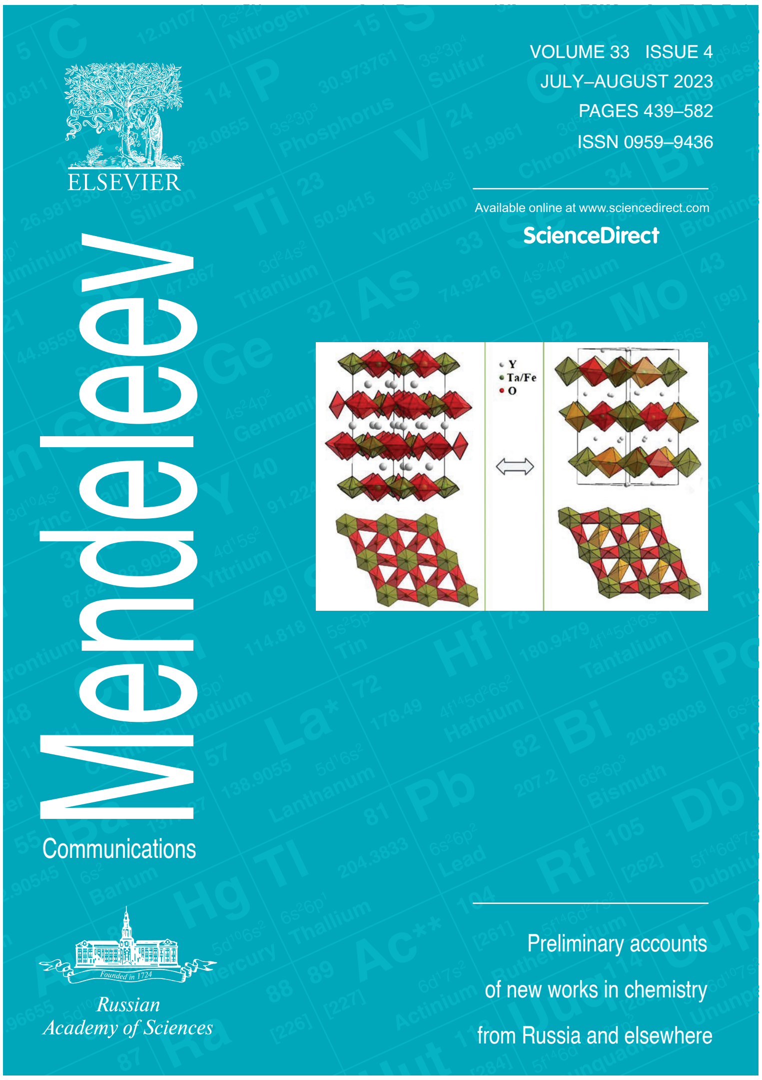

VOLUME 33 ISSUE 4
JULY–AUGUST 2023
PAGES 439–582
ISSN 0959-9436

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Wolmershäuser radicals: chemistry and materials science

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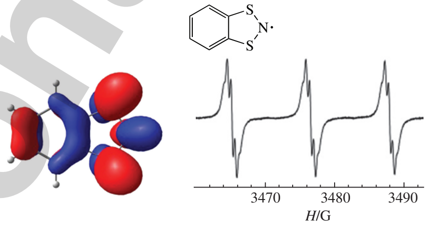
DOI: 10.1016/j.mencom.2023.06.001

Chemistry and materials science of stable 1,3,2-benzodithiazolyls (Wolmershäuser radicals) are discussed. These easily-accessible chromogenic and redox-active compounds are promising building blocks of conductive and magnetic molecular materials including spin-crossover materials. Their comparison with 1,2,3-isomers (Herz radicals), also involved in contemporary materials science, is given.



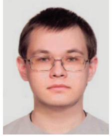
Keywords: 1,3,2-benzodithiazolyls, chalcogen–nitrogen π-heterocycles, conducting molecular materials, magnetic molecular materials, structure, synthesis, reactivity, Wolmershäuser radicals.

Introduction

1,3,2-Benzodithiazolyls or Wolmershäuser radicals (WRs) are isomers of 1,2,3-benzodithiazolyls or Herz radicals (HRs).[1,2] Together with their most common synthetic precursors – Wolmershäuser and Herz cations (WCs and HCs, respectively),[1,2] WRs and HRs (Scheme 1) belong to a broad family of stable π-heterocyclic derivatives of thiazyl $[SN]^•$ (ref. 3) and thiazolium $[SN]^+$;[4] besides labs, $[SN]^•$ and $[SN]^+$ are observed in the interstellar space.[5] A reference to $[SN]^•$ is meaningful since this specie is formed upon thermolysis and photolysis of various neutral sulfur–nitrogen rings and cages;[6] and its $[(SN)_3]^•$ trimer, upon thermolysis of polymer $(SN)_x$.[7] Furthermore, nontrivial chemical comparability of $[SN]^•$ and $[CN]^•$ is recognized.[8] Stable acyclic organic derivatives of $[SN]^•$ are thioaminyls;[9] the term is also used for some π-heterocyclic incarnations.[10] Amongst inorganic derivatives of $[SN]^•$, the most important are dimer $(SN)_2$, tetramer $(SN)_4$, and the aforementioned $(SN)_x$ also known as poly(thiazyl).[2,11]

For the first time, WRs were independently detected with EPR by G. Wolmershäuser *et al.* and L. H. Sutcliffe *et al.* in the

Scheme 1 The archetypal WR and WC (left) and HR and HC (right); the radicals are shown as N-centered to avoid resonance superpositions.



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early 1980s, and isolated and defined by XRD in the end of the decade.[12,13] At around the same time, their monocyclic analogues were isolated and unambiguously characterized by L. H. Sutcliffe *et al.* with EPR of ^{33}S and ^{15}N isotopomers, XRD and GED,[13] following by higher-level quantum chemical calculations;[14] the first EPR detection of these species in solution is dated by 1977 featuring incorrect structural assignment.[15]

Similar to HRs,[1,16] WRs (for selected examples **1–20**, see Scheme 2) are chromogenic and redox-active compounds. Isolated in the form of thermally stable solids, WRs are promising for materials science of conductive and magnetic materials including spin-crossover materials, obviously, together with other thiazyl-derived radicals,[1,2,17–28] *e.g.* **21**[27] (Scheme 2) prepared by G. Wolmershäuser *et al.* in 1989[12(*e*)] and not covered here except for selected physical properties. To certain extent, all such radicals are similar to atoms in alkali metals, and might afford a half-filled electron-energy band; in the solid state, however, they normally feature highly-correlated electron systems with strong spin–lattice correlations.[17(*c*),28]

Besides synthesis, chemistry of WRs is not well-studied. Any Se and Te congeners of WRs are still unknown despite attempted syntheses of the former; notably, the parent $[EN]^\bullet$ (E = Se, Te) species are also undescribed[3] (only calculated vibrational frequency of $[TeN]^\bullet$ is reported).[29] At the same time, heavier WRs are promising for materials science due to enlarged spin–orbit coupling (SOC),[†,30] polarizability,[31] and secondary bonding interactions (SBIs)[32]/chalcogen bonding (*ChB*)[33,34] associated with σ-holes at the chalcogen atoms.[‡]

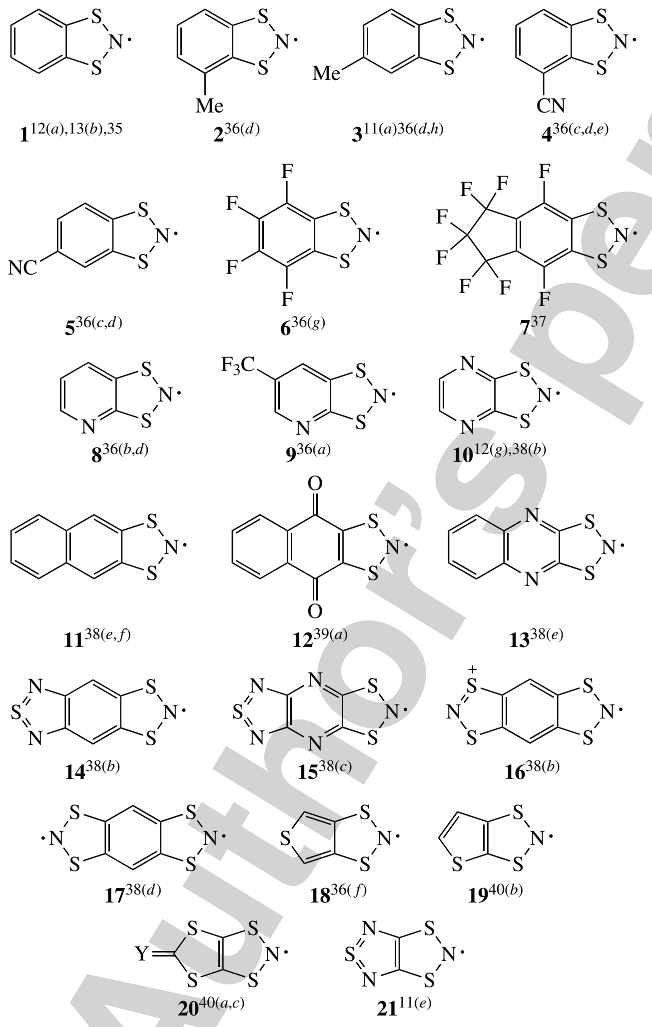
In this focus article, chemistry and materials science of WRs are discussed in comparison with those of their isomeric HRs.

Synthesis

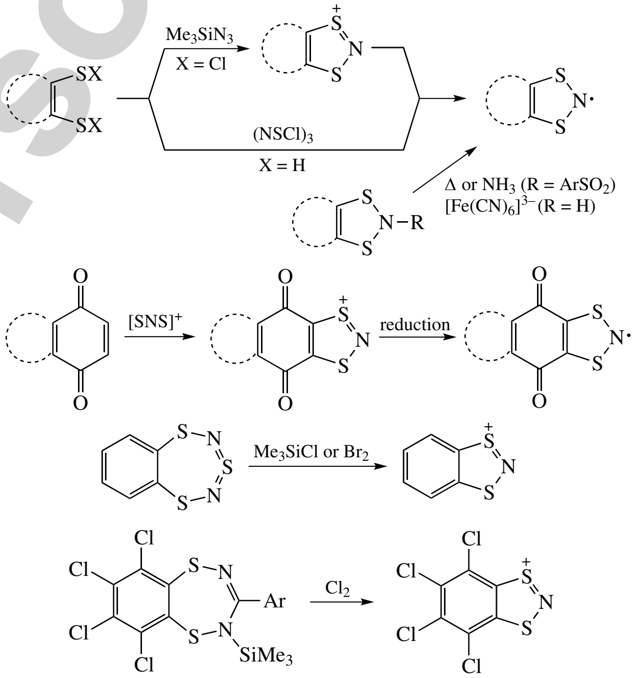
The most common starting materials for WRs are WCs. Generally, WCs are prepared by the ring-closure of 1,2-di(sulfenyl chlorides) (easily accessible from corresponding 1,2-dithioles and 1,2,5,6-tetrathiocines) with Me_3SiN_3 in the hydrocarbon and fluorocarbon series, or directly by the ring-closure of 1,2-dithioles with $(NSCl)_3$; and rarely by the cycloaddition/oxidative dehydrogenation reaction of 1,4-naphthoquinone with $[SNS]^+$; by the cleavage of 2-R-1,3,2-dithiazoles; and by the ring-contraction of 1,3,5,2,4-trithia- or 1,5,2,4-dithiadiazepines[2,12,36–46] (Scheme 3).

Chemical (with Ag, Cu, Zn, $SbPh_3$ or $[S_2O_4]^{2-}$) and electrochemical reduction of WCs provides WRs (see Scheme 3). In some cases, chemical approaches afford uncharacterized low-soluble products instead of the target WRs; the most recommended reducing agents are Ag and $SbPh_3$.[12] Together with WRs, these methods cover related radical cations and diradicals (see Scheme 2).[2,12,36–38,40,42–46] More complex species are mentioned only in passing.[12(*g*)]

The archetypal WR **1** together with $[SN]^\bullet$ was generated by thermolysis and photolysis of 1,3,5,2,4-benzotrithiadiazepine



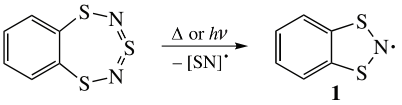
Scheme 2 Selected WRs and related fused 1,3,2-dithiazolyls, Y = O, S, $(NC)_2C$; (see refs. 18 and 41 for other hydrocarbon WRs and ref. 37 for fluorocarbon WRs).



Scheme 3 Synthesis of WCs and WRs.

[†] The SOC is quantum mechanical phenomenon consisting in the interaction between the electron's spin and orbital motion around the nucleus causing a shift in the electron's energy levels. For hydrogen-like atoms, the SOC increases with the atomic number Z as Z^4 to be considerable for $Z \geqslant 30$ ($Z = 16$ and 34 for S and Se, respectively). The SOC drives magnetic anisotropy and some other properties important for molecular magnetism and spintronics. In EPR spectra, SOC manifests itself in line-broadening and g-shift.

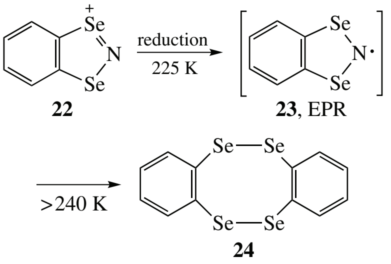
[‡] By the IUPAC definition, *ChB* is net attractive interaction between an electrophilic region associated with a chalcogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity. In molecular electrostatic potential (MEP) theory, such electrophilic regions, corresponding to MEP positive values, are termed σ-holes; recently, they were visualized with Kelvin probe force microscopy.



Scheme 4 Generation of WR **1** and [SN]• by thermolysis and photolysis of 1,3,5,2,4-benzotrithiadiazepine.

(Scheme 4); the similar processes are known for the archetypal HR and 1,2,4,3,5-benzotrithiadiazepine.[6(c)] These and analogous transformations of other neutral closed-shell sulfur–nitrogen rings and cages reflect their general propensity to form π-radicals.[6(a)]

Heavier chalcogen analogues of WRs were not isolated; most likely, Te derivatives were never tried. On electrochemical reduction of WC **22**, a 1 : 1 : 1 triplet was detected by EPR at 225 K; at temperatures $\geqslant 240$ K, however, the signal vanished. The triplet can be assigned to the target WR **23** due to typical (see below) $a_N = 1.19$ mT and $g = 2.0168$ enlarged by SOC at the Se atom. On chemical reduction with Ag, the isolated product was tetraselenocine **24** seemingly formed by self-condensation of **23** (Scheme 5);[2,12(g),47] for HRs, self-condensations are typical.[1,48]



Scheme 5 Attempted synthesis of WR **23**.

Structure and bonding

At the (U)B3LYP/6-31+G(d) level of DFT theory, the archetypal WC and WR are thermodynamically less preferable than the archetypal HC and HR by ~11 and ~14 kcal mol⁻¹, respectively; carbocyclic substitution, including tetrafluorination, changes this situation insignificantly.[37] These relative stabilities can be assigned to worse π-conjugation of carbo- and heterocycles through the C–S bond (2p–3p AO overlap) in WC/WR as compared with that through the C–N bond (2p–2p AO overlap) in HC/HR.

Both WRs and WCs are planar and π-delocalized. Four uppermost MOs of **1** are π-MOs $4b_1$ (Figure 1), $2a_2$, $3b_1$ and $1a_2$ with energies –6.66, –8.79, –9.51 and –10.46 eV, respectively, estimated from He(I) PES vertical ionization energies *via* Koopmans theorem.[38(d)] The spin density distribution of WRs depends on the nature of annulated rings.[18(d),35,36(b,f),38(d),39(a),49,50] In **1**, the spin density is mostly concentrated at the 5-membered ring, which is in striking contrast with HRs[1,50] (Scheme 6); in WRs having strongly electron-withdrawing substituents, *e.g.* **15**, the spin density is delocalized away from the 1,3,2-dithiazole ring.[38(g)]

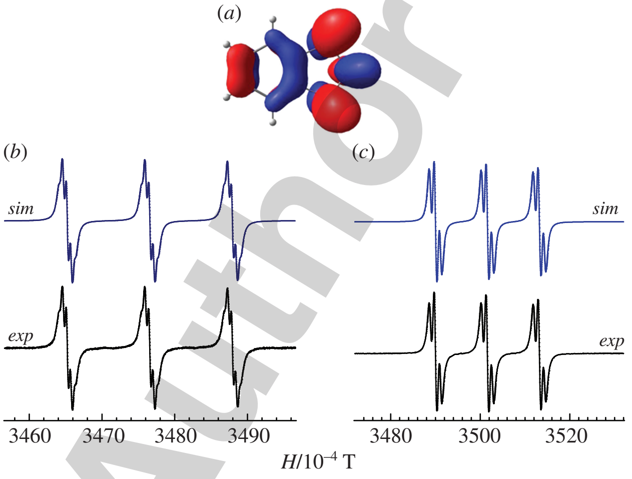
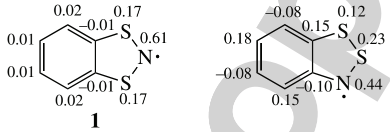


Figure 1 (*a*) The π*-SOMO $4b_1$ of WR **1** from DFT calculations, and experimental EPR spectra of (*b*) **1** and (*c*) its tetrafluoro congener **6** in solution.



Scheme 6 Spin density distribution in the archetypal WR and HR from (U)B3LYP/cc-pvdz calculations[50] (negative values are associated with a polarization of some of the doubly occupied MOs induced by the SOMO).

Many WCs and WRs are characterized by XRD[12,18,35–39,43,51–57] (for selected examples, see Figures 2 and 3; in this article, XRD structures are taken from CSD[58] and their CCDC numbers are given). Amongst WCs, notable are fluorinated derivatives, such as [**6**]⁺ and its congeners, isolated in the form of chloride salts;[36(g),37] whereas fluorinated HCs are unknown[1,16] and, thus, challenging.

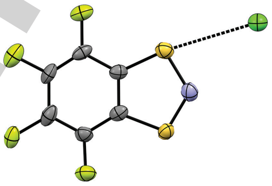


Figure 2 XRD structure of [**6**]⁺[Cl]⁻ [36(g),37] (CCDC 731911). Colour code: C, grey; Cl, green; F, light green; N, blue; S, yellow; dashed line indicates S···Cl⁻ shortened contact (here and below, as compared with the sum of the corresponding van der Waals (VdW) radii, *i.e.*, SBI/*ChB*; see discussion below).

For 5-membered cycles of [**1**]⁺/**1** pair, the bonds distances (Å) are: C–S, 1.708 and 1.714/1.741 and 1.746; S–N, 1.593 and 1.625/1.644 and 1.648; C–C, 1.410 and 1.411/1.394; and bond angles C–S–N, 98.2 and 99.1/99.1 and 99.4; S–N–S, 116.6 and 117.1/113.9; C–C–S 112.6 and 113.1/112.9 and 113.9.[35,43(a)] Typical distances of S–N and S=N bonds are ~1.60–1.70 and ~1.50–1.58, respectively;[59] the bond distances in [SN]•, $(SN)_4$ and $(SN)_x$ are 1.494, 1.625, and 1.588 and 1.625, respectively.[2,11(b,c),60] On transformation of WCs into WRs, the heterocyclic C–S and S–N bond distances elongate, and C–C shorten, in agreement with nodal properties of the WRs'

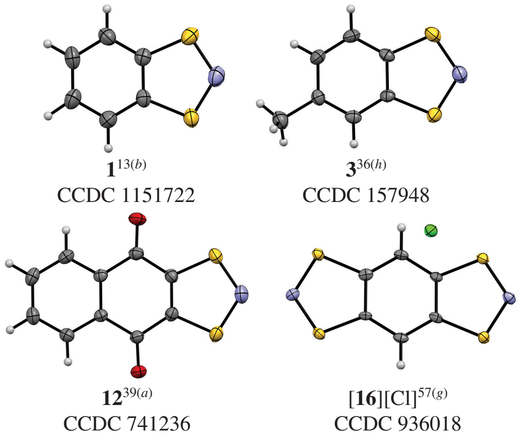


Figure 3 Selected XRD molecular structures of neutral radicals **1**, **3** and **12**, and radical cation **16**. Colour code: C, grey; H, light grey; Cl, green; N, blue; O, red; S, yellow.

π*-SOMOs (see Figure 1); whereas bond angles change insignificantly except decrease of S–N–S one by ~3°. In the Herz family,[1] the similar situation is observed for the similar reason.[61]

Notable non-equivalence of the S–N bond distances of WCs in their halide salts, *e.g.* [**1**]$^+$[Hal]$^-$ (Hal = Cl, Br, I)[44] and [**6**]$^+$[Cl]$^-$ (see Figure 2),[36(g),37] is caused by the markedly shortened non-equivalent contacts between S1 and S3 atoms and halide ions, *i.e.*, by *ChB* mainly (but not only) driven by σ-hole interactions.[‡,33,34] In solvate of [**1**]$^+$[Cl]$^-$ with SO$_2$, featuring no cation–anion shortened contacts, both S–N bond distances are equal to 1.598 Å.[35] A similar situation is observed for Se–N bonds in salt [**22**]$^+$[ClO$_4$]$^-$ with low-coordinating anion.[47] In contrast, heterocycles of HCs including 1-Se derivative are structurally very rigid and their geometries are almost the same in salts with various anion such as [Cl]$^-$, [BF$_4$]$^-$, [GaCl$_4$]$^-$, [SbCl$_6$]$^-$, [Te$_4$Cl$_{18}$]$^{2-}$ featuring both strong and weak cation–anion interactions.[61–63]

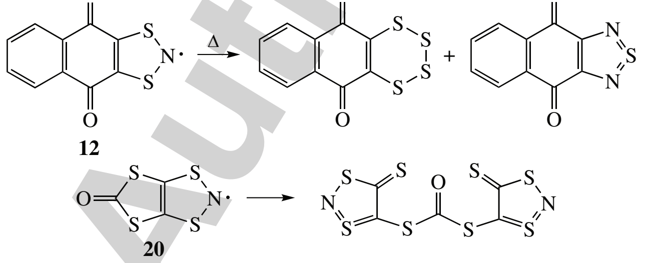
The WRs also reveal *ChB*, particularly in 1 : 1 complexes with 4-Ar-1,2,3,5-dichalcogenazolyls (chalcogen = S, Se);[64] in contrast to WCs acting as *ChB* donors,[44] WRs act as *ChB* acceptors[64(b)] (see below).

Solution EPR spectrum of natural isotopomer of **1** consists of a 1 : 1 : 1 triplet featuring hyperfine coupling (hfc) constant (mT) $a_N = 1.14$, together with two very minor $a_H = \sim 0.05$ (for ^{33}S isotopomer, $a_S = 0.39$), $g = 2.0069$;[37,49,50,65] and that of **6**, of triplet of triplets with $a_N = 1.12$ and $a_F = 0.12$ and 0.02; $g = 2.0044$[36(g),37] (see Figure 1). Typically, a_N are in the range 0.95 (**15**)–1.57 (**10**); a_H, 0.03 (**13**)–0.13 (**10**); and g, 2.0044 (**6**)–2.0073 (**12**).[12,13,35–40,49,50] Solution EPR spectra of diradical **17** are different from those of monoradicals;[1(b),38(d),42] it is suggested that **17** mainly exists in an EPR-silent π-dimerized form.[66(a)] The spectra display the exchange-coupled free **17** with uncoupled associated species; and UHF calculations estimates ΔE_{ST} as ~0.5 kcal mol^{-1}.[38(c)] The experimental g values and isotropic hfc constants of WRs, as well as hyperfine tensor components, are well-reproduced by DFT;[50,65(b,c),67] *e.g.* UPBE0 and UB1LYP functionals with EPR-II basis set exclude a need in more sophisticated methods.[66(a)]

Despite WRs are chromogenic, their Vis properties are not properly characterized. Monocyclic 4,5-(CF$_3$)$_2$-1,3,2-dithiazolyl is blue-coloured and reveals low-intensity Vis bands (λ_{max}, nm; hexane solution/post-HF CI calculations) at 560/573 (X^{2}B → B^{2}B) and 738 (gas phase, 708)/720 (X^{2}B → A^{2}B); the calculations also predict NIR band at 985 (X^{2}B → A^{2}A).[13(a),14] Notably, related closed-shell 4n π-electron 1,3,2-dithiazole-4-thione[68] and 1,3,2,4-benzodithiadiazines[69] are also blue-coloured. Due to the lack of data, it is impossible to compare WRs with WCs; transformation of HCs into HRs causes bathochromic shift of λ_{max} (typically from ~410–475 to ~500–520) and changes fine structure of the band.[16]

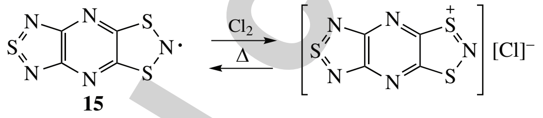
Reactivity

Reactivity of WRs is not well-studied; typically, they are air-sensitive. The WR **12** undergoes thermal transformation into the corresponding tetrathiine and thiadiazole (Scheme 7; *cf.* Scheme 5).[39(a)] Radicals **18–20** are inherently unstable, and **20** (R = O) reveals self-condensation featuring the loss of CO and rearrangement.[36(f),40]



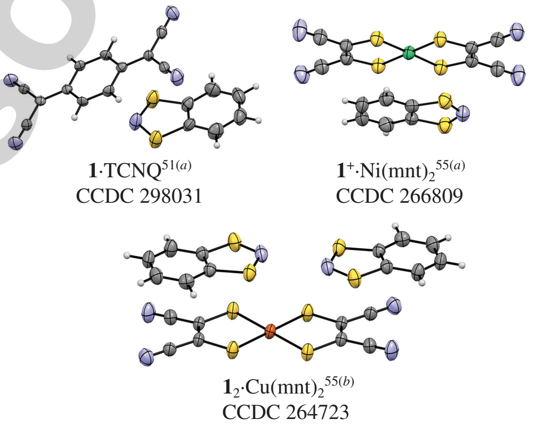
Scheme 7 Examples of chemical transformations of WRs.

The WRs are redox active and can be oxidized into WCs by the action of Hal$_2$ (Hal = Cl, Br, I) or Lewis acids, *e.g.* SbCl$_5$, or electrochemically; normally, potential $E_{1/2}$(ox) of WRs is slightly lower than that of relevant HRs (*e.g.* by 0.15 and 0.18 V for the archetypal WR and HR, respectively).[18(c),70] In most cases, electrochemical reduction of WRs is irreversible,[37] *i.e.*, similar to that of HRs, and proceeds at higher $E_{1/2}$(red) values.[71] With strongly electron-withdrawing substituents, however, it is fully reversible as exemplified by WR **15** and the corresponding HR.[38(g)] Some [WC][Cl] salts undergo thermal disproportionation to WR and Cl$_2$ (Scheme 8).[38(c)]



Scheme 8 Chlorine-assisted interconversion WR ↔ WC.

As electron donors, WRs form CT complexes with TCNQ and I$_2$ (**1** and I$_2$ give the corresponding WC);[2,12(f),43(b),51(a)] and, potentially, with fullerenes (only theoretical data are reported).[72] Also, WRs coordinate Cu, Zn, Co and Mn cations as N-ligands[24,51(b–f),52] (WCs also form salts with Co, Ni and Cu 1,2-dithiolenes)[51(a)] (Figure 4).



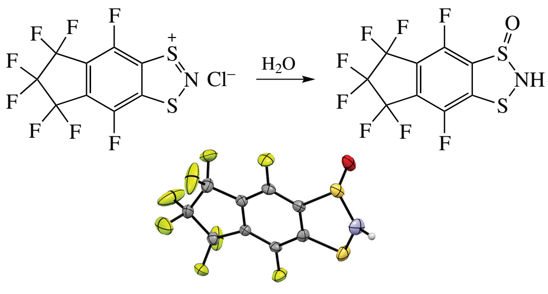
1·TCNQ[51(a)]
CCDC 298031

1$^+$·Ni(mnt)$_2$[55(a)]
CCDC 266809

1$_2$·Cu(mnt)$_2$[55(b)]
CCDC 264723

Figure 4 XRD molecular structures of WRs' complexes, coordination compounds and salts. Colour code: C, grey; H, light grey; Cu, red; N, blue; Ni, green; S, yellow.

Besides primary bonding interactions, WRs, similar to WCs, participate in SBIs, particularly in *ChB*. Thus, WRs form 1 : 1 complexes with 4-Ar-1,2,3,5-dichalcogenazolyls (chalcogen is S, Se),[64] and in the solid state the π-dimers of partners are linked by bifurcate *ChB*;[64(a)] *i.e.*, in contrast to WCs acting as *ChB* donors,[43] WRs act here as *ChB* acceptors.[64(b)]



Scheme 9 Water addition to polyfluorinated WC and XRD structure of the product;[37] colour code: C, grey; H, light grey; F, green; N, blue; O, red; S, yellow.

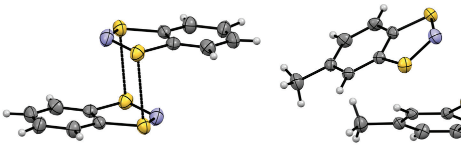
Reactivity of WCs is also poorly studied except for reduction into WRs (see Scheme 3). Cation [**1**]$^+$ is reported as stable in aqueous solution;[12(a),44] for polyfluorinated derivative, however, 1 : 1 addition of H_2O is observed (Scheme 9).[37]

Solid-state magnetic and electrical properties

The overall structural, magnetic and conductive topology of WRs is 3D but in many cases it can be effectively taken as 1D.[73] The WRs, which are monomeric in the solid state, are paramagnetics. However, and similar to HRs, crystalline WRs reveal propensity to scaffold-depending diamagnetic π-dimerization within π-stacks. Thus, WR **1** reveals a transoid π-dimer featuring shortened S···S contacts of 3.25 Å, whereas **3** is monomeric; diradical **17** is diamagnetic in the range 5–400 K. Typical is polymorphism (Figure 5), especially for salts of radical cation **16**.[12,13,35,36,38,39,53,54,57(c,g),74]

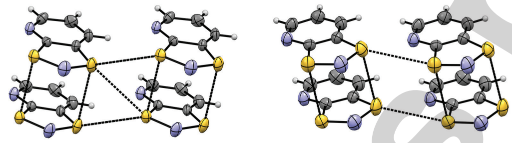
Within a certain temperature range, the uniform paramagnetic π-stacks are stable for two reasons, one is static and another dynamic: the stacks featuring both in-stack and lateral slippage of WRs with neighbors correspond to a local minimum on the potential energy surface (PES) of the system; and the stacks featuring only lateral slippage correspond to a dynamic interconversion between two degenerate π-dimerized configurations.[72(a)] This structural dichotomy is important for spin-Peierls transitions[§,73(b)] in switchable WRs-based magnets.

Some WRs possess magnetic bistability associated with hysteretic[¶] spin crossover between $S = 0$ for π-dimeric and $S = 1/2$ for monomeric species;[12(c,h),18,36(c,e,h),38(a,b,f),74,75] the hysteretic loop is broad (Table 1; *cf.* HRs[1] amongst which only all-S analogue of **27** with R = F (Scheme 10) reveals sharp crossover with ΔT of 15 K).[17] For materials science/crystal engineering, (near) room-temperature magnetic bistability is most promising, and the field manifests fast progress with prominent contribution from sulfur–nitrogen paramagnetic species.[54(a),76]

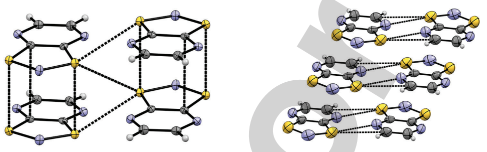


1[13(b),35]
CCDC 1151722

3[36(h)]
CCDC 157948



8[36(b)] CCDC 678356 and 678357
kinetically- (left) and thermodynamically- (right) favored polymorphs



10[12(g),38(b)] CCDC 244871 and 244872
low-temperature diamagnetic (left) and
high-temperature paramagnetic (right) polymorphs

Figure 5 Selected XRD crystal structures of WRs; dashed lines indicate SBIs.

Table 1 Magnetic bistability of WRs.[††]

T/K	**21**	**15**	**11**[a]	**10**	**9**	**5**[b]	**4**[c]
$T_{C\uparrow}$	305	180	188	343	50	304	250
$T_{C\downarrow}$	230	120	128	297	50	291	250
ΔT^d	92	60	60	46	0	13	0

[a] Diamagnetic phase consists of N–N σ-bonded dimers.[38(f)] [b] A low-temperature (<77 K) phase reveals additional transition with $T_{C\uparrow}$ = 28, $T_{C\downarrow}$ = 37 and ΔT = 9 K. [c] π-Dimeric **1** affords *via* melting and rapid cooling paramagnetic phase of unknown structure featuring magnetic ordering at 11 K;[35,53(c),75(b)] its nature (AF or spin-canted AF), is unclear and crystallographic investigations on this phase are needed. [d] Temperature range of two phases coexisting.

As mentioned, some WRs reveal high-temperature (HT) paramagnetic structure features $(\cdots R^{\bullet}\cdots R^{\bullet}\cdots)_n$ uniform π-stacks, and low-temperature (LT) diamagnetic structure features $(\cdots R^{\bullet}–R^{\bullet}\cdots)_n$ π-dimeric stacks stabilized by pancake bonds[77] between the partners. The $(\cdots R^{\bullet}\cdots R^{\bullet}\cdots)_n$ structures are not PES minima but average structures from $(\cdots R^{\bullet}–R^{\bullet}\cdots)_n \longleftrightarrow (–R^{\bullet}\cdots R^{\bullet}–)_n$ dynamic interconversion between two degenerate π-dimeric structures. With the dynamically-stabilized uniform π-stacks, the spin transition requires the thermal activation of the interconversion, and the transition temperature is controlled by the activation barrier. Such switching is exemplified by **4**[36(e)] and, likely, **9**[78] (LT crystal structure for **9** was not defined); the hysteretic transition in **10** and **21** is more complex as accompanied by a rearrangement of the SBIs between the π-stacks. Similar transition of [**16**][Cl] with alternation of both intra- and interstack distances at around 150 K, however, displays no thermal hysteresis.[57(g)] With the statically-stabilized stacks, the transition temperature is controlled by the energy difference between the LT and HT phases; of course, the energy barrier between the two forms of stacks cannot be fully ignored. Such switching is exemplified by **15**.[74(a,c)]

Thermal promotion of the discussed dynamics is a more common way for triggering spin transitions in WRs-based materials. However, it is not enough to generate bistability, which also requires a rearrangement of SBIs between the π-stacks. For instance, **4**, **10**, **15** and **21** display spin transition but **14** does not; the bistability of **10** and **21** embraces room temperature whilst requires much lower temperature with **15** (Table 2). Overall, changes in the magnetic response upon spin transition come from the changes in the magnetic interactions between neighboring WRs along the π-stacks; the latter are driven mostly by the changes in their in-stack and lateral slippage.[54,74]

Importantly, the spin crossover in WRs can be driven by light and pressure. In HRs, the crossover occurs between π-monomeric and σ-dimeric species and also can be driven by visible light.[17]

WRs-based solids feature both antiferromagnetic (AF; including spin-canted and metamagnetic) and ferromagnetic (FM) properties; the best-studied are salts of **16** (see Table 2).[14,18,19,53,54(a,c,d),55(a,f),57(a–d),67,75(b)] This is important particularly taking into account fast progress of AF spintronics.[79] The WR **1**, which is diamagnetic under normal conditions, at 346 K reveals phase transition to a paramagnetic state and a superheating process resulting in the double melting, *i.e.*, melt–crystallization–melt process, above 360 K; the supercooling of

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[§] One-dimensional spin/electron systems are inherently unstable towards many factors. Peierls transition is quantum mechanical phenomenon manifesting in linear dimerization of uniform 1D crystal lattice caused by coupling between the lattice and its spin/electron system. With this transition, paramagnetics become diamagnetics and metals become insulators/semiconductors. The 1D instabilities can be suppressed by dimensionality-increasing SBIs.

[¶] Hysteresis is a phenomenon in which the value of physical property lags behind changes in the effect causing it.

[††] Curie temperature T_C is the temperature at which paramagnetic substance loses its permanent magnetic properties, and Neél temperature T_N is the temperature above which AF substance becomes paramagnetic.

Table 2 Magnetic ordering temperatures[††] of [**16**][MX_4] and related salts.[a]

M	Tl		In	Ga		Fe
X	Br	I	I[b]	Br[c]	Cl	Cl[d]
T/K	T_N, 11.6	T_N, 8.9	T_N, 11.3	T_N, 15.5	T_C, 7[e]	T_N, 6.6/6.3

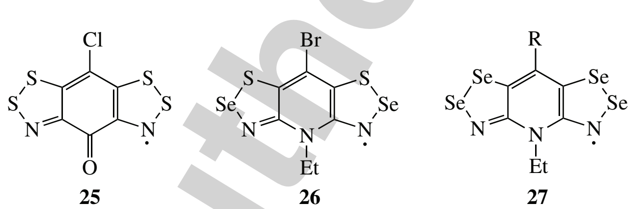
[a] [**16**][$Au(CN)_2$]: T_C, 8.2; [**16**]$_2$[$ReBr_6$]: T_N, 12.2. [b] X = Cl and Br, spin-Peierls transition at 108 and 250 K, respectively. [c] Spin-canted AF (α-phase); for β-phase $T_C = 0.4$ K.[56(c)] [d] MeCN/Me_2CO solvates, desolvated salts are ferrimagnetics below 44 K; [e] 14.5 at 1.6 GPa.

the paramagnetic phase leads to a magnetic ordering of unclear nature (AF or spin-canted AF – *i.e.*, weak FM) at 11 K.[53(d)] The WR **4** also has the AF ground state.[53,67] The diradical **17** reveals strong AF coupling, leading to an essentially diamagnetic ground state.[38(d)] For $\mathbf{1}^{+}\cdot Ni(mnt)_2$ and $\mathbf{1}_2\cdot Cu(mnt)_2$, FM and AF coupling, respectively, is observed (mnt is maleonitriledithiolate).[51(a),55(a,b)] In $\mathbf{3}_2\cdot M(hfac)_2$ (M = Zn, Co, Mn), strong AF interactions occur between WRs and paramagnetic Mn^{2+} and Co^{2+} cations (hfac is hexafluoroacetylacetonate); in the case of diamagnetic Zn^{2+} cations, weak AF interactions between WRs are detected. Strong intermolecular exchange coupling in the Mn^{2+} complex comes from WRs' π-contacts.[52] Polymeric $\mathbf{21}\cdot Cu(hfac)_2$ reveals FM interactions in coordination chains.[10,53]

The WRs' π-dimerization in the LT phase disallows intermolecular FM spin coupling J_{AB}, whereas the corresponding paramagnetic HT phases allow it. The macroscopic magnetic responses of the HT phases depend on microscopic J_{AB} interactions driven mostly by the changes in the in-stack and lateral slippage.[74(b)] In accordance with Kahn orbital model,[‡‡,80] specific geometrical dispositions enhance FM spin coupling, *i.e.*, those preventing the SOMOs of the neighboring WRs from π-overlap. Consequently, larger WRs, such as **15**, are not suitable for FM interactions due to high probability of the SOMOs' π-overlap in the crystal; for smaller WRs **21**, **10** and **4**, however, the regions featuring FM interactions are identified in magneto-structural correlation maps (matching magnetic properties and structures of rings annulated to 1,3,2-dithiazolyl core), *i.e.*, required geometrical dispositions are specified. Such maps can be useful in the quantum chemical/crystal engineering design of new WRs-based solid materials with dominant FM interactions. Overall energy demand, however, is high and only a few WRs have the FM ground state.[53,54,67,74]

With HRs,[1] record temperatures of magnetic ordering belong to **25**–**27** (Scheme 10);[18,81] one of radical-cation salts with a Kagome-coupled chain structure provides a rare example of spin frustration in an organic radical-ion salt.[82] Amongst other relevant magnets, spin-canted AF (*i.e.*, weak FM) 4-R-1,2,3,5-dithiadiazolyl (R = 4-NC-C_6F_4) reveals bulk magnetic ordering at 36 K at normal pressure and at 70 K at 1.6 GPa.[18(a),83]

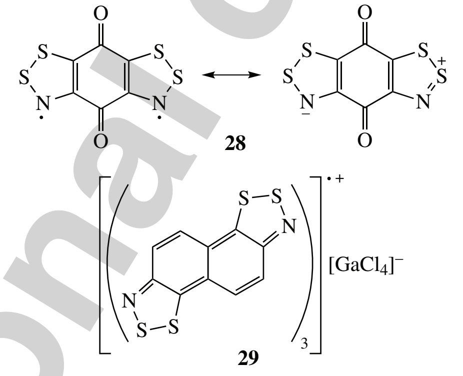
Monocyclic 4,5-$(CF_3)_2$-1,3,2-dithiazolyl, existing in the solid state as π-dimers, melts into paramagnetic liquids whose supercooling towards room temperature affords phases featuring thermal hysteresis.[13(a),84]



25 **26** **27**

Scheme 10 HRs **25**–**27** and their T_C or T_N (K) at normal 100 (kPa)/ enlarged (2 GPa) pressure: **25**, $T_N = 8$; **26**, $T_C = 14.1$; **27**, $T_N = 27$ (R = H, spin-canted AF), 17.5/24 (R = Br), and 10.5/27.5 (R = I).[81]

CT complexes of **1** and **3** with TCNQ and **13** with I_2 are semiconductors.[12(a,f)] Complex **1**·TCNQ reveals room-temperature conductivity σ_{RT} ~35 and activation energy E_a ~0.06;[85] and $\mathbf{1}\cdot[Ni(dmit)_2]_2$, χ_{RT} ~0.1 (dmit is 1,3-dithiol-2-thione-4,5-dithiolate)[51(a)] (here and below, σ_{RT} is in S cm^{-1} and E_a in eV). Diradical **17** features an E_a ~0.22.[23] Within HR species, the highest σ_{RT} belongs to the diradical / bipolar ion **28** revealing metallization at 8 GPa with σ_{RT} ~10 (~10^2 at GPa); and to the radical-cation salt **29** with normal-pressure σ_{RT} ~0.5 and E_a ~0.18.[86,87] (Scheme 11); for brief overview of organic conductors, see ref. 88. The best relevant molecular conductor $(SN)_x$, formally composed of $[SN]^{\cdot}$ units, has σ_{RT} ~10^3 along the macromolecules and becomes a BCS superconductor at ~0.3 K (0.54 K at 0.9 GPa).[11(c)]



28

29

Scheme 11 Best HRs-based conductors.

Quantum chemical consideration of magnetic and conductive properties reveals that the size of WR (as well as HR)[1] scaffolds directly controls the on-site Coulomb repulsion, whereas their chemical nature and crystal packing are less important; at the same time, the resonance integral is very sensitive to them, *i.e.*, there is a simultaneous demand for localization and delocalization hardly reachable with 1D crystal packings. Increased packings' dimensionalities might lead to coexistence of conductive and magnetic channels; conductive channel is associated with strong in-stack overlap, and magnetic channel, with lateral interactions between the stacks.[§,10,52(a)]

By gas-phase diffusion, WRs **1** and **3** were incorporated into porous crystalline framework, wherein they retained their π-dimeric and monomeric structures, respectively.[89]

Conclusions

The WRs contribute much in contemporary chemistry, crystal engineering and materials science, in the latter case especially as magnetically bistable materials. Their Se and Te incarnations are unknown; meanwhile, they are of keen interest due to stronger SOC, higher polarizability, and a larger propensity to SBIs suppressing 1D instabilities. Molecular design, synthesis, structural and functional characterization of such WRs are challenging for further research. The same is also true for all-S tri- and polyradicals. A special target is isolation and structural and functional characterization of (poly) halogenated WRs since fluorine and its heavier congeners in many cases improve properties of organic conductors and magnets.

The quantum chemical/crystal engineering design rules for new WRs-based switchable materials depend on chosen mode of π-stack stabilization. The rules for WRs with dominant either FM or AF interaction appeal to Kahn orbital model. Moreover, the rules should harmonize in some way a contradictive demand on localization and delocalization. Besides, Vis and NIR properties of WRs are worth a closer look.

[‡‡] For magnetically-coupled SOMOs, Kahn model requires for FM state their strict orthogonality making impossible spatial overlap; and for AF state, a non-orthogonality allowing small overlap.

Overall, and together with HRs, WRs represent enormously promising field for further development of chalcogen–nitrogen π-heterocyclic chemistry and its applications potentially covering smart materials, *i.e.*, designed materials having at least one functional property which can be controlled by external conditions.[90]

We are grateful to Dr. Irina G. Irtegova, Prof. Irina Yu. Bagryanskaya, and Prof. Leonid A. Shundrin for valuable discussions. This work was supported by the Ministry of Science and Higher Education of the Russian Federation (State Assignment project no. 122040800264-3).

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Received: 29th March 2023; Com. 23/7134