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Herz radicals: chemistry and materials science

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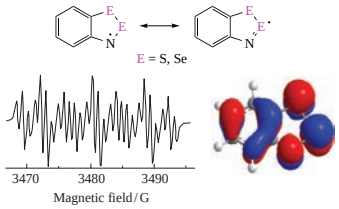
Chemistry and materials science of Herz radicals (1,2,3-benzodichalcogenazolyls; chalcogen is S or Se) are discussed including their synthesis, structure and reactivity. Preparation and functional characterization of radical-based molecular conducting and magnetic materials are considered.



Keywords: conducting molecular materials, magnetic molecular materials, Herz radicals, synthesis, structure, reactivity, organosulfur compounds, organoselenium compounds.

Introduction

Areno-fused 1,2,3-dithiazolyls, stable neutral π-radicals (*e.g.* **1**, Scheme 1),[†] were discovered with the use of solution EPR by R. Mayer *et al.* at the turn of the 1980s.[1,‡] They were isolated and characterized with XRD by R. T. Oakley *et al.* at the turn of the millennium in the form of related radical cations[2] and in 2005 in the form of authentic neutral derivatives.[3] These species were named Herz radicals in honor of R. Herz since they are the key

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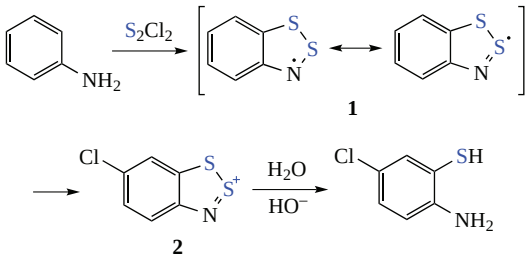
intermediates of the Herz reaction leading to Herz cations (*e.g.* **2**, Scheme 1). This reaction is known from 1920s and is used in industrial production of 2-aminothiophenols, precursors of various synthetic dyes.[1(a),(b),4] Shortly after S archetypes, Se congeners were reported[5] but properly characterized by EPR and XRD only recently.[3,6,7]



Scheme 1

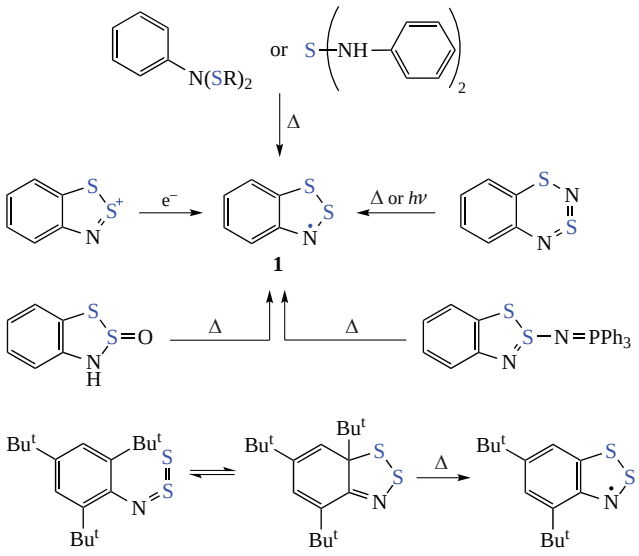
Originally being a kind of chemical curiosity, the Herz radicals then found interesting applications in chemistry beyond the Herz reaction.[8–10] Furthermore, they were actively used in the design and synthesis of all-organic (*i.e.* metal-free) molecular conductors and magnets.[11] This highlights their exceptional importance even in front of a wide variety of other isolated and functionally characterized neutral and charged organic paramagnetic species.[12,13] Chemically, Herz radicals belong to a broad family of main-group open-shell compounds consisting of sulfur–nitrogen π-radicals and their heavier-chalcogen analogues[9,11,14] named thiazyl radicals after SN• radical.[15] Notably, the main group chemistry becomes more and more important for molecular magnetism and conductivity.[16,§]

In this article, we discuss recent advances in chemistry and applications of the Herz radicals with chalcogens S and Se. Their congeners with O, Te and, obviously, Po and Lv are unknown.[17,¶] Monocyclic 1,2,3-dithiazolyls are not considered since they reveal propensity to C-centered recombination and are stable only when the position 5 is sterically hindered.[18] Isomeric 1,3,2-arenodithiazolyls and related radicals are also not discussed, although they are actively involved in the design and synthesis of magnetic and conductive molecular materials.[19,20] These radicals are worth a special review article.

Synthesis

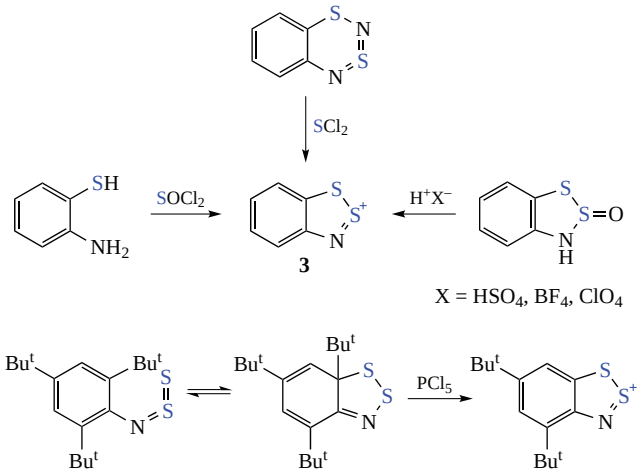
There are two main approaches to the Herz radicals: chemical or electrochemical reduction of 1,2,3-arenodithiazoliums (Herz cations); and thermolysis or photolysis of various sulfur–nitrogen derivatives, especially cyclic ones (Scheme 2), reflecting a general trend of neutral chalcogen–nitrogen rings and cages to form π-radicals.[21]

Normally, preparative chemical reduction of the Herz cations **3** (Scheme 3) with common reducing agents, *e.g.* Zn, Sn, Mg, Fe,



Scheme 2

Cu, $SbPh_3$, $FeCp^*_2$, *etc*. (see Scheme 2), proceeds smoothly. Therefore, the crucial point of this approach to the Herz radicals is synthesis of the Herz cations, which are thermodynamically attractive 10π-electron aromatics.[6(a)] For the Herz cations, five preparative methods are known including reaction of arylamines with S_2Cl_2 (the Herz reaction, see Scheme 1);[4] 2-aminothiophenols or their N–R (R = Me_3Si, Ac) derivatives with $SOCl_2$ or S_2Cl_2;[3,4,6] 1,3,2,4-benzodithiadiazines with SCl_2;[22] 7a*H*-1,2,3-benzodithiazoles with PCl_5; and 3*H*-1,2,3-benzodithiazole 2-oxides (Herz bases) with strong acids[23] (see Scheme 3).



Scheme 3

A scope of the Herz and Herz-like reactions is very broad. Besides $ArNH_2$ (see Scheme 1), many other differently N-functionalized aromatic and non-aromatic compounds are involved.[4,24–26] A special feature of the Herz reaction is chlorination of the carbocycle. For $ArNH_2$, the chlorination occurs at the position 4 if it is unsubstituted (see Scheme 1) or bearing an electron-acceptor group, whereas electron-donor group in this position retains. The mechanism of H replacement by Cl is not entirely clear. The general situation with the substitution in the Herz reaction, as well as with regioselectivity of the ring-closure, is rather sophisticated.[22–25,27] It requires further experimental and, especially, theoretical investigation. Non S_2Cl_2-based approaches (see Scheme 3)[4,22,23] normally avoid the carbocyclic chlorination with loss of the original substituents and provide additional opportunities as compared with the classical Herz reaction.

† For simplicity, Herz radicals are depicted as N-centered throughout the article. Where insignificant, carbocyclic substituents in Herz species, as well as anions in Herz salts, are omitted in Schemes (under conditions of the Herz reactions, the anion is obviously chloride, which can be easily exchanged if necessary). Overall, substitution pattern of Herz radicals is very rich, which is important for their fundamental chemistry and applications.

‡ Initially,[1(g),(h)] they were mistakenly assigned to 1,2-thiazetyls, which was corrected with ^{33}S labeling.

§ The main group chemistry involves all elements of the s- and p-blocks (groups 1 and 2, and 13–18, respectively) with conventional exception of H, C and N.

¶ Besides neutral radicals and radical cations, 1,2,3-dithiazolidyl radical anions are reported. With a few exceptions, they are unstable and not considered here.

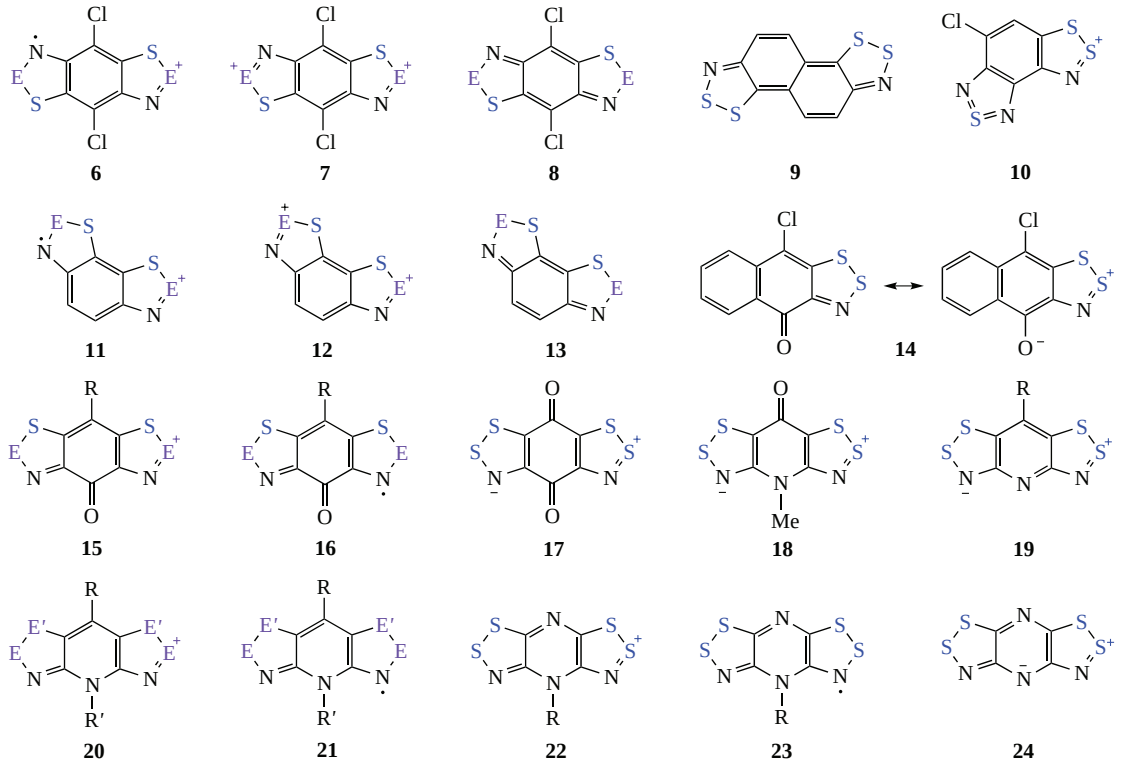
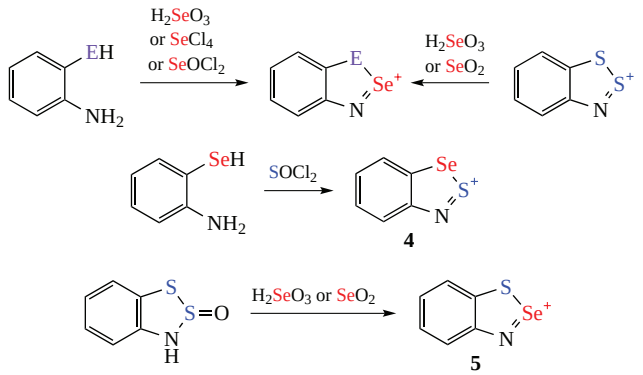


Figure 1 Selected Herz species including resonance-stabilized radicals, neutral quinoids/singlet diradicals, mono- and dications, radical cations, and bipolar ions (E, E′ is S, Se).

Selenium analogues of Herz cations (*e.g.* **4** and **5**) were synthesized by the ring-closure or chalcogen-exchange[13(a)] reactions (Scheme 4). 1,2,3-Thiaselena- and diselenazoliums were prepared from 2-amino thio- or selenophenols, respectively, and H_2SeO_3, $SeCl_4$ or $SeOCl_2$.[3,6,28] For direct chalcogen exchange, reaction of 1,2,3-benzodithiazoliums or 3*H*-1,2,3-benzodithiazole 2-oxides with H_2SeO_3 or SeO_2 was used.[4(a),6,28(c)] For indirect exchange, a transformation of dithiazoliums into amino thiols was applied followed by cyclization of the latter with $SeCl_4$.[28(a)] 2,1,3-Benzothiaselenazoliums were synthesized from 2-aminoselenophenols and $SOCl_2$[28(b),(c)] (see Scheme 4).



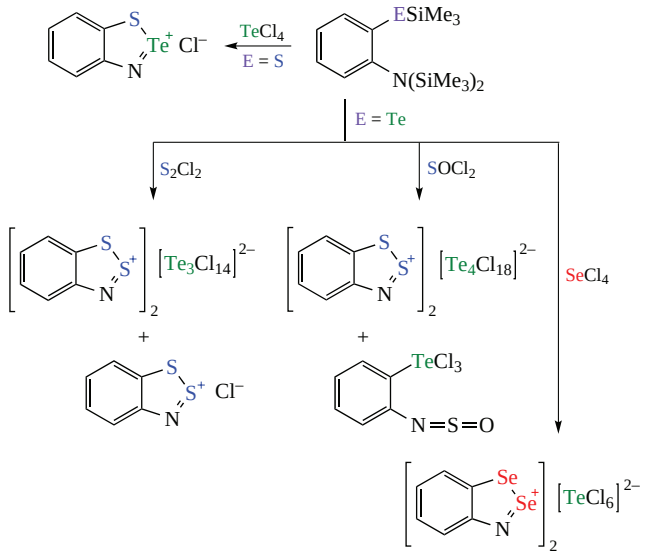
Scheme 4

Various Herz species **6**–**24** (Figure 1) were synthesized by the same methods. Quinoids **8**, **9** and **13** can be considered as either singlet diradicals[29,††] or 4n π-electron antiaromatics. The radical cations were oxidized/reduced into bis-cations/quinoids, respectively, whereas independently prepared quinoids were oxidized into radical cations.[2,7,8(a),25(b),(c),30–41]

1,2,3-Benzothiatellurazolium was synthesized by the ring-closure reaction,[6(c)] whereas the same approach applied to its 2,1,3-congener gave only Te-free Herz cations[28(a)] (Scheme 5).

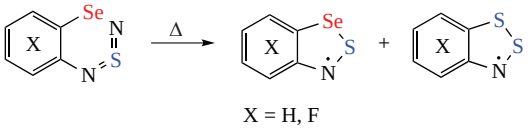
Numerous Herz radicals were prepared by chemical reduction of the discussed Herz cations (see Scheme 2) and isolated in the individual form followed in many cases by XRD characterization.[3,7,25,30,33,42(b)] In contrast, reduction of 1,2,3-benzothiatellurazolium afforded only unidentified diamagnetic products.[6(c)] It should be noted that only a few tellurium–nitrogen paramagnetic species are known,[43] and their design, synthesis and characterization are a serious challenge.

For mechanistic studies using spectroscopic methods (*e.g.* EPR, UV-VIS, IR), thermolysis and photolysis of various sulfur–nitrogen derivatives, particularly 1,3,2,4-benzodithiadiazines in the hydrocarbon and fluorocarbon series (see Scheme 2), are sometimes more suitable.[1(b),(f)–(h),8(c),10,21] This approach also



Scheme 5

†† Singlet diradical state is a real physical state which can be detected with a number of instrumental methods, *e.g.* two-photon absorption and/or phosphorescence spectroscopy.



Scheme 6

performs for Se containing radicals in both series, despite all-S congeners are observed as the second product (Scheme 6).[10(*a*),(*c*)]

Electronic, molecular and crystal structure

According to XRD and DFT data, Herz radicals are planar.[3,6(*a*),7,10(*e*),(*g*),21,25,30,33,34] The π*-SOMO, delocalized over a molecule, is essentially antibonding (Figure 2). According to EPR (including pulse technique), ENDOR and DFT data, the spin density is unevenly distributed over the whole molecule revealing a higher concentration at the positions 1–3 (chalcogen–nitrogen fragment) and a lower one at the positions 4, 6 and 7*a* (carbocycle). The replacement of S by Se leads to a limited perturbation of the electronic structure of the Herz radicals causing changes in the atomic charges, bond lengths, and bond orders only at the involved and neighbouring sites.[6(*a*)] At the same time, this noticeably affects EPR spectra of the Herz radicals inciting line-broadening and an increase in the g_{iso} and *g*-tensor anisotropy due to stronger spin–orbit coupling (SOC) in Se atoms compared to S atoms[3,6,7(*b*),10(*a*),(*c*),21,30(*f*),33(*h*),36–38] (Figure 3).

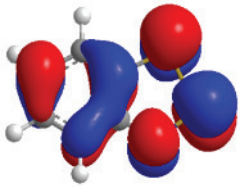


Figure 2 The π*-SOMO of 1,2,3-benzodithiazolyl from DFT calculations.

Comparison of 1,2,3- and 1,3,2-benzodithiazolyls reveals a striking contrast in the spin density distribution since in the latter the density is localized predominantly on the heterocycle.[6(*a*),10(*g*),11(*c*),15(*b*)]

The spin state of di-, tri- and polyradicals on the whole, and Herz species particularly, is an extremely sophisticated topic.[44]

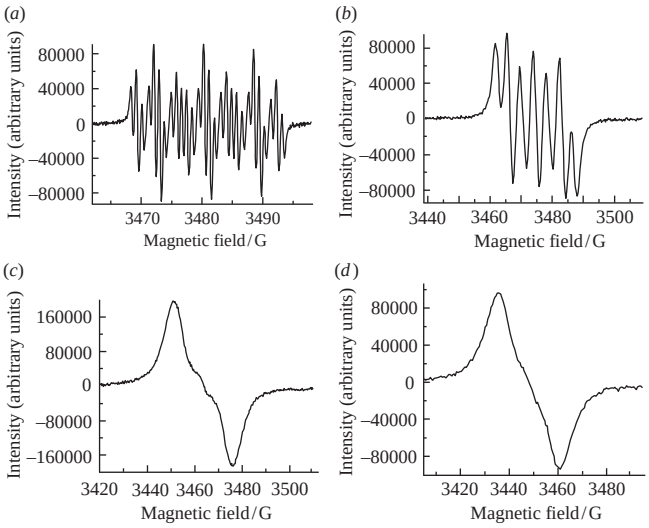


Figure 3 EPR spectra of (*a*) 1,2,3-benzodithiazolyl and its (*b*) 1,2-thiaselena, (*c*) -selenathia and (*d*) -diselena congeners in solution;[6(*a*),(*c*)] for spectra of naphtho-fused derivatives, see ref. 3.

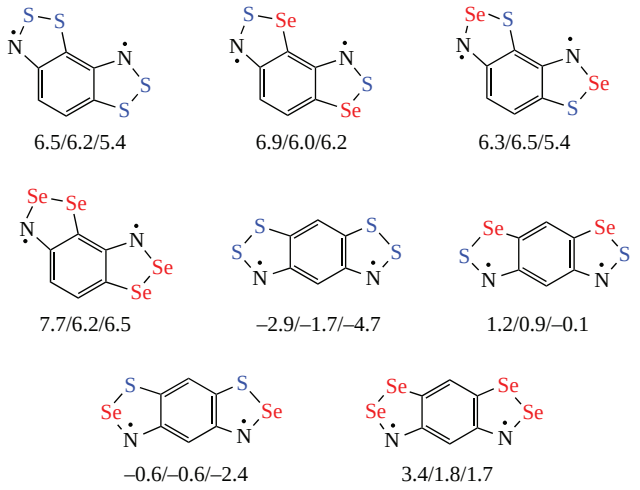


Figure 4 Calculated singlet–triplet splitting ΔE_{ST}/kcal mol^{-1} in Herz diradicals (left to right): CASSCF/CASPT2, only triplet state optimized; DFT, only triplet state optimized; CASSCF/CASPT2, both states optimized.

For unsubstituted benzo-fused bis(1,2,3-dichalcogenazolyls), both CASSCF/CASPT2 and broken-symmetry (BS) DFT calculations suggest dependence of the sign and value of the energy gap between the singlet and triplet states ($\Delta E_{ST} = E_S - E_T$) on the annulation mode. The replacement of S by Se affects ΔE_{ST} in different ways depending on the annulation mode and replacement position (Figure 4; for DFT data, see also ref. 41). For all angular species, the ground state is a triplet. Chalcogen exchange in one position only slightly affects the ΔE_{ST} value, whereas that in two positions produces a noticeable effect. With linear species, the situation is more variable. For S congeners, the ground state is a singlet. The replacement of S by Se reduces absolute value of ΔE_{ST} and even leads to the triplet ground state of the all-Se derivative, however, with ΔE_{ST} being much smaller than for angular species. Notably, conventional BS-DFT calculations are in reasonable agreement with the data of much more accurate CASSCF/CASPT2 ones (see Figure 4).[‡‡] Earlier, DFT calculations on substituted benzo- and azino-fused bis(1,2,3-dithiazoles) revealed that character of the ground state can be tuned by substituents in the central ring, namely, electron-acceptor substituents stabilize diamagnetic bipolar state and electron-donor substituent the paramagnetic state.[45]

For benzo-fused tris(1,2,3-dichalcogenazolyl)s, the CASSCF/CASPT2 and BS-DFT calculations suggest the quartet ground state. The replacement of S by Se produces only minor effect on the doublet-quartet splitting ($\Delta E_{DQ} = \Delta E_D - \Delta E_Q$) with two doublet states being almost degenerate (Figure 5).[‡‡]

Crystallographically, S and Se incarnations of the same Herz radicals can be both isomorphous and unisomorphous.[7,30(*c*),(*d*)]

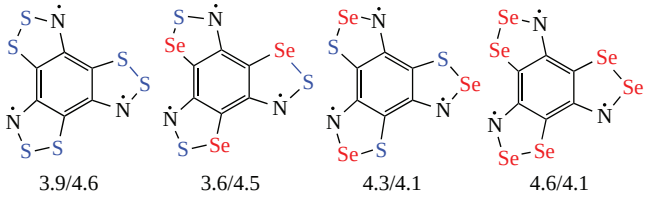
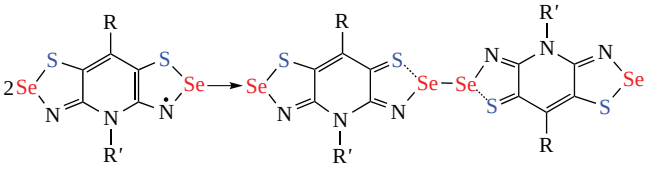


Figure 5 Calculated doublet–quartet splitting ΔE_{DQ}/kcal mol^{-1} in Herz triradicals with DFT-optimized geometry of the quartet state (left to right): CASSCF/CASPT2; DFT.

[‡‡] CASSCF/CASPT2: CASSCF(16,16)/CASPT2/ANO-RCC-dzp; DFT: BS-UB3LYP/def2-tzvp, ΔE_{ST} is taken as 2*J* and only the high-spin state geometries were optimized since BS singlet is not a real physical state. Full details will be published elsewhere.



25 **26**

Scheme 7

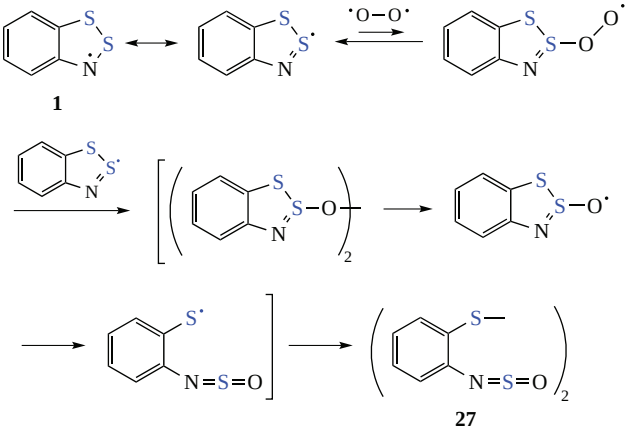
Thus, resonance-stabilized radicals **21** (see Figure 1; R = Me, R′ = Cl) crystallize in undimerized slipped π-stacked arrays but do not constitute an isomorphous set. With E = S, E′ = S, Se, the crystals belong to the orthorhombic space group $P2_12_12_1$; whilst with E = Se and E′ = S, Se the monoclinic space group $P2_1/n$ is arranged. The latter maximizes intermolecular Se···Se contacts, which are important, together with other shortened intermolecular contacts, for macroscopic electrical and magnetic properties of the compounds.[30(c)] Radicals **25** (Scheme 7; R = H, F, Me; R′ = Me) crystallize isomorphously in the monoclinic space group $P2_1/c$ in the form of centrosymmetric dimers **26**, in which an intramolecular Se−S bond of the radical is replaced by an intermolecular hypervalent 4-center 6-electron S···Se−Se···S σ-bond.[30(d)]

Overall, in the solid state Herz radicals systematically display both entropically-favored monomeric and enthalpically-favored dimeric structures.[3,7,25(b),(c),30,34,42(b)] The latter are normally composed of π-stacked pairs featuring pancake bonds,[3,18(b),46] sometimes lateral σ-pairs are also observed.[30(d),33(e),40] DFT calculations suggest that in a gas phase the π-dimers are inherently unstable, whereas Se-containing lateral σ-dimers can be stable.[6(a)] Paramagnetic monomeric structures are observed for oxobenzene-bridged radicals **16** (see Figure 1; E = S, R = F, Cl) packed in brick-wall or herringbone manner.[25(b),(c)] For crystal structures of this type radicals, covering also azine-bridged species **21** and **23**, alternating head-over-tail, herringbone and slipped-ribbon π-stacks are typical.[25(b),(c)] Higher-level quantum chemical calculations on radical **21** (E = E′ = S, R = H, R′ = Me, see Figure 1) revealed multicenter bonding between neighbouring species in slipped π-stacks, which is important for macroscopic magnetic properties of the compound.[47] Naphtho- and 1,4-naphthoquinono-fused 1,2,3-dithiazolyls and pyrazino-fused 1,2,5-thiadiazole/1,2,3-dithiazolyl hybrid revealed diamagnetic *cis*-cofacial, and slipped and centrosymmetric head-to-tail π-dimers, respectivelty.[3,9(b),42(b)]

Herz radicals demonstrate interesting polymorphism. Particularly, radicals **21** (see Figure 1; E = E′ = S, R = F, R′ = Me, Et) under normal conditions exist in the form of diamagnetic and paramagnetic polymorphs. The latter composed of π-stacks and the former of π-stacked dimers in which the radicals are linked laterally by hypervalent S···S–S···S σ-bonds (conceptually, π-radical → σ-dimer transition is similar to the HS → LS transition in metal coordination compounds; HS and LS are high- and low-spin states, respectively).[48] At elevated temperature or pressure, or visible/white light irradiation, the diamagnetic polymorph with R′ = Et undergoes phase transition to the paramagnetic state caused by a dimer-to-radical transformation accompanied by a cleavage of the hypervalent bonds. With R′ = Me, the diamagnetic polymorph is also thermo- and light-unstable, however, at elevated pressure its σ-dimers remain intact.[33(e),49] Pressurization of the related σ-dimerized thiaselenazolyl (E = Se, E′ = S, R = H, R′ = Me) causes its transformation into a π-dimer near 4–5 GPa.[49(d),50]

Reactivity

The Herz radicals are stable in a solid state and persistent in solution at room temperature. For isostructural species, thermal stability in a solution of Se derivatives is less than that of S ones.[3] In solutions, the Herz radicals are sensitive to moisture, oxygen, heat and, probably, UV light since in photochemical experiments a decrease of their concentration was observed during prolonged irradiation.[1(g),8(c),10(e)–(g),21]



1 **27**

Scheme 8

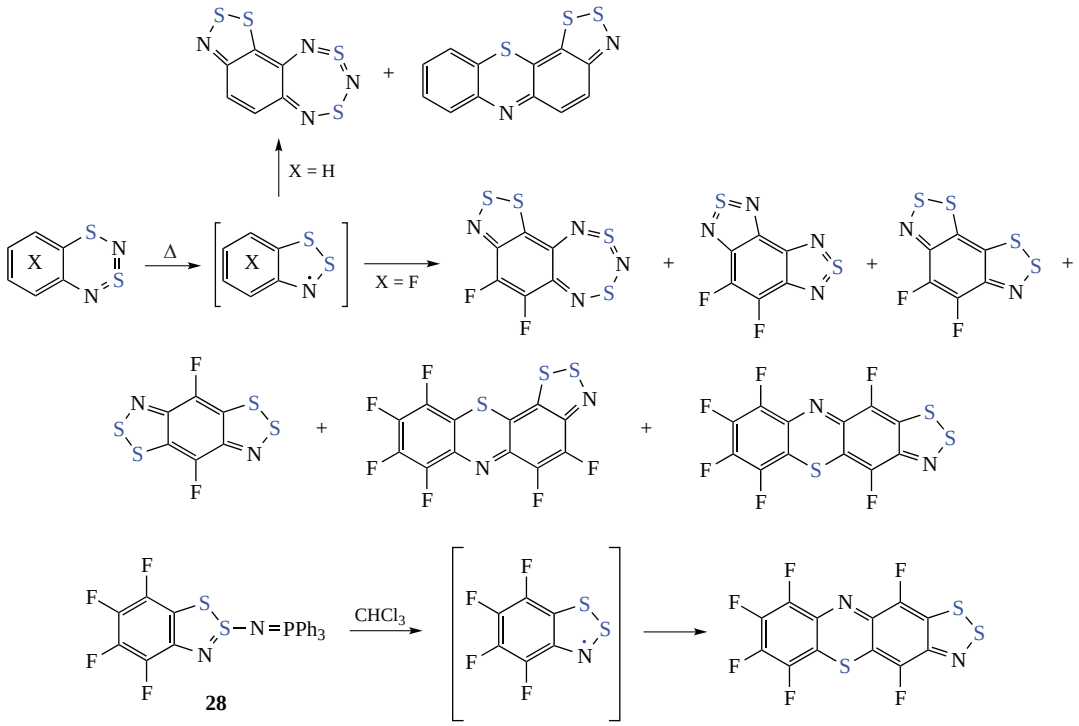
The interaction of Herz radical **1** with O_2 in hydrocarbon solutions leads to compound **27** (Scheme 8), with the radical decay kinetics corresponding to a self-termination reaction with an effective second-order rate constant linearly dependent on the concentration of dissolved O_2.[8(c),10(e)]

On heating in solution, naphtho-fused 1,2,3-dithiazolyl affords dibenzophenazine and elemental sulfur.[1(g)] Most likely, the reaction proceeds *via* a flipped co-facial π-dimer,[11(c)] *i.e.* it can be considered as self-condensation of the Herz radicals. The radicals obtained by thermolysis of concentrated (0.5 M) solutions of 1,3,2,4-benzodithiadiazines undergo condensations resulting, particularly, in differently fused polycyclic scaffolds (Scheme 9, *cf.* Schemes 2 and 6) whose structures were confirmed by XRD. The formation of the same polycyclic scaffolds in both the hydrocarbon and fluorocarbon series confirms the radical character of the carbocyclic substitution involved.[8(b)] Some of compounds R–N=PPh_3, such as **28** (Scheme 9), spontaneously produce Herz radicals in $CHCl_3$ solutions even at room temperature (*cf.* Scheme 2); for **28**, the final product of transformations is 5/6/6/6 tetracyclic system (Scheme 9).[8(b),10(c)]

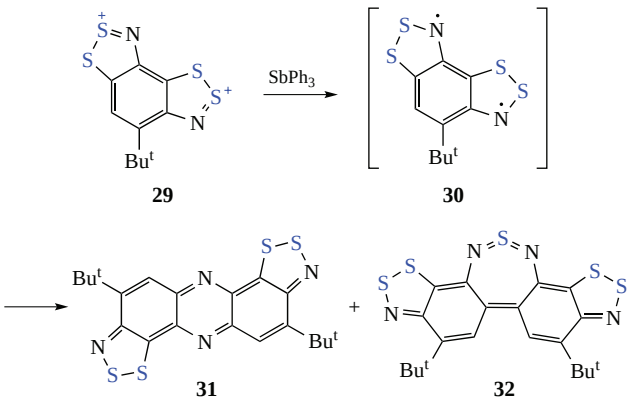
Synthetically, it is more convenient to generate the Herz radicals by chemical reduction of Herz cations under conditions favourable for the radicals' condensation. Particularly, condensation of tricyclic diradical **30**, generated *in situ* from dication **29**, gave pentacyclic scaffolds **31** and **32** (Scheme 10),[8(a),§§] most likely *via* its isomeric π-dimers and, in the latter case, rare –N=S=S derivatives, which are known to produce –N=S=N– linkage.[1(a),(f),24(b),51] Both **31** and **32** are near-IR dyes possessing the long-wavelength bands with λ_{max} at 689 (with a strong shoulder at 760) and 796 nm, respectively. Cyclic voltammetry, EPR and UV-VIS-NIR spectroelectrochemistry revealed that compound **31** possesses five differently-colored stable redox states covering dication, radical cation, neutral molecule, radical anion and dianion.[8(a)] In combination with near-IR absorption in the neutral state, it makes this compound very promising for the design and synthesis of tuneable functional materials.[52,53]

The pyridine-bridged Herz radical **33** transforms thermally into pyridone-bridged one **34** and then into bipolar ion **35**, whereas related radicals with H, Alk, Ar or Hal substituents

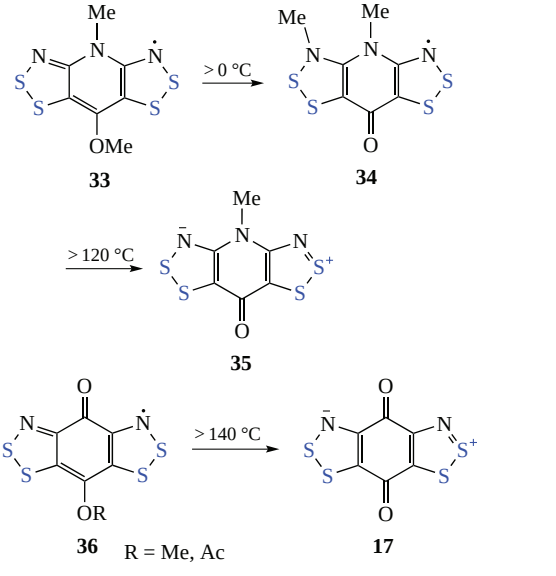
§§ The starting Herz diradical most likely has a triplet ground state. Heteroatom reactivity of singlet Herz diradicals can be different.



Scheme 9



Scheme 10



Scheme 11

instead of MeO, as well as their Se analogues, remain intact.[33(f)] Similar reaction was also observed for RO-substituted oxobenzene-bridged radicals **36** (Scheme 11).[54]

Herz radicals are redox active. For example, they are chemically (*e.g.* with halogens) and electrochemically oxidized to Herz cations,[1(b),4(a)] and 1,2-naphthoquinone-fused 1,2,3-dithiazolyl can be reduced into stable O-centered anion.[25(a)]

Herz radicals are promising paramagnetic ligands for metal coordination compounds. Particularly, 1,4-naphthoquinone-fused 1,2,3-dithiazolyl acts as bridging ligand in trinuclear Mn^{2+} complex where the cation's and radical's spins are coupled antiferromagnetically (AF) to give rise to the S = 13/2 ground state.[9] It should be emphasized that AF materials are of interest for spintronics.[55,56] It should also be noted that radical ligands are essentially important for the design and synthesis of single-molecule magnets. To the best of our knowledge, however, the only thiazyl radical involved does not belong to the Herz family.[57]

Materials science

Herz radicals are the building blocks of real or potential all-organic conductive and/or magnetic, including photomagnetic, molecular materials, as well as optoelectronic materials (for compilation of numerical conductive and magnetic data, see Online Supplementary Materials).[2,7,14,25,30–50,54,58–64] They form a unique domain of functional/smart materials science.[65] Replacement of S by Se strengthens intermolecular interactions (secondary bonding interactions, SBIs) in the solid state towards increasing electrical conductivity and magnetic exchange interactions. Stronger SOC in Se atom leads to magnetic anisotropy. Overall, many Se-containing Herz radicals are electrical conductors and low-temperature spin-canted antiferromagnets (AFMs; *i.e.* weak ferromagnets, FMs) or even bulk FMs.

All organic π-radicals with strong intermolecular interactions in a solid state are potential conductors.[58,66,¶¶] The electrical

¶¶ For S = 1/2 radicals in the solid state, a simple band theory suggests a half-filled (f = 1/2) electron energy band, *i.e.* metallic state, with bandwidth W. Electron–lattice and/or electron–electron interactions,

conductivity of solids formed by Herz radicals strongly depends on the nature and molecular positions of chalcogens, the nature and bulkiness of substituents, the type and dimensionality (including SBIs) of the crystal packing where regular 1D π-stacks or 2D π-sheets are the most favourable, and an external pressure. The conductivity of oxobenzo-bridged species **16** (see Figure 1) depends on the structure and energy of the radical's π*-SOMO constructed from group-orbitals of the heterocyles, C=O and R. In the solid state, these orbitals form electron–energy band, and in this sense the conductivity is driven by multiorbital effects. For some radicals, the external pressure leads to the activation energy E_a = ~0 eV, *i.e.* to band-gap closure with the formation of metallic state (see Online Supplementary Materials). In radical **16** with E = S and R = F, a 2D Fermi-liquid metallic state has been observed at 6 GPa.[58] Overall, a weak metallic state is caused by a complex interplay of the aforementioned factors.[30(c),33(a),34(b),58,59] In general, the electrical conductivity of Herz radicals in the solid state is facilitated by a low Coulombic barrier U to charge transfer between the radical π-SOMOs.§§ In radicals **16**, this barrier is further reduced by a multiorbital effect occasioned by the presence of a low-lying π*-LUMO.[54] The record conductivity for Herz species-based solids is σ = 0.5 S cm^{-1} at normal pressure for radical-cation salt [**9**$_3$]$^+$[GaCl$_4$]$^-$,[30(h),32(b)] and ~10^2 S cm^{-1} at 12 GPa for bipolar ion **17**.[34(b)] Amongst other species, radicals of types **16** (E = S, R = NO$_2$, MeCN solvate), **21** (E = Se, E′ = S, R = H, R′ = Me) and dimer **26** (R = H, R′ = Me) featuring σ ~ 10 S cm^{-1} at 8, 5 and 5 GPa, respectively, should be mentioned.[30(c),(d)] The best chalcogen–nitrogen molecular conductor polythiazyl (SN)$_x$, formally composed of SN$^{\bullet}$ radicals,[15] is a genuine metal in physical meaning. It reveals σ ~ 10^3 S cm^{-1} along the macromolecules and becomes a superconductor at ~0.3 K.[67–69,†††]

Neutral quinoid **9**[2(b)] (see Figure 1) exhibits nonlinear optical properties with a large third-order nonlinear susceptibility of 10^{-11} esu, which can be associated with a number of degenerate electronic states caused by its singlet diradical nature.[32(a)] Radical-cation mixed-valence salts [**9**$_3$]$^{2+}$[BF$_4$]$^-_2$ and [**9**$_3$]$^+$[MCl$_4$]$^-$ (M = Ga, Fe) demonstrate nonlinear electrical transport in the charge-ordered insulating state.[2(b),20(b)] With M = Ga, the low-field negative-resistance effect was observed at room temperature, which is rare and can be used in organic electronic devices such as switching units, information storage units and thyristors.[32(b)] Salts of its benzo-fused analogue **13** (see Figure 1; E = S) [**13**]$^+$[ClO$_4$]$^-$ and [**13**$_3$]$^{2+}$[X]$^-_2$ (X = ClO$_4$, FSO$_3$) have σ of 10^{-5} and 10^{-2}, respectively.[2(a)]

Conductive properties of Herz radicals-based solids are frequently combined with FM or AF ones[7(a),25(c),30(b),(h),61,64,70,71] (see Online Supplementary Materials). Particularly, conductive radical **16** (see Figure 1; E = S, R = Cl) orders as a spin-canted AFM at 8 K with a canting angle φ = 0.14° and coercive field H_C = 80 Oe at 2 K.[25(c)] Such type AFMs undergo a field-induced spin–flop transitions to FM states. The Se-containing radicals **21** (R = H, R′ = Me) reveal strong AF coupling at lower temperatures, whereas the all S-congener remains paramagnetic.[7(a)] Radical **21** (E = Se, E′ = S, R = Br, R′ = Et) at normal pressure (~100 kPa) undergoes the FM ordering with Curie temperature[‡‡‡] T_C = 14.1 K.[30(h)] In some cases external pressure increases T_C, with the record values of 24 K and 27.5 K at ~2 GPa for all-Se radicals **21** (E = E′ = Se; R = Br, I; R′ = Et), whose normal-pressure T_C is 17.5 and 10.5 K for R = Br, I, respectively.[30(b),(e),(g),33(g),64] Amongst other thiazyl magnetics, 4-R-1,2,3,5-dithiadiazolyl (R = 4-NCC$_6$F$_4$), which is spin-canted AFM (weak FM), has Néel temperature[‡‡‡] T_N = 36 K at normal pressure and 70 K at 1.6 GPa.[14(b),71]

For radical **21** (E = E′ = S, R = F, R′ = Et), hysteretic spin crossover between paramagnetic species and their S···S–S···S hypervalent σ-dimers was observed.[33(e)] Radical-cation salt [**6**][GaBr$_4$] (see Figure 1, E = S), having in crystal a kagome-coupled chain structure, reveals spin frustration.[30(a)]

The diamagnetic lateral σ-dimers of radicals **21** (E = E′ = S; R = F; R′ = Me, Et) dissociate into monomeric radicals under low-temperature irradiation by visible light with λ = 650 nm. The radical pairs are stable up to 150 and 242 K (R′ = Me, Et; respectively) before reverting to the dimer state. Therefore, corresponding solids can be considered as photomagnetic materials.[49(b)]

Overall, magnetic properties of Herz radicals-based solids can be affected by heat, pressure and light.[49(a)–(c)]

It should be emphasized that not only FM materials but also AF ones are promising for spintronics including the creation of nanoscale memory cells.[55] The experimental observation for AFMs of such an interesting physical phenomenon as the spin-liquid state[72] should also be mentioned.

In summary, amongst genuine Herz radicals those belonging to scaffolds **16**, **21** (see Figure 1) and **26** (see Scheme 7) are the most remarkable for materials science, and these scaffolds and their modifications are worth further attention.

Conclusions

Synthetically, Herz radicals with chalcogens S and Se, but not Te, are readily available. In many cases they can be isolated on a preparative scale in the form of stable solids. Their structural diversity is wide. Synthesis of Te-containing Herz radicals is a serious challenge. The same is also true for the synthesis, isolation and structural and functional characterization of Herz polyradicals.

The electrical and magnetic properties of solids formed by the Herz radicals contribute much to a contemporary *spin science*.[12(c)] They are promising for the further design and synthesis of all-organic conductors and magnets. An interesting direction of further research can be the co-crystallization of Herz radicals with other organic radicals, which can give metal-free ferrimagnets through AF interactions between the spins of dissimilar magnitude.[73] Promising is controlled reorganization of intermolecular interactions in the radicals' polymorphs, which can lead to bistable materials (*cf.* related 1,3,2-dithiazolyls).[74] Some of the Herz di- and triradicals can have high-spin ground states – triplet or quartet, respectively. Hopefully, they can find promising applications in both chemistry and materials science.

Heteroatom reactivity of Herz radicals, which, beginning with diradicals, should depend on their spin state, is less

however, lead to the Mott, Peierls or charge-ordered ground states, *i.e.* semiconductor/insulator situation. For good conductivity of such highly-correlated organic radicals, these interactions should be optimized. According to the Mott–Hubbard approach, the charge transport in 1D-arrays of radicals requires that the nearest-neighbour interactions expressed in the terms of the intermolecular resonance integral β or hopping integral t between the radicals' SOMOs are maximized, whereas the potential energy barrier for charge transfer, *i.e.* on-site Coulomb repulsion U, is minimized to the values that $W = 4\beta \sim 4|t| > U$. The conventional ranges for the conductivity σ of insulators and metals are 10^{-12}–10^{-6} and 10^4–10^6 S cm^{-1}, respectively, and σ of semiconductors is in between.

††† The metallic state of (SN)$_x$ is caused by its very special crystal packing leading to the degeneration of the frontier MOs of macromolecules and formation of half-filled 1D electron–energy band; numerous SBIs in the crystal, transform unstable 1D band into stable anisotropic 3D one. This situation is unique and all known oligomeric analogues of (SN)$_x$ with terminal or/and chain-incorporated arene groups are insulators. Therefore, the metallic state of (SN)$_x$ is *caprice of nature*.

‡‡‡ Curie temperature is the temperature at which paramagnetic substance loses its permanent magnetic properties. Néel temperature is the temperature above which AF substance becomes paramagnetic.

studied[8(a)–(c),10(c),(e),33(f),54] and worth massive further research. In this field, one can expect novel chemical reactions and novel structural types of their products possessing various properties useful for materials science.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.001.

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