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Stable heterocyclic radicals

O A Rakitin

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Abstract. Data on the synthesis and structural properties of stable heterocyclic radicals with the spin density on the carbon and nitrogen atoms are generalized and described systematically. The compounds isolated in a pure state and characterized by X-ray diffraction analysis over the last 15 years are considered. The bibliography includes 143 references.

I. Introduction

At present, there are many types of radicals that are sufficiently stable to be isolated and stored without special precautions. The dominating position among them belongs to the heterocyclic radicals. The wide diversity of their molecular architectures makes it possible to mark general factors that are responsible for the stability of such radicals, similarity of their geometrical and electronic structures, trend to dimerization and reactivity. The present review covers the main classes of heterocyclic radicals in view of their stability, molecular structure and methods of synthesis.

It should be noted that stable heterocyclic radicals have already been known for about 100 years. The development of their chemistry has shown that it is possible to build certain types of molecules that would be stable in the radical state. Moreover, there is a number of this kind of families that have been investigated for decades.

Stable molecules with an open electron shell are of interest to chemists working in different fields of chemistry. In the case of heterocyclic radicals, the research dealing with the development of new functional materials for electronics and spintronics [1, 2] is of prime priority. For example, the neutral 4-(4-cyanotetrafluorophenyl)-1,2,3,5-dithiazolyl radical ($[4\text{-}NCC_6F_4\overline{CNSSN}]^{\bullet}$) possesses ferromagnetic properties with $T_C = 36$ K (T_C is the Curie temperature) at normal pressure and $T_C = 65$ K at 16 kbar.[3] Several neutral radicals of the dichalcogenazolyl type (chalcogen is sulfur or selenium) possess electric conduction together with ferromagnetism ($T_C = 12$, 17 and 28 K depending on the structure).[4, 5] Other radicals of this type behaving as paramagnetic insulators under normal conditions (the Mott dielectric) undergo pressure-induced metallization.[6] In the solid state, some chalcogen – nitrogen heterocyclic π-radicals reveal spin crossover accompanied by magnetic hysteresis. The observed bistability is caused by the coexistence in the certain temperature interval of two phases, *viz*., paramagnetic radicals and their weakly coupled diamagnetic π-dimers.[7 – 10] It is believed that magnetically bistable materials may be used in molecular spintronic devices for the data storage and data processing.[11]

Investigations into organic radicals face first of all with the stability problem. There are two terms that define this property, *viz*., stable and persistent.[12 – 14] We adhere to Ingold's pragmatic definition,[15] which states that the radical that may be stored after isolation in the individual state for a long time in an inert atmosphere at room temperature is stable. The radical that is sufficiently long-living (usually in solutions) so that its structure can be established by spectroscopic methods (usually EPR) is persistent.

Recently, a series of reviews covering different types of radical species have been published.[2, 13, 14, 16 – 19] However, the reviews on the synthesis and general properties of stable heterocyclic radicals are lacking. It is clear that the properties of radicals include numerous aspects (*e.g*., see the recently published monograph edited by R G Hicks [18]). In the present review, the emphasis is made on the structural properties of heterocycilc radicals, especially on the crystal packing, which is essential for their physical properties and applications. The aim of this review is to attract the attention of the organic chemists working in the field of heterocyclic chemistry (including polynitrogen heterocycles) to the possibility of the synthesis of stable heterocyclic radicals on the basis of the structures that have been previously obtained by them.

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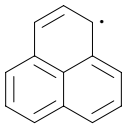
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Analysis of the available data shows that it is heterocyclic radicals where the spin density is mainly localized on the nitrogen atoms and on the nitrogen-bound oxygen atoms that are stable in general. Only several types of heterocycles with the spin density on the carbon atom are known. Of course, this classification is conventional, since the spin density is virtually always spread throughout the heterocyclic ring, which is discussed in detail below. In the present review, we do not discuss one of the most abundant classes of stable heterocyclic radicals, *viz*., nitroxide radicals since they are dealt with in a recent review by Tretyakov and Ovcharenko.[17] Data on the radicals containing elements different from carbon, nitrogen, sulfur and selenium in the ring (*e.g*., boron, phosphorus, germanium, silicon, metals) are also not discussed either, since they are dealt with in a review by Power.[13] Charged heterocyclic radicals, *i.e*., radical cations and radical anions are not considered as well. Chemistry and materials science of the former is the subject of numerous reviews (*e.g*., see Refs 20, 21 and others of this specialized issue).The study of the latter isolated as thermally stable salts of various cations is just at the beginning (see, *e.g*., Ref. 22 and papers cited therein). Collected here are data on the other types of heterocyclic radicals mainly over the last 15 years.

II. Heterocyclic radicals with spin denstity on the carbon atom

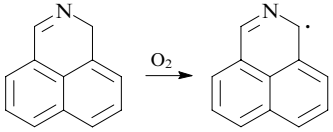
1. Azaphenalenyl radicals

As a rule, stable heterocyclic radicals in which the spin density is mainly localized on the carbon atom pertain to derivatives of phenalenyl radical (**1**). In itself, the radical **1** is characterised by the distribution of the spin density between six α-carbon atoms (α-positions relative to the common atoms). It is a striking example of a radical the stability of which is a result of delocalization of the unpaired electron. However, this can undergo dimerization to a considerable extent at the temperature below 20 °C.



1

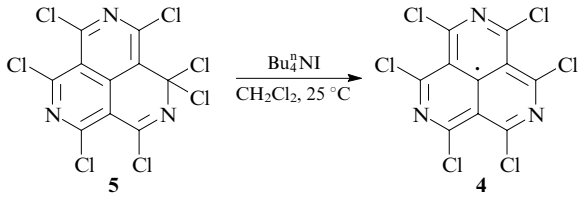
2-Azaphenalenyl radical (**2**) prepared by the oxidation of 3*H*-benzo[*de*]isoquinoline (**3**) with atmospheric oxygen [23] does not dimerize for several months at room temperature in a sealed tube.



3 **2**

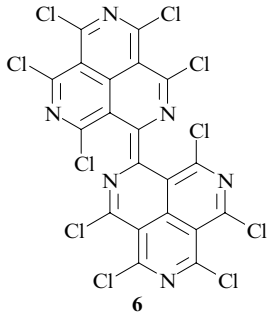
Data from EPR spectroscopy show that the spin density in this radical is localized on the carbon atoms as well and its distribution does not considerably differ from that in radical **1**. Only small increase in the spin density occurs on the carbon atoms nearest to the nitrogen atom.[23] Unexpectedly, an attempt of stabilization of the azaphenalenyl radical (**2**) by copper hexafluoroacetylacetonate led to a non-radical complex of divalent copper with a σ-dimer.[23]

Perchlorinated 2,5,8-triazaphenalenyl radical (**4**) [24] seems to be even more stable than radicals **1** and **2**. For example, it can be isolated by column chromatography on silica gel without substantial decomposition. It is obtained by the reduction of perchloro-derivative **5** with the tetrabutylammonium iodide at room temperature.



5 **4**

It should be noted that though radical **4** is stable, its synthesis is to be carried with certain precautions in order to avoid its further dimerization into compound **6** with removal of two chlorine atoms and the formation of the double bond C=C.[24]

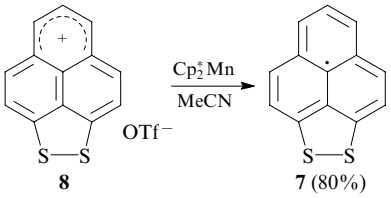


6

2. Thiophenalenyl radicals

Other examples of phenalenyl radicals stabilized by annulation of the heterocycle to a hydrocarbon ring are thiophenalenyl radicals. Two representatives of this class of heterocyclic radicals are known.

1,9-Dithiophenalenyl radical (**7**) was obtained by the reduction of 1,9-dithiophenalenylium triflate (**8**) with bis(pentamethylcyclopentadienyl)manganese in acetonitrile.[25]



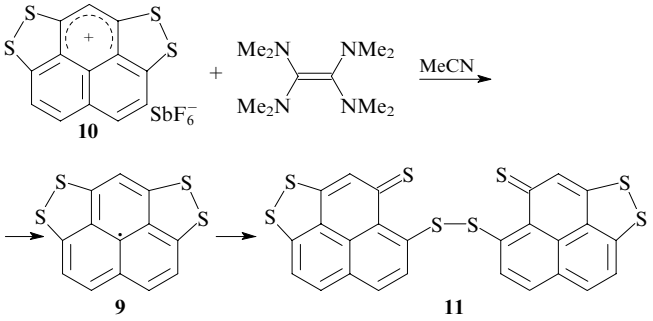
8 **7** (80%)

Cp* = η^5-C_5Me_5.

Radical **7** is stable in air in the crystalline state for 24 h, but easily decomposes in solutions even in the absence of oxygen. Crystallization of radical **7**, remaining in the radical state, forms a π-dimer. This is one more example of a radical stabilized by electronic rather than by steric factors.

Quite unexpectedly, phenalenyl radical **9** containing two 1,2-dithiole rings is less stable than radical **7**.[26] It is obtained by slow reduction of the tetrathiophenalenylium hexafluoroantimonate (**10**) with tetrakis(dimethylamino)ethylene in acetonitrile at room temperature. The presence of the radical in the solution at room temperature has been confirmed by EPR spectroscopy. It has been shown that in the absence of oxygen the radical may be stored for

infinitely long time. However, in the solid state salt **10** forms S–S-dimer **11** with a decomposition of one of the dithiole rings. Thus the increase of the number of disulfide moieties can lead to the ring-opening of one of the dithiole rings and σ-dimerization.



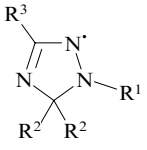
10 **9** **11**

III. Heterocyclic radicals with the spin density on the nitrogen atom

1. Radicals based on five-membered heterocycles

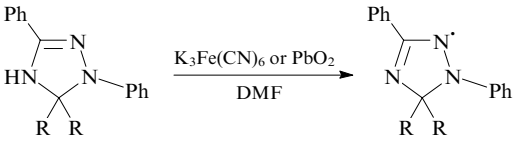
a. 1,2,4-Triazolyl radicals

1,2,4-Triazolyl radicals contain a hydrazine group incorporated in the cyclic structure (often unsaturated) contributing to π-delocalization. A series of stable dihydrotriazolyl radicals **12** are known. The conditions of stability are the following: substituent R^1 should be aromatic and substituents R^2 and R^3 may be both aliphatic and aromatic.



12 R^1 = Ar; R^2, R^3 = Alk, Ar.

Several representatives of this series have been characterized by X-ray diffraction analysis.[23,24] It turned out that they all exist as monomers both in the solid state and in solutions. The spin density in triazolyl radicals **12** is concentrated mainly on the hydrazine nitrogen atom devoid of an exocyclic substituent. Though, the spin density is partially localized on the imine nitrogen atom, too. 1,2,4-Triazolyl radicals are obtained by the oxidation of 4,5-dihydro-1*H*-1,2,4-triazoles **13** with potassium ferricyanide[27] or lead dioxide in dimethylformamide.[28] The yields of the radical may come up to 90%.

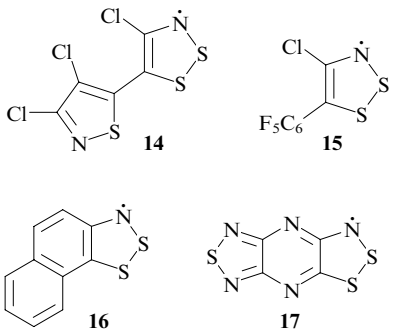


13 **12** (34%–90%)

R = Ph, Me; R–R is biphenyl-2,2-diyl.

b. 1,2,3-Dithiazolyl radicals

Recently, Oakley and co-authours have isolated several stable monocyclic and fused 1,2,3-dithiazolyl radicals. Studies of their structures by X-ray diffraction analysis have unexpectedly shown that dithiazolyls **14**–**17** possess different types of structures in the solid state.

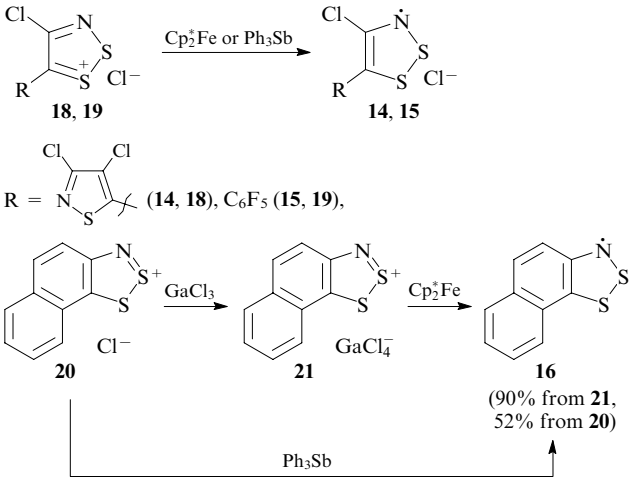


14 **15** **16** **17**

The only radical that does exist in the monomer state is 1,2,3-dithiazolyl radical **14** with the isothiazolyl substituent in position 5.[29] In the crystal state, its molecules are involved in π-stacking interactions. At the same time, another non-fused dithiazolyl **15** has a structure of a *gauche*-π-dimer bound by intramolecular S···S bonds (3.2987 Å) in positions 1.[30]

1,2,3-Dithiazolyl **16** with a fused naphthalene ring forms cofacial π-dimers (the distance between the radicals in the dimer is 3.0534 Å),[31] and tricyclic radical **17** forms π-dimers with the antiparallel arrangement of the heterocycles (the distance between the radicals in the dimer is 3.2331 Å).[32] Thus, in the dimers of the species **15**–**17** the distances between the sulfur atoms range from 3.0 to 3.3 Å, which is larger than the sum of the two covalent radii but is less than the sum of the two van der Waals radii of the S atom. EPR spectroscopy and quantum chemical calculations show that the spin density in the fused 1,2,3-dithiazolyl radicals **16** and **17** is delocalized. Obviously, it may be a reason of the higher stability of the isolated radicals. However, the situation with the stability of this type of heterocyclic radicals is not as simple as it seems. For example, their selenium analogues occurred to be thermally unstable.[31]

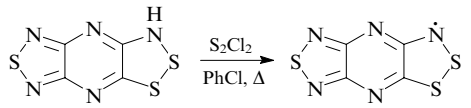
As a rule, 1,2,3-dithiazolyl radicals **14**–**16** are obtained by the reduction of the corresponding 1,2,3-dithiazolium salts **18**–**21** with decamethylferrocene[30,31] or triphenylantimony.[29,31]



18, **19** **14**, **15**

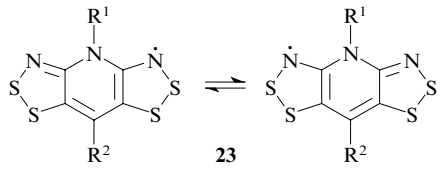
20 **21** **16** (90% from **21**, 52% from **20**)

The radical species also form in the oxidation of 1,2,5-thiadiazolo-1,2,3-dithiazolopyrazine (**22**).[32] The best result among the oxidants studied (S_2Cl_2, SO_2Cl_2, bromine, chlorine) was obtained with sulfur monochloride in boiling chlorobenzene. The yield of radical **17** was 78%.



22 **17** (78%)

An undoubtful recent achievement by Oakley and co-workers is the development of approaches[33–36] to the so-called resonance-delocalized 1,2,3-dithiazolyl radicals **23**. The latter unlike other fused dithiazolyls (*e.g.*, **16** and **17**) exist as monomers in solutions and in the solid state.

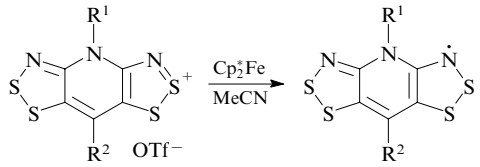


23

R^1 = H, Me, Et, Pr^n; R^2 = H, Me, Ph, Cl.

One of the compounds **23** ($R^1 = R^2$ = Me) exists in the solid state as monomers forming stacks through π-interactions. The S···S contacts of the lateral type are the shortest intermolecular distances (3.368 Å).[36]

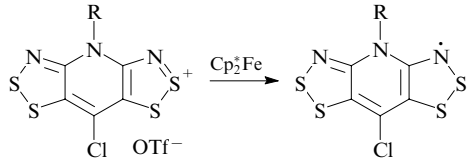
Bis(1,2,3-dithiazolo)pyridyl radicals **23** were obtained from the corresponding salts **24** under the action of decamethylferrocene in acetonitrile.[36]



24 **23** (56%–58%)

R^1 = Me, Et; R^2 = Me, Ph.

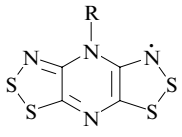
Under these conditions, chlorinated cations **25** also form the corresponding radicals **26**.[34,35]



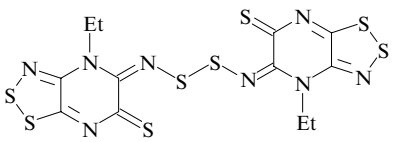
25 **26** (64%–83%)

R = Me, Et.

The pyrazine analogues of radicals **23**, compounds **27a**,**b**, are characterised as radical species by EPR spectroscopy and cyclic voltammetry in solutions. In the solid state, they unexpectedly demonstrate quite different behaviour. Thus ethyl derivative **27a** forms σ-dimer **28** due to the S–S-bonding (2.82 Å).[37]



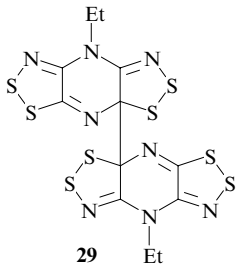
27a,**b**



28

R = Et (**a**), Me (**b**).

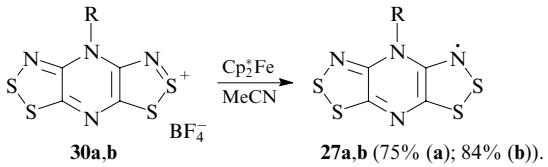
Interestingly, it may crystallize in another form with the formation of a σ-bond C–C (1.607 Å) (dimer **29**). Presumably, the reason of the formation of such dimers is the presence of significant spin density on the carbon atoms and on the sulfur atom of the radical **27a**.



29

Crystals of the methyl derivative **27b** consist of non-dimerized radical species π-stacked in an alternating ABABAB fashion. There are numerous S···S and S···N contacts in this packing.[38]

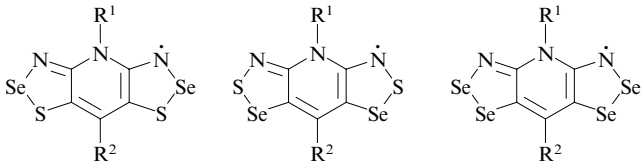
Pyrazine radicals **27a**,**b** are obtained by the reduction of 1,2,3-dithiazolium tetrafluoroborates **30a**,**b** with decamethylferrocene in acetonitrile.[38]



30a,**b** **27a**,**b** (75% (**a**); 84% (**b**)).

R = Et (**a**), Me (**b**).

In the search for practically useful thiazolyl radicals, Oakley and co-workers[31] have synthesized a series of resonance-delocalized 1,2,3-dithiazolyl radicals in which some or all sulfur atoms were replaced by selenium. It turned out that the selenium derivatives **31**–**33** are stable unlike the selenium analogues of monocyclic 1,2,3-dithiazolyl radicals, which are so unstable that they cannot be isolated in the individual state (see previous Section).[31] It has been determined that in the solid state they may consist of both monomeric radicals or σ-dimers bound by the Se–Se bond. The latter dimers are similar to dimer **28**.



31a–**d** **32a**–**d** **33a**–**c**

R^2 = H: R^1 = H (**a**), Me (**b**); R^2 = Cl: R^1 = Et (**c**), Me (**d**).

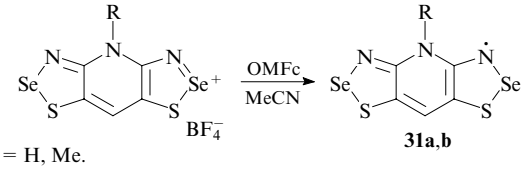
R^1 = Me: R^2 = H (**a**), Me (**b**); R^2 = Cl: R^1 = Et (**c**), Me (**d**).

R^1 = Me, R^2 = H (**a**); R^2 = Cl: R^1 = Et (**b**), Me (**c**).

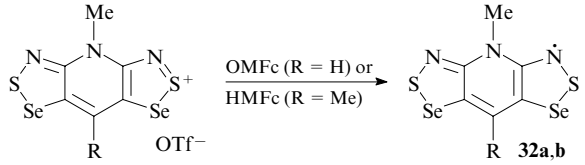
Radicals **31a**,**b** form isostructural crystals consisting of the Se–Se bound π-stacked σ-dimers. The latter are bound by numerous intermolecular contacts: Se···Se, Se···S and Se···N.[39,40] However, radicals **32a**,**b** and **33a** crystallize as non-dimerized molecules forming π-stacks[41] bound into bands through intermolecular contacts element–element. Radicals **31c**, **32c** and **33b** have the same crystalline struc-

tures.[42] Methyl derivatives **31d**, **32d** and **33c** also crystallize as monomers but the crystals are not isomorphous.[43]

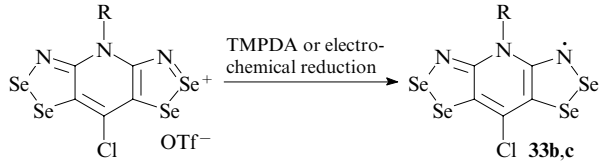
The diversity of reducing agents used for the synthesis of bis(thiaselenazolo)pyridinyls **31**–**33** from the corresponding salts is wider than for the bis(dithiazolo)pyridinyls **27**. Octamethylferrocene (OMFc)[39,41] and hexamethylferrocene (HMFc),[43] *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPDA),[42] and electrochemical reduction[42,43] have been used.



R = H, Me.

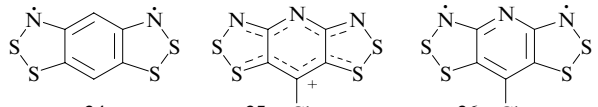


R = H, Me.

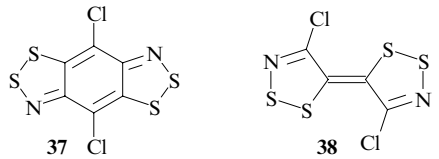


R = Me, Et.

The synthesis of the compounds containing two 1,2,3-dithiazolyl rings each with an unpaired electron was of a particular interest. The ground triplet state has been predicted for the benzobis(1,2,3-dithiazolyl) (**34**),[44] but this compound has not been obtained yet. However, a tricycle **35** in which the nitrogen atom is substituted for the carbon atom has been obtained. X-ray diffraction analisys and quantum chemical calculations have revealed that this tricycle is an antiaromatic zwitterion rather than a biradical **36**.[45]



The attempts to obtain other biradicals with dithiazole rings annulated (compound **37**)[46] or bound by an exocyclic double bond C=C (compound **38**)[47] resulted in the quinonoid structures with closed electron shell. The analisys of dichotomy 'biradical–compound with a closed shell' is given in a review.[19]

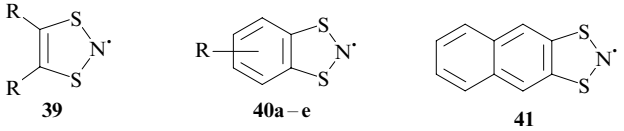


The solution reaction of areno-1,2,3-dithiazolyl radicals with atmospheric oxygen has been specially studied. It turned out that the reaction is accompanied by the rearrangement resulting in *N*-sulfinyl derivatives of 2,2′-diaminodiaryl sulfides.[48,49]

c. 1,3,2-Dithiazolyl radicals

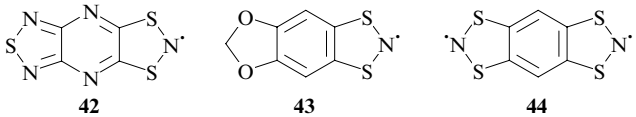
1,3,2-Dithiazolyl radicals are the structural isomers of 1,2,3-dithiazolyl radicals considered in the previous section. More than ten of them are characterised by X-ray diffraction analysis. Generally, these radicals are particularly stable in the solid state, and they may react with atmospheric oxygen in solutions.

1,3,2-Dithiazolyl radicals may form different types of crystals. As a rule, the delocalization of an unpaired electron is significant and that is why the influence of the substituent electronic effects is great for these radicals. Monocyclic 1,3,2-dithiazolyls **39** in the crystalline state form cofacial π-dimers.[50,51] The benzoannuled radical **40a** may form centrosymmetric antarafacial† π-dimers.[52,53] The crystals of naphtho-1,2,3-dithiazolyl (**41**),[54] 1,2,5-thiadiazolo-1,3,2-dithiazolopyrazinyl (**42**)[55] and cofacial π-dimers of benzodithiazolyls **40b**–**d**[56–58] have herringbone packing, and tricyclic radical **43** forms slightly distorted π-stacks.[59] Quite recently, it has been established that benzoannuled radicals (*e.g.*, **40e**) may remain monomeric in the crystalline state forming a complex packing without π-dimerization.[59]



R = CN, CF_3, CO_2Me.

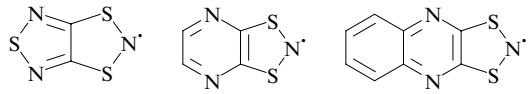
R = H (**a**), 3-Me (**b**), 3-CN (**c**), 4-CN (**d**), 5,6-$(OMe)_2$ (**e**).



It should be noted that in the case of 1,3,2-dithiazolyls it is possible to obtain biradical structures, for example, benzo-1,2:4,5-bis(1,3,2-dithiazolyl) (**44**), whose crystals consist of individual molecules forming slipped π-stacks; molecular planes make an angle of 32.4°, interplanar spacing is 3.49 Å.[60] EPR spectroscopy shows that in some solvents (*e.g.*, in toluene) biradical **44** may exist in equilibrium with the π-dimers of both centrosymmetric and cofacial types.[60]

Oakley and co-workers[10,55,61–65] have found that the structures of the fused 1,3,2-dithiazolyls **42**, **45** and **46** depend on the temperature and manifest magnetic hysteresis. It has been determined[65] for radical **46** that at temperatures from 297 to 343 K these radicals are packed in 'head-to-tail' chains. However, at a higher temperature they exist as monomers and at a lower temperature they exist as π-dimers. Hysteresis demonstrates the transition between the dimeric and monomeric structures. Between these temperatures, the radicals have a property of bistability, that is, they may exist as both the monomers or dimers depending on the direction of the temperature change.

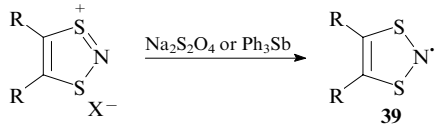
† In literature, the cofacial and antarafacial dimers are sometimes called *cis*- and *trans*-dimers, but these terms do not conform to the IUPAC Recommendations.



45 **46** **47**

It should be noted that quinoxalino-1,3,2-dithiazolyl (**47**) also consists of the monomers packed in slipped π-stacks [54, 55] though no hysteresis has been revealed in this case, which shows fine structure – property relationship in 1,3,2-dithiazolyl radicals.

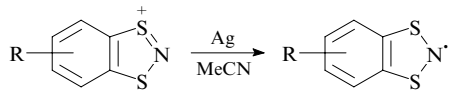
1,3,2-Dithiazolyl radicals are mainly obtained by the reduction of the corresponding 1,3,2-dithiazolyl salts. For the monocyclic derivatives **39**, either sodium dithionite in sulfur dioxide [51] or triphenylantimony in dichloromethane [66] are usually employed.



39

R = CO_2Me, CF_3, CN; X = AsF_6, SbF_6.

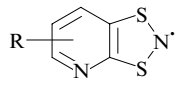
Elemental silver in acetonitrile is used for the synthesis of benzoannuled radicals **40** from 1,3,2-dithiazolyl salts **48**.



48 Cl^- **40**

R	Ref.	R	Ref.
H	67	5-CN	57
5-Me	67	4,5,6,7-F_4	68
4-CN	58	5,6-$(OMe)_2$	59

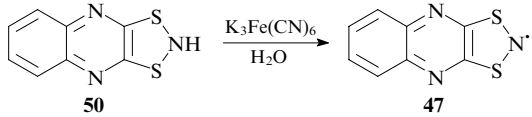
Various reducing agents may be used for the synthesis of 1,3,2-dithiazolyl radicals fused to heterocycles. They are triphenylantimony for the production of the biradical **44** [60] and radicals **42**,[55] **45**,[53] sodium dithionite (for the synthesis of **44**),[63] silver in acetonitrile (for the preparation of pyridodithiazolyls **49a – d**).[56] Recently it has been demonstrated that polymethylferrocenes are suitable reducing agents since their reducing power depends on the number of the methyl groups. In particular, dimethylferrocene has been proposed to prepare radical **49a**.[69]



49a – d

R = H (**a**), 2-CN (**b**), 3-CN (**c**), 2-Me (**d**).

Yet another known, but non-popular method for an access to 1,3,2-dithiazolyl radicals is the oxidation of unsubstituted 1,3,2-dithiazoloquinoxaline (**50**) with potassium ferricyanide in water.[55]

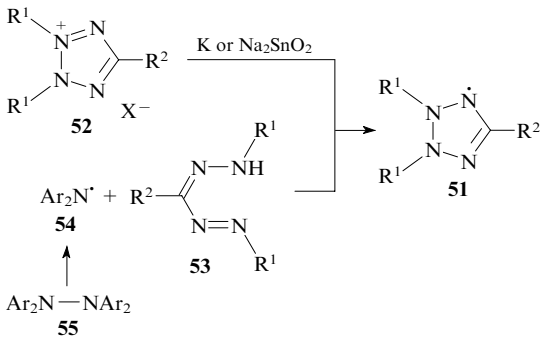


50 **47**

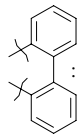
d. 1,2,3,4-Tetrazolyl radicals

Though the synthesis of a series of tetrazolyl radicals **51** is described in literature, these compounds have not attracted chemist's attention for more than 30 years. There are no examples of tetrazolyl radicals studied by X-ray diffraction analysis. It is known that these radicals exist as monomers both in the solid state and in solutions at low temperatures (below 90 K).[70] It has been found that the stability of such radicals increases with the increase in the strength and the number of electron-withdrawing substituents.[70, 71]

Tetrazolyl radicals are obtained by the reduction of the corresponding tetrazolium salts **52** by metallic potassium in dimethoxyethane [72] or by sodium stannite in a mixture water – benzene.[73]



52 **54** **53** **55** **51**

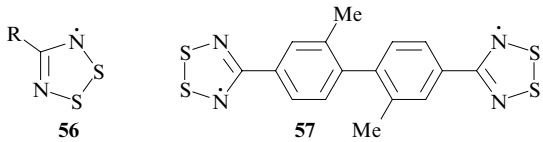
51, **52**: $R^1 - R^1$ =  : R^2 = H, Me, Ph;

51, **53**: R^1 = 4-$O_2NC_6H_4$, 4-NCC_6H_4, 4-MeC_6H_4, 4-$MeCO_2C_6H_4$, *etc.*; R^2 = Bu^t;
Ar = 4-MeC_6H_4.

Yet another method includes the hydrogen abstraction from formazans **53** followed by the cyclization into a tetrazole ring under the action of bis(4-tolyl)aminyl radical (**54**), which forms *in situ* from tetrakis(4-tolyl)hydrazine (**55**) if heated to 60 °C.[70]

e. 1,2,3,5-Dithiazolyl radicals

1,2,3,5-Dithiazolyl radicals **56** comprise one of the most important and widely studied classes of heterocyclic thiazolyl radicals. As a rule, they are stable in the solutions in the absence of oxygen and in the solid state. They also show high thermal stability.



56 **57**

1,2,3,5-Dithiazolyl radicals exist as monomers only in solutions and even then the monomer – dimer equilibrium may often be found. They form dimers in the solid state. The X-ray diffraction analysis of dithiazolyl radicals **56** has revealed that depending on the steric characteristics of the substituent R they may form different types of π-dimers.

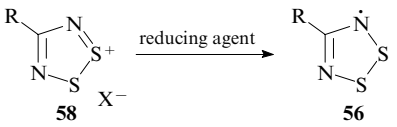
4-Phenyl-1,2,3,5-dithiazolyl **56** (R = Ph) forms a cofacial π-dimer with two S···S contacts.[74] A series of other derivatives with aromatic substituents also have similar structures.[75 – 82] The shortest intermolecular contacts

(3.0–3.1 Å) in the dimers are formed by the sulfur atoms as in many other thiazolyl radicals. 1,2,3,5-Dithiazolyls with nonplanar substituents (R = Me, CF_3, NMe_2) crystallize as somewhat different cofacial π-dimers.[83–86] Due to the steric hindrance, the heterocycles are rotated relative to each other, with only one S···S contact remaining (such dimers are called twisted).

On the other hand, 1,2,3,5-dithiazolyl **56** with the CN group in the phenyl ring (R = 3-NCC_6H_4)[75] forms antarafacial centrosymmetric π-dimers with the S···S distance 3.075 Å. Similarly, the dimers of dithiazolyl **56** (R = 3-F-4-$CF_3C_6H_3$)[82] (the S···S distances are 2.096–3.076 Å) and the biradical **57**[87] are formed.

Some of the fluoroaryl derivatives of 1,2,3,5-dithiazolyls do not form dimeric structures at all.[88–91] Other 1,2,3,5-dithiazolyls crystallize as a mixture of monomers and π-dimers with different orientation of the heterocyclic rings.[92]

The main if not the only method for the synthesis of these radicals is the reduction of the corresponding 1,2,3,5-dithiazolium salts **58** (chlorides are commonly used). Triphenylantimony in acetonitrile is widely used,[80, 89, 90, 93, 94] the yields of the radicals reaching 73%.



58 **56**

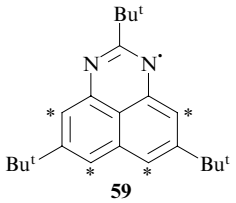
Other reducing agents are used occasionally. These may be zinc and copper in tetrahydrofuran[88] or in liquid sulfur dioxide,[82, 92] silver in the same solvent.[91] Currently, polyalkylferrocenes are preferred.[95]

2. Radicals based on six-membered heterocycles

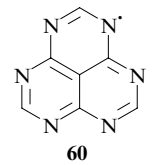
a. Diazaphenalenyl radicals

One of the possibilities of modification of phenalenyl radical (**1**) (see Section II.1) in order to increase its stability is the introduction of heteroatoms into the six-membered aromatic ring so that the spin density is concentrated on the heteroatom. So far, this approach in combination with the introduction of bulky substituents has been realized by Nakasuji and co-workers[96] by an example of 2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl (**59**). It turned out that the introduction of two nitrogen atoms and three *tert*-butyl groups in the structure of phenalenyl radical (**1**) leads to a sufficient increase in its stability. According to the X-ray diffraction analysis, in the crystalline state diazaphenalenyl **59** forms π-dimers in which the heterocycles are almost parallel to each other and are rotated by about 60°. The dimers are packed into columns which is essential for the electroconductivity of organic solids. According to data from EPR spectroscopy and quantum chemical calculations, the spin density on the two nitrogen atoms significantly decreases. As for the four remaining carbon α-atoms (marked with asterisks) the spin density increases in comparison with its distribution in phenalenyl radical. This makes these four positions more reactive which is balanced by the introduction of bulky *tert*-butyl groups in the positions 5 and 8.

It should be mentioned that a potentially more stable hexa-analogue of phenalenyl radical (**60**) in which the spin density is distributed between the nitrogen atoms could not be obtained from the corresponding anion.



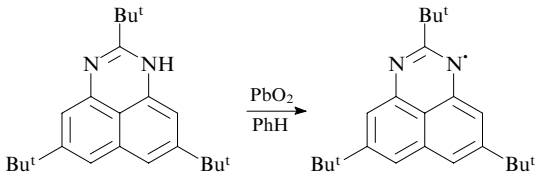
59



60

The study of the electrochemical behaviour of the latter has revealed that it has a higher reduction potential then other azaphenalenyl anions. This indicates an abnormally high stability of this anion.[97]

Diazaphenalenyl radical **59** is obtained by the oxidation of 2,5,8-tri-*tert*-butyl-1,3-diazaphenalene (**61**) by lead dioxide in benzene.[96]



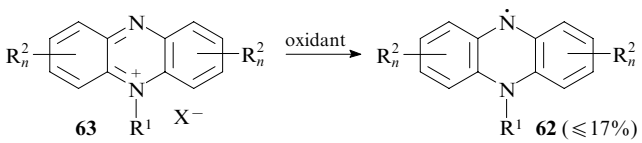
61 **59** (42%)

b. Phenazinyl radicals

Along with phenoxazinyl and phenothiazinyl radicals, phenazinyl radicals **62** pertain to the family of aminyl radicals [$R_2N^{\bullet}$]. If the aminyl radical is incorporated into a heterocycle surrounded by the aromatic rings, the stability of the radical sufficiently increases.

A series of stable phenazinyl radicals is known.[98–102] The substituent at the nitrogen atom of the piperazine ring may be represented by an alkyl, aryl or benzyl group, but not a hydrogen atom. The aromatic rings may be unsubstituted or may contain alkyl substituents, the most stable compounds containing two bulky *tert*-butyl groups. Phenazinyls **62** exist as monomers in solution at room temperature, In the solid state, they may crystallize as the chains of monomers,[98] mixtures of the monomers and π-dimers differently located in the unit cell,[101] and as a mixture of different π-dimers.[100, 102] π-Dimers are characterized by short intermolecular (intradimer) contacts (< 3.3 Å). The absorption spectra contain low-energy maxima missing in the monomeric molecules. All this suggests a strong electronic interaction in π-dimer structures. But in the case of phenazinyl radical **62** (R^1 = 4-$O_2NC_6H_4$, R^2 = 3-Bu^t), the π–π interactions between the nearest neighbours are lacking due to the strong steric hindrance in the crystal.[102]

The main starting compounds for the synthesis of phenazinyl radicals **62** are phenazinylium salts **63**. Apparently, the character of the anions of these salts is of no importance for their successful oxidation. Hexafluorophosphates and hexafluoroborates are used most often. Ascorbic acid[99, 101] and potassium ferrocyanide[101] are used as reducing agents. In all cases, the yields of the radicals are low.

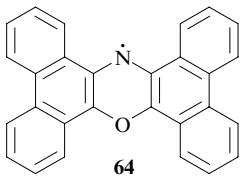


63 **62** (≤17%)

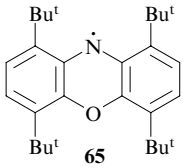
R^1 = Me, Et, Pr^n, Pr^i, Ph, 4-$O_2NC_6H_4$, Bn; R^2 = Me, Bu^t; n = 0–2; X = PF_6, BF_4, *etc.*

c. Phenoxazinyl radicals

There are not so many known radicals of this class isolated in the solid state (less than 10 examples). As a rule, they are sufficiently stable to allow registation of their EPR spectra. However, it was shown that the EPR signal of even the stable polycyclic phenoxazinyl **64** virtually disappears within five months.[103] Data from X-ray diffraction analysis have been obtained for another radical of this type (**65**),[104] but the data on the packing of the molecules in the crystal are lacking.

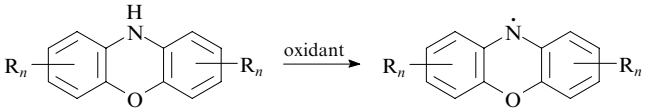


64



65

The phenoxazinyl radicals **66** are synthesized by the oxidation of the corresponding phenoxazines **67** by bromine,[105] or atmospheric oxygen.[104]

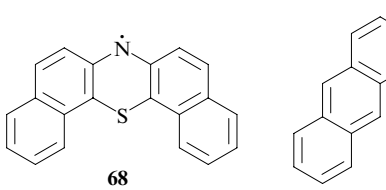


67 **66**

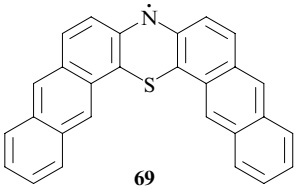
These radicals were also obtained by the electrochemical reduction of the corresponding salt with participation of the Mohr's salt. [106]

d. Phenothiazinyl radicals

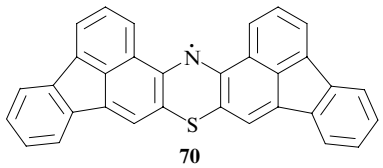
Like the phenoxazinyl radicals discussed in the previous section, not all of the representatives of the phenothiazinyl radicals possess high stability. Polycyclic derivatives **68**–**70** in which the heterocycles are fused to aromatic rings are sufficiently stable. Their melting points exceed 300 °C.[107–109] Perchlorinated phenothiazinyl **71** is stable as well.[110]



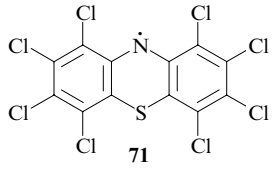
68



69

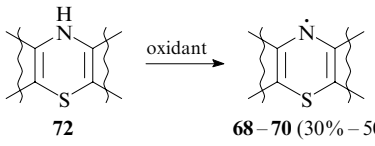


70

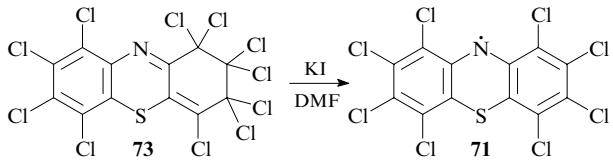


71

Polycyclic phenothiazinyls **68**–**70** are obtained by dehydrogenation of the corresponding fused phenothiazinyls **72** by mercury oxide in boiling toluene (in the case of compound **68**) [107] or lead dioxide in boiling xylene or 1,2,4-trichlorobenzene (for phenothiazinyls **69**, **70**),[108, 109] while the polychlorinated derivative **71** is obtained by the dechlorination of 1,1,2,2,3,3,4,6,7,8,9-undecachloro-2,3-dihydro-1*H*-phenothiazine (**73**) by potassium iodide in dimethylformamide.[111]



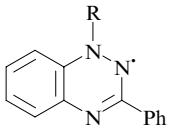
72 **68**–**70** (30%–50%)



73 **71**

e. 1,2,4-Triazinyl radicals

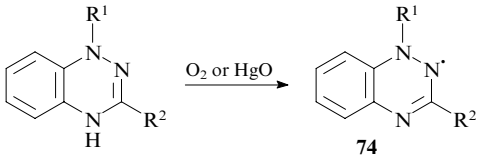
1,4-Dihydro-1,2,4-benzotriazin-4-yl radicals **74a**,**b** were first synthesized in 1968.[112] They have a prominent stability among the nitrogen-centred heterocyclic radicals. For example, it was reported [113] that the sample of compound **74a** obtained in 1973 did not change its properties till 2002.



74a,**b** R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**).

In the crystal, the π–π-interaction of the electron systems of the bicyclic fragments of the molecules results in π-stacking (*i.e.*, the formation of the stacks of molecules).[113–115] Besides π-stacking and the hydrogen bonds C–H···N, the coplanar arrangement of the phenyl substituent in position 3 relative to the plane of the heterocycle involved in the π–π-interactions should be mentioned. It was inferred that the stability of the radicals **74a** is a result of the high degree of the delocalization of the unpaired electron in the amidrazone moiety of the triazine ring and partially in the annuled benzene ring, these characteristics being independent of substituents in the phenyl ring in the position 1.[113] Similar results were obtained for the radical **74b** as well.[116]

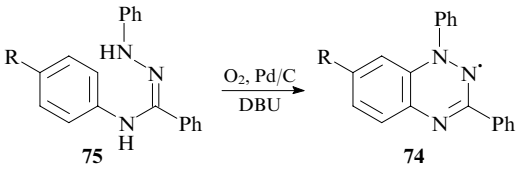
Benzotriazinyl radicals **74** are synthesized by the oxidation of the corresponding benzotriazines by the atmospheric oxygen [112–115] or mercuric oxide.[116]



74

R^1 = Ph, 4-$O_2NC_6H_4$, 4-ClC_6H_4, *etc.*; R^2 = Ph, Bu^t, $O(CH_2CH_2)_2N$, *etc.*

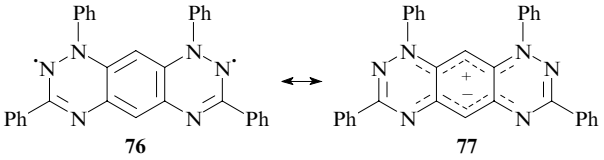
Yet another procedure consists of the catalytic oxidation of amidrazones **75** by the atmospheric oxygen in the presence of palladium-on-carbon and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[117]



75 74

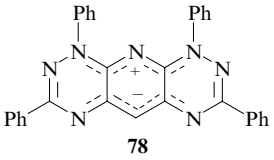
R = H, Me, OMe, CF_3, Cl, Br, I.

Fusion of two triazine rings to a benzene ring could afford the biradical **76**; moreover, a compound with this composition has been obtained.[118] However, no EPR spectrum for this compound has been observed. Data from X-ray diffraction analysis and quantum chemical calculations have revealed that it has a zwitterionic structure **77** with a low-lying triplet state.



76 77

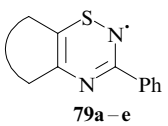
It is of note that this compound possesses solvatochromism, *i.e.*, it changes the absorption spectrum in parallel with the changes in the solvating capacity of the solvent. Remarkably, the introduction of the nitrogen atom into the central ring (compound **78**) does not lead to the formation of the biradical structure, the most stable structure being the zwitterionic one (**78**).[119]



78

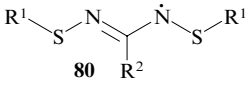
f. 1,2,4-Thiadiazolyl radicals

Cyclic 1,2,4-thiadiazolyl radicals **79** pertain to the family of the resonance-delocalized thioaminyl radicals **80**. A series of non-cyclic radicals **80** is identified as intermediates (see, *e.g.*, Ref. 120), however, on the whole they are not sufficiently stable to be isolated and characterized.



79a–e

= CH=CH–CH=CH (**a**),
CH=CH–CH=N (**b**),
N=CH–CH=N (**c**),
CF=CF–CF=CF (**d**),
CCl=CCl–CCl=CCl (**e**).



80

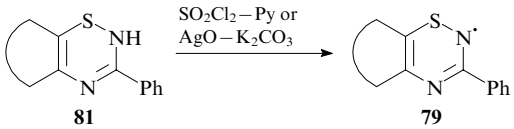
R^1, R^2 = H, Ph.

Cyclic representatives of this class (**79**) are much more stable. Kaszynski *et al.*[121] synthesized a series of fused 1,2,4-thiadiazolyls **79a–e**.

Quantitative EPR spectroscopy showed that the stability of these radicals increases in the series **79c** < **79a** < **79b** < **79e** < **79d**. All the radicals are stable in the toluene solutions at −80 °C, but at a higher temperature they gradually decompose, the main process being their oxidation by the atmospheric oxygen into S-oxides. At room temperature, the half-life of the most stable fluorinated compound **79d** is 4 months.

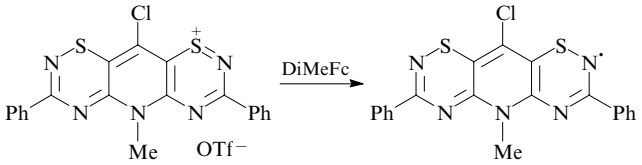
According to the data from X-ray diffraction analysis, the radicals in the crystal form interpenetrating stacks in which the molecules are arranged in an antiparallel mode and are bound into weak dimeric pairs by numerous intermolecular N···S contacts.

The radicals **79** are obtained by the oxidation of the corresponding fused thiadiazines **81** by a mixture sulfuryl chloride–pyridine in toluene or silver oxide–potassium carbonate in a mixture of toluene and acetonitrile, the highest yields (86%–98%) of the product being obtained in the former case with the exception of the radical **79b**, which is better synthesized using silver oxide (yield 38%).[121]



81 79

Reduction of salt **82** by dimethylferrocene (DiMeFc) in acetonitrile allowed Oakley and co-workers[122] to obtain a resonance-stabilized analogue of the compounds **79**, *viz.*, bis(thiadiazinyl) radical **83**.

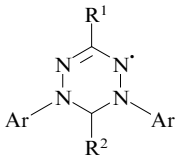


82 83

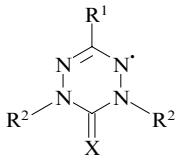
This compound is extremely thermally stable in both the solution and the solid state, it is also stable against atmospheric oxygen and heating. Data from X-ray diffraction analysis show that the radicals **83** are not dimerized. They have a planar structure (considering phenyl rings, too), which provides a high delocalization of the spin density. In the crystal, the radicals **83** form π-stacks. Data from EPR spectroscopy and quantum chemical calculations show that the spin density is mainly localized on the four nitrogen atoms of the thiadiazine rings.

g. Verdazyl radicals

There are two types of verdazyl radicals corresponding to the structures **84** and **85**.



84



85a,b

R^1 = Alk, Ar;
R^2 = H, Alk, Ar.

R^1, R^2 = Alk, Ar;
X = O (**a**), S (**b**).

Since their discovery, over 100 stable verdazyl radicals of **84** and **85** types have been obtained, both classes belonging to the most stable among heterocyclic radicals. Such radicals can be isolated in the solid state and stored for a long time without decomposition even in the presence of atmospheric oxygen and moisture. The basis of their stabil-

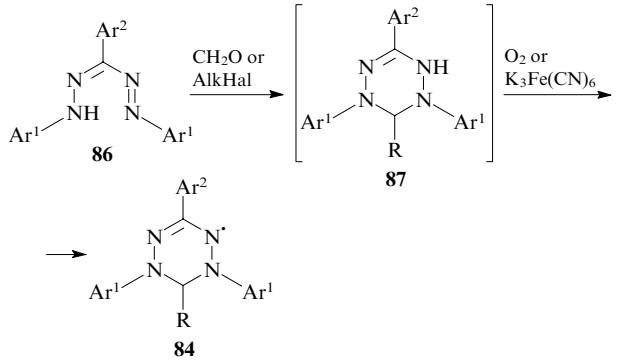
ity is the possibility of the delocalization of the unpaired electron between two chemically equivalent parts of the molecule. These radicals neither associate nor dimerize. The fact that the structures without bulky substituents are also stable is the significant feature of such radicals.

The presence of the phenyl substituent in position 6 of the radical **84** (R^2 = Ph) prevents the stacking of the molecules in the crystal. As a result, ladder-type chain structures with a shift are formed.[123] In case of the verdazyl radicals **84** without bulky substituents in position 6 (*e.g.*, R^2 = H) the molecules are packed in columns.[124]

Examples with both the aryl and alkyl substituents at the heterocyclic nitrogen atoms are known for oxoverdazyls **85a**, the stability of the radicals depending significantly on the character of the substituents.Thus for the radicals **85a** (R^2 = Me), the stability varies over a wide range from the unlimited to the moderate one (several hours) depending on the substituent R^1. It has recently been shown that upon the substitution of the isopropyl group for the methyl group (R^2 = Pr^i) the stability of the radicals **85a** increases greatly.[125]

In the crystalline state, the molecules of oxoverdazyls **85a** form linear π-stacks in which the verdazyl ring of one molecule partly superimposes on the aromatic (heterocyclic) ring of the substituent in position 6 of the neighbouring molecule in the stack. A series of intermolecular contacts (3.6–3.9 Å) slightly exceeding the van der Waals contacts for the stacked rings (3.35 Å) are observed but substantial interactions between stacks are lacking.[126] Quite recently, it has been shown that 1,5-dimethyl-6-oxoverdazyl radicals **85a** (R^1 = H, Me; R^2 = Me) in the solid state form π-dimeric particles with close contacts between the radicals (3.10 Å) that are arranged in an antiparallel manner and are characterized by a series of interatomic (C···C and N···N) contacts that are less then the sum of the van der Waals radii for these atoms.[127]

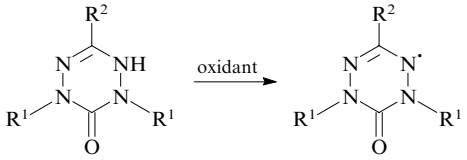
The verdazyl radicals **84** are synthesized by reactions of formazans **86** with formaldehyde or alkyl(benzyl) halides in the presence of a base to give tetrahydrotetrazynes **87**, which are oxidized by the atmospheric oxygen [123, 128, 129] or by potassium ferricyanide [130] to the target products. Tetrahydrotetrazine is oxidized so easily that it is usually not isolated from the reaction medium.



86 **87** **84**

Ar^1 = Ph, 4-YC_6H_4 (Y = Me, OMe, Cl, CN);
Ar^2 = Ph, 4-ZC_6H_4 (Z = NO_2, Me, OMe); R = H, Alk.

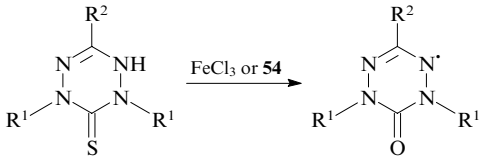
Oxoverdazyls **85a** are obtained by the oxidation of the easily accessible tetrazanes **88** by a wide range of the oxidants: benzoquinone,[125, 128, 131–134] potassium ferricyanide,[134–136] sodium periodate,[134, 137] lead dioxide.[138]



88 **85a**

R^1 = Me, Pr^i; R^2 = Ar, Het.

Sometimes potassium ferricyanide is not suitable for the synthesis of thioverdazyls **85b**.[139] It is better to use such oxidants as bis(4-tolyl)aminyl radical (**54**), which is obtained from tetrakis(4-tolyl)hydrazine (**55**) upon heating, or iron(III) chloride.[130, 139]

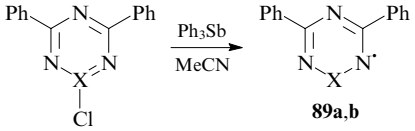


85a

R^1 = Me, Ph; R^2 = H, Ph, Bu^t.

e. Thiatriazinyl radicals

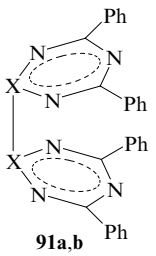
Only one example of a stable 1,2,4,6-thiatriazinyl radical is described in literature. It is the 3,5-diphenyl derivative **89a**, which is obtained by the reduction of the 1-chloro-3,5-diphenyl-1,2,4,6-thiatriazine (**90a**) by triphenylantimony in acetonitrile.[140]



90a,b **89a,b**

X = S (**a**), Se (**b**).

The radical **89a** forms π-dimers **91a**. The intermolecular S···S distance (2.66 Å) in these radicals is significantly shorter than the S···S distance in other thiazinyl radicals. This is reflected partially in the spin density distribution in the radical **89a**. The main part of the spin density is located on the sulfur atoms. Thus, the dimeric structure **91a** may be presented as an intermediate between the π-dimer and S–S-dimer bound by the σ-bond.

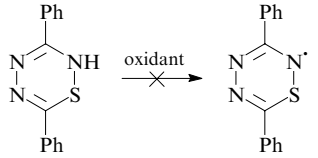


91a,b X = S (**a**), Se (**b**).

Compound **89b** is a selenium analogue of the radical **89a**. It is synthesized similarly to the sulfur-containing derivative.[141] It crystallizes as a dimer **91b** with the Se–Se bond. The Se···Se distance (2.792 Å) is shorter than in similar dimers (3.12–3.18 Å) and longer than the typical Se–Se bond (2.335 Å). Thus, the substitution of the selenium atom for the sulfur atom in 1,2,4,6-thiatriazinyl **89a**

does not significantly change the packing of the molecules in the crystal.

1,2,4,5-Thia(seleno)triazinyl radicals are not described in literature. According to the quantum chemical calculations, this type of a radical should be one of the most stable thiazinyl radicals,[142] however, all attempts to synthesize the diphenyl derivative **92** by the oxidation of 3,6-diphenyl-1,2,4,5-thiatriazine (**93**) by lead dioxide, thiantrenium perchlorate or iodine have failed.

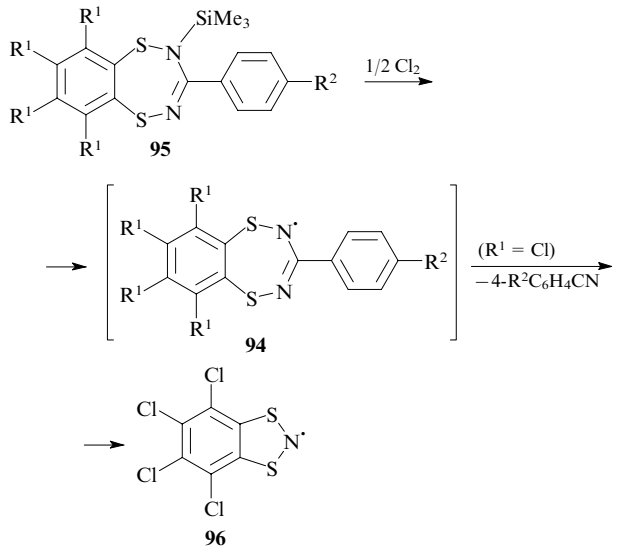


93 **92**

3. Radicals based on seven-membered heterocycles

a. Dithiadiazepinyl radicals

Though the DFT calculations have shown that seven-membered thiazepinyl radicals should possess low energies of disproportionation and dimerization, these radicals are poorly studied. No stable representatives have been described yet. The attempts to prepare a series of the dithiadiazepinyl radicals **94** by the oxidation of the trimethylsilyl derivatives of benzodithiadiazepines **95** by chlorine have been undertaken.[143] However, these radicals turned out to be thermally unstable. Thus, for $R^1 = Cl$, the abstraction of the molecule of an aromatic nitrile with the formation of the 1,3,2-thiadiazolyl radical **96** occurred during the reaction.



R^1 = H, Cl; R^2 = H, Me.

IV. Conclusion

The stability of heterocyclic radicals, as for all kinds of radicals, is a crucial problem. Taking into consideration structural and electronic characteristics of compounds discussed in the present review, it is possible to mark two factors that increase the stability of the heterocyclic radicals.

The introduction of bulky substituents that hinder the interactions of the radicals with other molecules (including oxygen) is probably the most obvious method to increase the kinetic stability of the radical species. To date, it remains one of the most popular approaches. However, it is not often used in the case of the heterocyclic radicals.

Delocalization of the spin density is another stabilizing factor. It is an effective way to decrease both the total energy of the molecule and its reactivity since the distribution of the spin density of the unpaired electron between more atoms decreases its value on each atom. The latter correlates with the decrease in the reactivity. That is why the stability of the heterocyclic radicals discussed in the present review is significantly higher then that of the acyclic molecules. However, one should not oversimplify this situation assuming that the higher the delocalization the better. Different reactivities of different atoms should be taken into consideration.

The chemistry of the stable heterocyclic radicals has been rapidly developing for the last 20 – 30 years. Though the discovery of virtually every new type of the stable heterocyclic radicals have been accidental, it often led to the fundamental researches of the application of these radicals in technology. At present, the ultimate goal of the choice of the structures to be synthesized is the study of such properties as electric conductivity (including superconductivity) and (or) magnetism. It is thought that a more reasonable point of view on stable heterocyclic radicals will be formed in future and these structures will be considered as practically important rather than exotic ones. The diversity of the obtained heterocyclic radicals makes a strong impression. The author supposes that almost every synthetic chemist working in the field of heterocyclic compounds may find a niche in the chemistry of radicals as well.

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