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Verdazyls: synthesis, properties, application

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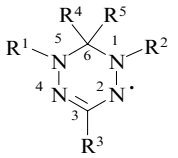
Abstract. Synthesis, structure, properties and reactivity of stable heterocyclic radicals, verdazyls, are considered. Special attention is focused on metal verdazyl complexes. Major areas of application of such radicals are discussed. The bibliography includes 164 references.

I. Introduction

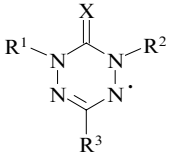
Stable radicals play an important role not only in the development of theoretical concepts of organic chemistry, but also in the solution of some practical problems. Among the most intensively studied stable organic radicals are triphenylmethyl, nitroxide and various heterocyclic radicals. Verdazyls belong to heterocyclic radicals and can be divided into three types depending on the nature of the group in the 6-position: verdazyls of the first type (structure **I**) are radicals with a saturated carbon atom (Kuhn verdazyls), and verdazyls of the second type (structure **II**) are compounds containing carbonyl or thiocarbonyl function. So-called phospha- and borataverdazyl radicals (structure **III**) containing a phosphorus or boron atom in the 6(3)-position should be placed in a separate category.

The high chemical stability and synthetic potential and the ability to form metal complexes render verdazyls one of the most attractive classes of stable radicals. They are used in various fields of chemistry, physics, and biology as stabilizers, spin labels and 'building blocks' for design of single-molecule magnets.

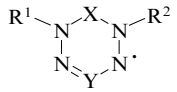
Structures **I** – **III**



I



II (X = O, S)



III [X = P(O)R^4, B(OAc)$_2$; Y = CR^3, PR$^3_2$]

Since their discovery in 1964,[1] numerous publications have appeared dealing with the synthesis, properties and application of new verdazyl representatives. In recent years, several reviews have been published, but they are either limited to a summary of verdazyls along with other classes of radicals,[2,3] or are a chapter in a book,[4] or are devoted to special issues. For example, only magnetic properties of such radicals have been discussed in two reviews,[5,6] and Lemaire[7] has focused on the coordination chemistry of verdazyls. As for the Russian literature, it is represented by only one book by O M Polumbrik published in 1984.[8] At the same time, there is a significant number of original works in Russian, which are unavailable to foreign researchers and, therefore, poorly cited.

In the present review, we have tried to summarize the available data on verdazyl chemistry, with the intention of discussing — more fully than in previous publications — the results obtained by researchers in Russia and former Soviet Union countries.

II. Synthesis and structure of verdazyls

1. Synthesis and structure of verdazyls with a saturated carbon atom in the 6-position

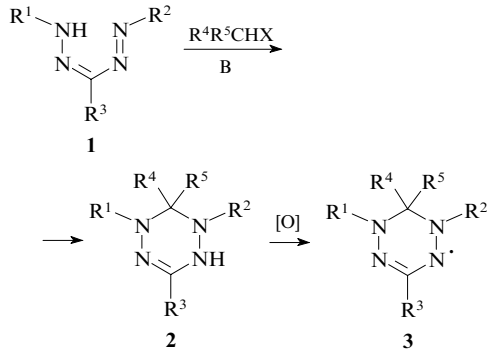
The basic strategy for the synthesis of verdazyl radicals of type **I**, developed by Kuhn and Trischmann,[1] is alkylation of formazans **1**. Intermediate alkyl derivatives are easily cyclized to leuco-verdazyls **2**. Under the action of oxidants

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[air oxygen, lead dioxide, ferric chloride, potassium hexacyanoferrate(III) [1, 8]], leuco-verdazyls are converted into corresponding free radicals **3** (Scheme 1).

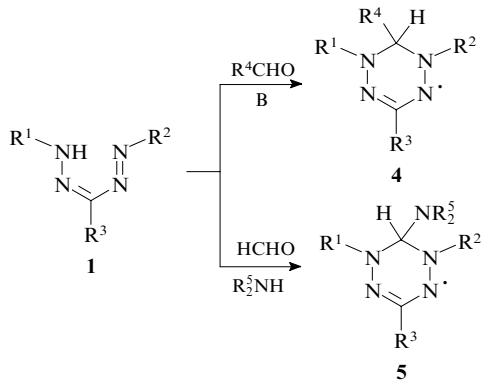
Scheme 1



B is base

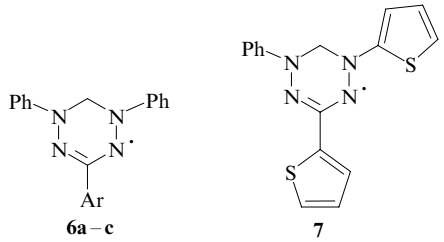
Another convenient method of synthesis of verdazyls (for example, compounds **4** and **5**) is by the reaction of formazans with aliphatic aldehydes, in particular, with formaldehyde, in a basic medium.[8, 9] This reaction also occurs through the formation of leuco-verdazyls (Scheme 2).

Scheme 2



It is worth noting that the methods of synthesis of Kuhn verdazyls from formazans have become widespread because of the availability and diversity of initial compounds, as well as because of rather high yields of radicals. In addition, this approach enables the synthesis of bis- and tris(verdazyl) radicals and is the basis for synthesis of verdazyl-containing polymers. Works on the synthesis of new verdazyl radicals and verdazyl-containing polymers were carried out most actively in the 1980–1990s. Most of these works were included in the monograph of Polumbrik.[8] Among the verdazyls of this type synthesized later, compounds **6a–c** and **7**, containing bulky aromatic and heterocyclic fragments are worthy of notice.[10–12]

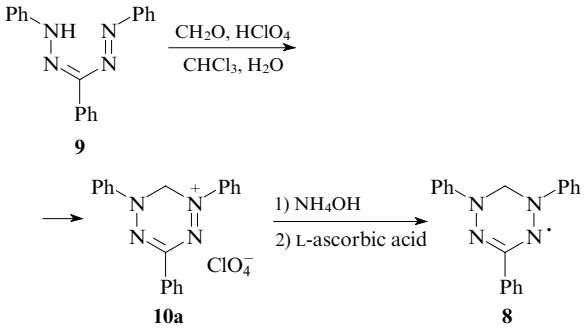
Structures **6**, **7**



Ar is anthracen-9-yl (**a**), 4-pyridyl (**b**), 3-pyridyl (**c**)

Active study of physicochemical (magnetic, luminescent) properties of stable radicals, as well as the improvement of the methods of structural analysis of organic compounds, has shaped the development of the chemistry of verdazyls, including the extension of the range of these radicals. For example, Katritzky and Belyakov [13] have suggested a one-pot method of preparation of triphenylverdazyl **8** from triphenylformazan **9,** without isolation of triarylverdazylium salt **10a** formed at the first stage Scheme 3).

Scheme 3



These researchers have also contributed to the development of the procedure for the preparation of 1,3,5-triphenylverdazyls with heterocyclic substituents in the 6-position.[9] The method uses the $Ba(OH)_2 \cdot H_2O$–dicyclohexano-18-crown-6 (DC18C6) catalytic system for alkylation of triphenylformazan **9** or 1-(aminomethyl)benzotriazoles **11** as a source of alkylamino group. In both cases, the reaction occurs through intermediates **12–15** and yields radicals **16** (Scheme 4).

To study redox processes in biological systems, a water-soluble sodium salt of 1,3,5-tris(*p*-sulfophenyl)verdazyl (**17**) has been synthesized.[14] The reaction of 1,3,5-triphenylverdazyl (**8**) with chlorosulfonic acid is accompanied by disproportionation of the radical to form salt **10b** and leuco-verdazyl **18**, which are then neutralized to give compound **17** (Scheme 5).

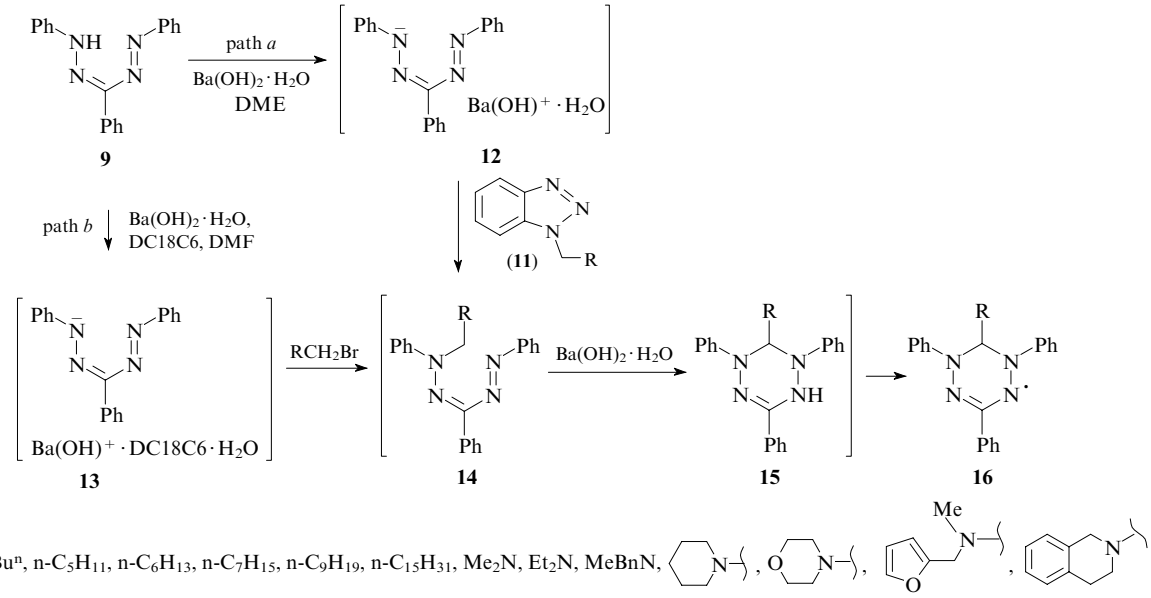
The effect of negative spin density induced at the 3-nitro or 3-nitrophenyl group and of the steric factor of the substituent in the 6-position on the magnetic properties of verdazyls in crystals has been studied for radicals **20a–c** synthesized from formazans **19a**,**b** (Scheme 6).[15, 16] The alkylation of the initial compounds is carried out in the presence of potassium *tert*-butoxide or barium oxide as a base.

According to X-ray crystallography data for verdazyl **20a** (Fig. 1), the methyl group in the 6-position is almost perpendicular to the plane passing through the nitrogen atoms of the verdazyl moiety, and the *N*-phenyl groups are distorted in a mutual antipropeller fashion. The magnetic properties of this compound have been studied. The plot of inverse magnetic susceptibility *versus* temperature enables the suggestion of the existence of intermolecular antiferromagnetic interactions at temperatures below 100 K.

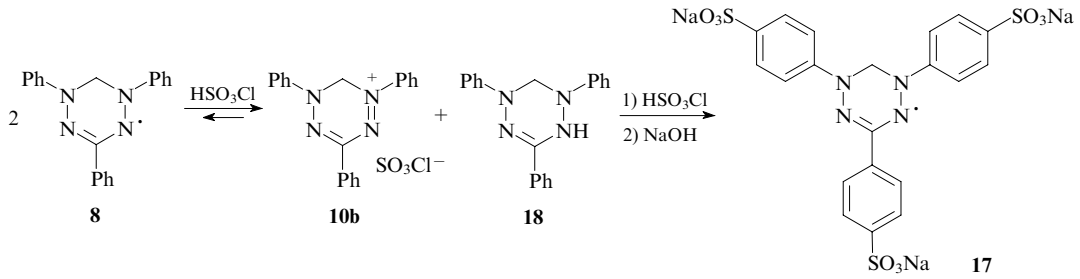
For a series of verdazyl radicals **21** with different substituents in the 6-position, it has been revealed that even a small modification of the molecule leads to a change in the crystal packing and has a significant effect on the magnetic properties.[17, 18]

The nature of the substituent at the C(6) atom has a noticeable effect on the spin–spin coupling constants

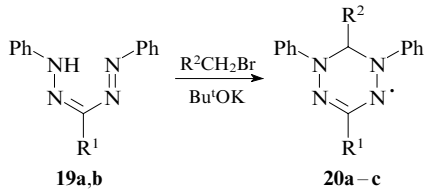
Scheme 4



Scheme 5



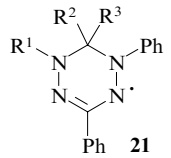
Scheme 6



19: R^1 = NO_2 (**a**), 4-$NO_2C_6H_4$ (**b**);
20: R^2 = Me: R^1 = NO_2 (**a**), 4-$NO_2C_6H_4$ (**b**);
R^2 = Ph: R^1 = 4-$NO_2C_6H_4$ (**c**)

(SSCC) of protons in the *ortho* and *para* positions of *N*-phenyl moieties. The structure of 1-(4-isopropylphenyl)-3,5-diphenylverdazyl (**21a**) has been determined by X-ray crystallography (Fig. 2).[18]

Structure **21**



R^1 = Ph, R^2 = H: R^3 = Me, XC_6H_4 (X = H, 4-Br, 4-CF_3, 3-CF_3), 1-Naph, 2-Naph; R^1 = R^2 = R^3 = Ph; R^2 = R^3 = H: R^1 = 4-YC_6H_4 (Y = Br, Pr^i); Naph is naphthyl

Another stable radical is 3-(4-azidophenyl)-1,5,6-triphenylverdazyl (**22**), and its structure has also been confirmed by X-ray crystallography (Fig. 3).[19] Photolysis of a frozen solution of verdazyl **22** leads to 3-(4-nitrophenyl)-1,5,6-triphenylverdazyl (**23**), containing a heterospin system in which the nitrene and radical spins are coupled by exchange interaction (Scheme 7).

Dormann and co-workers[20] synthesized a new tris(verdazyl) radical — 1,3,5-tris(1,3,5-triphenylverdazyl-6-yl)ben-

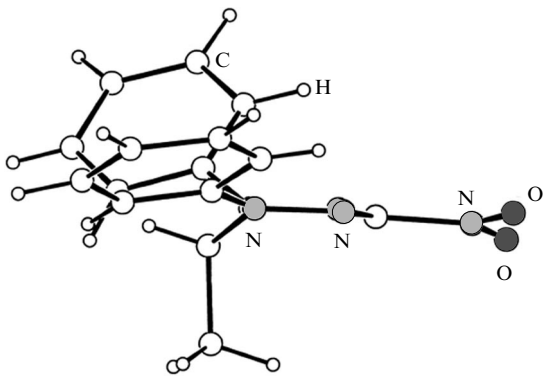


Figure 1. Molecular structure of 6-methyl-3-nitro-1,5-diphenylverdazyl (**20a**).[16]

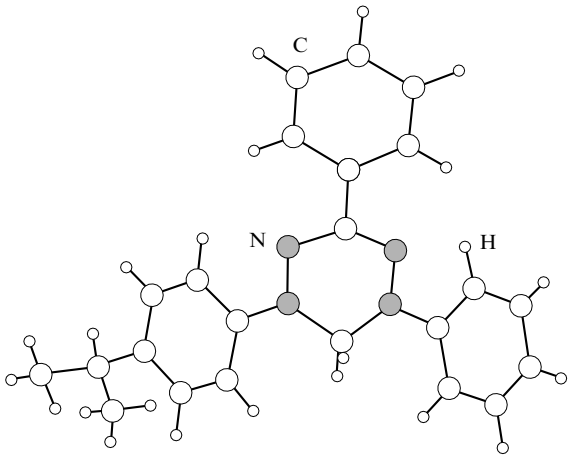


Figure 2. Molecular structure of 1-(4-isopropylphenyl)-3,5-diphenylverdazyl (**21a**).[18]

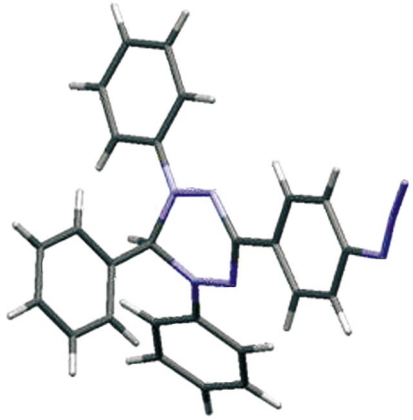
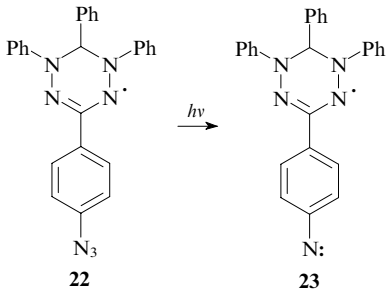


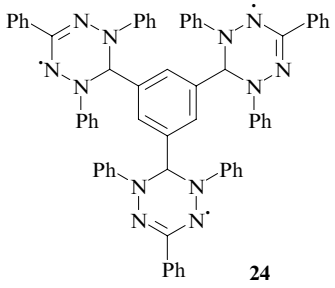
Figure 3. Molecular structure of 3-(4-azidophenyl)-1,5,6-triphenylverdazyl (**22**).[19]

Scheme 7



zene (**24**), which was characterized by ^{1}H NMR and EPR data.

Structure **24**

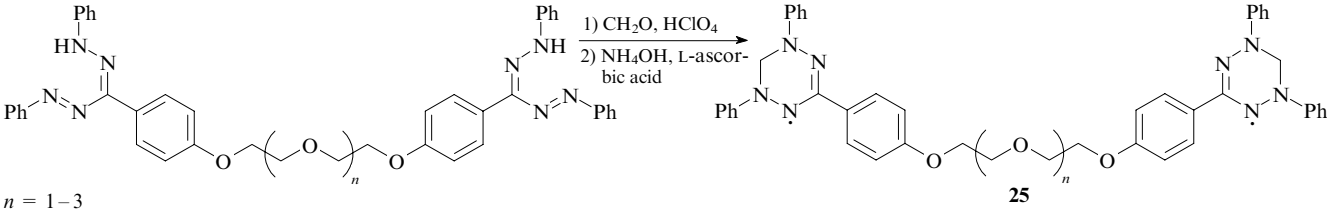


Katritzky *et al.*[21] have described bis(verdazyl) radicals **25** — new open-chain podands with terminal chromogenic moieties (Scheme 8).

Roughly at the same time, Egyptian researchers[22] synthesized, from compounds **26**, bis(verdazyl) radicals **27**, in which the verdazyl moieties are linked with the bridge through nitrogen atoms (Scheme 9).

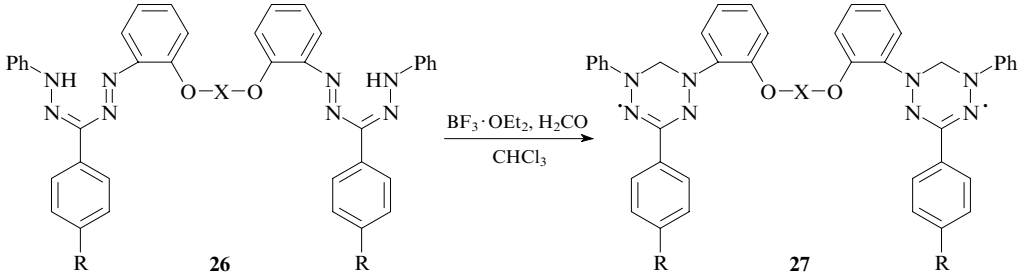
Synthesis and study of organic polyradicals attract the attention of researchers owing to their unique ferro- and superferromagnetic properties.[12,23,24] One of the examples of preparation of such materials is the synthesis of polyverdazyl **28**.[23] First, compound **29** is converted into radical **30**, then an isocyanide group is formed, and resulting 3-(4-isocyanophenyl)-1,5-diphenylverdazyl (**31**) is polymerized

Scheme 8



n = 1–3

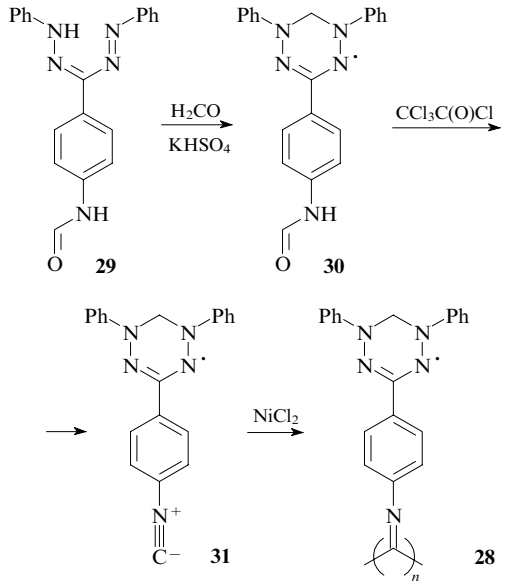
Scheme 9



X = $(CH_2)_3$: R = H, OMe, CN; X = $(CH_2CH_2)_2O$, R = CN

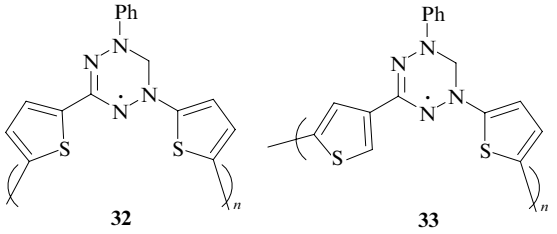
in the presence of nickel chloride as a catalyst (Scheme 10). Magnetic susceptibility measurements indicate that polymer **28** contains a limited concentration of radical centres (0.45 spin per repeating unit), which produces an ideal paramagnetic behaviour.

Scheme 10



Electropolymerization of 1,3-di(2-thienyl)-5-phenylverdazyl and 1-(2-thienyl)-3-(3-thienyl)-5-phenylverdazyl produces respective polyverdazyls **32** and **33** — solid polymeric materials.[12, 24] Analogous verdazyl derivatives of polypyrrole have been synthesized earlier.[25]

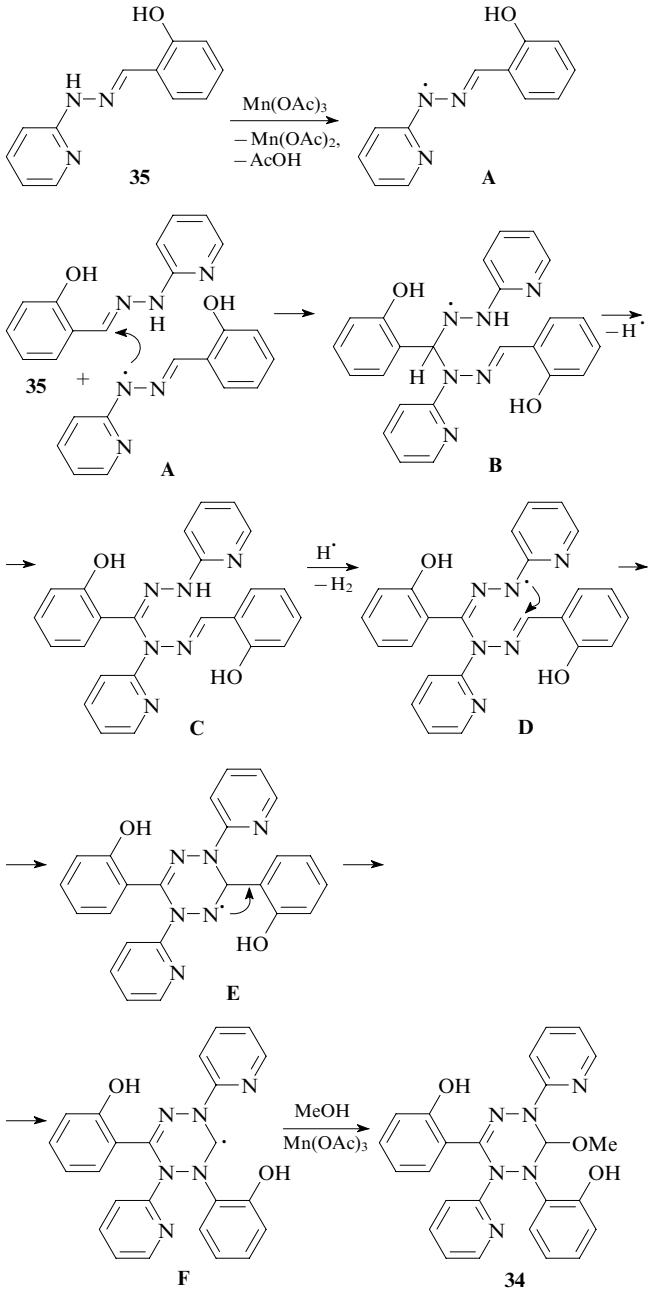
Structures **32**, **33**



An unusual method of synthesis of leuco-verdazyl **34** from 6-[(2-pyridyl)hydrazonomethyl]phenol (**35**), rather than from formazan, has been described.[26] The proposed mechanism of the reaction is shown in Scheme 11.

N-Radical **A** formed under the action of Mn^{III} reacts with the second molecule of **35** at the C=N group to form radical **B**, which then loses a hydrogen atom to produce dimer **C**. After the formation of N-radical **D** and its conversion into cyclic radical **E**, the latter undergoes radical 1,2-migration of the phenol moiety to generate carbon-centred intermediate **F**. Under the reaction conditions, this intermediate is converted into neutral compound **34**. The proposed scheme is supported by EPR data, which indicate the formation of Mn^{II} from Mn^{III} in the reaction mixture and the presence of organic radical species in the course of synthesis of leuco derivative **34**. The structure of 1,3-bis(2-hydroxyphenyl)-6-methoxy-2,5-di(2-pyridyl)leuco-verdazyl (**34**) has been confirmed by X-ray crystallography (Fig. 4).

Scheme 11



Many of verdazyl radicals synthesized in the 1970 – 1980s exhibit useful properties (for example, magnetic), which stimulates further studies of their structures. In particular, 3-[*p*-(methacryloyloxymethyl)]-1,5-diphenylverdazyl (**36**), synthesized for the first time in 1972, has later been studied by X-ray crystallography to reveal specific features of crystal structure and their correlation with magnetic properties (Fig. 5).[27]

The bond lengths and angles in the molecule of **36** are very close to those in other verdazyls described earlier.[8] However, intricate intermolecular interactions in the crystal structure of this radical are different from those in the known verdazyls.

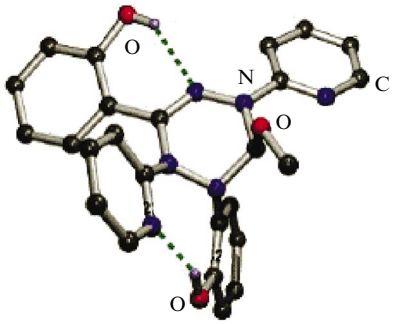


Figure 4. Molecular structure of 1,3-bis(2-hydroxyphenyl)-6-methoxy-2,5-di(2-pyridyl)leuco-verdazyl (**34**).[26] The hydrogen atoms of the benzene ring are omitted for clarity.

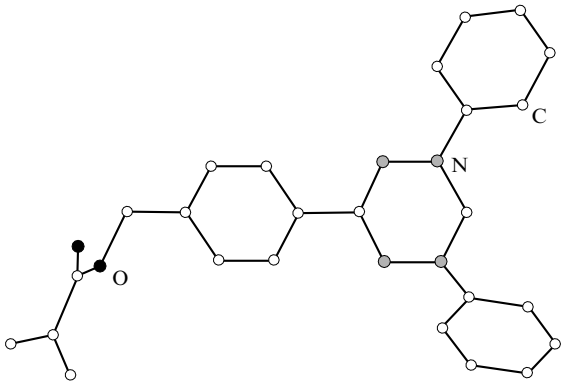


Figure 5. Molecular structure of 3-[*p*-(methacryloyloxymethyl)-phenyl]-1,5-diphenylverdazyl (**36**).[27] The hydrogen atoms are omitted for clarity.

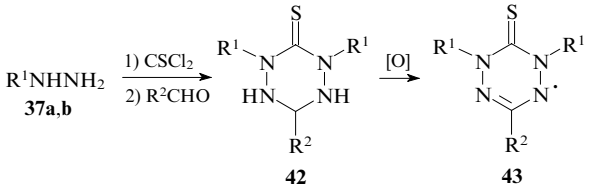
2. Synthesis and structure of oxo- and thioxoverdazyls

Methods of synthesis of type **II** verdazyls (6-oxoverdazyls) have been developed by Neugebauer *et al.*[28] Alkylhydrazines **37a**,**b**, with the use of benzylidene protecting groups (compounds **38a**,**b**), are converted into 2,4-disubstituted bis(carbohydrazides) **39a**,**b**. The latter are condensed with different aldehydes to produce 1,2,4,5-tetrazin-6-ones **40**, which can be oxidized to 6-oxoverdazyls **41**. Silver(I) oxide, potassium hexacyanoferrate, lead(IV) oxide, periodate and benzoquinone are most frequently used as oxidants (Scheme 12).

Later, it has been shown that bis(hydrazides) **39a**,**b** can be synthesized directly from monoakylhydrazines by the reaction with either phosgene at low temperatures or triphosgene.[29]

The use of triphosgene rather than phosgene as a reagent affords 1,2,4,5-tetrazine-6-thiones **42**, which are oxidized to the corresponding 6-thioxoverdazyls **43** (Scheme 13).[28]

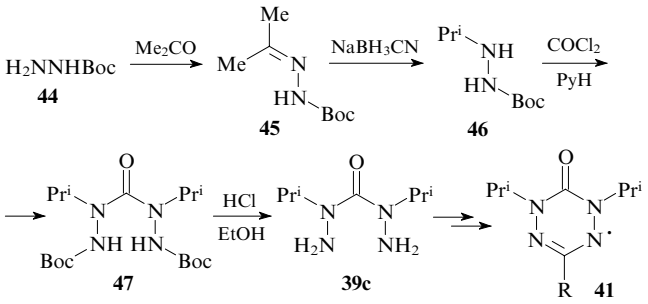
Scheme 13



R^1 = Me (**a**), Bn (**b**); R^2 = H, Me, Ph

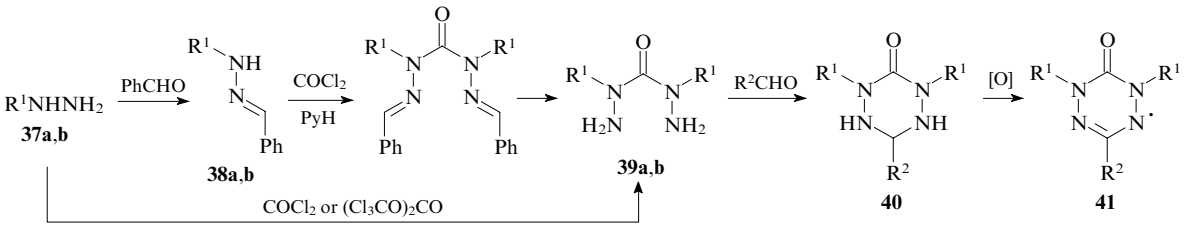
A major limitation of the above methods of synthesis of 6-oxo- and 6-thioxoverdazyls is a relatively narrow range of available bis(verdazyl) redicals **39**; until recently, it included only derivatives with methyl and benzyl groups. Brook and coworkers[30, 31] have developed a method of synthesis of 2,4-bis(isopropylhydrazide) **39c**, based on the use of *tert*-butyloxycarbonyl (Boc) protective groups. The initial compound is hydrazide **44**, which is converted, through the stages of formation of compounds **45** – **47**, into compound **39c** and then into *N,N*-di(isopropyl)-6-oxoverdazyls **41** (R^1 = Pr^i) with a wide range substituents in the 3-position. Such derivatives are stable in air at room temperature (Scheme 14).

Scheme 14



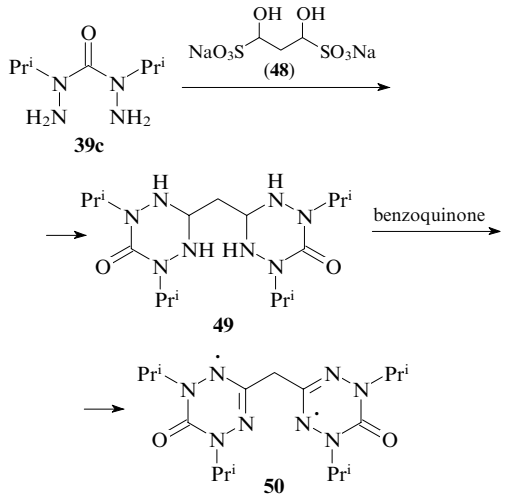
The use of the disulfite derivative of malondialdehyde **48** affords bis(1,5-diisopropyl-6-oxotetrazan-3-yl)methane (**49**), which is treated with benzoquinone to give the corresponding bis(verdazyl) **50** (Scheme 15).[32]

Scheme 12



R^1 = Me (**a**), Bn (**b**); R^2 = H, Me, Ph, 2-MeC_6H_4, 2-$MeOC_6H_4$, 4-$H_2NC_6H_4$, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-$O_2NC_6H_4$, CO_2Et, 1-Naph

Scheme 15



X-Ray crystallographic analysis of bis(verdazyl) **50** (Fig. 6) shows that the bond lengths in the verdazyl moieties are close to the bond lengths in other 6-oxoverdazyls. The rings are almost flat and are at an angle of 73° to each other. Each of the C–H bonds of the methylene moiety forms an angle of 13.5° with the plane of one verdazyl ring and is almost perpendicular to the other ring (an angle of 76.3°). The isopropyl moieties are oriented in such a way that the C–H groups are parallel to the C=O bonds.

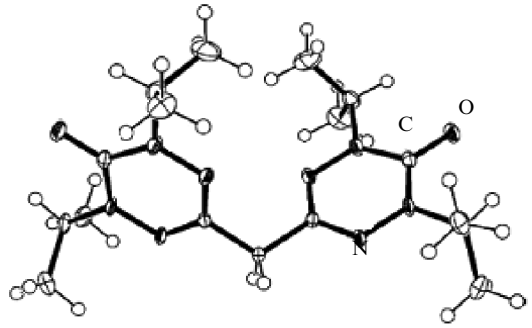


Figure 6. Molecular structure of bis(1,5-diisopropyl-6-oxoverdazyl)methane (**50**).[32]

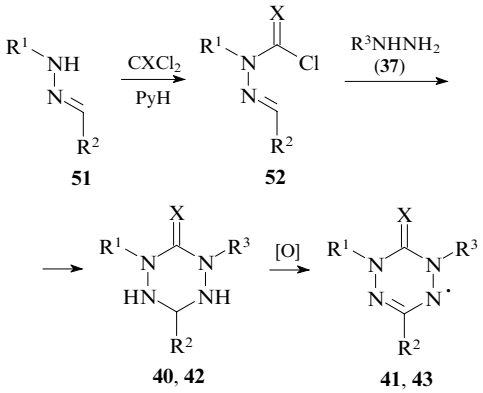
Research teams headed by Neugebauer [33] and Milcent [34] have extended the range of substituents at the nitrogen atoms in verdazyl radicals by step-by-step construction of the tetrazine ring. In particular, the reactions of hydrazone **51** with phosgene and thiophosgene yield *N*-chloroformylhydrazones **52** (X = O, S), and their treatment with monosubstituted hydrazine **37** produces tetrazines **40** and **42**, which are oxidized to the corresponding verdazyls. This method has enabled the synthesis of a large number of 6-oxo- (**41**) and 6-thioxoverdazyls (**43**), since it makes it possible not only to introduce aromatic substituents into the 1- and 5-positions of the tetrazine ring but also to obtain asymmetrically substituted radicals (Table 1, Scheme 16).

Neugebauer *et al.*[28, 33] have synthesized and for the first time studied the structures of 6-oxo- and 6-thioxoverdazyls by EPR, electron nuclear double resonance (ENDOR), ^{2}H NMR and X-ray crystallography (Fig. 7).

Table 1. 6-Oxo- (**41**) and 6-thioxoverdazyls (**43**) synthesized by Schemes 12, 13 and 16.

R^1	R^3	R^2	X	Ref.
Me	Me	Me, C_6D_5, CO_2Et, 1-Naph, 2-MeC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-$H_2NC_6H_4$, 4-NCC_6H_4, 4-$O_2NC_6H_4$, CO_2H	O	28, 35
Bn	Bn	H, Me, Ph	O	28, 35
Me	Me	H, Me, Ph, C_6D_5	S	28, 35
Bn	Bn	H, Me, Ph	S	28, 35
Ph	Ph	Ph, C_6D_5, Bu^t	O	33
C_6D_5	C_6D_5	Ph, C_6D_5	O	33
Me	Ph	Ph	O	33
Me	C_6D_5	C_6D_5	O	33
Ph	Ph	Ph, C_6D_5, Bu^t	S	33
C_6D_5	C_6D_5	Ph, C_6D_5	S	
Me	Ph	Ph	S	33
Me	C_6D_5	C_6D_5	S	33
Ph	Ph	4-$MeOC_6H_4$, 4-$O_2NC_6H_4$, 4-$MeO_2CC_6H_4$, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$	O	34
Ph	4-MeC_6H_4	Ph, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$	O	34
Ph	4-$MeOC_6H_4$	Ph, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$	O	34
Ph	4-$NO_2C_6H_4$	Ph	O	34
Ph	Me	4-$MeO_2CC_6H_4$	O	34

Scheme 16



X = O (**40**, **41**), S (**42**, **43**)

The tetrazine ring of 6-oxo-1,3,5-triphenylverdazyl **41a** ($R^1 = R^2 = R^3 = Ph$) is almost planar with an insignificant (±0.01 Å) deviation of the nitrogen atoms. The *N*-phenyl groups are twisted with respect to each other in a propeller fashion, the benzene ring in the 3-position of the ring is twisted in the same direction, but to a much lower degree. The tetrazine ring of 3-*tert*-butyl-6-thioxo-1,5-diphenylverdazyl **43a** ($R^1 = R^3 = Ph$, $R^2 = Bu^t$) has a flat boat conformation in which the C(3) and C(6) atoms are shifted from the plane passing through the nitrogen atoms in the same direction by 0.053 and 0.100 Å, respectively. Owing to the bulky sulfur atom, the *N*-phenyl groups are considerably twisted out of the plane of the verdazyl ring in an antipropeller fashion. Noteworthy is strong electronic interaction between the lone electron pair at the N(1) atom and the carbonyl (or thiocarbonyl) group, which is responsible for a slight elongation of the C(6)–N(1) bonds [1.381(1) Å in oxoverdazyl and 1.369(2) Å in thioverdazyl] and for an insignificant decrease in the C=O [1.208(2) Å] and C=S

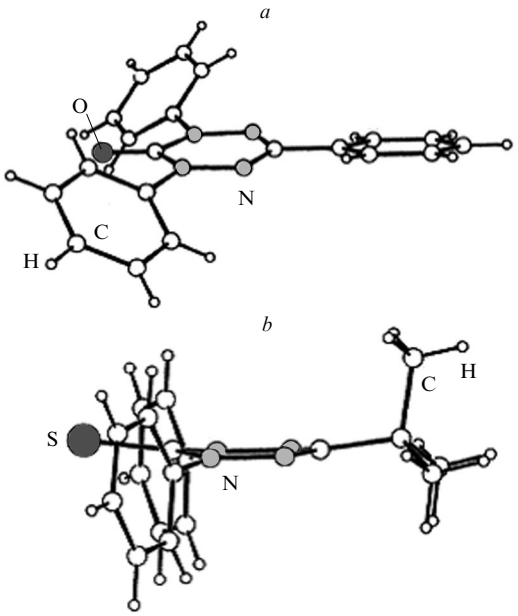


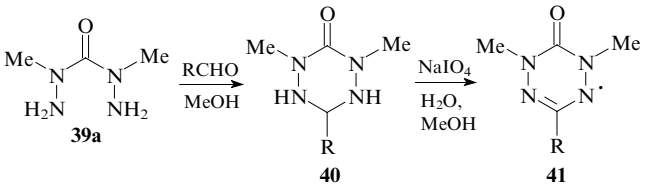
Figure 7. Molecular structures of 6-oxo-1,3,5-triphenylverdazyl (**41a**) (*a*) and 3-*tert*-butyl-6-thioxo-1,5-diphenylverdazyl (**43a**) (*b*).[33]

[1.652(3) Å] bond lengths as compared with the corresponding bonds in nonradical structural analogues: tetrahydro-1,2,4,5-tetrazine-3,6-dione [the C–N and C=O bond lengths are 1.363(12) and 1.224(2) Å] and in the corresponding 3,6-dithione [the C–N and C=S bond lengths are 1.349(5) and 1.667(2) Å].

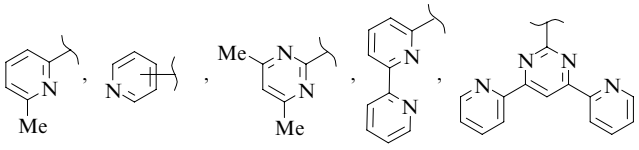
The verdazyl radicals described by Milcent *et al.*[34] (see Table 1), have been characterized mainly by elemental analysis and IR spectroscopy data. It has been noted that many radicals containing alkyl or benzyl group [R^3 = Bn, CH_2CO_2Et, $(CH_2)_2CN$)] could not be isolated in the pure form.

A search for novel organic ferromagnetic materials has served as an impetus for synthesis of some verdazyl radicals containing heterocyclic moieties or ferrocenyl substituent. By the reaction of hydrogenated tetrazinones **40** ($R^1 = R^3$ = Me), obtained from bis(hydrazide) **39a**, with (hetero)aromatic aldehydes and subsequent oxidation, a series of 3-(het)aryl-6-oxoverdazyls **41** ($R^1 = R^3$ = Me) has been synthesized (Scheme 17).[29, 36–40]

Scheme 17

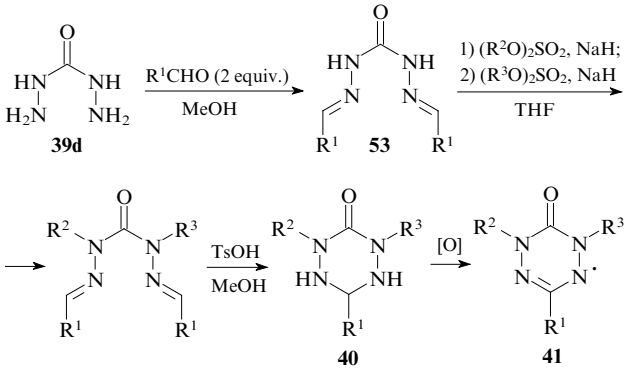


R = 3,5-$Bu^t_2C_6H_3$, 2-HO-5-$HO_2CC_6H_3$, 2-HOC_6H_4, 3-HOC_6H_4, 4-HOC_6H_4, 4-$Ph_2NC_6H_4$, 4-MeC(O)NHC_6H_4, ferrocenyl (Fc),



The range of available 6-oxoverdazyl radicals has been significantly extended by Georges and co-workers[41, 42] with the aim of using them as building blocks for synthesis of new heterocyclic systems. The authors have developed a new approach to the synthesis of verdazyls **41**, implying the use of carbohydrazide **39d** as an initial compound and successive alkylation of compound **53**. The method enables the synthesis of both symmetric and asymmetric verdazyls without using phosgene and alkylhydrazines (Scheme 18).

Scheme 18

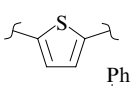
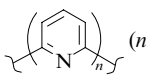
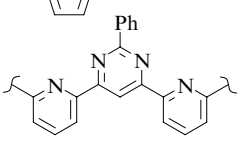
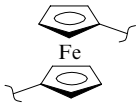


$R^2 = R^3$ = Me: R^1 = Bu^t, Bn, $(CH_2)_2Ph$, 4-FC_6H_4, 3-$CF_3C_6H_4$, 6-Ind, 2-Fu, 3-Th; R^1 = Ph, R^2 = Me: $R^3 = Pr^n$, Pr^i, Bn; $R^2 = R^3$ = Et: R^1 = Ph, 4-$(CH_2{=}CH)C_6H_4$; R^1 = Ph, R^3 = Bn: R^2 = Et, Bn (Ind is indolyl, Fu is furyl, Th is thienyl)

The condensation of carbohydrazide **39d** with aldehydes protects the NH_2 groups and makes it possible to introduce a required substituent in the 3-position of the verdazyl moiety. Successive alkylation of the corresponding condensation products by alkyl sulfates (or alkyl iodides) in the presence of sodium hydride is possible owing to the fact that monoalkylated carbohydrazides are less reactive than the unsubstituted carbohydrazides. Methanolysis and cyclization in the presence of *p*-toluenesulfonic acid lead to the corresponding leuco-verdazyls.

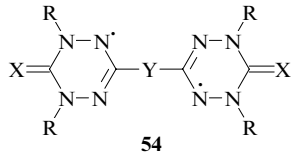
The ability of polydentate verdazyl radicals to form chelates renders them efficient ligands in transition metal complexes. With the aim of creating paramagnetic analogues of oligopyridine metal-containing supramolecular building blocks, an abundant series of biradicals **54**, includ-

Table 2. Bis(verdazyl) biradicals **54** containing oxo and thioxo groups.

R	Y	X	Ref.
Me	none	O	43
Me	none	S	44
Me	*p*-phenylene, *m*-phenylene; 	O	44
Me	 (*n* = 1, 2, 3); 	O	36
Me		O	37
Pr^i	*p*-phenylene, *m*-phenylene	O	45

ing those with multitopic fragments, has been synthesized (Table 2).

Structure **54**



54

Among the bis(verdazyl) radicals presented in Table 2, one of the most interesting radicals is 1,1′-bis(verdazyl)ferrocene. Its structure is shown in Fig. 8. According to X-ray crystallography data, the verdazyl rings of compound **54a** (R = Me, X = O, Y is ferrocene-1,1′-diyl) in the solid state are arranged exactly one above the other, which is evidence of formation of an intramolecular π-dimer. The torsion angles between the planes of the verdazyl rings and cyclopentadienyl moieties of ferrocene to which they are bonded are nearly zero. The N – N distances between the rings are on average 3.15 Å, which is substantially smaller than the common interplanar distance in the ferrocene molecule (3.3 Å). The internal parameters of verdazyl moieties of compound **54a** differ only slightly from those of other verdazyls, but the methyl and carbonyl groups are noticeably twisted out of the plane of the verdazyl ring. This complex is the first dimer of verdazyl radicals. In crystal, the two verdazyl rings linked through the ferrocenyl moiety in the dimer are intramolecularly associated.

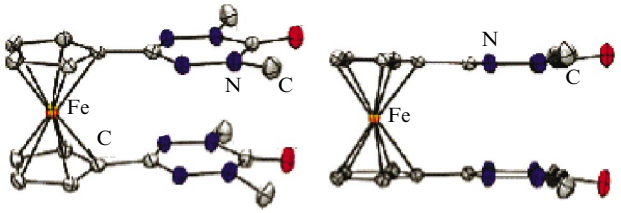
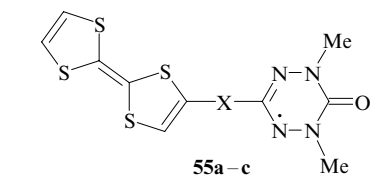


Figure 8. Two views of molecular structure of 1,1′-bis(verdazyl)-ferrocene **54a** (R = Me, X = O, Y is ferrocene-1,1′-diyl).[37]

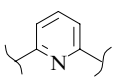
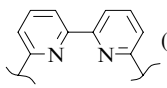
In crystals, verdazyl **54a** is diamagnetic, which points to spin coupling owing to π-dimerization. However, in solution this diradical is not a π-dimer since exchange interaction is very weak.

At present, an important challenge is to design molecular materials exhibiting two or more useful properties (for example, electrical conductivity and magnetism). Tetrathiafulvalene (TTF) derivatives represent one of the classes of organic compounds widely used for fabricating hybrid materials. A combination of the TTF and verdazyl moieties in the same molecule has enabled the synthesis of novel donor ligands **55a – c**, in which the localized spin of the stable radical and the π-spin generated at the TTF moiety are ferromagnetically coupled.[46,47] Such ligands are of interest for the synthesis of transition metal chelates.

Structure **55**

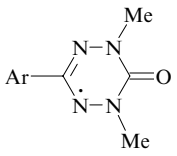


55a – c

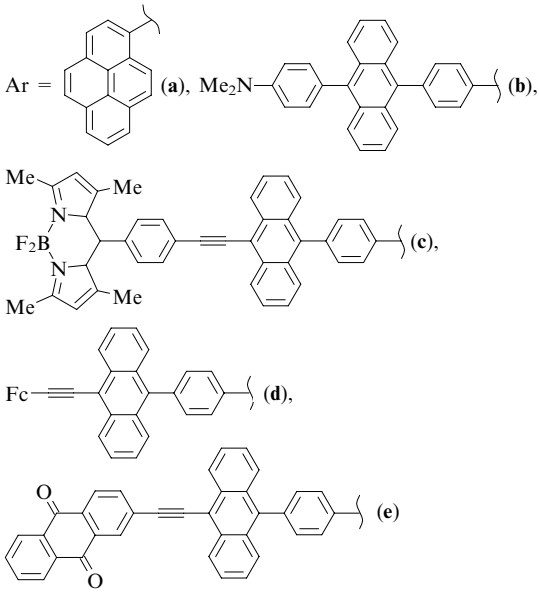
X = CH=CH (**a**),  (**b**),  (**c**)

A search for new π-conjugated spin systems involved in spin ordering process has triggered the synthesis of a series of verdazyl derivatives **56a – e** containing polyaromatic moieties in the 3-position.[48 – 52]

Structure **56**

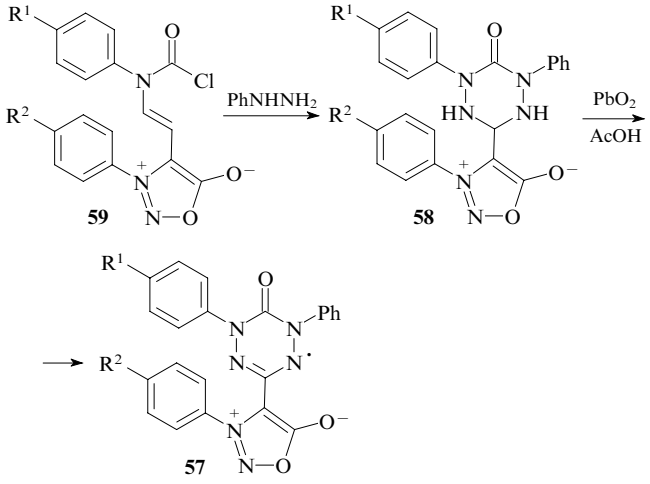


56a – e



A team of Chinese researchers[53] has synthesized sydnonylverdazyls **57**. The precursors — 6-sydnonyl-1,2,4,5-tetrazin-3-ones **58**, which are obtained by the reaction of α-chloroformylarylhydrazones **59** with phenylhydrazine, are oxidized by lead(IV) acetate in acetic acid (Scheme 19).

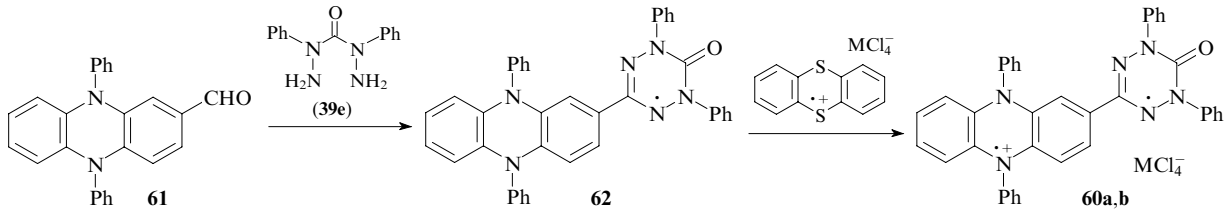
Scheme 19



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

Compounds **57** have been characterized by elemental analysis, ^{1}H NMR and IR spectroscopy and by mass

Scheme 20



M = Fe (**a**), Ga (**b**)

spectrometry. Verdazyl derivatives **57** are very stable: samples remained unaltered on storage at room temperature for one year.

As novel ferro- and ferrimagnets, 1,5-diphenyl-6-oxoverdazyl containing diphenyldihydrophenazinyl radical cation in the 3-position has been suggested.[54] This species has been isolated as salts **60a**,**b** with $FeCl_4^-$ and $GaCl_4^-$ counterions. The reaction of 5,10-diphenyl-5,10-dihydrophenazine-2-carbaldehyde **61** with 2,4-diphenylcarbohydrazide (**39e**) in the presence of pyridinium tosylate yields verdazyl **62**, and its treatment with corresponding salts of the thianthrenyl radical anion gives salts **60a**,**b** (Scheme 20).

According to X-ray crystallography data, the molecular structures and crystal packings of salts **60a**,**b** are similar to each other. The crystal lattice reveals intermolecular interactions that have an effect on magnetic properties (the C–Cl, C–N and C–C contacts are within the ranges 3.39–3.59, 3.25–3.26 and 3.28–3.50 Å, respectively) (Fig. 9). As a whole, the crystal lattice is a 3D network with parameters pointing to the possibility of considerable antiferromagnetic intermolecular interactions.

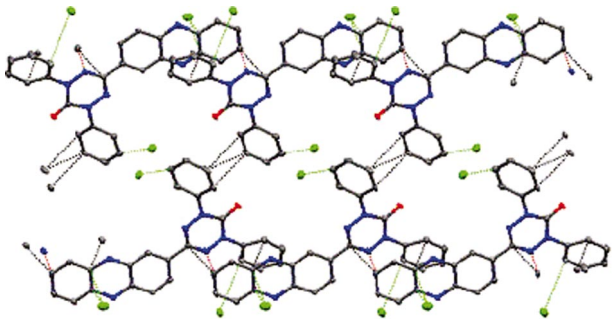


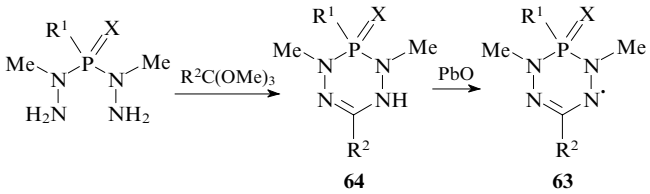
Figure 9. Crystal structure of salt **60a**.[54]

3. Synthesis and structure of phospha- and borataverdazyls

In previous sections, we have considered verdazyl radicals with very different substituents, but with the same structure of the verdazyl ring as a whole. This section deals with so-called heteroverdazyls in which the carbon atoms in the 3- or 6-position are replaced by heteroatoms (phosphorus or boron) that carry a noticeable positive charge.

The first representatives of phosphaverdazyls have been described by Polumbrik [8]. 6-Phosphaverdazyls **63** have been synthesized by oxidation of 1,2,4,5-tetraza-6-phosphorines **64**, the products of the reaction of bis(1-methylhydrazide) derivatives of the corresponding R^1-phosphoric acid with orthoesters (Scheme 21).

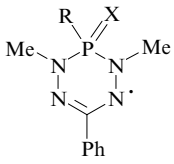
Scheme 21



X = O, R^1 = Ph: R^2 = H, Me, Ph; X = S: R^1 = H, Me, Ph, Me_2N; R^2 = H, Me, Ph

Radicals **63** synthesized by Scheme 21 are rather stable: a noticeable change in the EPR spectrum intensity is observed only after several days. At the same time, the formation of phosphaverdazyls **3a**–**d**, prepared by oxidation of corresponding leuco-phosphaverdazyls, has been detected only owing to colouration and observation of corresponding signals in EPR spectra.[8]

Structure **63**

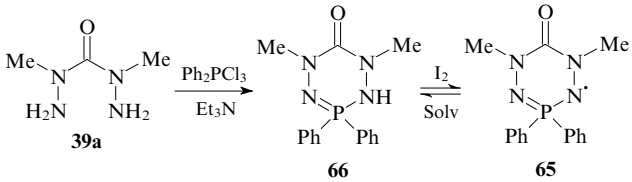


63a–**d**

X = O, R = OPh (**a**); X = S, R = NMe_2 (**b**);
X = NSO_2Ph: R = Ph (**c**), H (**d**)

A representative of phosphaverdazyls **65** containing the phosphorus atom in the 3-position was first synthesized by Hicks and Hooper [55] through the reaction of bis(1-methylhydrazide) of carboxylic acid **39a** with trichlorodiphenylphosphorane in the presence of triethylamine to give 1,2,4,5-tetraza-3-phosphorine **66** and its subsequent oxidation (Scheme 22).

Scheme 22



Solv is solvent

Radical **65** is stable on storage at −30 °C in the solid state. However, at room temperature or in solution, it decomposes within 1–2 weeks, mainly returning to leuco species **66**, so that 3-phosphaverdazyl could not been studied by X-ray diffraction. EPR data (in particular,

hyperfine coupling constants of the phosphorus atom) demonstrate that the minimal spin density is on the phosphorus atom. This is evidence of the planar geometry of the phosphaverdazyl ring. In contrast, the significant hyperfine coupling constant of the phosphorus atom in 6-phosphaverdazyl **63c** implies a nonplanar half-boat conformation.

Modification of the method shown in Scheme 21 affords P-dimethylamino-substituted 6-phosphaverdazyl **63e** (X = O, $R^1 = Me_2N$, R^2 = Ph).[56] The hyperfine coupling constants of the four nitrogen atoms of the verdazyl ring and six *N*-methyl protons of this compound are consistent with those for related structures. A surprising fact is the lack of hyperfine splitting at the phosphorus atom, as distinct from that observed in EPR spectra of phosphaverdazyl **63f** (X = O, $R^1 = R^2$ = Ph). The experimental data, supported by density functional theory (DFT) calculations, are indicative of a significant effect of the substituent at the phosphorus atom on the conformation and spin distribution in phosphaverdazyl molecules. In addition, the EPR spectra of compound **63e** reveal extraordinary high hyperfine coupling (HFC) constants for the exocyclic nitrogen atom. Quantum chemical calculations enable the suggestion that the spin transfer in phosphaverdazyls arises from spiroconjugation-type overlap of the *p* orbital of the exocyclic nitrogen atom with the π-system of the verdazyl radical (Fig. 10).

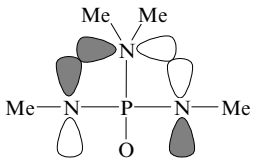


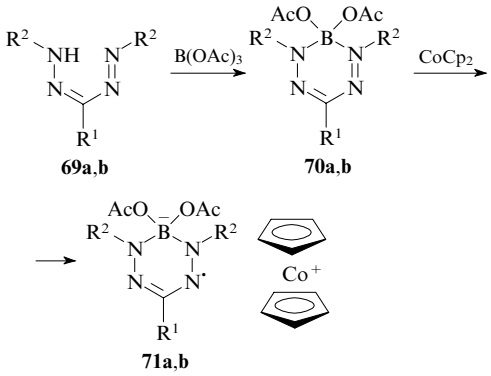
Figure 10. Overlap of the *p* orbital of the exocyclic nitrogen atom and the verdazyl π-system in compound **63e**.[56]

Spiroconjugation of another ring with phosphaverdazyl can enhance spin scattering through spiro binding and appearance of a new spin delocalization mechanism. This suggestion has been an impetus for synthesis of compound **67** in which the phosphaverdazyl moiety forms a spiro system with the phosphazene ring (Scheme 23).[57]

Radical **67** is rather stable, but it gradually disproportionates in the solid state or solution to leuco species **68**. The EPR spectrum of radical **67** consists of at least 14 poorly resolved lines, which makes its interpretation impossible, despite numerous attempts to improve the spectral resolution. However, the isotropic hyperfine structure has been interpreted by means of the ENDOR method. The spectral data point to significant spin polarization through the spirocyclic phosphorus atom into the phosphazene ring to the distant phosphorus and nitrogen atoms. The spin density on the nitrogen atoms of the phosphazene ring is much lower than on the exocyclic nitrogen atom in radical **63e**. The presence of small spin density on the distant phosphorus atoms indicates that spin distribution in the phosphazene ring occurs *via* another mechanism.

Complexation of formazans with boron trihalides leads to inseparable mixtures. However, the reaction of compounds **69a**,**b** with boron triacetate yields boratatetrazines **70a**,**b**, and the products of their reduction — radical anions — can be formally classified with stable neutral verdazyls. The reaction of tetrazines **70a**,**b** with cobaltocene suggested by Hicks and coworkers[58] yields borataverdazyl radical anions **71a**,**b** (Scheme 24).

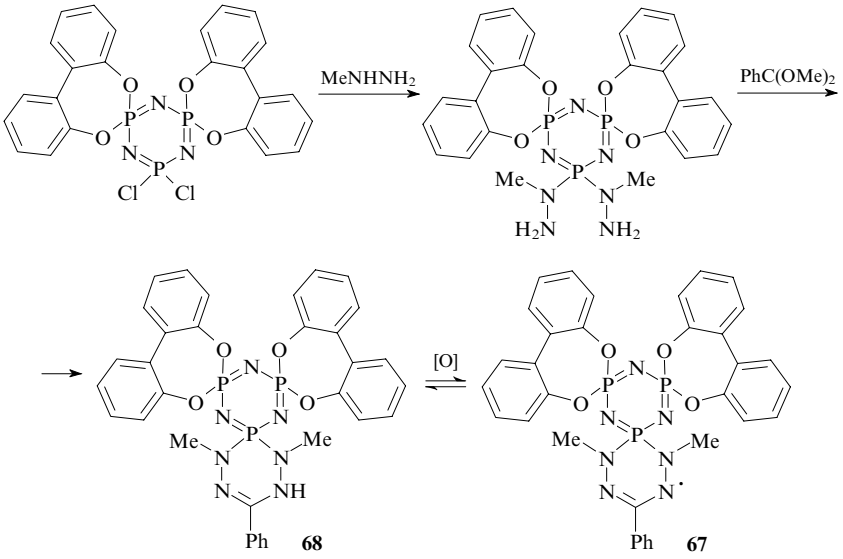
Scheme 24



69a,**b** **70a**,**b** **71a**,**b**

R^1 = 4-MeC_6H_4, R^2 = Ph (**a**); R^1 = Ph, R^2 = 4-MeC_6H_4 (**b**); Cp is cyclopentadienyl

Scheme 23



68 **67**

Salts **71a**,**b** are extremely sensitive to the presence of air and are decomposed in solution even in an inert atmosphere, which hinders their purification. However, both compounds have been characterized by elemental analysis data and EPR spectroscopy in the solid state.

III. General characteristics of verdazyl radicals

1. Verdazyl stability

One of the major problems that emerge in consideration and use of organic radicals is their stability. Analysis shows that stable heterocyclic radicals are mainly those in which spin density is localized on the nitrogen atoms and their bonded oxygen atoms.[3] In this respect, verdazyls are among the most stable radicals. Almost all synthesized verdazyls can be stored without decomposition for a long time in the presence of air and moisture. Their stability is based on the possibility of delocalization of the unpaired electron between two chemically equivalent parts of the molecule. However, it is worth noting that the nature of substituents in oxoverdazyls has a significant effect on their stability. Verdazyls are neither associated nor dimerized in solution. Their important specific feature is that even the structures without bulky substituents are stable.

2. Crystal structure

The crystal structures of many verdazyl derivatives have been determined by X-ray crystallography.[11, 16, 18, 19, 26, 27, 32, 33, 37, 54, 59] Analysis of the available data enables some conclusions to be drawn.[3] In particular, in 6-oxo- (**41**) and 6-thioxoverdazyls (**43**), the ring comprising four nitrogen atoms and two carbon atoms is roughly planar, and the *N*-aryl substituents in compounds **41** are twisted in a propeller or antipropeller fashion with respect to the tetrazine moiety (torsion angle $\sim 30^\circ$). At the same time, in 6-thioxoverdazyl **43a** ($R^1 = R^3 = Ph$, $R^2 = Bu^t$), *N*-phenyl rings are perpendicular to the tetrazine plane.[33] The major conformation of Kuhn verdazyls **3**, with a methylene group in the 6-position, is a half-chair. When an alkyl or aryl fragment is substituted for one of the hydrogen atoms of the methylene group, the bulkier group occupies the axial position.[16]

The effect of substituents at different positions of verdazyl on crystal packing, which is of crucial importance for the physical properties and application, has been considered in review [3]. The presence of the phenyl substituent in the 6-position of radical **20c** prevents an upright columnar stacking of the molecules in crystals. As a result, the molecules are mutually shifted and build up a stairlike chain structure.[16] In the absence of bulky substituents in this position, the molecules are packed in stacks.[11]

The molecules of oxoverdazyls **41** is crystals form linear π-stacks in which the verdazyl ring of one molecule partially overlaps with the aromatic (heteroaromatic) ring of the substituent in the 6-position of a neighbouring molecule in the stack. A number of intermolecular contacts (3.6–3.9 Å) have been revealed in the stacks; however, there are no noticeable interactions between the stacks.[60] Detailed consideration of the crystal structure of oxoverdazyls **41**, without bulky substituents, invoking quantum chemical calculations, reveals the existence of separate π-dimers with the 'head-to-tail' monomer orientation. Evaluations of the frontier orbitals show that these π-associates are formed *via* nitrogen-based multicenter (2e/8c) long-distance bonding.

A specific feature of the highest occupied molecular orbitals (HOMO) of the π-dimers of oxoverdazyl radicals is that they are mainly made up of nitrogen orbitals, whereas in the previously studied systems, multicentre bonding mainly involves carbon atoms. This fact emphasizes the universal character of the phenomenon of long-distance π-bonding in organic radical systems.[61]

3. Electronic spectra

Verdazyls are π-electron free radicals, and all of them are intensely coloured. In particular, Kuhn verdazyls **3** are, as a rule, green and absorb light in the range 700–750 nm [extinction coefficient (ε) $\sim 10^3$ litre mol^{-1} cm^{-1}]. 6-Oxoverdazyls **41** absorb light in a shorter wavelength range of 400–560 nm and 6-thioxoverdazyls **43**, in a range of 450–600 nm (Refs 28 and 33). The maximum absorptions for 6-X-substituted 1,3,5-triphenylverdazyls in dioxane are observed at 720 nm for $X = CH_2$, 608 nm for X = S and 563 nm for X = O.

For all radicals, the substituent in the 3-position also has a strong effect on the electronic spectrum: for verdazyls with H and Alk in this position, λ_{max} is 50 nm smaller than for the 3-phenyl derivatives. The presence of electron-releasing groups in the ring leads to an even larger red shift.[31] This is consistent with the suggestion that the lowest energy absorption involves electron transfer from the occupied orbital to the singly occupied molecular orbital.

The nature of substituents at the nitrogen atoms is also essential. In particular, 6-oxoverdazyls with the *N*-alkyl group absorb light in the range 400–450 nm (the solution is from yellow to dark orange), whereas *N*-aryl-substituted 6-oxoverdazyls **41** in solution become red (absorption maximum from 500 to 550 nm).

4. EPR and NMR spectra

The spin distribution in verdazyls has been studied by experimental and theoretical methods.[4, 8] EPR spectroscopy plays a decisive role in evaluation of the degree of spin distribution. The EPR spectrum of the Kuhn verdazyls consists of nine broad lines with the intensity ratio 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 caused by coupling of the unpaired electron to the four spectrally equivalent nitrogen atoms of the tetrazine ring. Although there are two chemically nonequivalent pairs of nitrogen atoms [N(1) and N(5), N(2) and N(4)], the hyperfine coupling constants usually have close values. For Kuhn 3-substituted 1,5-diarylverdazyls **3** (R^1, R^2 = Ar), the hyperfine coupling constants are in the range 5.7–6.2 Hz for the N(1) and N(5) atoms and 5.4–6.1 Hz for the N(2) and N(4) atoms.

The EPR spectra of 6-oxo- (**41**) and 6-thioverdazyls (**43**) differ from those for the Kuhn verdazyls. For them, the constants of the N(1) and N(5) atoms are smaller than those of the N(2) and N(4) atoms. Typical values for the former are 5.1–5.4 Hz if $R^1 = R^3 = Alk$ and ~ 4.5 Hz if $R^1 = R^3 = Ar$; the constants of the N(2) and N(4) atoms are in the range 6.3–6.6 Hz. The EPR spectra of 1,5-dialkyl-6-oxoverdazyls **41** ($R^1 = R^3 = Alk$) are more complicated because of additional coupling of the unpaired electron to hydrogen atoms: the HFC constants of the α-protons of alkyl groups are in the range 5.2–5.8 Hz, 2.9–3.0 Hz and 1.2–1.5 Hz, respectively, for methyl, benzyl and isopropyl groups in the 1- and 5-positions. As an

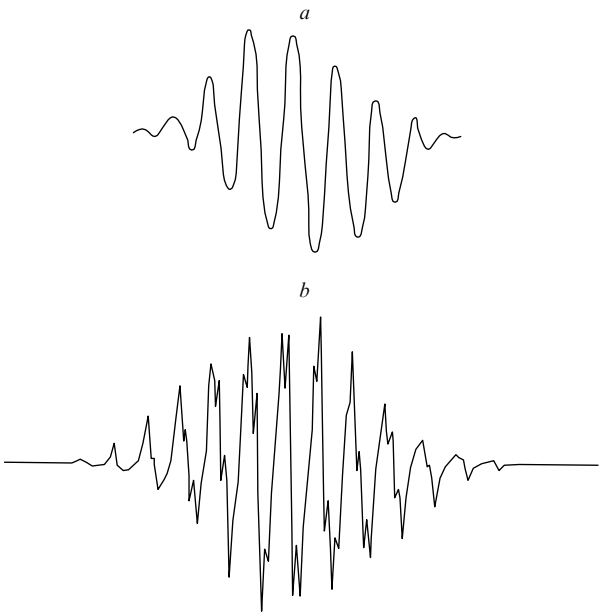


Figure 11. Room-temperature EPR spectra of 1,3,5-triphenylverdazyl (**8**) (*a*) and 1,5-dimethyl-3-(4,6-dimethylpyrimidin-2-yl)-6-oxoverdazyl (**41b**) (*b*) in benzene.[28, 33]

example, Fig. 11 shows the EPR spectra of 1,3,5-triphenylverdazyl (**8**) and one of the 1,5-dimethyl-6-oxoverdazyls — compound **41b** ($R^1 = R^3 =$ Me, R^2 is 4,6-dimethylpyrimidin-2-yl).[28, 33]

The use, in addition to EPR, of other spectral methods, first of all NMR, including ENDOR, dynamic nuclear polarization (DNP) and electron – electron magnetic resonance (ELDOR), has provided a more complete pattern of spin distribution over all nuclei, including the protons of all substituents and the methylene group in Kuhn verdazyls **3**.[28, 33]

^{1}H NMR spectra can provide additional information on HFC constants and spin density signs. In particular, Lang *et al.*[18] have compared the ^{1}H NMR spectrum of 1,3,5,6-tetraphenylverdazyl (**21b**; $R^3 = H$: $R^1 = R^2 =$ Ph) with those of triphenylverdazyl **8** and 6-methyltriphenylverdazyl **16a** (R = Me) and have determined the paramagnetic shifts, HFC constants for each proton and the spin density on the neighbouring carbon atoms. It has been shown that there is a correlation between the nature of substituents in the 6-position and the HFC constants for the protons of the *N*-phenyl groups. In another work of the same research team,[20] a new triradical — 1,3,5-tris(1,3,5-triphenylverdazyl-6-yl)benzene (**24**) has been studied, its ^{1}H NMR spectra and EPR spectra of liquid and frozen solutions have been described, and magnetic susceptibility for solid samples has been measured. Conclusions have been drawn concerning the doublet – quartet ground state of this triradical and the influence of molecular packing on the magnetic properties.

5. Quantum chemical calculations and magnetic properties

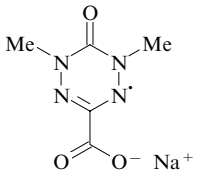
Quantum chemical calculations of verdazyl radicals have been performed by different methods.[4, 5, 8] The calculations have enabled the conclusion that the unpaired electron in all types of verdazyls is part of a 7π-electron system delocalized over the N(1) – N(2) – C(3) – N(4) – N(5) atoms of the heterocycle. The four nitrogen atoms account for about 80% – 85% of total positive spin density and the C(3) carbon atom, for about 3% – 6% of negative spin density.[5]

Specific features of exchange interaction of unpaired electrons are responsible for the specific behaviour of the magnetic susceptibility of verdazyls as a function of temperature. The paramagnetic properties of verdazyls persist even with a strong decrease in temperature.[8] Owing to the chemical stability and ability to be functionalized, verdazyls attract ever-increasing attention as building blocks for design of organic magnets. Numerous studies have focused on their magnetic properties (see, for example, Refs 15, 27, 40, 59, 62 – 67). Both antiferromagnetic and ferromagnetic interactions can be observed in verdazyls. Differences in magnetic properties are caused to a significant extent by structural features of crystals. Some correlations between the character of interaction and spin density distribution have been revealed.[5, 68]

Magnetic properties of verdazyls, including three types of exchange coupling — through-bond exchange coupling in di- and polyverdazyl radicals, through-space exchange coupling in crystals of radical molecules and magnetochemistry of metal verdazyl complexes, have been discussed in sufficient detail.[4, 5, 69, 70]

In this review, only some of new publications concerning the magnetic properties of verdazyl systems have been cited. In particular, very strong antiferromagnetic exchange coupling has been revealed in clathrate hydrate of deprotonated 1,5-dimethyl-6-oxoverdazyl-3-carboxylic acid (**72**).[71] Crystal packing of **72** has a stack structure with intermolecular contacts between the carboxylate oxygen atoms and the nitrogen atoms of the radical anion (Fig. 12).

Structure **72**



72

Quantum chemical calculations predict very strong ferromagnetic interaction in mixed diradicals involving oxoverdazyl and nitronyl nitroxide moieties connected by a polyene linker.[72] Calculations have been used to prove the possibility of spin crossover in verdazyl systems.[73]

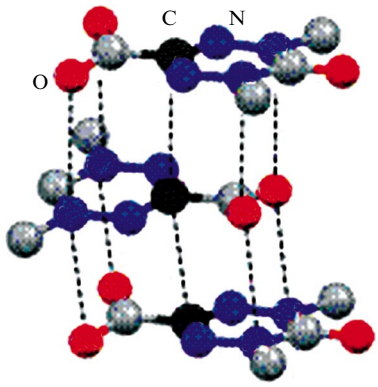
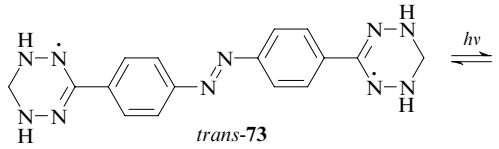


Figure 12. Intermolecular contacts in the crystal of radical anion **72**.[71]

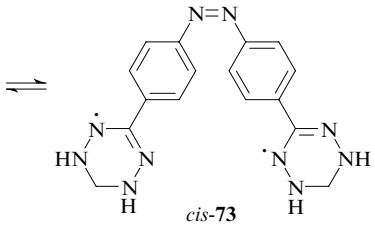
Studying spin ordering in the photoexcited state is essential for photocontrol of molecular magnetism. Spin delocalization upon photoexcitation has been experimentally and theoretically studied for oxoverdazyls **56**.[51, 52]

The photomagnetic properties of azobenzene **73**, containing verdazyl moieties have been theoretically studied.[74] It has been predicted that excitation of this system by light is accompanied by magnetic crossover. The antiferromagnetic *trans* isomer (*trans*-**73**) is converted into the ferromagnetic *cis* species (*cis*-**73**) under irradiation with light at 340 – 380 nm (Scheme 25).

Scheme 25



trans-**73**



cis-**73**

Magnetic interactions in π-conjugated systems consisting of the verdazyl radical and the tetrafulvalene radical cation have been studied by the DFT method.[75] The broken symmetry density functional theory (BS-DFT) approach has been used for studying the magnetic interaction of oxo- and thioxoverdazyl diradicals **54** containing different π-conjugated linkers.[76, 77] The intermolecular magnetic exchange coupling constants have been calculated, and their values have been explained using spin polarization maps and magnetic orbitals. It has been found that some of radicals **54** have ferromagnetic character, while the others are antiferromagnetic in nature. The use of spectroscopy oriented configuration interaction (SORCI) calculations, along with the BS-DFT approach, enabled the prediction of the antiferromagnetic character of the ground state of 6,6′-dioxo-3,3′-biverdazyl **54b** (X = O, R = Me, Y is absent).[78] It has been demonstrated that the SORCI method can be used for the computation of the magnetic properties of large molecules.

IV. Reactivity of verdazyls

Verdazyls as stable radicals can be involved in different chemical transformations. The general stability of verdazyls makes it possible to carry out reactions not affecting the radical centre.

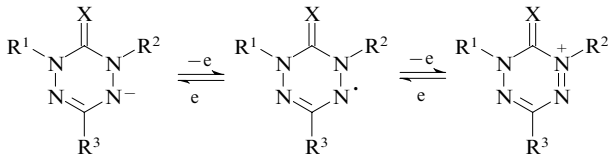
For example, amino-substituted Kuhn verdazyls **5** can be converted into amide or imine derivatives.[8] Sulfonation of 1,3,5-triphenylverdazyl (**8**) leads to water-soluble derivatives **17**.[14] Many verdazyl-containing polymers (for example, compounds **28**, **32** and **33**) are synthesized through multistep transformations, so that verdazyl used as a precursor is involved in several reactions that do not affect the radical centre.

However, most of the chemical transformations of verdazyls involve the unpaired electron.

1. Electrochemical properties and electron-transfer reactions

Verdazyl radicals, like other free radicals, can accept or donate one electron, converting into an anion or cation. They are characterized by a triad of reversible states (shown for verdazyls **I** and **II** as an example) (Scheme 26).

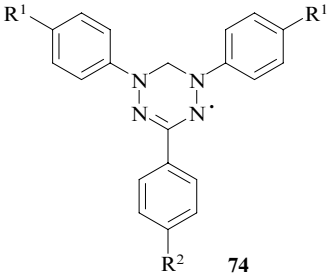
Scheme 26



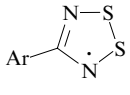
X = 2H, O, S

The electrochemical characteristics of verdazyl radicals have been described in a number of studies where it has been shown that the redox potentials strongly depend on the verdazyl structure, the nature of substituents and solvent.[8, 29, 44 – 47, 79 – 83] Hicks and co-workers[84] have performed systematic electrochemical study of redox properties as a function of structure for a series of verdazyls **74** and 6-oxoverdazyls **41** ($R^1 = R^3$ = Me, Pr^i, Ph; R^2 = Ph, 2-Py, imidazol-2-yl, 1-methylimidazol-2-yl).

Structures **74**, **75**



74



75

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

Cyclic voltammetry shows that almost all verdazyls can be reversibly reduced and oxidized. The oxidation potentials of verdazyls **8** and **74** are in the range from −0.39 to −0.15 V, which characterizes them as good electron donors. The reduction of these radicals occurs at considerably negative potentials (from −1.14 to −1.33 V). The effect of substituent in this case is qualitatively predictable. For example, in the series of **74** with R^1 = OMe, Me, H, Cl and R^2 = Me, the electron-withdrawing properties of the substituents become more pronounced, and the oxidation potentials increase from −0.39 V (for R^1 = OMe) to −0.15 V (for R^1 = Cl) (the range is ∼250 mV). For comparison, electrochemical study of a wide series of 4-aryl-1,2,3,5-dithiadiazolyl radicals **75** with different electron-withdrawing substituents in the benzene ring has revealed the change in the oxidation potentials within the range of only 100 mV, although the substituent effect for these radicals is mitigated since the radical centre is located in the plane of the molecule.[85, 86]

The effect of the substituent in the 3-position of the verdazyl ring in **74** on the oxidation potential is much weaker than the effect of substituents in the 1- and 5-positions.

The redox properties of 6-oxoverdazyls **41** differ from those of verdazyls **74**. These differences are well demonstrated by the voltammograms for 1,3,5-triphenylverdazyl

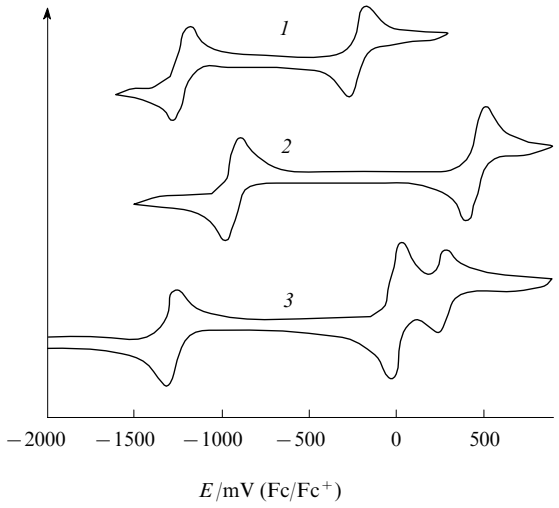


Figure 13. Cyclic voltammograms of 1,3,5-triphenylverdazyl (**8**) (curve *1*), 6-oxo-1,3,5-triphenylverdazyl (**41a**) (*2*) and 1,5-dimethyl-6-oxo-3-phenylverdazyl (**41c**) (*3*).

(**8**), 6-oxo-1,3,5- triphenylverdazyl (**41a**) and 1,5-dimethyl-6-oxo-3-phenylverdazyl (**41c**) (Fig. 13).

This comparison shows that, on the whole, verdazyl radicals **41** are much more difficult to oxidize than verdazyls **74**. This is likely due to the inductive electron-withdrawing effect of the carbonyl group in the 6-position of compounds **41**. As for the effect of substituents, the electron-withdrawing properties of substituents in the 3-position of the tetrazine ring of 6-oxoverdazyls **41**, like those in the Kuhn verdazyls, have a weak effect on the oxidation potential: the stronger the electron-withdrawing properties of the substituent, the easier the reduction and the more difficult the oxidation of verdazyl radical.

In design of neutral conducting materials, an important electrochemical characteristic of radicals is the cell potential ($E_{cell} = |E_{ox} - E_{red}|$), since this parameter correlates with the disproportionation energy. For verdazyl radicals **74**, the E_{cell} is close to 1.0 V and is roughly independent of the nature of substituents in the *para* position of aromatic moieties. For 1,5-dialkyl-3-aryl-6-oxoverdazyls, $E_{cell} \approx 1.5$ V, and intermediate values ($E_{cell} = 1.38$ V) have been obtained for 1,3,5-triaryl-6-oxoverdazyls. The electrochemical cell potentials for all available verdazyls are much larger than for other types of neutral radicals suggested as building blocks for design of conducting materials, such as polycyclic thiazyl radicals and spirocyclic phenalenyls.[84]

Voltammetry has shown that the electrochemical characteristics of bis(verdazyl) diradicals **54c**,**d** [X = O, R = Pr^i: Y is *p*-phenylene (**c**) and *m*-phenylene (**d**)] are nearly the same: both compounds can be reversibly oxidized to dications or reduced to dianions.[45] Bis(verdazyl) diradicals **54c**,**d** have higher redox potentials than the corresponding monoderivative **41d** ($R^1 = R^3 = Ph$, $R^2 = Pr^i$), which points to a strong electron-withdrawing character of the verdazyl moiety. The shape of the voltammograms for compounds **54c**,**d** enables the conclusion that the oxidation of these diradicals occurs as two pseudo-independent one-electron processes.

On the basis of the electrochemical redox potentials used for evaluation of the donor – acceptor properties of triarylverdazyls, a conclusion has been drawn that triphenylverdazyl **8** is one of the strongest nucleophilic agents among the known stable radicals.[8]

Because of low redox reaction potentials, one-electron transfer is rather typical of verdazyl radicals and their cations. In many transformations, verdazyls act as one-electron donors. In particular, in the reaction with strong electrophiles, such as halogens, triarylverdazyls are rapidly converted into the corresponding cations.[1,8,82,83] The reaction is accompanied by the change in colour of solution from green to violet, and the reaction rate depends on the halogen nature and the donor activity of the radical. Reactions of the Kuhn verdazyls with other oxidizing agents [silver, copper(II) and manganese(II) chlorides; Lewis acids] have also been studied.[8] In all cases, the reactions yield diamagnetic salts, and their stability depends on the nature of the solvent and counterion. The reaction of 1-(*p*-tolyl)-3,5-diphenylverdazyl with tetracyanoethylene leads to the verdazylium cation and the stable tetracyanoethylene radical anion identified from its EPR spectrum.[82,83]

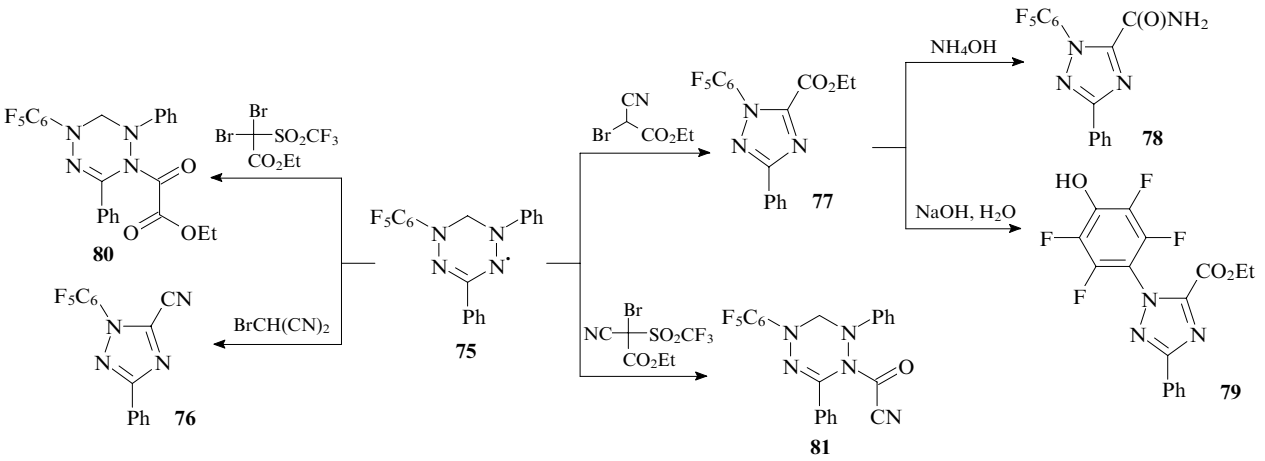
The oxidation of the Kuhn verdazyls by peroxy acids, peroxides or hydroperoxides or the action of air on verdazyl solutions in the presence of activated carbon leads to the opening of the tetrazine ring to form *N*-formylformazans and/or 1,2,4-triazoles.[87,88] Later,[89] autocatalysis in the oxidation of verdazyl radicals with hydroperoxides has been described.

Reactions of 1,3,5-triarylverdazyls with compounds containing a 'positive' halogen atom (for example, substituted bromomethanes) yield several products depending on the structures of both reagents, including 1,3,5-trisubstituted 1,2,4-triazoles.[90–92] Such a reaction has been suggested for synthesis of 5-cyano(ethoxycarbonyl)-substituted 1,2,4-triazoles under mild conditions.[90] The reaction of triphenylverdazyl **8** with trifluoromethylsulfonyl(ethoxycarbonyl)dibromomethane yields, in addition to a small amount of 5-ethoxycarbonyl-1,2,4-triazole, a product of radical N-acylation — 2-ethoxalyl-1,3,5-triphenylleucoverdazyl.[91] For 1,3-diphenyl-5-pentafluorophenylverdazyl (**75**) as an example, it has been shown[91] that dicyano- and cyano(ethoxycarbonyl)bromomethanes promote the fragmentation of the verdazyl radical to 1,3,5-trisubstituted 1,2,4-triazoles **76**–**79** (Scheme 27). At the same time, trifluoromethylsulfonylcyano- and trifluoromethyl(ethoxycarbonyl)dibromomethanes acylate the radicals to form 2-substituted 1,3-diphenyl-5-pentafluorophenyltetrahydrotetrazines **80**, **81**.[92]

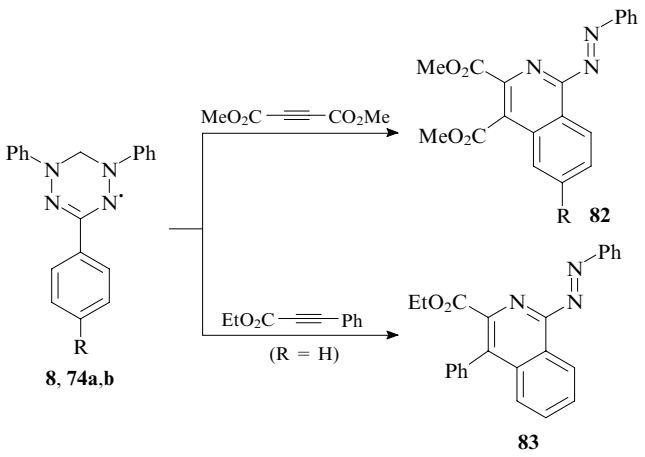
1,2,4-Triazole derivatives and leuco-verdazyls have also been synthesized by the reactions of triarylverdazyls with methacrylate and styrene.[93] However, the reaction of dimethyl acetylenedicarboxylate (DMAD) with 1,3,5-triphenylverdazyl (**8**) at 60 °C for 24 h yielded another product — dimethyl 1-(phenyldiazenyl)isoquinoline-3,4-dicarboxylate (**82**, R = H). Its structure has been confirmed by X-ray crystallography. Using a wide series of verdazyls and acetylene derivatives, Bancerz *et al.*[93] have developed a synthetic route to other substituted isoquinolines, for example, to compound **83** (Scheme 28).

On the basis of their experiments, the authors[93] have proposed the radical mechanism of this transformation,

Scheme 27



Scheme 28

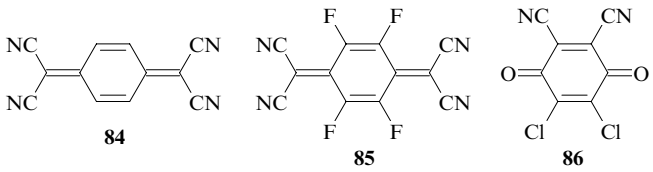


R = H (**8**), OMe (**74a**), Cl (**74b**)

which implies that product **83** is formed by the retro-Diels–Alder reaction.

Nakatsuji *et al.*[81] have studied the reaction of triarylverdazyl radicals with electron acceptors, such as tetracyanoquinodimethane (TCNQ, **84**), tetrafluorotetracyano-*p*-quinodimethane ($TCNQF_4$, **85**) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **86**).

Structures **84**–**86**



Their interaction with verdazyl radicals leads to formation of charge-transfer complexes composed of the verdazylium cation and the acceptor radical anion, which exhibit magnetic properties.

The same research team has studied the effect of substituent R in verdazyls **8** and **74a**–**e** [R^1 = H: R^2 = OMe (**a**), Cl (**b**), Me (**c**), NO_2 (**d**), NH_2 (**e**)] on the formation of complexes with $TCNQF_4$ and DDQ, as well as on the magnetic properties of such structures.[94]

According to elemental analysis data and X-ray crystallography, the complexes are stable crystalline compounds with the ratio donor : acceptor = 1 : 1. The molecular structure of the **74c** · $TCNQF_4$ complex, as an example, is shown in Fig. 14. Examining this structure enables the conclusion that verdazyl cation **74c** is converted into the verdazylium cation through one-electron transfer to $TCNQF_4$, since both N–N bonds in the tetrazine moiety [N(5)–N(6), 1.311 Å; N(7)–N(8), 1.313 Å] are considerably shorter than the N–N bond in the radical [1.348–1.353 Å], and the $TCNQF_4$ molecule thereby transforms into the radical anion. A strong decrease in the magnetic susceptibility and weak antiferromagnetic interactions have been revealed in each complex. A correlation between the magnetic properties and crystal structure of such complexes has been considered.

Mixed charge-transfer complexes have been synthesized from verdazyl **8** and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (**87a**,**b**) with the ratio radical : salt = 1 : 1 (complexes **88a**,**b**),

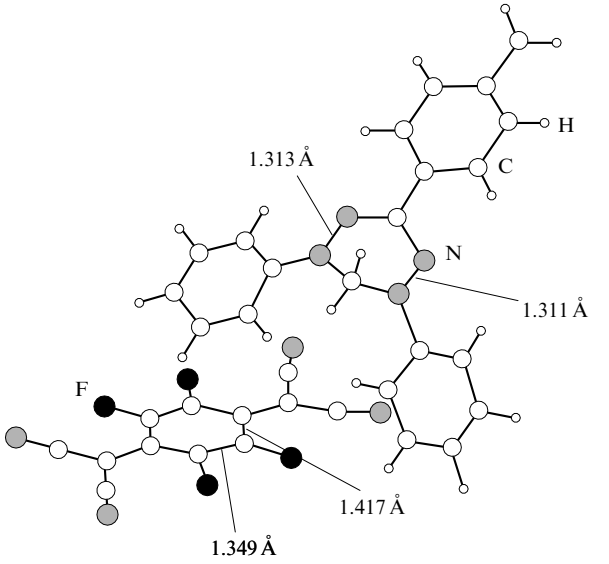
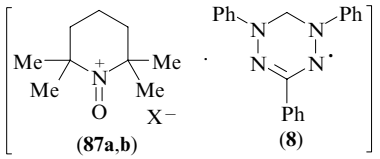


Figure 14. Crystal structure of complex **74c** · $TCNQF_4$.[94]

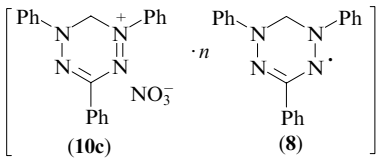
and from radical **8** and verdazylium nitrate **10c** with the radical : salt ratio being 1 : 1 (**88c**) or 2 : 1 (**88d**).[54]

Structures **87**, **88**



(**87a**,**b**) (**8**)

X = NO_3 (**88a**), Br (**88b**)



(**10c**) (**8**)

n = 1 (**88c**), 2 (**88d**)

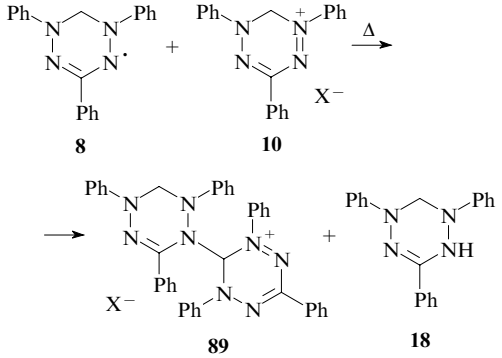
In complexes **88a**–**c** with the ratio radical : salt = 1 : 1, a large decrease in magnetic susceptibility is observed, which is evidence of electron transfer from the radical to the cation and electron delocalization between both partners. The magnetic characteristics of complex **88d** of the 2 : 1 composition are close to those of the initial radical.

Complexation of 1,3,5-triphenyl- and 1,2,3,5-tetraphenylverdazyls with their bromides has been studied by spectrophotometry.[95] It has been shown that the complexes have the 1 : 1 molar ratio; the stability constants of the complexes have been calculated, and their dependence on temperature and solvent polarity has been found.

The kinetics of outer-sphere electron transfer between Kuhn radicals **8** and **74a**–**c** and Co^{3+}, Fe^{3+} and Fe_3 cluster complexes has been studied.[96–99] In all cases, one-electron transfer occurs from the radical to the complex to give a derivative of the metal in the oxidation state +2 and the verdazylium cation. This process is monitored spectrophotometrically. Anomalously slow rates of reduction of Fe^{3+} polypyridine complexes by verdazyl radicals have been revealed.[99]

One-electron transfer reactions are also typical of verdazylium cations.[8] They readily react with compounds acting as one-electron donors, and owing to the high stability of verdazyls, the reaction often stops at this stage. An interesting fact is that heating a mixture of triphenylverdazyl **8** and its salt **10** leads to the formation of the C(6)–N(2) coupling product of **89** and leuco-verdazyl **18** (Scheme 29).[100]

Scheme 29



8 **10**

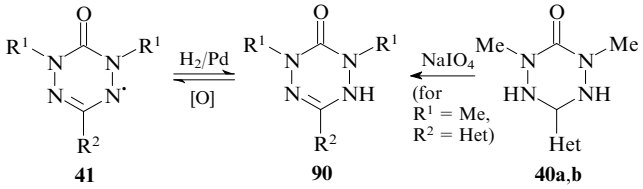
89 **18**

X = Br, OTs

In reactions with different organometallic reagents, Kuhn triarylverdazyls act as electron acceptors, converting to a mixture of leuco-verdazyl and tetrasubstituted tetrazine.[8] The N–H bond in leuco-verdazyls is relatively weak (bond energy of ~70 kcal mol^{-1}).[101] Such verdazyls can also be converted into leuco-verdazyls under the action of various reducing agents.[1, 8, 102, 103]

As for leuco derivatives of 6-oxoverdazyls **90**, it should be noted that they have been little studied. Similar compounds have been synthesized by hydrogenation of radicals **41** (see Scheme 12 for information on substituents)[28] or (only two examples!) by oxidation of tetrazanes **40a**,**b**.[29] Atmospheric oxygen easily oxidizes leuco-verdazyls **90** to the corresponding verdazyl radicals (Scheme 30).

Scheme 30



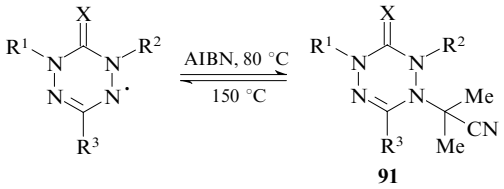
41 **90** **40a**,**b**

Het = 2-Py (**a**), 4,6-dimethylpyrimidin-2-yl (**b**)

2. Interaction of verdazyls with free radicals

Verdazyls of types **I** and **II** readily react with carbon-centred radicals. In particular, heating them in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) leads to 2-cyanopropyl-substitituted tetrazines **91**, which can be converted back into verdazyls in high yield by heating to 150 °C (Scheme 31).[8]

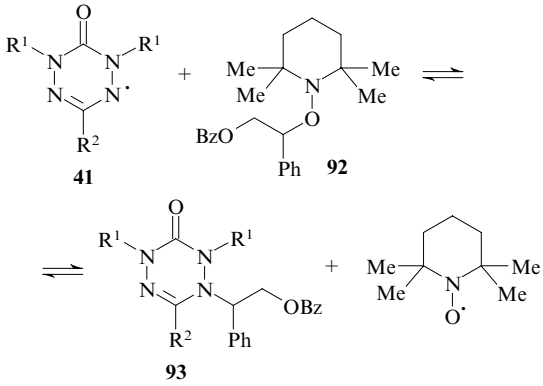
Scheme 31



91

N-Alkyltetrazines have been synthesized from verdazyls with the use of radical–alkyl adducts as the alkyl radical source. For example, on heating a mixture of 6-oxoverdazyls **41** and alkoxyamine **92**, the substituted benzyl radical is transferred from compound **92** to verdazyl to form N-substituted tetrazines **93** (Scheme 32).[104]

Scheme 32



41 **92**

93

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

Owing to the thermal lability of the C–N bonds in tetrazines **93** and the C–O bond in alkoxyamine **92**, the process is equilibrium; however, in some cases, *N*-alkyltetrazines have been isolated in high yield. The introduction of ascorbic acid also shifts the equilibrium toward *N*-alkylverdazyl, since it reduces the *N*-oxyl radical faster than verdazyl.

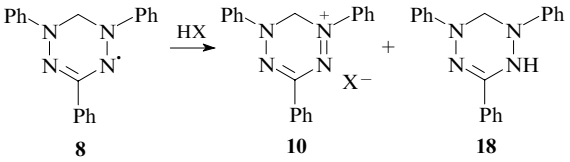
It is worth noting that the reaction of verdazyls with free radicals is a rather complicated process and, depending on the reaction conditions, can occur *via* different routes. It has been shown for 1,3,5-triarylverdazyls of type **I** that the major routes of such transformations are recombination of the active radical and verdazyl to give the addition product, formation of a verdazyl salt through electron transfer from the verdazyl to an active or stable radical, elimination of a hydrogen atom from the CH_2 group of verdazyl by the active radical, elimination of a hydrogen atom from the active radical by verdazyl to form leuco-verdazyl and carbene, as well as equilibrium addition of the active radical to the verdazyl radical.[8]

Fast reactions of verdazyls with carbon-centred radicals have been extensively studied in the context of using verdazyls as inhibitors of radical polymerization.

3. Disproportionation reactions

One of the first described reactions of triphenylverdazyl **8** is that with HCl that yields verdazylium cation **10** and leuco-verdazyl **18**.[1] Disproportionation of triarylverdazyls can be induced by other protonic acids, Lewis acids and Zn^{2+} and Cd^{2+} ions (Scheme 33).[1, 105]

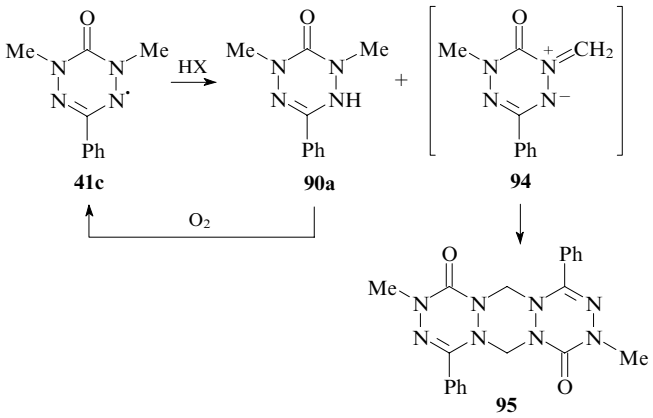
Scheme 33



The kinetic and thermodynamic behaviour of the reaction of triarylverdazyls with organic acids has enabled the conclusion that this reaction is equilibrium.[8] The equilibrium position depends on the donor–acceptor properties of the reactants, their structure and concentration, the solvent nature and temperature. The equilibrium is established almost instantaneously. The equilibrium of the reaction of verdazyls with strong carboxylic and mineral acids is completely shifted toward the reaction products; leuco-verdazyl, being in contact with oxygen, is oxidized to the verdazyl radical, and the radical is completely converted into the salt with time.

Disproportionation of 6-oxoverdazyls **41** is still the subject of investigation at present. However, this process differs from the above process for type **I** verdazyls. In particular, 1,5-dimethyl-6-oxo-3-phenylverdazyl **41c** ($R^1 = R^3 = Me$, $R^2 = Ph$) disproportionates initiating hydrogen atom transfer from the *N*-methyl group to give leuco-verdazyl **90a** ($R^1 = Ph$, $R^2 = R^3 = Me$) and azomethine imine intermediate **94**.[28] The formation of the intermediate could not been detected, since it dimerizes into the product of [3 + 3] cycloaddition — tricyclic compound **95** (Scheme 34). Leuco-verdazyl **90a** is oxidized to the initial radical. In this case, disproportionation is responsible for the lack of long-term stability of many 1,5-dimethyl-6-oxoverdazyls.

Scheme 34

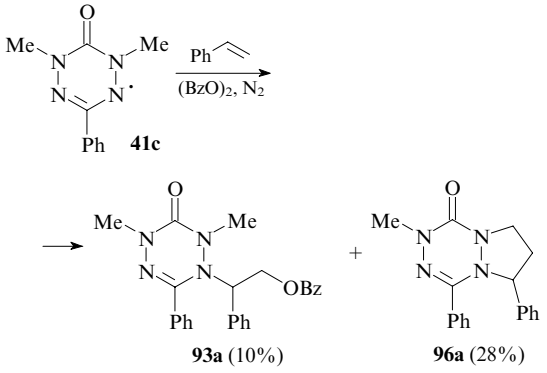


It should be noted that 3-substituted 1,5-diisopropyl-6-oxoverdazyls **41** ($R^1 = R^3 = Pr^i$) are more stable with respect to disproportionation reactions, although they contain proton in the α-position to the nitrogen atom.[30]

4. [3 + 2] Cycloaddition reactions

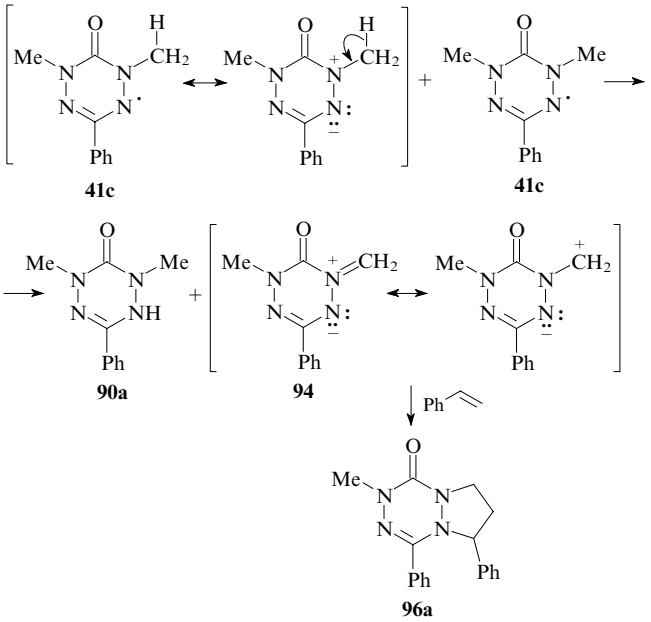
Georges and co-workers [106] were the first who used verdazyl radicals (namely, 1,5-dimethyl-3-phenyl-6-oxoverdazyl **41c**) as precursors of azomethine imines, which enter into [3 + 2] cycloaddition reactions with dipolarophiles. With the aim of synthesizing compounds promoting free radical polymerization, 6-oxoverdazyl **41c** was made to react with styrene and benzoyl peroxide in an inert atmosphere. However, the yield of the expected monomolecular initiator 1-benzoyloxy-2-(6-oxoverdazyl)-2-phenylethane (**93a**) was only 10%, whereas the major reaction product was unexpectedly bicyclic compound **96a** (Scheme 35).

Scheme 35



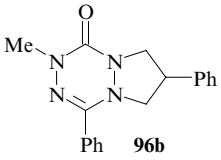
Compound **96a** is a result of cycloaddition of azomethine imine **94**, a product of disproportionation of two molecules of verdazyl **41c**, to styrene (Scheme 36).

Scheme 36



The proposed mechanism has been confirmed by quantum chemical calculations [B3LYP/6-31G(d)].[84] The reaction occurs regiospecifically; therefore, regioisomer **96b** has not been identified in the reaction mixture.

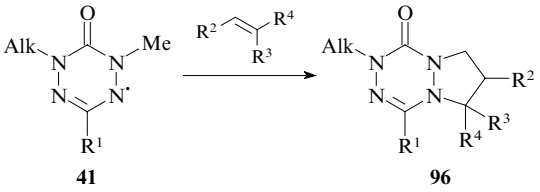
Structure **96b**



Since this mechanism rules out the participation of benzoyl peroxide, reactions have been carried out in its absence, which afford bicyclic product **96a** in 70% yield. The yield can be improved by increasing reaction duration and in the presence of oxygen.

Later, this reaction has been carried out with other alkenes and oxoverdazyls **41** (Scheme 37).[41, 106, 107]

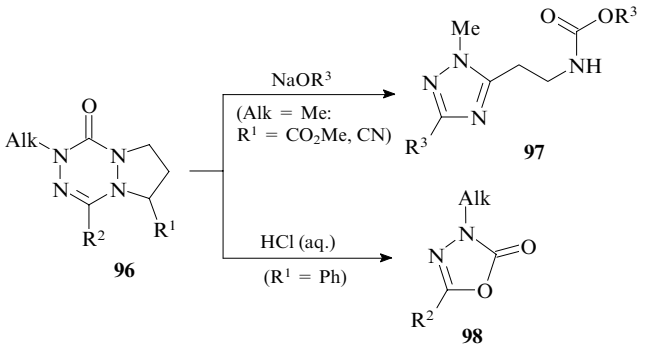
Scheme 37



Alk = Me: R^1 = Bu^t, $CHPh_2$, 4-XC_6H_4 [X = H, CN, NO_2, F, OMe, CF_3, CH_2NHAc, $CH_2NHC(O)Pr^i$], 2-Fu, 2-Th, 2-Im, 2-Py, benzimidazol-2-yl; R^1 = Ph: Alk = Pr^i, Bn; R^2 = R^3 = H: R^4 = Ph, CO_2Me, CO_2Pr^i, CO_2Bu^t, CN, $CONMe_2$, CH_2NHBoc, CH_2NHAc; R^2 = H, R^3 = Me: R^4 = CO_2Me, $CH{=}CH_2$; R^3 = H: R^2 = R^4 = CO_2Et, CO_2Me, CN; R^2 = Ph, R^3 = SMe, R^4 = CN

A wide range of substituents in cycloadducts **96** is due to the possibility of their further modification to obtain new biologically active derivatives, such as triazolylcarbamates **97** and 5-aryl-1,3,4-oxodiazolones **98** (Scheme 38).[41, 108]

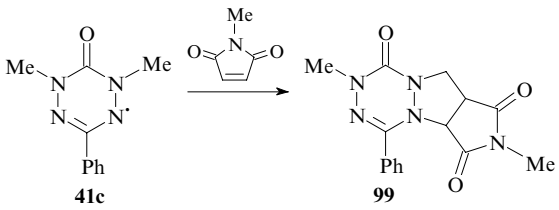
Scheme 38



Alk = Me, Pr^i, Bn; R^1 = Ph, CO_2Me, CN; R^2 = $CHPh_2$, 4-XC_6H_4 (X = H, F, OMe, CF_3, CH_2NHAc, $CH_2NHC(O)Pr^i$, $CH_2NHC(O)$-Bu^t), 2-Fu, 2-Th, 2-Py, 2-fluoro-4-pyridyl, benzimidazol-2-yl; R^3 = Me, Et, Pr^i

The use of cyclic dipolarophiles, such as *N*-methylmaleimide, makes it possible to synthesize tricyclic products **99** from verdazyls (Scheme 39).[106]

Scheme 39



However, the structure of isolated products of reaction with some alkene and acetylene derivatives is inconsistent with the expected results of [3 + 2]-dipolar cycloaddition. In particular, the reaction of 1,5-dimethyl-6-oxo-3-phenylverdazyl (**41c**) with 1-chloroacrylonitrile affords 1,3-dipolar cycloaddition product **100** in a yield of < 5%. Major product **101** is a result of the addition of verdazyl **41c** at the double bond of 1-chloroacrylonitrile, the subsequent reaction of radical **102** with another molecule of initial

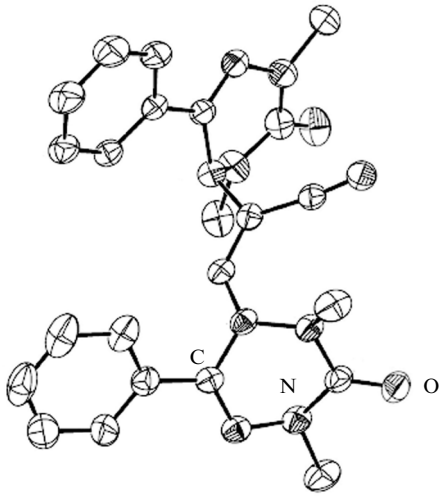
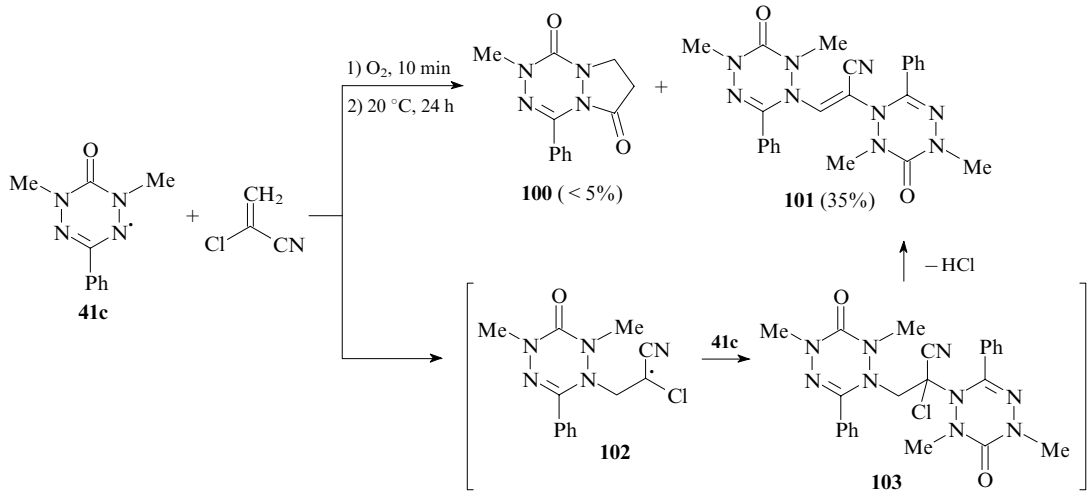


Figure 15. Molecular structure of compound **101**.[107] The hydrogen atoms are omitted for clarity.

Scheme 40

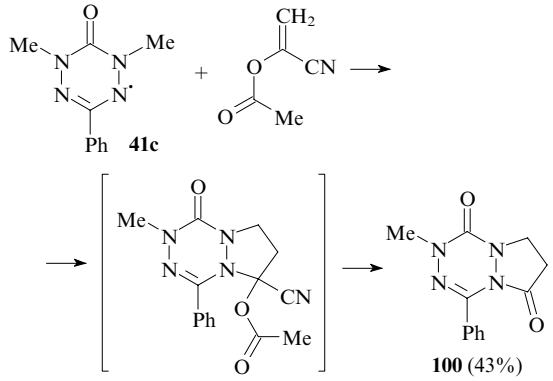


compound **41c** and the elimination of HCl from dimer **103** (Scheme 40).[107]

The structure of dimer **101** has been confirmed by X-ray crystallography (Fig. 15).

Compound **100** was synthesized in moderate yield by the reaction of verdazyl derivative **41c** with 1-acetoxyacrylonitrile (Scheme 41).[107]

Scheme 41



The reaction of methyl α-acetoxyacrylate with 1,5-dimethyl-6-oxoverdazyl **41c** yields 5-methyl-7-phenylpyrazolo[1,5-*d*]-1,2,4-triazin-4(5*H*)-one (**104**), which cannot be formed as a result of 1,3-dipolar cycloaddition or radical addition (Scheme 42). The structure of this products has been determined by ^{1}H and ^{13}C NMR and X-ray crystallography (Fig. 16).[107]

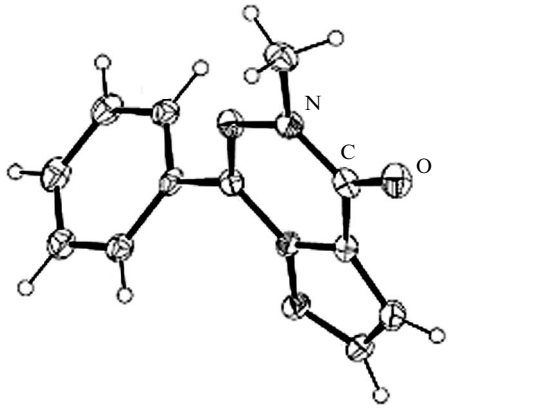
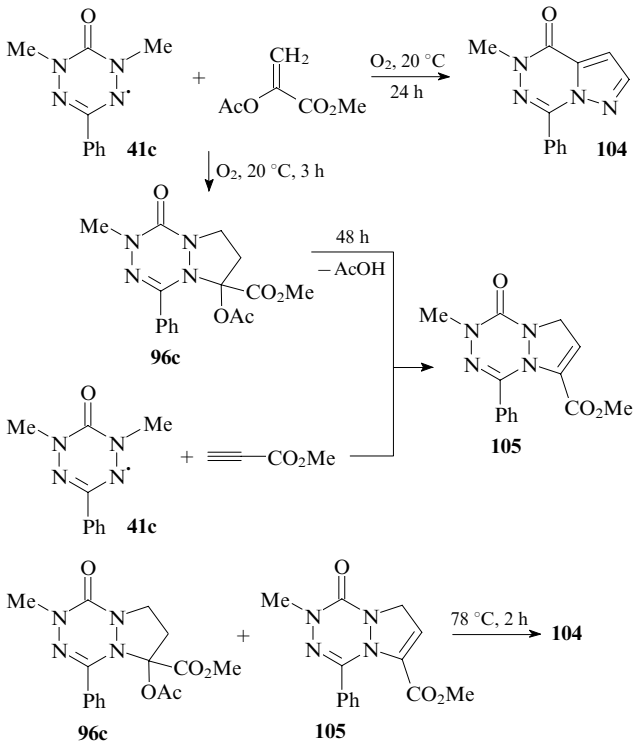


Figure 16. Molecular structure of 5-methyl-7-phenylpyrazolo-[1,5-*d*]-1,2,4-triazin-4(5*H*)-one (**104**).[107]

Scheme 42

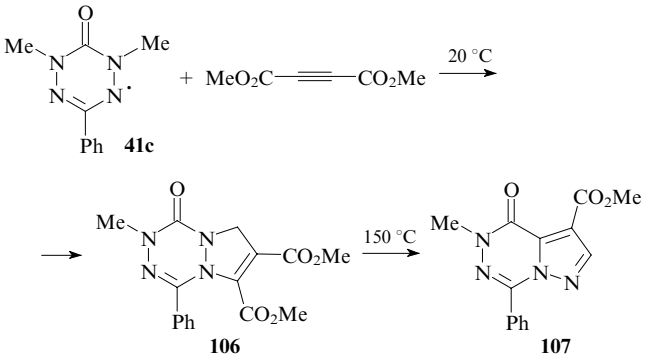


The decrease in the reaction time to 3 h made it possible to isolate the [3 + 2]-dipolar cycloaddition product **96c** in low yield. The cycloadduct turned out to be unstable and spontaneously transformed into compound **105** within two days. Refluxing compounds **96c** and **105** in ethyl acetate for 2 h or adding a NaH excess to a solution of product **96c** in THF at ambient temperature leads to 5-methyl-7-phenylpyrazolo[1,5-*d*]-1,2,4-triazin-4(5*H*)-one (**104**) in, respectively, 89% and 76% yield.[108] The major product of the reaction of 1,5-dimethyl-3-phenyl-6-oxoverdazyl (**41c**) with

methyl propiolate is ester **105**, and triazinone **104** is isolated as a minor product.

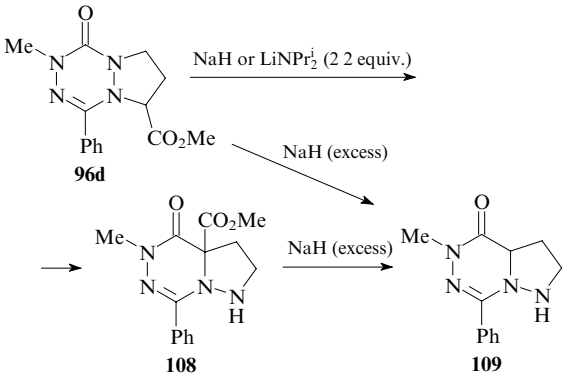
The use of disubstituted alkynes, such as DMAD, extends the possibilities of functionalization of the resulting triazinones. In particular, the reaction of verdazyl **41c** with DMAD yields cycloadduct **106**, and subsequent heating of the latter leads to rearrangement product **107** (Scheme 43).[107]

Scheme 43



To elucidate the mechanism of this rearrangement, additional studies have been carried out. It has been shown that a hydrogenated analogue of methyl ester **105** — compound **96d** — is stable on heating in ethyl acetate; however, treatment with a twofold NaH excess or lithium diisopropylamide leads to its rearrangement into pyrazolo[1,5-*d*]-1,2,4-triazine **108.** Decarboxylation of the latter leads to compound **109** with the free NH group (Scheme 44).[107]

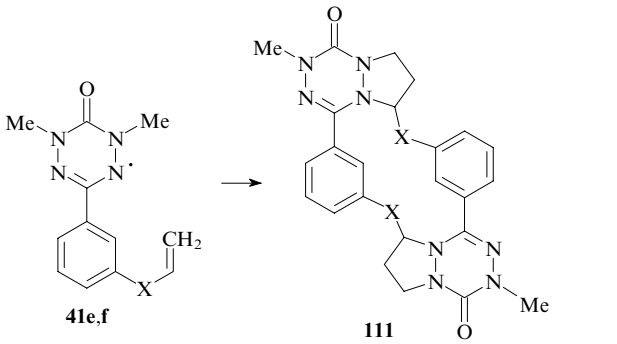
Scheme 44



A mechanism of rearrangement of compound **96d** to product **108** has been proposed, and quantum chemical calculations support the possibility of formation of intermediate **110** (Scheme 45).[107]

The 1,3-dipolar cycloaddition reaction of verdazyl radicals **41e**,**f**, which contain a moiety acting as a dipolarophile, affords cyclophanes **111** (Scheme 46).[109, 110]

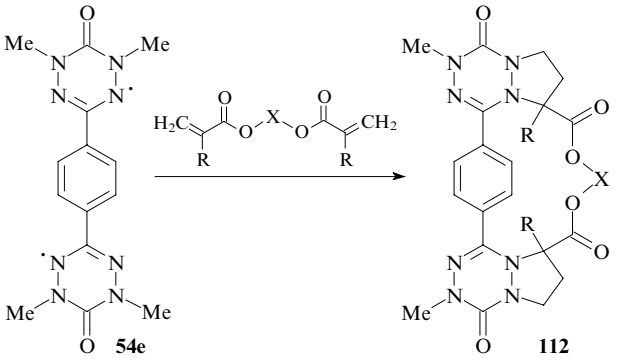
Scheme 46



X = O (**e**), *p*-phenylene (**f**)

Another method of synthesis of paraheterophane derivatives **112**, also based on the [3 + 2] cycloaddition reaction, uses diacrylates as dipolarophiles and bis(verdazyl) **54e** (R = Me, X = O, Y is *p*-phenylene) as a dipole (Scheme 47).[111]

Scheme 47



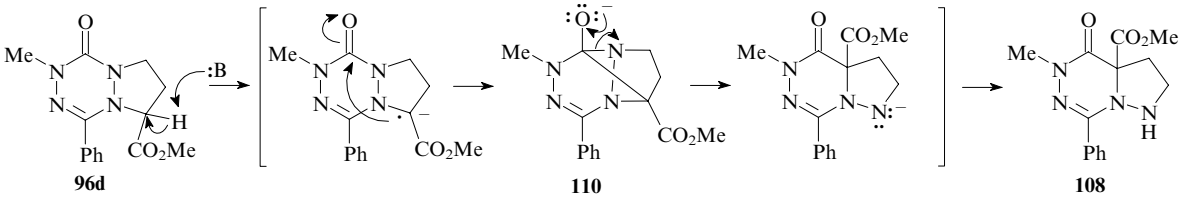
R = H, Me; X = CH_2CH_2, $CH_2CMe_2CH_2$, $CH_2(OCH_2CH_2)_3CH_2$

X-Ray crystallographic study of the resulting macrocyclic compounds enables the conclusion that their structures are symmetric with respect of the mirror plane containing the undistorted benzene ring. Rotation of the benzene ring is affected by the size of the macrocyclic cavity: when the linker is neopentyl glycol diacrylate, there are some signs of twisting of the macrocyclic ring to reduce steric hindrances caused by the presence of two methyl groups in the linker.

V. Metal verdazyl complexes: synthesis and properties

The ability of verdazyl radicals to form metal complexes has attracted the attention of researchers much later than their other properties. First complexes were synthesized by Brook *et al.*[43] in 1997. Since that time, the coordination chemistry of verdazyls has rapidly developed, which is reflected in the appearance of reviews.[2, 5, 7] Rapt attention

Scheme 45



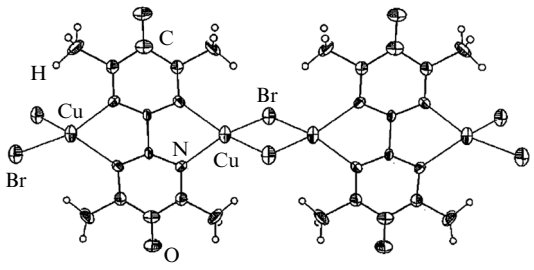
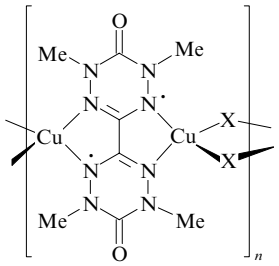


Figure 17. Molecular structure of complex **113a**.[43]

to metal complexes of these stable radicals is caused by the possibility to use them for the design of hybrid magnetic materials.

The reaction of 1,5-dimethyl-6-oxoverdazyl diradical **54b** (R = Me, X = O, Y is absent) with Cu(I) halides yields complexes **113a–c**. Their polymeric structure has been determined by X-ray crystallography The crystal structure of bromide complex **113a** as an example is shown in Fig. 17.[43]

Structure **113**



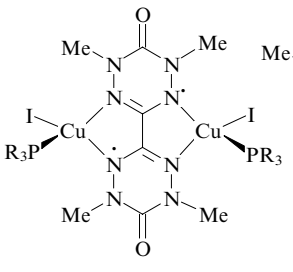
113a–c

X = Br (**a**), Cl (**b**), I (**c**)

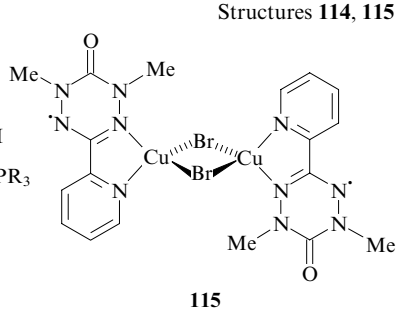
The bis(bidentate) molecule of the diradical is coordinated to two copper atoms, and these moieties are linked by bromide bridges to form chains. The magnetic properties have been studied, and exchange coupling parameters (J) have been determined. The latter point to the existence of strong antiferromagnetic interactions. There is a correlation between J and the halogen nature (X): Cl = Br < I.

For comparison of the magnetic properties, Cu(I) complexes based on the same diradical **54b**, but with binuclear structure **114** rather than with a polymeric structure, have been studied.[112] It has been shown that stronger donor properties of phosphines are responsible for weaker antiferromagnetic interactions in the complex.

Structures **114**, **115**



114

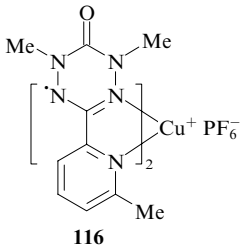


115

Later, bi- and tridentate monoverdazyl radicals have been used for synthesis of complexes. In particular, copper(I) complex **115** with 1,5-dimethyl-6-oxo-3-(2-pyridyl)-verdazyl (**41g**; $R^1 = R^3 = Me$, $R^2 = 2$-Py) has been synthesized.[113] X-Ray crystallography confirms the dimeric structure of the complex, with weak antiferromagnetic exchange coupling of free radicals. It should be noted that the reaction of a precursor of radical **41g** with copper(I) bromide and oxygen leads to the same complex.

The coordination polyhedron of Cu(I) complex **116** on the basis of 1,5-dimethyl-3-(6-methylpyridin-2-yl)-6-oxoverdazyl (**41h**; $R^1 = R^3 = Me$, $R^2 = 6$-Me-2-Py) is a flattened pseudotetrahedron (Fig. 18).[114]

Structure **116**



116

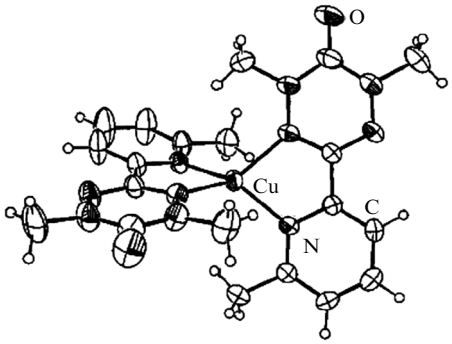


Figure 18. Molecular structure of complex **116**.[114]

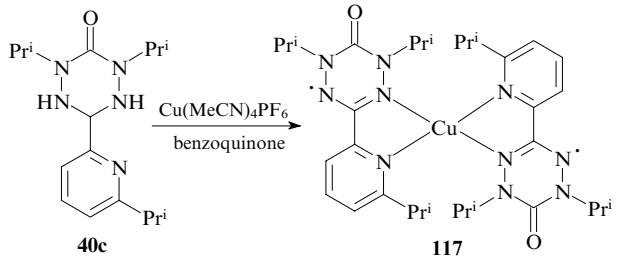
The angle between two coordinated verdazyl ligands is 115.8°. Studying the magnetic properties at different temperatures points to the existence of very weak antiferromagnetic interaction ($J = -2$ cm^{-1}); exchange between the radicals occurs through the diamagnetic Cu(I) centre.

At the same time, quantum chemical calculations (DFT) predict the triplet ground state for structure **116** ($J = +58.6$ cm^{-1}).[115] The inconsistency between the theoretical and experimental data has been explained by strong intermolecular interactions in the crystal structure.

The oxidation of tetrazane **40c** by benzoquinone in the presence of Cu(I) leads to copper(I) complex **117** with 1,5-diisopropyl-3-(6-isopropylpyridin-2-yl)-6-oxoverdazyl ligand [116] (Scheme 48).

The coordination core is a distorted tetrahedron. The angle between the planes of the verdazyl ligands is 75°. The magnetic susceptibility of complex **117** has been measured in the temperature range 5–300 K. It has been shown that the ground state of the diradical at this geometry is a triplet, and ferromagnetic interaction with $J = +47$ cm^{-1} is observed. Geometry control of ground state multiplicity in copper(I) bis(verdazyl) complexes is discussed.

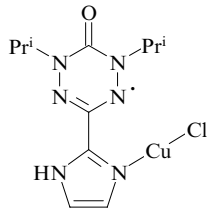
Scheme 48



40c **117**

Recently,[117] copper(I) complex **118** with 3-(imidazol-2-yl)-1,5-dimethyl-6-oxoverdazyl (**41i**; $R^1 = R^3 = Pr^i$, R^2 = 2-Im) has been described (Fig. 19).

Structure **118**



118

It is worth noting that the complex is synthesized from copper(II) chloride and 3-(imidazol-2-yl)-1,5-dimethyl-6-oxo-1,2,4,5-tetrazane — a precursor of radical **41i**. In the course of reaction, the tetrazane is oxidized and Cu(II) is reduced. Although radical **41i** seems to be bidentate, the structure of the complex is not quite common for verdazyls. The copper ion is bonded to a nonbridging chloride ion and the N(1) nitrogen atom of the imidazole ring (see Fig. 19) and has a quasi-linear environment. The N(1)—Cu(1)—Cl(21) angle changes from 175.37(8) to 174.5(1)° with a change in temperature from 120 to 320 K. The absence of the Cu(1)—N(14) bond indicates that the ligand is monodentate. The existence of H···O and H···Cl hydrogen bonds in crystals leads to formation of chains of pseudodimers of imidazole moieties. Inside the stacks, the complexes are arranged in a head-to-tail fashion, and the verdazyl moieties are positioned face to face, which is responsible for strong exchange coupling. The *J* values are high. Temperature dependence of this constant has been determined.[117]

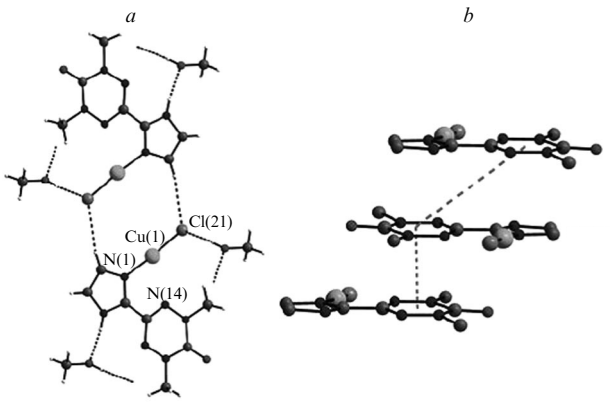
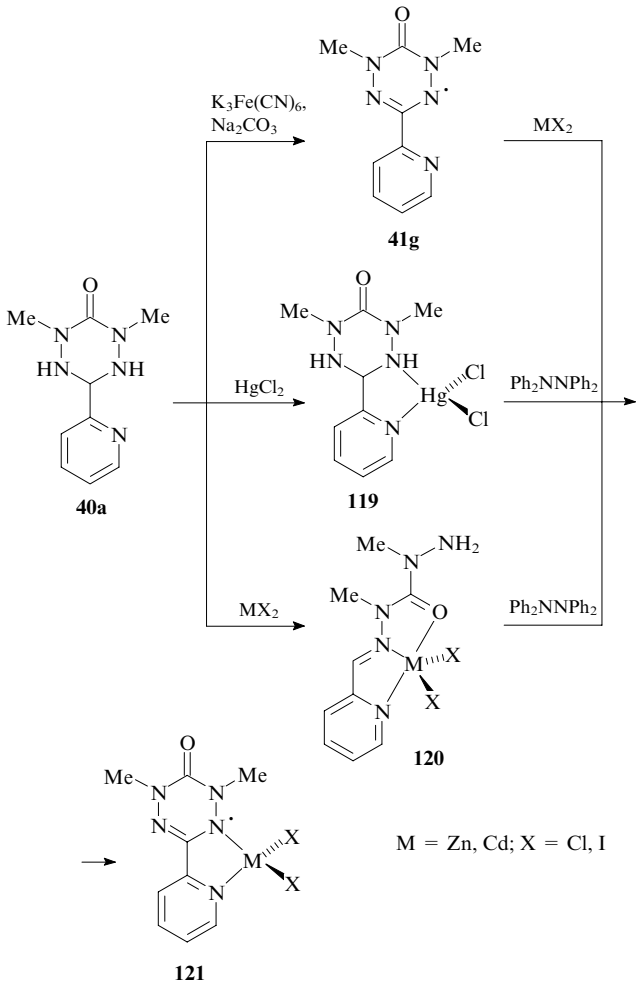


Figure 19. Molecular structure (*a*) and a fragment of the crystal packing of complex **118**·MeOH (*b*).[117]

Complexes of 1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl (**41g**; $R^1 = R^3$ = Me, R^2 = 2-Py) and its precursor **40a** with halides of diamagnetic metals, such as Zn(II), Gd(II) and Hg(II), have been synthesized.[118] The reaction of ligand **40a** with Hg(II) chloride leads to complex **119** with a distorted trigonal planar geometry of the coordination core (Scheme 49).

Scheme 49

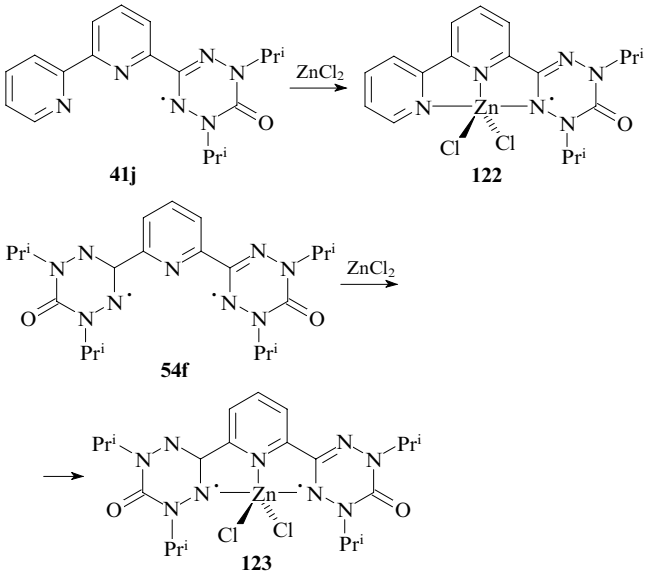


41g **40a** **119** **120** **121**

In the reaction of precursor **40a** with cadmium(II) iodide or zinc(II) iodide, the tetrazine ring is opened to form pentacoordinated complexes **120** with a hydrazone ligand. The structures of all three complexes have been confirmed by X-ray crystallography. The oxidation of these complexes by tetraphenylhydrazine gives metal complexes **121** with the corresponding verdazyl. Complexes **121** can be obtained by the direct reaction of radical **41g** with metal halides. The formation of verdazyl-containing complexes **121** in all cases has been proved by EPR and UV spectra; however, these compounds have not been isolated and characterized.

The reaction of zinc(II) chloride with 2,2′-bipyridine-substituted verdazyl **41j** ($R^1 = R^3 = Pr^i$, R^2 = 2,2′-bipyridin-6-yl) and 2,6-pyridine-linked diradical **54f** (R = Pr^i, X = O, Y is pyridine-2,6-diyl) leads to trigonal pyramidal complexes **122** and **123** (Scheme 50).

Scheme 50



In these complexes, the Zn–N bond to verdazyl is longer than the bonds to pyridine (Fig. 20).[119]

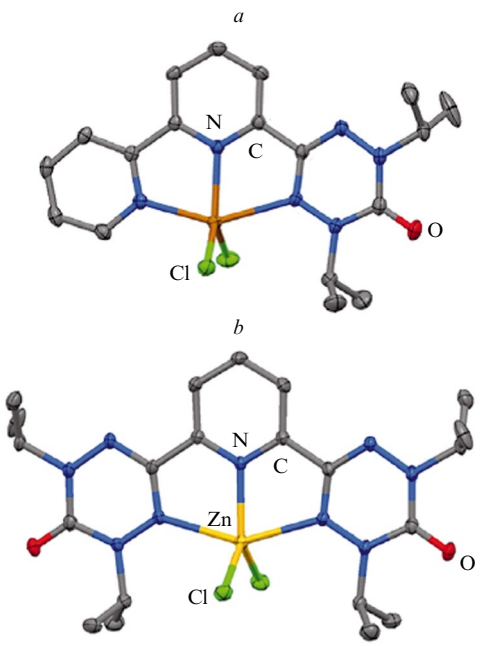
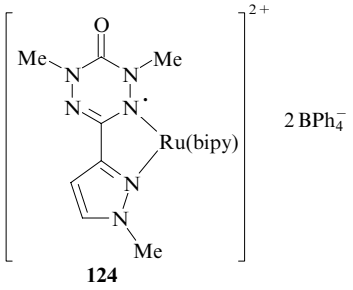


Figure 20. Molecular structures of complexes **122** (*a*) and **123** (*b*).[119]

Studying the UV and EPR spectra and magnetic susceptibility suggests minimal perturbation of the verdazyl chromophore in the complexes, but the redox properties considerably differ from those of the free ligands.

1,5-Dimethyl-3-(1-methylpyrazol-3-yl)-6-oxoverdazyl (**41k**; $R^1 = R^3 = Me$, R^2 is 1-methylpyrazol-3-yl), synthesized by Wu *et al.*,[120] reacts with *cis*-[Ru-(bipy)$_2$Cl$_2$] (bipy is 2,2′-bipyridine) and NaBPh$_4$ to form complex **124** with the diamagnetic ion Ru(bipy)$_2^{2+}$.

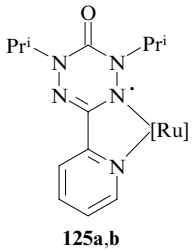
Structure **124**



The absence of luminescence and the electrochemical behaviour of this complex are explained by that the lowest triplet excited state is localized on the verdazyl ligand. Data on the magnetic properties of this complex are not reported.

The reaction of 1,5-diisopropyl-6-oxo-3-(2-pyridyl)verdazyl (**40l**; $R^1 = R^3 = Pr^i$, R^2 = 2-Py) with ruthenium acetylacetonate (acac) or hexafluoroacetylacetonate (hfac) affords complexes **125a**,**b**.[121]

Structure **125**



[Ru] = Ru(acac)$_2$ (**a**), Ru(hfac)$_2$ (**b**)

According to X-ray crystallography evidence, these complexes have similar structures (Fig. 21 shows the structure of complex **125a** as an example). Considerable difference in EPR spectra and electrochemical properties of complexes **125a**,**b** shows that charge delocalization is very sensitive to the nature of the ancillary β-diketonate ligand.

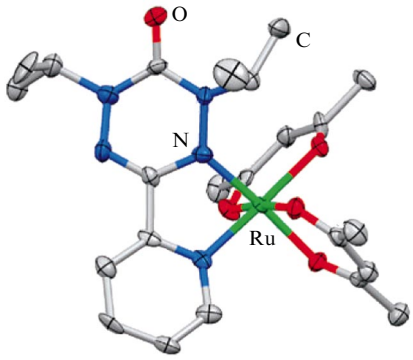
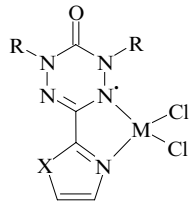


Figure 21. Molecular structure of complex **125a**.[121]

The same research team[122] has continued studying the electronic structure of **125a**,**b** and their charged species. Cationic complexes were synthesized by the oxidation of the neutral compound with a silver salt and an anionic complex, by the reduction of neutral complex **125b** with cobaltocene. Experimental and theoretical studies reveal a strong effect of the nature of the ancillary ligand on the properties of the complexes.

Palladium(II) and platinum(II) complexes **126a–c** with 3-hetaryl-substituted 6-oxoverdazyls have been described.[123]

Structure **126**



126a–c

R = Me, X = CH=CH (**a**); R = Pr^{i}: X = CH=CH (**b**), NMe (**c**); M = Pd^{II}, Pt^{II}

In all such complexes, the metal environment is planar (X-ray crystallographic data for complex **126a** are shown in Fig. 22). In the solid state, the complexes assemble into different kinds of π-stacked architectures. Variable temperature magnetic susceptibility studies reveal relatively weak magnetic interactions which can be correlated with the mode of stacking.

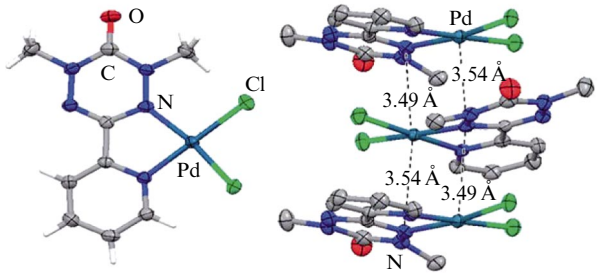
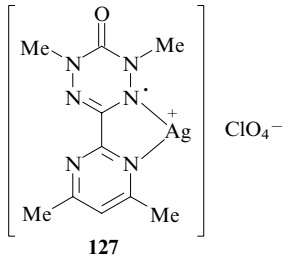


Figure 22. Molecular structure of palladium complex **126a**.[123]

The reaction of 1,5-dimethyl-3-(4,6-dimethylpyrimidin-2-yl)-6-oxoverdazyl (**41b**; $R^1 = R^2 = Me$, $R^3 = 4,6\text{-}Me_2\text{-}2\text{-}Prm$; Prm is pyrimidine) with silver(I) perchlorate affords complex **127**, in which two nitrogen atoms are coordinated to the silver ion.[124]

Structure **127**



127

X-Ray crystallography (Fig. 23) shows that complex **127** is built of cationic chains of silver ions bridged by bidentate ligands. The complex is characterized by intrachain antiferromagnetic exchange interaction ($J = -7.5$ cm^{-1}) between two radicals through the diamagnetic silver ion.

In all above metal complexes of verdazyls, metal centres are diamagnetic, and this rules out metal–verdazyl exchange interactions. With the aim of creating magnetic materials with such interactions, studies of the synthesis and properties of verdazyl complexes with paramagnetic transition metals have been initiated. In particular, Hicks *et al.*[125] have synthesized Mn(II) (**128a**) and Ni(II) (**128b**) complexes with 1,5-dimethyl-6-oxo-3-(2-pyridyl)verdazyl (**41g**).

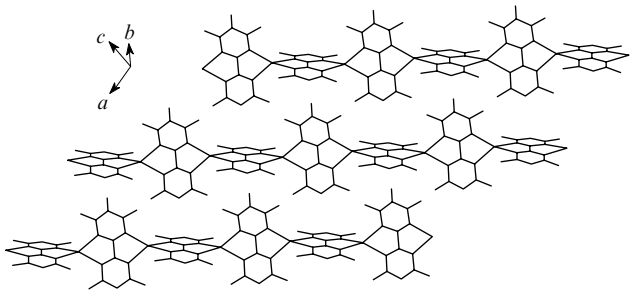
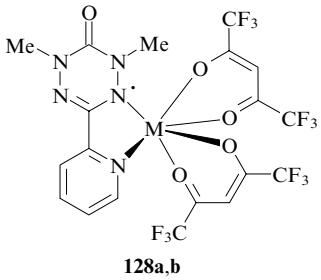


Figure 23. Crystal packing of complex **127**.[124]

Structure **128**



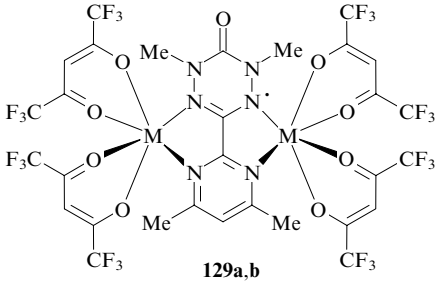
128a,b

M = Mn (**a**), Ni (**b**)

X-Ray crystallography confirms a mononuclear pseudooctahedral structure of these complexes. They have different magnetic behaviour: very strong ferromagnetic exchange coupling is observed for the nickel complexes ($J \geqslant +240$ cm^{-1}) and weaker antiferromagnetic exchange coupling, for the manganese complex ($J = -45$ cm^{-1}).

The same researchers[126] have studied the magnetic properties of novel bimetallic Mn(II) and Ni(II) complexes **129a,b** based on bis(bidentate) pyrimidine-containing verdazyl **41b** (Fig. 24).

Structure **129**



129a,b

M = Mn (**a**), Ni (**b**)

The structure and magnetic behaviour of these compounds are similar to those for mononuclear complexes **128a,b**: the same differences depending on the metal nature and close J values are observed.

With the use of tridentate 3-(2,2′-bipyridin-6-yl)-1,5-dimethyl-6-oxoverdazyl (**41m**; $R^1 = R^3 = Me$, $R^2 = 2,2'$-bipyridin-6-yl) is a kind of analogue of terpyridine, metal complexes **130a–d** of general formula $[M(\mathbf{41m})_2]X_2$, where

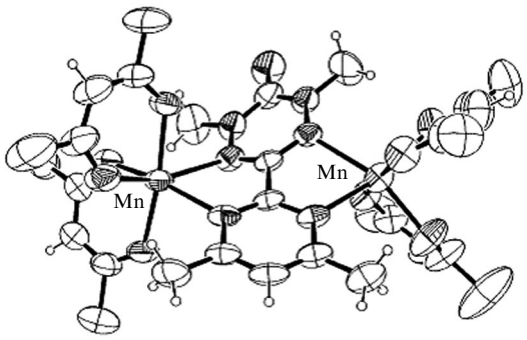
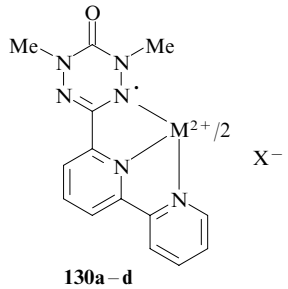


Figure 24. Molecular structure of complex **129a**.[126]

M(II) = Mn, Ni, Cu, Zn; X = PF_6, ClO_4, have been synthesized and structurally characterized.[38,127]

Structure **130**



130a–d

M = Mn (**a**), Ni (**b**), Cu (**c**), Zn (**d**)

In all cases, the two verdazyl ligands are arranged almost perpendicular to each other in meridional positions, yielding pseudooctahedral metal complexes. The structure of nickel complex **130b** is shown in Fig. 25. The intramolecular metal–verdazyl magnetic exchange coupling in the complexes of tridentate ligand **41m** depends on the metal nature. The intramolecular metal–verdazyl magnetic exchange coupling is strongly ferromagnetic in nickel complex **130b** ($J > +240$ cm^{-1}), and strongly antiferromagnetic in manganese complex **130a** ($J = -93$ cm^{-1}). Copper complex **130c** exhibits weak antiferromagnetic exchange coupling ($J = -4.5$ cm^{-1}). Intramolecular radical–radical exchange is rather weak in the four complexes.

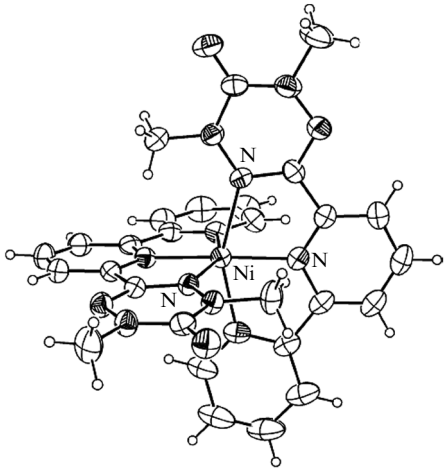


Figure 25. Molecular structure of complex **130b**.[127]

The first summary of the results of studying the structure and magnetic properties of Ni(II) and Mn(II) complexes of verdazyl radicals has been made by Hicks,[128] and later new information on such complexes has appeared. The reaction of recently synthesized 3-(imidazol-2-yl)-1,5-dimethyl-6-oxoverdazyl (**41i**) with Mn(hfac)$_2$ and Ni(hfac)$_2$ affords mononuclear manganese (**131a**) and nickel (**131b**) complexes.[129] According to X-ray crystallography, complexes **131a**,**b** are isostructural. The metal ion is coordinated to the four oxygen atoms of the hfac ligand and two nitrogen atoms of verdazyl **41i**, forming a distorted octahedral structure (Fig. 26). In crystals, the initial radical and its complexes exhibit imidazole–oxoverdazyl π-stacking. Experimental and theoretical study of magnetic properties reveals that radical **41i** behaves as an antiferromagnet with $J = -100$ cm^{-1}, the behaviour of complexes **131a**,**b** is interpreted as metal–radical intramolecular interaction ($J_{Mn} = -62.5$ cm^{-1} and $J_{Ni} = -193$ cm^{-1}), and there is antiferromagnetic intermolecular interaction ($J_{Mn} = -12.6$ cm^{-1} and $J_{Ni} = -4.3$ cm^{-1}) related to imidazole–oxoverdazyl π-stacking.

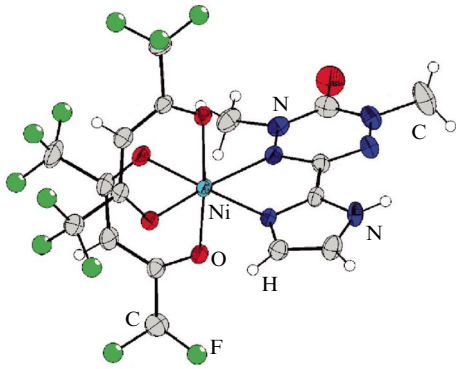


Figure 26. Molecular structure of complex **131b**.[129]

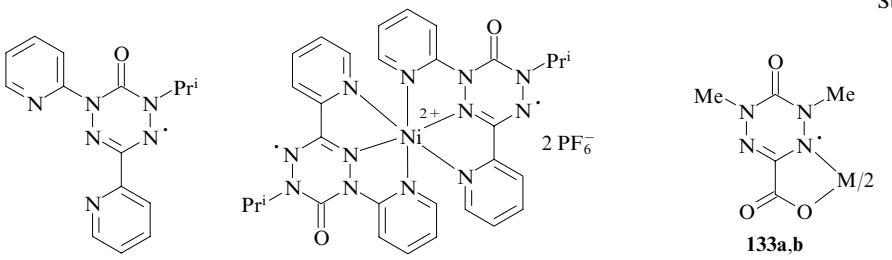
Inspecting the magnetic behaviour of Mn(II) and Ni(II) complexes with different oxoverdazyl radicals, Rota *et al.*[130] have noted that the character and magnitude of intramolecular interactions in the complexes are sensitive to the nature of both the metal and radical. Different quantum chemical computations suggest the duality of 6-oxoverdazyl **41i** in transition metal complexes: this radical acts as a π* donor, which allows ligand-to-metal charge transfer, and as a magnetic partner.[130]

5-Isopropyl-6-oxo-1,3-di(2-pyridyl)verdazyl (**41n**; $R^1 = Pr^i$, $R^2 = R^3 = 2$-Py), synthesized from the corresponding dipyridyl hydrazone, reacts with Ni(II) triflate to give complex **132**.[131]

The complex has a pseudooctahedral NiN_6 coordination core (Fig. 27), in which the Ni–verdazyl bonds (1.98 Å) are shorter than in complexes with other radicals. The complex exhibits strong Ni–radical ($J = +300$ cm^{-1}) and radical–radical ($J = +160$ cm^{-1}) ferromagnetic exchange coupling.

An interesting complexing agent is 3-carboxyl-1,5-dimethyl-6-oxoverdazyl (**41o**; $R^1 = R^3 = Me$, $R^2 = CO_2H$). Its deprotonated form is readily soluble in water, which enables the synthesis of complexes in an aqueous medium, including synthesis under hydrothermal conditions. It is essential that not radical **41o** but rather its precursor — the corresponding tetrazane — is introduced into the

Structures **41n**, **132**, **133**



41n **132** **133a**,**b**

M = Ni (**a**), Co (**b**)

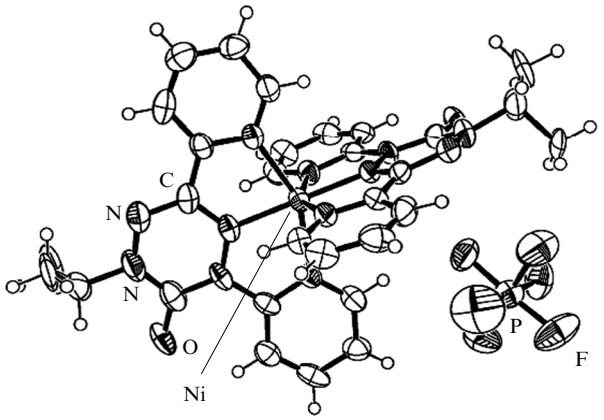


Figure 27. Molecular structure of complex **132**.[131]

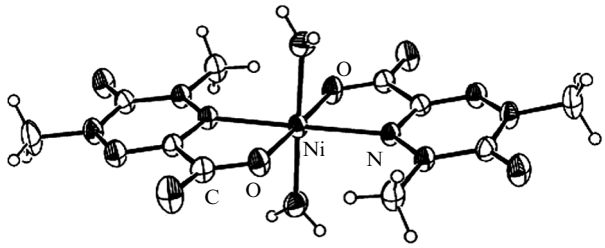


Figure 28. Molecular structure of complex **133a**.[35]

reaction with Ni(II) and Co(II) chlorides or perchlorates in an aqueous alkaline medium.[35] Keeping this reaction mixture for several days at room temperature in the presence of air oxygen leads to formation of complexes **133a**,**b** containing radical **41o**.

The metal ions in both complexes have a pseudooctahedral environment comprising two N,O-chelating verdazyl radicals in the *anti* conformation in the equatorial plane and two *trans*-aqua ligands in the axial positions (Fig. 28). Study of magnetic properties demonstrates that nickel complex **133a** exhibits strong metal – radical exchange ($J = +94$ cm^{-1}). For cobalt complex **133b**, preliminary data point to ferromagnetic cobalt – radical exchange coupling ($J = +34$ cm^{-1}); however, further study is required.

The synthesis of Co(II) complex with 1,5-dimethyl-6-oxo-3-[4,6-bis(2-pyridyl)pyrimidin-2-yl]verdazyl [**41p**; $R^1 = R^3 = Me$, $R^2 = 4,6$-(2-Py)-2-Prm] has been reported.[132] The attempt to obtain a complex directly from **41p** failed because of the insufficient stability of the latter. On the contrary, the reaction of the corresponding tetrazane **40d** with cobalt chloride in methanol saturated with oxygen for 15 h affords complex **134**, in which the radical acts as a tridentate ligand for one metal ion (Scheme 51).

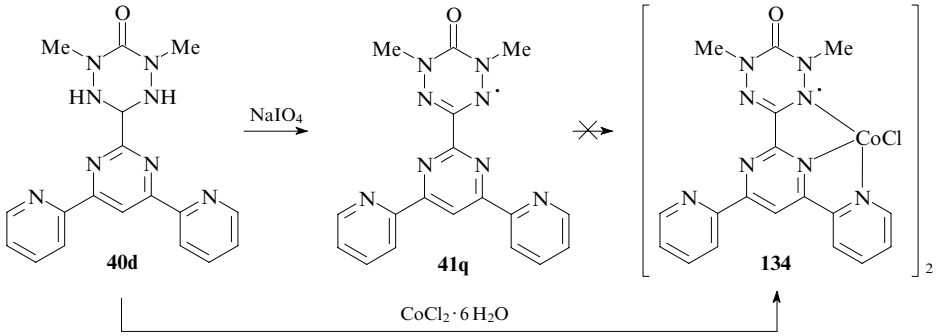
The second tridentate position of the radical remains vacant. In crystal, the complex is a dimer in which the cobalt ions are linked through chloride bridges (Fig. 29).

The Co_2Cl_2 core is asymmetric and has two short and two long Co – Cl bonds. The structure shows relatively short intermolecular contacts between the coordinated verdazyl radicals ($d_1 - d_3$, see Fig. 29). Magnetic susceptibility measurements in the range 2 – 300 K attest to intramolecular ferromagnetic Co – radical exchange coupling ($J = +20$ cm^{-1}).

Magnetostructural studies of Cu(II) complexes with 3-hetaryl-substituted 6-oxoverdazyls **41g**,**l**,**q** [$R^1 = R^3 = Me$, $R^2 = 2$-Py (**g**); $R^1 = R^3 = Pr^i$: $R^2 = 2$-Py (**l**), *N*-methylimidazol-2-yl (**q**)] have been reported[60]. The complexes are synthesized by the reaction of verdazyls with $CuCl_2$ (compounds **135a**,**c**) or Cu(hfac)$_2$ (**135b**,**d**).

According to X-ray crystallographic data, the copper ion in complexes **135a**,**c** has a pseudosquare-pyramidal environment, with the verdazyl ligands in the equatorial positions (Fig. 30). The copper ions in complexes **135b**,**d** have an octahedral environment, with the coordinated

Scheme 51



40d **41q** **134**

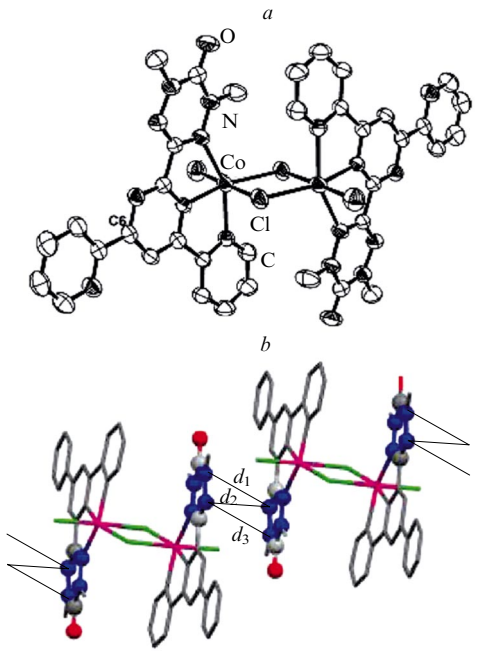


Figure 29. Molecular structure (*a*) and crystal packing of complex **134** (*b*).[132]

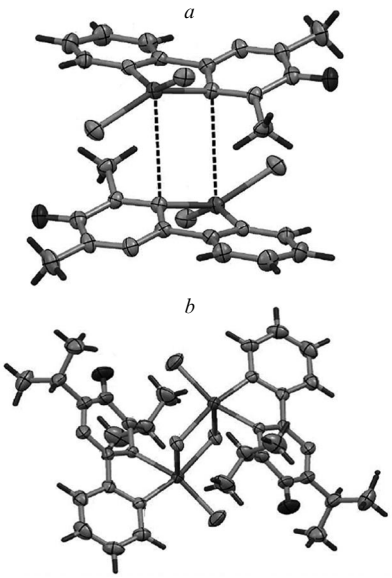


Figure 30. Molecular structures of complexes **135a** (*a*) and **135c** (*b*).[60]

verdazyl N atoms in the axial positions (Fig. 31). Analysis of the magnetic behaviour of complexes **135a**–**d** reveals a correlation with the structure: the radicals in the equatorial positions are characterized by strong antiferromagnetic exchange coupling and axially bound radicals, by weak ferromagnetic exchange coupling.

The synthesis, structure and magnetic properties of the first copper(II) complex containing 1,5-dimethyl-3-(pyridin-2-yl)-6-thioxoverdazyl, with hexafluoroacetylacetonate as an ancillary ligand, have been described (structure **136**).[133]

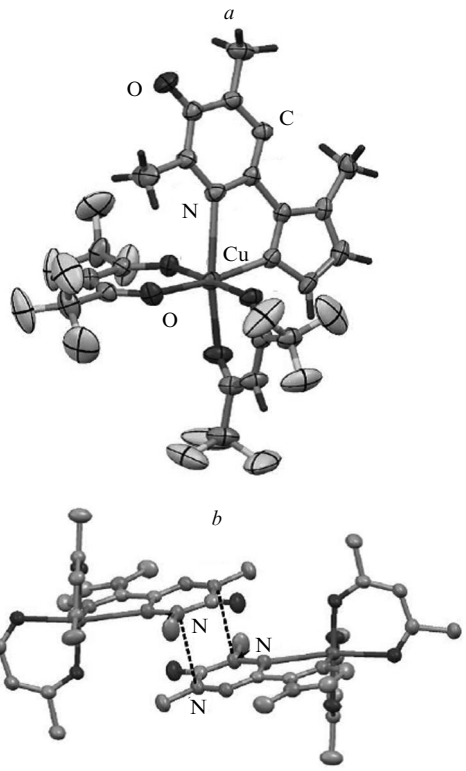
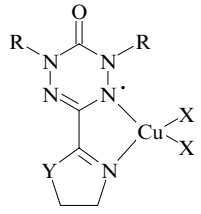
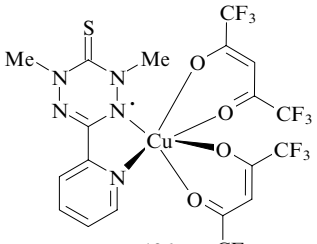


Figure 31. Molecular structure (*a*) and crystal packing of complex **135d** (*b*).[60]

Structures **135**, **136**



135



136

R = Me, Y = CH=CH:
X = Cl (**a**), 2 X = hfac (**b**);
R = Pr^i; Y = CH=CH,
X = Cl (**c**); Y = NMe, 2 X = hfac (**d**)

X-ray crystallography reveals that the CuN_2O_4 coordination core is a prolate octahedron, and the radical acts as a bidentate ligand. Experimental and theoretical studies of the magnetic behaviour point to ferromagnetic intramolecular metal–radical exchange coupling and antiferromagnetic exchange coupling due to stacking in the crystal. Analysis of the magnetic properties of complex **136** and analogous complexes with oxoverdazyls shows that the substituent at the 3-position has a stronger effect on exchange interactions than the heteroatom in the 6-position.

An oxoverdazyl radical has been attached to one of the β positions of the metalloporphyrin ring (compounds **137a**,**b**) in order to obtain a hybrid spin system in which the paramagnetic ligand bound to the paramagnetic metal is a mediator of ferromagnetic exchange between neighbouring centres.[134]

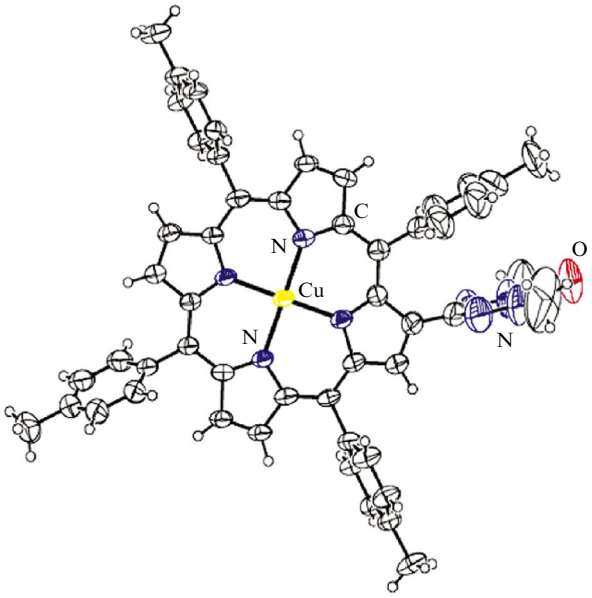
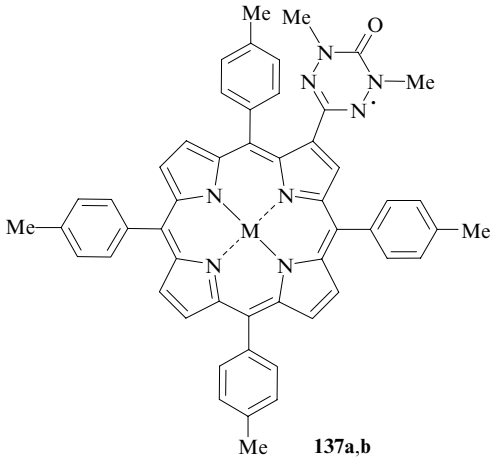


Figure 32. Molecular structure of complex **137a**.[134]

The X-ray crystal structure of complex Cu(II) **137a** shows that the plane of the verdazyl moiety is oriented such that it is nearly perpendicular to the plane of the porphyrin ring (Fig. 32). As expected for such a structure, the metal and radical are weakly antiferromagnetically coupled.

Structure **137**



137a,b

M = Cu (**a**), VO (**b**)

First lanthanide complexes of verdazyls have been synthesized. In particular, the reaction of 3-(imidazol-2-yl)-1,5-dimethyl-6-oxoverdazyl [**41i**; $R^1 = R^3 = Me$, R^2 = 2-Im] with $Ln(hfac)_3$ yields complexes **138a–c** [Ln = Gd (**a**), Tb (**b**), Dy (**c**)].[135]

All complexes are isomorphous. The structures contain one-dimensional chains in which the verdazyl ligand bridges two lanthanide ions. The molecular structure of Dy(III) complex **138c** is shown in Fig. 33. The metal ion is surrounded by six oxygen atoms of the hfac ligands, the nitrogen atom of the imidazole moiety of the radical and the oxygen atom of the second radical. The coordination polyhedron is asymmetric and can be described as a distorted dodecahedron. Magnetic properties of these complexes have been studied, and exchange coupling parameters have been determined.

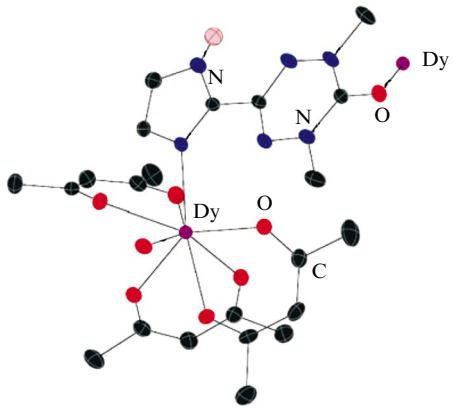
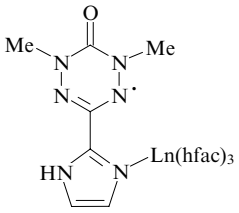


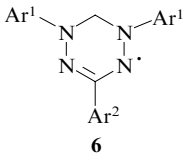
Figure 33. Molecular structure of complex **138c**.[135] The H and F atoms are omitted.

Structures **6**, **138**



138a–c

Ln = Gd (**a**), Tb (**b**), Dy (**c**)



6

Ar^1 = 4-Py, 3-Py, 4-PyC_6H_4;
Ar^2 = Ph, 4-Py, 3-Py

It should be noted that, in complexes **18**, **137** and **138**, the verdazyl ring over which the unpaired electron is distributed is not directly bound to the metal.

Another group of complexes based on verdazyl radicals includes compounds in which the donor centres for binding to the metal are specially distant from the tetrazinyl ring. In such complexes, aryl(pyridyl)- or tri(pyridyl)verdazyls of general formula **6** have been used as ligands.[136]

In particular, stirring a mixture of 4 equiv. of 1,3,5-tris(4-pyridyl)verdazyl (L, **6d**) and 6 equiv. of [Pd(bipy)$(NO_3)_2$] (M, **140**) in water at room temperature leads to self-assembly of the Pd(II) complex of composition M_6L_4

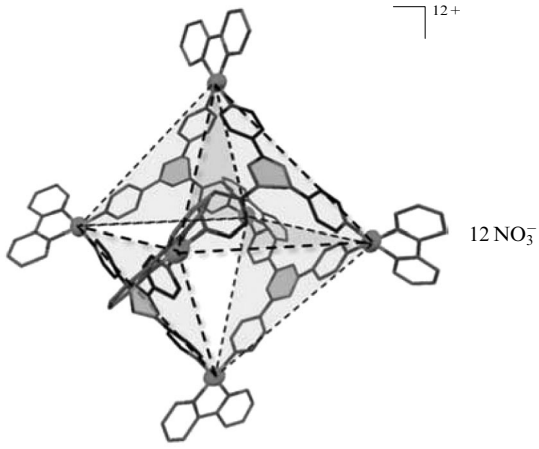
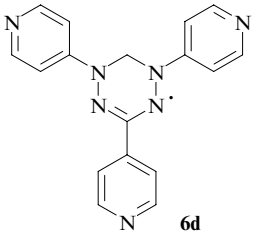


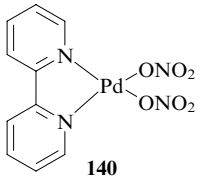
Figure 34. Crystal structure of complex **139**.[137]

(**139**) (Fig. 34).[137] The ligand in this case is a building block for formation of a cage ion with four spin centres. The hexanuclear structure of complex **139** has been determined by X-ray single crystal diffraction.

Structures **6d**, **140**



6d



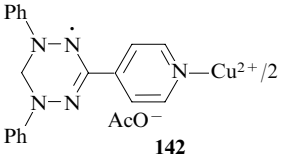
140

Yet another example of self-assembly of Pd(II) complex **141** with the use of 1,3,5-tris(4-pyridyl)verdazyl (**6d**) has been described[138] (Scheme 52).

X-Ray crystallography shows that complex **141** consists of two parallel radical moieties aligned in a face-to-face fashion and linked by palladium atoms and pyrazine molecules, with inclusion of triphenylene as a 'guest'. The EPR spectra of this complex show radical–radical coupling. Encapsulation of planar copper(II) complexes into the 'spin cage' makes it possible to observe through-space spin–spin interactions.

On the basis of 3-(4-pyridyl)-1,5-diphenylverdazyl (**6b**; Ar^1 = Ph, Ar^2 = 4-Py), binuclear Cu(II) complex **142** has been synthesized and structurally characterized (Fig. 35).[139]

Structure **142**



142

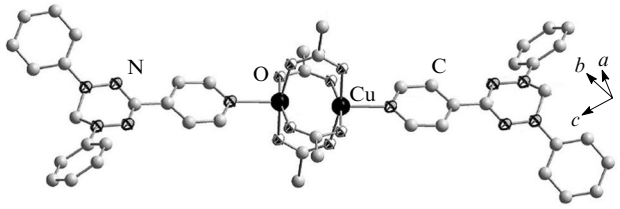


Figure 35. Molecular structure of complex **142**.[139]

The magnetic properties of this complex have been studied in a wide temperature range. It has been shown that the radicals in the crystal structure are antiferromagnetically coupled. Exchange interactions between Cu(II) and the radical are weak as compared with strong intramolecular antiferromagnetic Cu···Cu interactions.

VI. Some areas of application of verdazyls

The use of verdazyls in various fields of chemistry, physics, biology, electronics and spintronics has been addressed rather well in monographs.[2, 4, 5, 8] In this review, we present a summary of the main application areas.

Verdazyl radicals are widely used in polymer chemistry. They are efficient inhibitors of polymerization of styrene, methyl methacrylate, acrylonitrile, vinyl chloride and other important monomers.[140, 141] It has been shown by the example of radical polymerization of oligo(urethane acrylate) that verdazyls have an inhibitory effect and can be used for visual control and as paramagnetic probes.[142]

The preparation of spin-labeled styrene–divinylbenzene copolymers has been described.[143] Approaches to controlled polymerization of styrene and acrylates with the use of 6-oxoverdazyl radicals have been developed.[104, 144, 145]

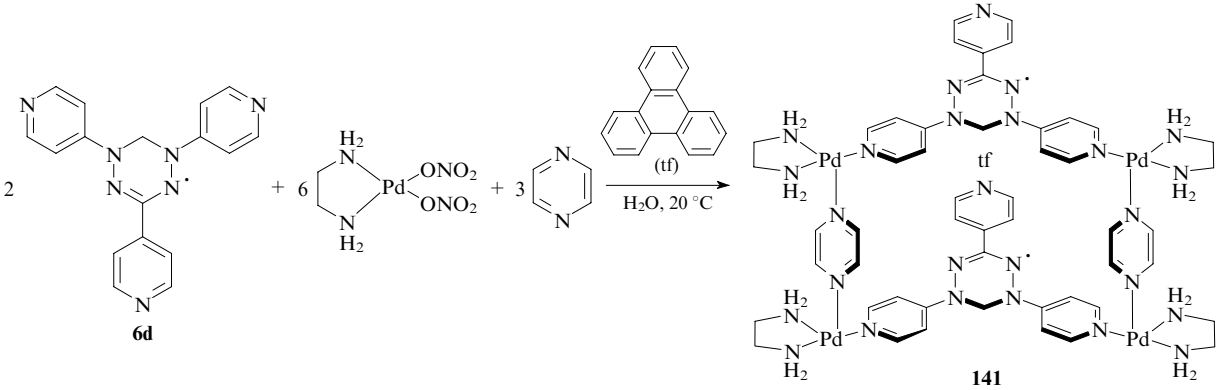
The Kuhn verdazyls are used as internal indicators for determining the rate of heterolysis of organic compounds. This method is based on the fact that verdazyls rapidly and quantitatively react with reaction products or with a cationoid intermediate, which makes it possible to monitor the reaction rate based on the consumption of verdazyl and/or its salt. The reaction is easily monitored spectrophotometrically.[146–154]

The use of verdazyls as active electrode materials (electrolyte) in solar cells have been described in a number of patents.[155–157] Since verdazyls are electrochromic dyes, various verdazyl radicals have been used as elements of electroluminescent displays.[158]

Polymers containing verdazyl moieties are active components of organic magnets for various purposes.[159] The ability of verdazyls to form covalent bonds with functional groups of proteins makes it possible to obtain spin-labelled molecules and extends the application of stable radicals in biological and medical studies.[160]

A promising application of verdazyls for creation of magnetic semiconductors has been developed by Mukai *et al.*[161–164] They have synthesized salts **143**, composed of the verdazylium cation and the $Ni(dt)_2$ anionic complex (dt = 1,3-dithiol-2-thione-4,5-dithiolate).

Scheme 52



6d **141**

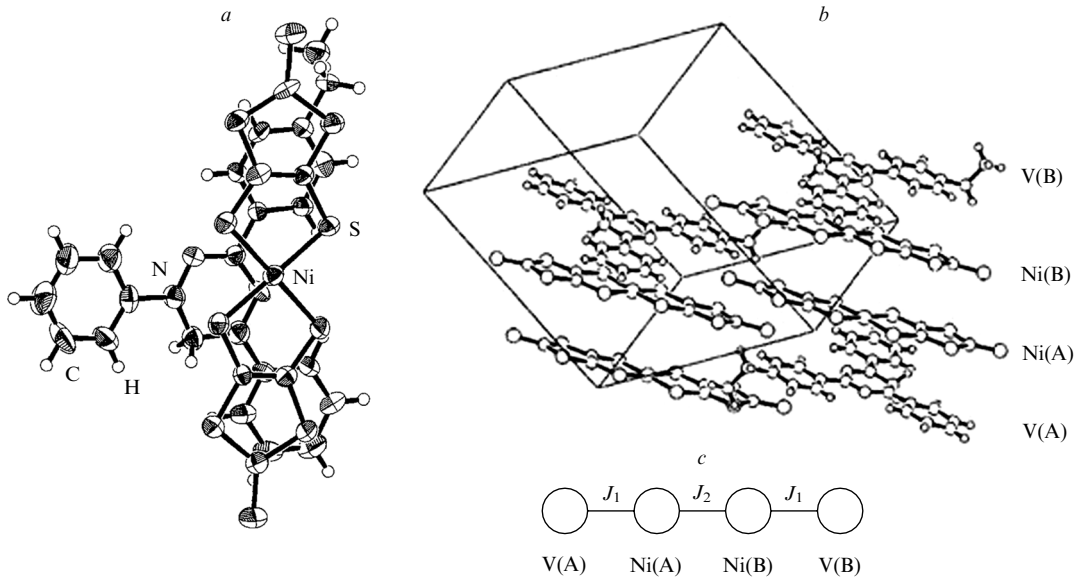
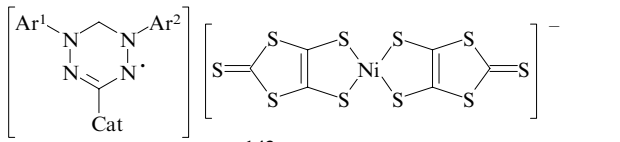
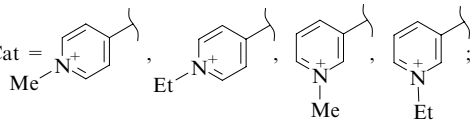


Figure 36. Molecular structure (*a*), crystal packing (*b*) and magnetic parameters of salt **143a** (*c*).[163]
V is verdazyl.

Structure **143**



143

$Ar^1 = Ar^2$ = Ph: Cat = 

Cat = 4-$Me_3N^+C_6H_4$: $Ar^1 = Ar^2$ = 4-MeC_6H_4;
Ar^1 = Ph, Ar^2 = 4-MeC_6H_4

The crystal structure of salt **143a** ($Ar^1 = Ar^2$ = Ph, Cat is *N*-ethylpyridinium) contains dimers of anionic complexes located between two verdazyl cations. In such a manner, magnetic linear tetramers of sandwich type are formed (Fig. 36). The magnetic properties of such a salt have been studied, and the exchange coupling constants J_1 and J_2 have been determined. The conductivity of the salts has been measured, and it has been demonstrated that they are molecular paramagnetic semiconductors.

VII. Conclusions

The above analysis of literature data shows that, in spite of intensive recent studies of verdazyls, the chemistry of these compounds is far from being exhausted. The present review mainly focuses on two types of verdazyls (**I** and **II**) differing by the substituent at the 6-position and presents the developed approaches to their synthesis. A large number of such compounds have been described, and their structures and properties have been studied. Comparison of verdazyls of different types reveals the similarity in the properties caused by the existence of the unpaired electron delocalized over the four nitrogen atoms. At the same time, verdazyls **I** and **II** differ in methods of synthesis and reactivity (see disproportionation and complexation reactions).

The most promising directions of development of this field of chemistry are related to the use of verdazyls as substrates for synthesis of new nitrogen-containing heterocycles and building blocks for design of organic magnets, paramagnetic probes, magnetic semiconductors and active materials in solar cells. An advantage of verdazyl radicals is, first of all, their stability, which is a key difficulty when operating with species containing an unpaired electron. Their synthetic availability and a variety of types of bonds — from strong covalent to weak intermolecular — are also attractive. In addition, verdazyl heteroatoms are capable of binding metal ions and forming coordination compounds characterized by strong radical – metal exchange coupling. The nature of substituents in a verdazyl radical has a significant effect on its complexation ability, intra- and intermolecular interactions and molecule packing in the solid state and, hence, the magnetic properties of verdazyl-based materials. Verdazyl complexes of paramagnetic lanthanide and transition d-metal ions are believed to be promising.

It is worth noting that verdazyls are also attractive for studying the kinetics and mechanisms of different reactions.

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References

1. R Kuhn, H Trischmann *Monatsh. Chem.* **95** 457 (1964)
2. C Train, L Norel, M Baumgarten *Coord. Chem. Rev.* **253** 2342 (2009)
3. O A Rakitin *Russ. Chem. Rev.* **80** 647 (2011)

4. R G Hicks, in *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds* (Ed. R G Hicks) (Bognor Regis: Wiley, 2010) p. 246
5. B D Koivisto, R G Hicks *Coord. Chem. Rev.* **249** 2612 (2005)
6. B Pilawa *Ann. Phys.* **8** 191 (1999)
7. M T Lemaire *Pure Appl. Chem.* **76** 277 (2004)
8. O M Polumbrik *Khimiya Verdazil'nykh Radikalov* (The Chemistry of Verdazyl Radicals) (Kiev: Naukova Dumka, 1984)
9. A R Katritzky, S A Belyakov, H D Durst, R Xu, N Dalal *Can. J. Chem.* **72** 1849 (1994)
10. L Parkanyi, C Kertesz, A J Mayr, M P Eastman *J. Mol. Struct.* **447** 141 (1998)
11. K Mukai, M Matsubara, H Hisatou, Y Hosokoshi, K Inoue, N Azuma *J. Phys. Chem. B* **106** 8632 (2002)
12. M Hmyene, H Naarmann, H Winter, B Pilawa, E Dormann *J. Phys.: Condens. Matter* **6** L511 (1994)
13. A R Katritzky, S A Belyakov *Synthesis* 17 (1997)
14. I A Bezvershenko, V Kh Premyslov *Khim. Geterotsikl. Soedin.* 1129 (1985) [a]
15. P-M Allemand, G Srdanov, F Wudl *Synth. Met.* **41 – 43** 3245 (1991)
16. M Mito, K Takeda, K Mukai, N Azuma, M R Gleiter, C Krieger, F A Neugebauer *J. Phys. Chem. B* **101** 9517 (1997)
17. E Dormann, H Winter, W Dyakonow, B Gotschy, A Lang, H Naarmann, N Walker *Ber. Bunsen-Ges. Phys. Chem.* **97** 922 (1992)
18. A Lang, H Naarmann, N Walker, E Dormann *Synth. Met.* **53** 379 (1993)
19. P R Serwinski, B Esat, P M Lahti, Y Liao, R Walton, J Lan *J. Org. Chem.* **69** 5247 (2004)
20. A Lang, H Naarmann, G Rösler, B Gotschy, H Winter, E Dormann *Mol. Phys.* **79** 1051 (1993)
21. A R Katritzky, S A Belyakov, O V Denisko, U Maran, N S Dalal *J. Chem. Soc., Perkin Trans. 2* 611 (1998)
22. A H M Elwahy, A A Abbas, Y A Ibrahim *J. Chem. Res. (S)* 184 (1998)
23. J Bosch, C Rovira, J Veciana *Synth. Met.* **55** 1141 (1993)
24. M Hmyene, A Hakam, H Naarmann, E Dormann *Ann. Chim. Sci. Mater.* **29** (4) 55 (2004)
25. H Winter, B Gotschy, E Dormann, H Naarmann *Synth. Met.* **38** 341 (1990)
26. J Tang, S Nayak, J S Costa, A Robertazzi, R Pievo, I Mutikainen, O Roubeau, S J Teat, P Gamez, J Reedijk *Dalton Trans.* **39** 1361 (2010)
27. J Bosch, E Molins, C Miravitlles, F Palacio, J Veciana *Mol. Cryst. Liq. Cryst.* **187** 67 (1990)
28. F A Neugebauer, H Fischer, R Siegel *Chem. Ber.* **121** 815 (1988)
29. C L Barr, P A Chase, R G Hicks, M T Lemaire, C L Stevens *J. Org. Chem.* **64** 8893 (1999)
30. E C Pare, D J R Brook, A Brieger, M Badik, M Schinke *Org. Biomol. Chem.* **3** 4258 (2005)
31. V Chemistruck, D Chambers, D J R Brook *J. Org. Chem.* **74** 1850 (2009)
32. D J R Brook, G T Yee *J. Org. Chem.* **71** 4889 (2006)
33. F A Neugebauer, H Fischer, C Krieger *J. Chem. Soc., Perkin Trans. 2* 535 (1993)
34. R Milcent, G Barbier, S Capelle, J P Catteau *J. Heterocycl. Chem.* **31** 319 (1994)
35. T M Barclay, R G Hicks, M T Lemaire, L K Thompson, Z Xu *Chem. Commun.* 1688 (2002)
36. R G Hicks, B D Koivisto, M T Lemaire *Org. Lett.* **6** 1887 (2004)
37. B D Koivisto, A S Ichimura, R McDonald, M T Lemaire, L K Thompson, R G Hicks *J. Am. Chem. Soc.* **128** 690 (2006)
38. T M Barclay, R G Hicks, M T Lemaire, L K Thompson *Chem. Commun.* 2141 (2000)
39. M J Plater, J P Sinclair, S Kemp, T Gelbrich, M B Hursthouse, C J Gomez-Garcia *J. Chem. Res.* 515 (2006)
40. M J Plater, S Kemp, E Coronado, C J Gomez-Garcia, R W Harrington, W Clegg *Polyhedron* **25** 2433 (2006)
41. M Bancerz, M K Georges *J. Org. Chem.* **76** 6377 (2011)
42. M Bancerz, B Youn, M V DaCosta, M K Georges *J. Org. Chem.* **77** 2415 (2012)
43. D J R Brook, V Lynch, B Conklin, M A Fox *J. Am. Chem. Soc.* **119** 5155 (1997)
44. R M Fico Jr , M F Hay, S Reese, S Hammond, E Lambert, M A Fox *J. Org. Chem.* **64** 9386 (1999)
45. J B Gilroy, S D J McKinnon, P Kennepohl, M S Zsombor, M J Ferguson, L K Thompson, R G Hicks *J. Org. Chem.* **72** 8062 (2007)
46. M Chahma, X S Wang, A Est, M Pilkington *J. Org. Chem.* **71** 2750 (2006)
47. M Chahma, K Macnamara, A Est, A Alberola, V Polo, M Pilkington *New J. Chem.* **31** 1973 (2007)
48. Y Teki, M Kimura, S Narimatsu, K Ohara, K Mukai *Bull. Chem. Soc. Jpn.* **77** 95 (2004)
49. T Toichi, Y Teki *Polyhedron* **24** 2337 (2005)
50. Y Teki, H Tamekuni, J Takeuchi, Y Miura *Angew. Chem., Int. Ed.* **45** 4666 (2006)
51. N Mihara, Y Teki *Inorg. Chim. Acta* **361** 3891 (2008)
52. Y Teki, H Tamekuni, K Haruta, J Takeuchi, Y Miura *J. Mater. Chem.* **18** 381 (2008)
53. W-F Kuo, I-T Lin, S-W Sun, M-Y Yeh *J. Chin. Chem. Soc.* **48** 769 (2001)
54. Y Masuda, M Kuratsu, S Suzuki, M Kozaki, D Shiomi, K Sato, T Takui, K Okada *Polyhedron* **28** 1950 (2009)
55. R G Hicks, R Hooper *Inorg. Chem.* **38** 284 (1999)
56. R G Hicks, L Öhrsrtöm, G W Patenaude *Inorg. Chem.* **40** 1865 (2001)
57. T M Barclay, R G Hicks, A S Ichimura, G W Patenaude *Can. J. Chem.* **80** 1501 (2002)
58. J B Gilroy, M J Ferguson, R McDonald, B O Patrick, R G Hicks *Chem. Commun.* 126 (2007)
59. P M Allemand, G Srdanov, F Wudl *J. Am. Chem. Soc.* **112** 9391 (1990)
60. J B Gilroy, B D Koivisto, R McDonald, M J Ferguson, R G Hicks *J. Mater. Chem.* **16** 2618 (2006)
61. S V Rosokha, J Zhang, J Lu, J K Kochi *J. Phys. Org. Chem.* **23** 395 (2010)
62. M Fujiwara, M Tamaru, M Hara, K Suzuki, K Mukai *J. Phys. Chem. B* **111** 9492 (2007)
63. J Jornet, M Deumal, J Ribas-Arino, M J Bearpark, M A Robb, R G Hicks, J J Novoa *Chem. – Eur. J.* **12** 3995 (2006)
64. R G Hicks, M T Lemaire, L Öhrsrtöm, J F Richardson, L K Thompson, Z Xu *J. Am. Chem. Soc.* **123** 7154 (2001)
65. K Mukai, M Nuwa, K Suzuki, S Nagaoka, N Achiwa, J B Jamali *J. Phys. Chem. B* **102** 782 (1998)
66. E Dormann, W Dyakonow, B Gotschy, A Lang, H Naarmann, B Pilawa, N Walker, H Winter *Synth. Met.* **55 – 57** 3273 (1993)
67. M Kamachi, H Enomoto, M Shibasaka, W Mori, M Kishita *Polymer J.* **18** 439 (1986)
68. V I Buzulukov, K N Nishchev, V N Yuzhalkin, O B Tomilin *Zh. Fiz. Khim.* **71** 949 (1997) [b]
69. K Mukai, in *Carbon-Based Magnetism* (Eds T Makarova, F Palacio) (Amsterdam: Elsevier, 2006) p. 75
70. K Mukai, M Yanagimoyo, S Tanaka, M Mito, T Kawae, K Takeda *J. Phys. Soc. Jpn.* **72** 2312 (2003)
71. J B Gilroy, M T Lemaire, B O Patrick, R G Hicks *Cryst. Eng. Commun.* **11** 2180 (2009)
72. I A Latif, A Panda, S N Datta *J. Phys. Chem. A* **113** 1595 (2009)
73. J-B Rota, B Le Guennic, V Robert *Inorg. Chem.* **49** 1230 (2010)

74. S Shil, A Misra *J. Phys. Chem. A* **114** 2022 (2010)
75. V Polo, A Alberola, J Andres, J Anthony, M Pilkington *Phys. Chem. Chem. Phys.* **10** 857 (2008)
76. D Bhattacharya, A Misra *J. Phys. Chem. A* **113** 5470 (2009)
77. D Bhattacharya, S Shil, A Misra, D J Klein *Theor. Chem. Acc.* **127** 57 (2010)
78. S M Mattar, H M Dokainish *J. Phys. Chem. A* **114** 2010 (2010)
79. J S Jaworski *J. Electroanal. Chem.* **300** 167 (1991)
80. J S Jaworski, I Krawczyk *Monatsh. Chem.* **123** 43 (1992)
81. S Nakatsuji, A Kitamura, A Takai, K Nishikawa, Y Morimoto, N Yasuoka, H Kawamura, H Anzai *Z. Naturforsch., B* **53** 495 (1998)
82. O M Polumbrik, I G Ryabokon', N G Vasil'kevich, N V Ignat'ev, L N Markovskii *Zh. Org. Khim.* **21** 185 (1985) [c]
83. O M Polumbrik, A V Misyura, N G Vasil'kevich, L N Markovskii *Zh. Org. Khim.* **21** 871 (1985) [c]
84. J B Gilroy, S D J McKinnon, B D Koivisto, R G Hicks *Org. Lett.* **9** 4837 (2007)
85. R T Boere, K H Moock, M Parvez *Z. Anorg. Allg. Chem.* **620** 1589 (1994)
86. C M Aherne, A J Banister, I B Gorrell, M I Hansford, Z V Hauptman, A W Luke, J M Rawson *J. Chem. Soc., Dalton Trans.* 967 (1993)
87. I G Ryabokon', O M Polumbrik, L N Markovskii *Dokl. Akad. Nauk Ukr. SSR, Ser. B* 47 (1984)
88. V I Buzulukov, L A Zhivechkova *Zh. Obshch. Khim.* **64** 306 (1994) [d]
89. V I Buzulukov *Zh. Obshch. Khim.* **80** 1843 (2010 [d]
90. E I Tomilenko, A M Nesterenko, V N Kalinin, V I Staninets *Khim. Geterotsikl. Soedin.* 981 (1987) [a]
91. E I Tomilenko, P I Ogoiko, V I Staninets *Khim. Geterotsikl. Soedin.* 1532 (1987) [a]
92. E I Tomilenko, P I Ogoiko, V I Staninets *Khim. Geterotsikl. Soedin.* 1251 (1989) [a]
93. M Bancerz, E Prack, M Georges *Tetrahedron Lett.* **53** 4026 (2012)
94. S Nakatsuji, A Kitamura, K Nishikawa, Y Morimoto, N Yasuoka, H Kawamura, H Anzai *Mol. Cryst. Liq. Cryst.* **313** 235 (1998)
95. S Nakatsuji, A Takai, M Mizumoto, H Anzai, K Nishikawa, Y Morimoto, N Yasuoka, J Boy, G Kaupp *Mol. Cryst. Liq. Cryst.* **334** 177 (1999)
96. V I Buzulukov, S Yu Shchipakin *Zh. Obshch. Khim.* **79** 1577 (2009) [d]
97. L Keeney, M Hynes *Dalton Trans.* 133 (2005)
98. L Keeney, M Hynes *Dalton Trans.* 1524 (2005)
99. S Conway, L Keeney, M Hynes *Dalton Trans.* 2878 (2009)
100. P V Tarasenko, E A Ponomareva, G F Dvorko *Khim. Heterotsikl. Soedin.* 270 (1983) [a]
101. A V Misyura, O M Polumbrik, L N Markovskii *Zh. Obshch. Khim.* **25** 424 (1989) [d]
102. A V Misyura, O M Polumbrik, L N Markovskii *Dokl. Akad. Nauk Ukr. SSR, Ser. B* 58 (1988)
103. N I Buryak, O M Polumbrik, A A Yasnikov *Ukr. Khim. Zh.* **51** 1111 (1985) [e]
104. E K Y Chen, S J Teertstra, D Chan-Seng, P O Otieno, R G Hicks, M K Georges *Macromolecules* **40** 8609 (2007)
105. N G Strizhikova, Yu A Maletin, I A Shcheka *Zh. Obshch. Khim.* **53** 498 (1983) [d]
106. A Yang, T Kasahara, E K Y Chen, G K Hamer, M K Georges *Eur. J. Org. Chem.* 4571 (2008)
107. E K Y Chen, M Bancerz, G K Hamer, M K Georges *Eur. J. Org. Chem.* 5681 (2010)
108. E K Y Chen, Ph.D. Thesis, University of Toronto, Toronto, 2010
109. J Dang, Master of Science Thesis, University of Toronto, Toronto, 2010
110. J Dang, G K Hamer, M K Georges *Tetrahedron Lett.* **53** 4877 (2012)
111. A A Cumaraswamy, G K Hamer, M K Georges *Eur. J. Org. Chem.* 1717 (2012)
112. M T Green, T A McCormick *Inorg. Chem.* **38** 3061 (1999)
113. D J R Brook, S Fornell, B Noll, G T Yee, T H Koch *J. Chem. Soc., Dalton Trans.* 2019 (2000)
114. T M Barclay, R G Hicks, M T Lemaire, L K Thompson *Inorg. Chem.* **40** 6521 (2001)
115. J E Stevens, D J R Brook, V W Abeyta *Polyhedron* **22** 2241 (2003)
116. D J R Brook, G T Yee, M Hundley, D Rogow, J Wong, K Van-Tu *Inorg. Chem.* **49** 8573 (2010)
117. L Norel, J-B Rota, L-M Chamoreau, G Pilet, V Robert, C Train *Angew. Chem., Int. Ed.* **50** 7128 (2011)
118. D J R Brook, S Fornell, J E Stevens, B Noll, T H Koch, W Eisfeld *Inorg. Chem.* **39** 562 (2000)
119. K J Anderson, J G Gilroy, B O Patrick, R McDonald, M J Ferguson, R G Hicks *Inorg. Chim. Acta* **374** 480 (2011)
120. J-Z Wu, E Bouwman, J Reedijk, A M Mills, A L Spek *Inorg. Chim. Acta* **351** 326 (2003)
121. S D J McKinnon, B O Patrick, A B P Lever, R G Hicks *Chem. Commun.* **46** 773 (2010)
122. S D J McKinnon, B O Patrick, A B P Lever, R G Hicks *J. Am. Chem. Soc.* **133** 13587 (2011)
123. S D J McKinnon, J B Gilroy, R McDonald, B O Patrick, R G Hicks *J. Mater. Chem.* **21** 1523 (2011)
124. F Pointillart, C Train, P Herson, J Marrot, M Verdaguer *New J. Chem.* **31** 1001 (2007)
125. R G Hicks, M T Lemaire, L K Thompson, T M Barclay *J. Am. Chem. Soc.* **122** 8077 (2000)
126. T M Barclay, R G Hicks, M T Lemaire, L K Thompson *Inorg. Chem.* **40** 5581 (2001)
127. T M Barclay, R G Hicks, M T Lemaire, L K Thompson *Inorg. Chem.* **42** 2261 (2003)
128. R G Hicks *Aust. J. Chem.* **54** 597 (2001)
129. L Norel, F Poitillart, C Train, L-M Chamoreau, K Boubekeur, Y Journaux, A Brieger, D J R Brook *Inorg. Chem.* **47** 2396 (2008)
130. J-B Rota, L Norel, C Train, N B Amor, D Maynau, V Robert *J. Am. Chem. Soc.* **130** 10380 (2008)
131. D J R Brook, C J Richardson, B C Haller, M Hundley, G T Yee *Chem. Commun.* **46** 6590 (2010)
132. M T Lemaire, T M Barclay, L K Thompson, R G Hicks *Inorg. Chim. Acta* **359** 2616 (2006)
133. O Oms, J B Rota, L Norel, C J Calzado, H Rousseliere, C Train, V Robert *Eur. J. Inorg. Chem.* 5373 (2010)
134. P K Poddutooori, M Pilkington, A Alberola, V Polo, J E Warren, A van der Est *Inorg. Chem.* **49** 3516 (2010)
135. L Norel, L-M Chamoreau, Y Journaux, O Oms, G Chastanet, C Train *Chem. Commun.* 2381 (2009)
136. Patent JP 2008214316 (2008)
137. K Nakabayashi, Y Ozaki, M Kawano, M Fujita *Angew. Chem., Int. Ed.* **47** 2046 (2008)
138. Y Ozaki, M Kawano, M Fujita *Chem. Commun.* 4245 (2009)
139. A V Yakovenko, S V Kolotilov, O Cador, S Golhen, L Ouahab, V V Pavlishchuk *Eur. J. Inorg. Chem.* 2354 (2009)
140. Patent US 5550272 (1996)
141. B Yamada, H Tanaka, K Konishi, T Otsu *J. Macromol. Sci., Part A: Pure Appl. Chem.* **31** 351 (1994)
142. A V Misyura, O M Polumbrik, I G Ryabokon' *Ukr. Khim. Zh.* **51** 885 (1985) [e]
143. A R Katritzky, S A Belyakov, S Strah, B Cage, N S Dalal *Tetrahedron Lett.* **40** 407 (1999)
144. S J Teertstra, E Chen, D Chan-Seng, P O Otieno, R G Hicks, M K Georges *Macromol. Symp.* **248** 117 (2007)
145. Patent US 0244274 (2007)
146. G F Dvorko, E A Ponomareva *Russ. Chem. Rev.* **60** 1071 (1991)

147. G F Dvorko, E A Ponomareva, N N Golovko, T L Pervishko *Zh. Obshch. Khim.* **75** 105 (2005) [d]
148. N E Ponomarev, M V Stambirskii, G F Dvorko *Zh. Obshch. Khim.* **75** 937 (2005) [d]
149. N E Ponomarev, V V Zaliznyi, G F Dvorko *Zh. Obshch. Khim.* **75** 1503 (2005) [d]
150. G F Dvorko, E A Ponomareva, N E Ponomarev, V V Zaliznyi, I V Koshchii *Zh. Obshch. Khim.* **77** 1535 (2007) [d]
151. N E Ponomarev, V V Zaliznyi, G F Dvorko *Zh. Obshch. Khim.* **77** 1204 (2007) [d]
152. G F Dvorko, A F Vasil'kevich, I V Koshchii, K V Mikhal'chuk *Zh. Org. Khim.* **45** 1336 (2009) [c]
153. G F Dvorko, M E Ponomarev, E A Ponomareva *Adv. Chem. Res.* **5** 191 (2010)
154. I M Serebryakov, E B Kryzhanovskaya, S S Dzhurinskaya, A V Kladova, E A Azarova *Zh. Obshch. Khim.* **75** 1402 (2005) [d]
155. Patent WO 121900 (2010)
156. Patent JP 124567 (2011)
157. Patent US 0195297 (2011)
158. Patent JP 198770 (2009)
159. Patent JP 6264013 (1994)
160. Patent JP 291974 (2005)
161. K Mukai, T Hatanaka, N Senba, T Nakayashiki, Y Misaki, K Tanaka, K Ueda, T Sugimoto, N Azuma *Inorg. Chem.* **41** 5066 (2002)
162. K Mukai, N Senba, T Hatanaka, H Minakuchi, K Ohara, M Tanigochi, Y Misaki, Y Hosokoshi, K Inoue, N Azuma *Inorg. Chem.* **43** 566 (2004)
163. K Mukai, D Shiba, K Yoshida, Ky Mukai, H Hisatou, K Ohara, Y Hosokoshi, N Azuma *Bull. Chem. Soc. Jpn.* **78** 2114 (2005)
164. K Mukai, D Shiba, Ky Mukai, K Yoshida, H Hisatou, K Ohara, Y Hosokoshi, N Azuma *Polyhedron* **24** 2513 (2005)

[a] — *Chem. Heterocycl. Compd. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem., Ser. A (Engl. Transl.)*
[c] — *Russ. J. Org. Chem. (Engl. Transl.)*
[d] —*Russ. J. Gen. Chem. (Engl. Transl.)*
[e] — *Ukr. Chem. J. (Engl. Transl.)*