Translated from *Uspekhi Khimii*, 47, 1444-1478 (1978) U.D.C. 547.883

Advances in the Chemistry of Verdazyl Radicals

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Data relevant to the methods of synthesis of various verdazyl mono-,, bi-, tri-, and poly-radicals as well as their analogues (tetra-azapentenyl, tetrazolinyl, and phototetrazolinyl radicals) are discussed, and the reactions of verdazyls not involving the free valence are considered; data are presented on the structures, spectra, and physical and chemical properties of verdazyls. Attention has been concentrated on problems of the kinetics and mechanisms of chemical reactions involving verdazyls. Problems of the practical applications of verdazyls in chemical, physical, and biological research (inhibition of free-radical reactions, stabilisation of polymeric materials, spin labels, redox indicators, galvanic cells, etc.) as well as the prospects for the development of this new class of stable radicals are discussed.
The bibliography includes 242 references.

CONTENTS

I. Introduction 767
II. Methods of synthesis of verdazyls 767
III. Structure and spectra 769
IV. Chemical properties 772
V. Tetrazinyl radical-ions and tetra-azapentenyl, tetrazolinyl, and phototetrazolinyl radicals 779
VI. Applied aspects of the chemistry of verdazyl radicals 780

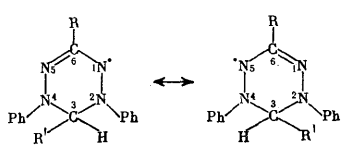
I. INTRODUCTION

Verdazyls (tetrahydrotetrazinyls) occupy a special place amonst stable radicals. The striking stability of verdazyls, the ease with which their reactions may be studied by spectroscopic methods, and their ready solubility make them suitable objects for the solution of many chemical and physicochemical problems. Since the discovery of verdazyls by Kuhn and Trischmann[1-3] (1963), more than 150 papers have been published on the synthesis, structures, and physicochemical properties of verdazyls. Certain aspects of the chemistry and physicochemical properties of verdazyls are dealt with in a number of publications[4-6].

In the present review attention has been concentrated on the structures, methods of synthesis, reactivities, and practical applications of verdazyls; other problems (EPR, NMR, and quantum-chemical calculations) are dealt with in less detail.

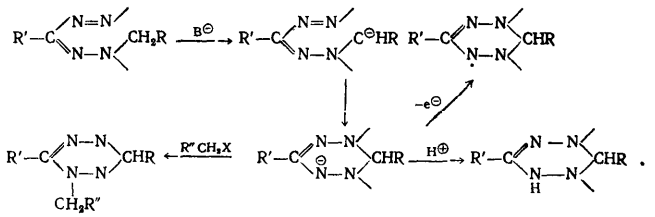
II. METHODS OF SYNTHESIS OF VERDAZYLS

Verdazyls were discovered in studies on the alkylation of formazans[7,8]. A characteristic feature of verdazyls is the obligatory presence in the 2- and 4-positions of aromatic substituents (the substituents at the carbon atoms in the 3- and 6-positions may be varied[9,10]):

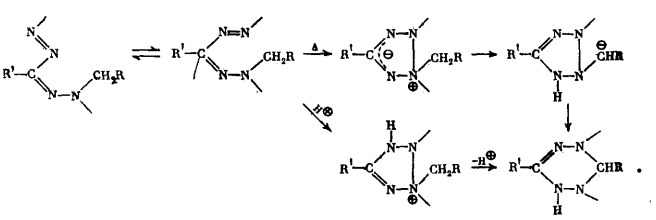


(I) R' = H, R = Ph;
(II) R' = H, R = *p*-X-C_6H_4;
(III) R' = CH_3, R = Ph;
(IV) R' = H, R = $(CH_3)_3$.

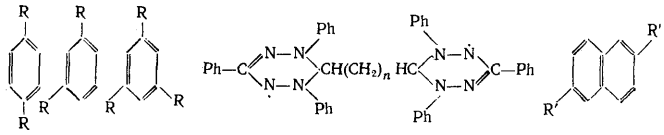
The alkylation reaction is the main method for synthesising verdazyls. The cyclisation of *N*-alkylformazans with the formation of tetrahydro-*syn*-tetrazines (leucoverdazyls), which constitutes formally the addition of the alkyl group to the –N=N– bond, has been studied in detail[11]. The capacity of *N*-alkylformazans for cyclisation depends greatly on the size of the substituents at the central carbon atom, which influences the *trans*-(*anti*-*syn*) isomerisation of formazans[12,13]. Bulky substituents (phenyl, t-butyl) tend to fix the chelate form with a strong intramolecular hydrogen bond, while alkyl substituents weaken the hydrogen bond and lead to the opening of the chelate ring (*trans*-*anti*-form). Thus the energy of the intramolecular hydrogen bond is approximately 7 kcal mole^{-1} in triphenylformazan and approximately 2 kcal mole^{-1} in diphenylformazan[14]. The cyclisation of *N*-alkylformazans can proceed under the influence of strong bases (NaOH, t-BuK, $NaOC_2H_5$), acids, or thermally. The *N*-alkylformazan anion formed under the influences of bases cyclises to the leucoverdazyl anion, which undergoes further transformations:



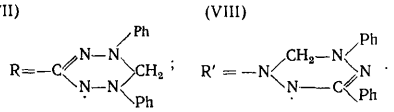
The rate of thermal cyclisation of *N*-alkylformazans follows first-order kinetics and increases rapidly with temperature (ΔH = 25 kcal mole^{-1}). It is suggested[11] that the rate-limiting stage in such cyclisations is the formation of a delocalised zwitter-ion, which is converted into the isomeric ylid and then into the leucoverdazyl via the Stevens rearrangement. The ease of cyclisation of *N*-alkylformazans under the influence of acids is associated with the formation of a protonated form of the delocalised zwitter-ion:



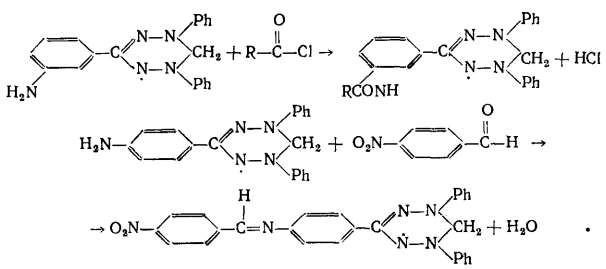
Under the influence of oxidants [$FeCl_3$, $K_3Fe(CN)_6$, PbO_2], leucoverdazyls are dehydrogenated to verdazyls. In many cases *N*-alkylformazans are stable[15-17] and cyclise only at high temperatures. Under the influence of alkalis, verdazyl salts may recyclise[9,18,19]. Compound (I) is also obtained by the reduction of tetrazolium salts with diazomethane[9]. Verdazyls can give rise to bi- and tri-radicals by being joined together in the 3-, 6- and 4-positions:



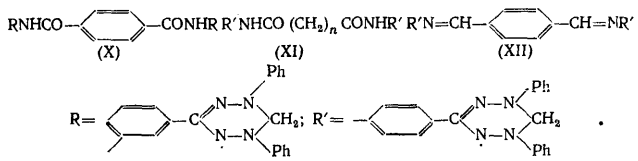
(V) (VI) (VII) (VIII) (IX)



Many mono-, bi-, and tri-verdazyls have now been synthesised from the corresponding formazans[20-23]. Aminoalkylation of formazans yields verdazyls with amino-groups in the 3-position[9]. It has been found recently[24] that 6-aminoverdazyls may be acylated by acyl chlorides or may be converted into imines by reaction with aldehydes without involving their free valence (reactions of this type are well known for *N*-oxide radicals[25]:

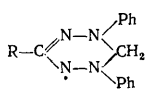


(In order to avoid the disproportionation of verdazyls under the influence of the hydrogen chloride liberated, the first reaction is carried out in the presence of triethylamine.) Bifunctional acyl chlorides or aldehydes give rise to verdazyl biradicals:



(X) (XI) (XII)

Aldose formazans have been used to synthesise water-soluble verdazyls[26]:



XIII

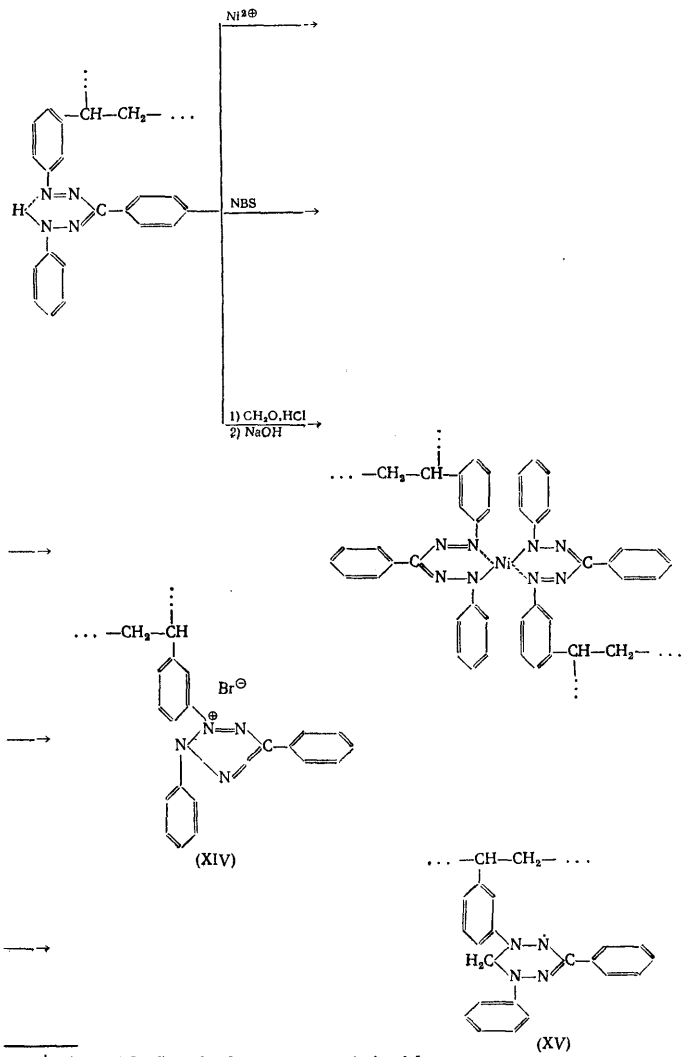
where R = D-*galacto*pentahydroxypentyl, D-*gluco*pentahydroxypentyl, D-*manno*pentahydroxypentyl, L-*rhamno*tetrahydroxypentyl, D-*arabino*tetrahydroxybutyl, or D-*xylo*tetrahydroxybutyl.

The photochemical formation of triphenylformazan on irradiation of (I),[2] on oxidation of (I) with atmospheric oxygen in the presence of activated charcoal[27], and when 3-aminoverdazyls are acted upon by acids and alkalis[9] constitutes chemical proof of the retention in verdazyl of the order of atoms in the initial formazan chain.

After long heating (at 80°C), (I) decomposes with formation of leucoverdazyl and 5-anilino-1,3-diphenyl-1,2,4-triazole in 1 : 1 proportions[28]. On thermal decomposition of (I) (at 200°C), aniline is formed in addition to these products[2]. Photochemical irradiation of (I) yields aniline, leucoverdazyl, and 1,3-diphenyl-1,2,4-triazole[29].

Formazans containing heteroaromatic substituents in the 1-, 5-, or 3-positions tend to undergo amine–imine tautomerism[30]. Formazans in which the heterocycle is not involved in tautomerism are most suitable for the synthesis of verdazyls[30-35].

Polymeric verdazyls and oligomers containing verdazyls in a polymer matrix are obtained by alkylating formazans or substituting them, by the anionic polymerisation of vinyl- and methacryloyl-verdazyls, and by the substitution of diaminoverdazyls with terephthalic aldehyde, terephthalic acid chloride, or styrene–maleic anhydride copolymers[36-45]. Polyurea containing verdazyls in the main chain has been obtained by the polyaddition of diverdazyldiamine and phenyl di-isocyanate[39]. Polycondensation of bisformazan with *p*-phenylenedimethylene dibromide yielded oligomers containing verdazyls[36]. A polymeric chelate, a polyverdazyl, and a polytetrazolium salt (a polymeric redox indicator) have been obtained by the polymerisation of polyvinylformazan[38]†:



(XIV) (XV)

† Here NBS = *N*-bromosuccinimide.

III. STRUCTURE AND SPECTRA

The geometry of the verdazyl skeleton was established by X-ray diffraction[46-49]. The heterocyclic verdazyl ring has the shape of an asymmetric boat with four coplanar nitrogen atoms and the $C_{(3)}$ and $C_{(6)}$ atoms at distances of 0.590 and 0.099 Å from the plane of the nitrogen atoms. The verdazyl heterocycle has a structure close to that of the planar *syn*-tetrazine and 3,6-diphenyl-*syn*-tetrazine[50,51]. The verdazyl ring contains N and C atoms of different valence, which leads to differences between the C–N distances in different parts of the ring (1.443 Å in the saturated component and 1.338 Å in the aromatic component). Fig. 1 presents the bond lengths and angles in radical (I) obtained by the X-ray diffraction analysis of a single crystal. The benzene rings at the $N_{(2)}$ and $N_{(4)}$ atoms are somewhat deformed owing to intermolecular forces and the planes of the rings deviate from the plane of the nitrogen atoms by 9° and 12°. The $N_{(1)}C_{(6)}N_{(5)}$ angle is close to the trigonal value, as a result of which the structure of the radical is favourable for the delocalisation of the unpaired electron. The benzene rings at the $N_{(2)}$, $N_{(4)}$, and $C_{(6)}$ atoms are also rotated relative to the $N_{(2)}$–C_{Ar}, $N_{(4)}$–C_{Ar}, and $C_{(2)}$–C_{Ar} bonds by 23°, 13.1°, and 1.6°. The appreciable dipole moment of (I) (2.94 D in benzene)[2] shows that the radical has a non-planar configuration in solution.

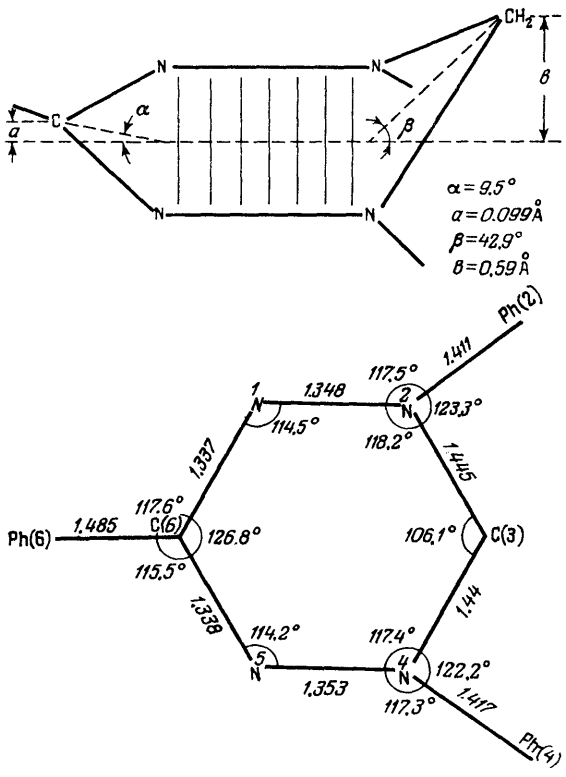


Figure 1. The bonds length and angles in the 2,4,6-triphenylverdazyl radical[46,47].

The electronic structures of verdazyls and the bond orders have been calculated by the simple and extended Hückel method[52-55] and also by the self-consistent field method in terms of the INDO approximation[56]. Calculation of ρ^{π} in radical (I) and in 2,4-diphenyltetrahydro-*syn*-tetrazinyl (XVI) by the Hückel method showed that the unpaired electron is localised mainly at the nitrogen atoms, where the spin densities are approximately the same (Fig. 2). The spin densities at the nitrogen atoms in the bi- and tri-radicals differ little from those in monoverdazyls[52].

We carried out a quantum-chemical calculation on the heterocycle in verdazyls by the unrestricted Hartree-Fock method in terms of the INDO approximation with complete optimisation of the geometry on the basis of a program employing a gradient method to find the proton energy minimum[216]. Fig. 3 presents the optimised bond lengths and angles in the boat conformer of a model verdazyl radical (the benzene rings have been replaced by hydrogen atoms). The calculations made it possible to explain satisfactorily the dipole moment found for triphenylverdazyl and the spectroscopic equivalence of the four nitrogen atoms of the verdazyl ring.

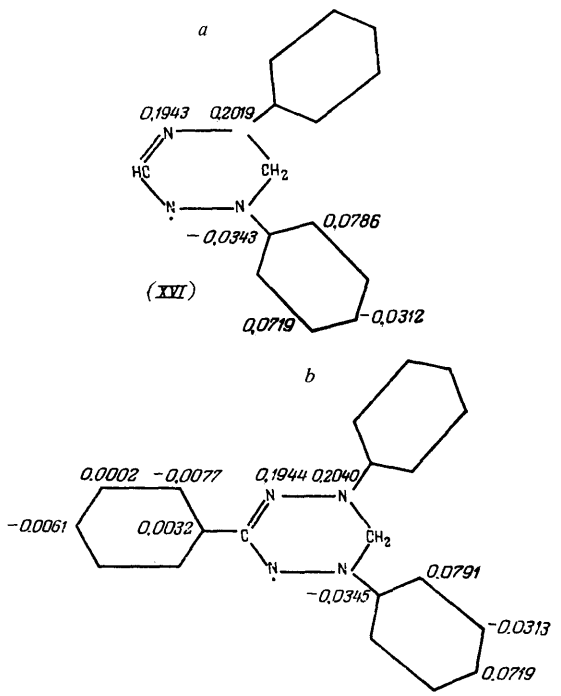


Figure 2. Distribution of spin densities: *a*) in the diphenylverdazyl radical (XVI); *b*) in the triphenylverdazyl radical[52].

The EPR spectrum of radical (I) consists of nine broad lines with a binomial intensity distribution (1 : 4 : 10 : 16 : 19 : 16...), which is due to the interaction of the unpaired electron with the four equivalent nitrogen atoms of the verdazyl ring[2,57]. The hyperfine interaction (HFI) constant $a^{N} \simeq 6$ G and the *g*-factor is 2.0033–2.0036.

The introduction of substituents in the *o*- and *p*-positions in the benzene rings of (IV) leads to the non-equivalence of the nitrogen atoms in pairs; the dependence of $a^N_{2,4}$ on the properties of the substituents then obeys the Hammett equation, while the constants $a^N_{1,5}$ are virtually independent of the nature of the substituent[22]. Arylverdazyls into which F, Cl, D, and Br atoms have been introduced selectively give rise to well resolved EPR spectra at room temperature. Splittings are observed due to protons in the equivalent benzene rings attached to the $N_{(2)}$ and $N_{(4)}$ atoms: $a^H_o = a^H_p = 1.06–1.09$ G; $a^H_m = 0.41–0.49$ G.[15]

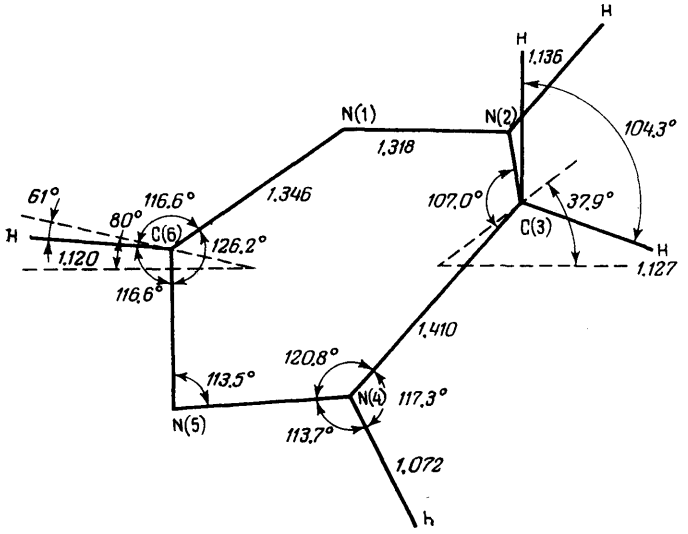
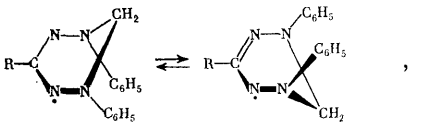


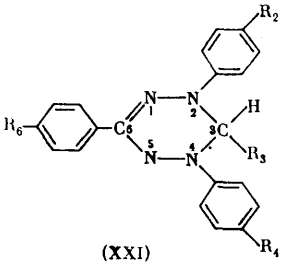
Figure 3. The steric structure of a model verdazyl radical[216].

The paramagnetic shifts relative to diamagnetic leuco-verdazyls have been determined from the NMR spectra for many verdazyl radicals with aliphatic substituents and the isotropic HFI constants have been found[10,53,58–61]. The HFI constants (in G) have been obtained from the NMR spectra of (I) in $CDCl_3$ for all its protons[53]: for the protons of the benzene rings attached to $N_{(2)}$ and $N_{(4)}$ ($a^H_p = 1.195$, $a^H_o = 1.12$, $a^H_m = 0.425$), for the protons of the $C_{(6)}$-benzene ring ($a^H_p = 0.31$, $a^H_o = 0.425$, $a^H_m = 0.16$), and for the $C_{(3)}$-methylene protons ($a^H = 0.027$)[53]. The electronic-nuclear double resonance (ENDOR) spectra of dilute liquid solutions of verdazyls have been investigated[62]; the constants for the hyperfine interaction with the protons in the *o*-, *m*-, and *p*-positions in the aromatic rings agree with the values measured previously by EPR and NMR (Table 1). The signs and values of the HFI constants found by the NMR method agree with the spin densities calculated from the experimental data using the McConnel and Stone–Maki equations[15,53], and with the spin densities obtained by the Hückel and McLachlan quantum-chemical calculations[52]. The constant for the hyperfine interaction with the protons of the CH_2 group in the 3-position of the verdazyl ring is positive for all the monoverdazyls and amounts to 0.027–0.031 G.[15,58,62] The temperature dependence of the NMR spectrum of this group indicates the inversion of the verdazyl ring[10,60]:



Hyperfine interaction with protons located at large distances from the point at which the initial spin density is localised (separated by 3–4 σ bonds) has been observed for verdazyls with aliphatic substituents in the 3- or 6-positions and in the *p*-positions in the *N*-phenyl rings (Table 2). The characteristics of the distribution of spin density in verdazyl σ systems depend on the geometrical structure of the radicals[53,58–61].

Table 1. The hyperfine splitting constants of verdazyls (G) measured by the ENDOR method[62].



(XXI)

a) $R_2 = R_3 = R_4 = R_6 = H$;
b) $R_2 = R_3 = R_4 = H$; $R_6 = CH_3$;
c) $R_2 = R_4 = CH_3$; $R_3 = R_6 = H$;
d) $R_2 = R_4 = R_6 = CH_3$; $R_3 = H$;
e) $R_2 = R_4 = R_6 = H$; $R_3 = CH_3$

Radical	a^{*N}	$a^H_{2,4\text{-p}}$	$a^H_{2,4\text{-}o}$	$a^H_{2,4\text{-}m}, a^H_{6\text{-}o}$	$a^{CH_3}_{6\text{-p}}$	$a^{CH_3}_3$
(XXIa)	5.79	1.22	1.11	0.42	—	—
(XXIb)	5.67	1.28	1.11	0.42	0.30	—
(XXIc)	5.75	1.29	1.12	0.41	—	—
XXId)	5.62	1.29	1.12	0.41	0.30	—
(XXIe)	5.60	1.26	1.15	0.42	—	0.97

* According to EPR data in 2-methyltetrahydrofuran.

^{19}F dynamic nuclear polarisation (DNP) has been investigated in solution in the presence of verdazyls. The heterocyclic group of verdazyls has a high spin density and readily forms complexes with C_6F_6, the contact interaction making a significant contribution to the polarisation[63,64].

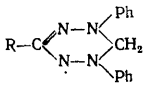
The EPR spectra of the polymers based on verdazyl radicals are non-characteristic and usually consist of a single or several broadened lines[37,38,65].

The EPR spectra of verdazyl bi- and tri-radicals[20,21,24] are less well resolved than those of the monoradicals, which is primarily due to the electron–electron interaction‡. A detailed study of the verdazyl biradicals (V) and (VI) by EPR and NMR showed that the constant for the

‡ An increase in molecular size can also lead to an impairment of the averaging of the anisotropic HFI.

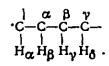
hyperfine interactions with the protons of the aromatic rings joining the verdazyl moieties are equal to the average HFI constants for the corresponding protons in monoverdazyl, while the temperature dependence of the paramagnetic shifts is linear. Hence it follows that the exchange energy in the verdazyl biradicals obeys the relation $RT > J > a^N$. In the spectra of radicals (XI) with $n = 0$ splitting by the eight equivalent nitrogen atoms is observed ($a^N = 2.9$ G) but, when $n = 6$, the usual spectrum of verdazyl monoradical is observed (four N atoms, $a^N = 5.8$ G). The exchange interaction energy J then changes from $J > 6$ G ($n = 0$) to $J \simeq 0$ ($n = 6$).[24] In dilute solid solutions of verdazyl bi- and tri-radicals, dipole splitting is observed. The dipole interaction constants D of the electrons in verdazyl biradicals are 10–55 Oe, depending on the structure[66-69]. The values of D for (V) and (VI) are respectively 43.1 and 52.7 G, whence the average distances between the paramagnetic centres (8.7 and 8.1 Å) were found.

Table 2. The isotropic constants (G) for the hyperfine interaction with protons in the 3-position in verdazyls*[60].

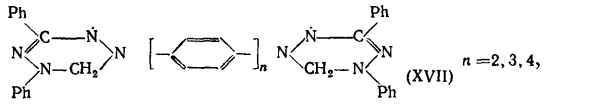


R	a_{H_α}	a_{H_β}	a_{H_γ}	a_{H_δ}
H	0.72	—	—	—
CH_3	—	−2.03	—	—
$C(CH_3)_3$	—	—	0.105	—
CH_2CH_3	—	−1.63	0.168	—
$CH(CH_3)_2$	—	−1.17	0.120	—
$CH_2C_6H_5$	—	−1.34	—	—
$CHCH_3C_6H_5$	—	−1.04	0.124	—
$CH_2CH(CH_3)_2$	—	−1.50	0.275	0.038
$CH_2CHCH_3C_2H_5$	—	−1.63; −1.41	0.260	—
$CH_2CHCH_3C_6H_5$	—	−1.57; −1.41	0.282	0.037
$CH{=}CHC_6H_5$	—	−0.953	0.832	

* The positions of the atoms relative to the radical centre are as follows:



The study of EPR spectra and magnetic susceptibility over a wide temperature range showed that radicals (VIII) ($n = 4$) and (V) are biradicals with a virtually degenerate singlet–triplet ground state, while triradical (VII) has a virtually degenerate doublet–quartet ground state[6,67]. Biradicals (IX) and (XVII),



(XVII) $n = 2, 3, 4,$

exhibit a decrease of paramagnetism on reducing the temperature, which is believed[21] to be a result of equilibrium with the corresponding diamagnetic zwitter-ionic forms.

In order to study diverdazyl radicals in frozen solid solutions (toluene or polystyrene matrices at 77 K), two- and three-pulse EPR spectroscopy has also been used[70]. Transitions from the triplet level (for which $\Delta M = 1$) are then observed.

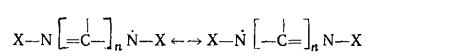
In order to find the parameters of the g-tensor and the tensor of the HFI constants, a study was made of the EPR spectra of radical (I) in a 2,4,6-triphenylbenzene diamagnetic single crystal matrix[71]. When the single crystal is rotated in a magnetic field, the EPR spectrum changes and additional splitting (seven lines), attributed to radical pairs and three-membered radical clusters, is observed. Studies of this kind are of interest from the standpoint of using verdazyls as paramagnetic probes in studies on molecular mobility in crystals and phase transitions.

Like other stable radicals, verdazyls catalyse the ortho-para conversion of hydrogen; the catalytic property depends strongly on the magnetic moment and structure of the verdazyl[72-74].

The characteristics of the behaviour of magnetic susceptibility in crystalline verdazyl radicals, determined by the exchange interaction of the electrons, have been studied[21,48,49,75,76]. The magnetic susceptibility of verdazyls obeys the Curie–Weiss law with negative θ constants [$\theta = -14.6$ K for (I)], over a wide temperature range (300–30 K). However, below 30 K the curves for the temperature dependence of this susceptibility have maxima indicating the occurrence of antiferromagnetic interactions [at 6.9 K for (I) and at 12 K for (III)]. At temperatures below T_{max} the EPR lines are broadened and the g-factor shifts, which indicates the occurrence of magnetic phase transitions. The magnetic properties of the radicals are extremely sensitive to the distribution of the unpaired electron and to the way in which the molecules are packed in the crystal. The different magnetic properties of (I) and substituted triarylverdazyls are associated mainly with the different types of molecular packing of the radicals. Azuma and coworkers[48,49] showed that verdazyls are linear spin systems and can serve as convenient model compounds for the investigation of ferromagnetic interactions in stable radicals.

The study of the frequency and temperature dependence of the EPR line width in the spectrum of (I) yielded information about the exchange and dipole–dipole interactions[77]. The EPR line width for (I) is independent of frequency and temperature (in the range 300–100 K) and approaches the limit corresponding to maximum narrowing. The spin exchange frequency (111 GHz) and the upper limit for the dipole interaction ($D = 288$ G) have been estimated[77]. The high spin exchange frequency is associated with the strong intermolecular overlapping of the $2p\sigma$ and $2p\pi$ orbitals of the aromatic rings of the verdazyl radical in the solid state.

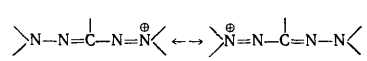
According to Dahne[78], verdazyls are electrically neutral polymethine cyanines having the general formula



where the CH_2 bridge links the ends of the cyanine chain in the *cis-cis* positions with formation of a six-membered ring. Monoverdazyls[2,9,22,79] as well as verdazyl bi-, tri-, and poly-radicals[21,36-45] absorb in the visible region of the spectrum (at 400 and 700 nm). In polar solvents the bands undergo a bathochromic shift which makes it possible to assign them to $\pi \rightarrow \pi^*$ transitions[29]. A bathochromic shift of both bands has been observed for triarylverdazyls with electron-donating or electron-accepting substituents, because this entails an increase in the conjugation system, which stabilises the first excited state to a greater extent than the ground state and thus reduces the excitation energy regardless of the nature of the substituent[22]. The substituent in the 3-position, which is not

involved in the conjugation system, causes a small hypsochromic shift (20–30 nm) of the long-wavelength absorption band. For the colourless leucoverdazyls substituted in the *p*-position of the $C_{(6)}$-phenyl ring, the shift of the long-wavelength absorption band maximum (~330 nm) is satisfactorily correlated with the Hammett σ constants for the substituents[80].

Verdazyl cations are regarded as azacyanine cations having the general formula

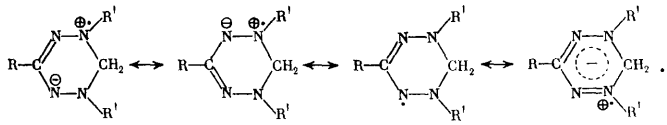


in which two –CR= groups have been replaced by –N=.[22,78] The introduction of substituents in the $C_{(6)}$-ring of triarylverdazyl cations leads to a bathochromic shift of λ_{max} in the presence of electron-donating substituents and to a small hypsochromic shift in the presence of electron-accepting substituents[22,79,81]: NO_2 (535 nm), Cl (545 nm), H (548 nm), CH_3 (553 nm), and OCH_3 (576 nm). Solutions of verdazyl radicals, cations, and leuco-bases obey the Beer–Lambert law. The monomeric state of verdazyl radicals in solutions has also been demonstrated by EPR.[82] Quantum-chemical calculations (LCAO-MO and SCF LCAO-MO in terms of the INDO approximation)[52–56] do not provide an interpretation of the electronic absorption spectra of verdazyls.

The infrared spectra of verdazyls and their cations and leuco-bases have been studied in detail[2,54,55,83–86]. The similarity of the atomic weights of carbon and nitrogen leads to a strong interaction of the vibrations, so that the interpretation of the spectral lines in terms of the vibrations of individual bonds is not sufficiently rigorous[54]. When the ^{15}N label is introduced into (I) all the bands in the infrared spectrum are displaced towards longer wavelengths compared with the species containing ^{14}N, which indicates the presence of a conjugation chain in the verdazyl system[6]. The infrared spectra of the leuco-bases showed the characteristic bands of the N–H bonds (~3300 cm^{-1}). The bands in the region of 1600 cm^{-1} have been assigned to the vibrations of the $C_{(6)}=N_{(5)}$ bond; in triphenylverdazyl and its leuco-base it is intense, while in the cations it is weaker (these bands, which are superimposed on the vibration bands of benzene rings, become resolved in the presence of the ^{15}N label[6]). The 1155–1165 cm^{-1} band, assigned to the –N=N– stretching vibrations, characterises the distribution of electron density in the ring. The spectrum of (I) shows in this region a doublet at 1122–1165 cm^{-1}, which is absent from the spectra of the leuco-bases. The intense 1260 cm^{-1} band, assigned to the $N_{(5)}–C_{(6)}–N_{(1)}$ bond[54,55,83–86], is observed for verdazyl radicals and cations but not for the leuco-forms. It is located at a higher level than in the spectra of formazans having the symmetrical $N_{(2)}–C_{(3)}–N_{(4)}$ linkage[87]. The infrared spectra of verdazyls in general confirm a symmetrical distribution of the unpaired electron.

IV. CHEMICAL PROPERTIES

Verdazyls belong to the class of the most stable free radicals. Crystalline (I) remains unchanged for many years. This is due to the strong delocalisation of the unpaired electron, which lowers the energy of the ground state of the radical, and to the steric shielding of the verdazyl ring. It can also be accounted for on the basis of the principle of the "merostabilisation" of free radicals[88]:



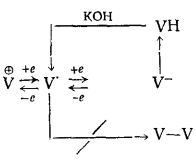
The stability of verdazyls is to a large extent determined by the ability of the 6-substituent in the 6-position to cause the steric stabilisation of the verdazyl ring[6] and varies in the sequence[2,10,15,57,89]

$$RS < H < CH_3 < COOR < C(CH_3)_3 < C_6H_5.$$

The introduction of alkyl or phenyl substituents in the 3-position increases the stability of the verdazyl radical[6,27]. Leucoverdazyls are readily dehydrogenated by other stable radicals—DPPH and tri-t-butylphenoxyl[90]. In the reaction with 2,2,6,6-tetramethylpiperidin-1-yloxy-radical the equilibrium is displaced towards (I). Thus the stability of triarylverdazyls greatly exceeds that of phenoxy- and hydrazyl radicals and is not inferior to that of the ultrastable iminoxy-radicals.

1. Electrochemical Reactions

The polarographic oxidation-reduction of substituted triarylverdazyl radicals (V·) in solution in DMF, CH_3CN, and propylene carbonate (PC) at a dropping mercury electrode takes place reversibly with transfer of one electron and may be described schematically as follows[91–93]:



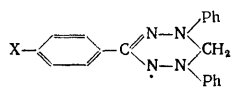
The half-wave oxidation and reduction potentials ($E_{1/2}$) for (II) depend on the nature of the substituents (Table 3). As was to be expected, as the electron-donating properties become more pronounced, the oxidation-reduction half-wave potential shifts towards lower values. The effect of the substituent is described satisfactorily by the modified Hammett–Zuman equation: $\Delta E_{1/2} = E^{X}_{1/2} - E^{0}_{1/2} = \rho_{\pi}\sigma$. The reaction constants characterising the polarisability of the electrochemically active group depend little on the nature of the solvent (Table 4). However, in methanol ρ_{π} for the reduction reaction changes sign, which indicates an electrophilic mechanism. It appears that the kinetics of the protonation in the electrode field preceding electron transfer play a decisive role in the reduction[94]. Comparison of the oxidation-reduction half-wave potentials of (I) and the water-soluble verdazyl (XIII) (R = D-*galacto*-pentahydroxypentyl), whose molecules are capable of forming an intramolecular hydrogen bond, shows that the oxidation half-wave potentials in various solvents differ little (within the limits of the differences between the potential of the liquid compound and the value in solvents and water)[94]. However, there is a difference between the reduction half-wave potentials of (I) and (XIII). The formation of an intramolecular hydrogen bond is accompanied by a small change in $E_{1/2}$ (intramolecular protonation). Thus, when (XIII) is transferred from CH_3CN to CH_3OH, $E_{1/2}$ increases by 0.08 V, while the corresponding increase for (I) is by 0.51 V,[91,94] the reduction half-wave

potentials of triarylverdazyls depending to a greater extent on the specific solvation effects than on the substituent effects. This is apparently associated with the involvement of mobile hydrogen atoms of alcohols in the potential-determing stage of the electrode process. Indeed the reduction half-wave potentials of (I) and (XIII) vary in parallel with pK_a for the autoprotolysis of the organic solvents[91,94]. These data demonstrate the importance of taking into account the proton transfer reactions when the reactivities of verdazyls are considered.

Comparison of electrochemical data for stable radicals makes it possible to estimate qualitatively their donor–acceptor properties. The radicals can be arranged in the following activity series in terms of their reducing capacity: perchlorodiphenylmethyl[95], tri-t-butylphenoxyl[96], DPPH,[97] di-t-butylnitroxide[98], *N*-oxides[99], triphenylmethyl[100], triphenylverdazyl[91].

In this series the most powerful electron donor is the triphenylverdazyl radical, which must be regarded as a Lewis base. Thus chlorinated triphenylmethyl radicals are virtually inert with respect to powerful electrophiles such as the halogens and concentrated nitric acid[5,101], phenoxyls are oxidised only under the influence of powerful oxidants ($SbCl_5$ and other metal halides)[102], while (I) or triphenylmethyl radicals react almost instantaneously with halogens to form cations[2,101].

Table 3. The half-wave potentials for the polarographic oxidation-reduction of triarylverdazyls in propylene carbonate and methanol at 25 °C.[21,93]



X	Reduction		Oxidation		X	Reduction		Oxidation	
	angular coeffi-cient, mV	$E_{1/2}$, V	angular coeffi-cient, mV	$E_{1/2}$, V		angular coeffi-cient, mV	$E_{1/2}$, V	angular coeffi-cient, mV	$E_{1/2}$, V
	Propylene carbonate					Methanol			
NO_2	65	−0.68	65	0.305	NO_2	90	−0.300	55	0.250
Cl	60	−0.72	60	0.235	CO_2CH_3	90	−0.270	65	0.190
CO_2CH_3	70	−0.71	65	0.240	Cl	90	−0.275	65	0.180
H	60	−0.725	70	0.200	H	90	−0.270	65	0.160
CH_3O	70	−0.755	75	0.165	CH_3O	90	−0.250	60	0.120
CH_3O*	80	−0.770	75	0.110	CH_3O *	90	−0.250	65	0.070

* 2,6-Bis-(4-methoxyphenyl)-4-phenylverdazyl.

2. One-Electron Transfer Reactions

One-electron transfer reactions play an important role in the mechanisms of the elementary steps of many organic and bio-organic reactions[103]. Model reactions involving triphenylverdazyls and their salts, in which the one-electron transfer stage has been clearly detected by physicochemical methods, are discussed below. Verdazyls are some of the most powerful nucleophiles and in their reactions with electrophiles give up an electron and are converted into stable cations. Such reactions include those of (I) with halogens[2,104], Lewis acids[2,21,79,105–107], and various inorganic oxidants[2,108]. When a green solution of (I) is mixed with oxidants, a violet verdazyl salt is formed instantaneously. The stability of the diamagnetic cation depends on the nature of the substituent in the radical, the nature of the oxidant and the medium, and other conditions.

Table 4. Correlation equations for chemical reactions involving verdazyls.

X-R*	Reaction of substrate	T, °C	Solvent	Reaction constants (parameters of the substituents with which they are correlated)	Corresponding correlation coefficient	Isokinetic temp.**	Refs.
X—R	electrochemical oxidation	25	DMF	1.99 (σ)	0.990	—	91
X—R	ditto	25	CH_3OH	2.02 (σ)	0.992	—	91
X—R	electrochemical reduction	25	DMF	1.36 (σ)	0.995	—	91
X—R	ditto	25	CH_3OH	−0.71 (σ)	0.936	—	91
X—R	$ClCH_2CO_2H$	20	C_2H_5OH	−3.13 (σ), −23.42 ($E_{1/2}$), −0.81 (pK_a)	0.993; 0.989; 0.989	—	90
X—R	ditto	20	DMF	−2.17 (σ), −16.74 ($E_{1/2}$)	0.994, 0.997	—	90
X—R	PhSH	20	CH_3CN	−0.90 (σ), −8.65 ($E_{1/2}$)	0.999, 0.987	363	90
X—R	$C(NO_2)_4$	20	C_6H_{12}	−2.17 (σ), −20.8 ($E_{1/2}$)	0.999, 0.981	—	107
X—R	ditto	20	THF	−1.13 (σ), −11.0 ($E_{1/2}$)	0.994, 0.985	—	107
X—R	HB	25	DMF	−0.31 (σ), −0.23 (σ^+), −2.51 ($E_{1/2}$)	0.977; 0.992; 0.970	—	147
X—R	ditto	25	C_2H_5OH	−0.42 (σ), −0.31 (σ^+), −3.54 ($E_{1/2}$)	0.983; 0.995; 0.992	—	147
X—R	BDN	25	DMF	0.23 (σ), 2.96 ($E_{1/2}$)	0.990, 0.991	335	90, 129
X—R	HE	25	DMF	0.14 (σ), 1.81 ($E_{1/2}$)	0.994, 0.988	—	90, 129
X—R	BDN	25	C_2H_5OH	−0.16 (σ^+), 4.81 ($E_{1/2}$)	0.967, 0.960	—	90, 129
X—R	HE	25	C_2H_5OH	−0.40 (σ^+), 12.36 ($E_{1/2}$)	0.976, 0.963	—	90, 129
X—R	$(C_6H_5CO_2)_2$	20	propylene carbonate	−0.35 (σ), −2.81 ($E_{1/2}$)	0.995, 0.997	370	125
H—R	$(p\text{-}XC_6H_4CO_2)_2$	20	ditto	1.17 (σ°), 32.87 ($E_{1/2}$)	0.993, 0.981	—	167
H—R	ditto	20	C_6H_6	1.22 (σ°), 34.15 ($E_{1/2}$)	0.995, 0.984	—	167
X—R+	$C_6H_5NHC_2H_5$	20	CH_3CN	0.37 (σ)	0.976	—	81
H—R+	$p\text{-}XC_6H_4NH_2$	20	ditto	−5.01 (σ), −5.75 ($E_{1/2}$), 1.86 (pK)	0.967; 0.987; 0.960	—	81
X—R+	HB	20	"	0.97 (σ), 9.38 ($E_{1/2}$)	0.993, 0.992	—	162
H—R+	X-HE***	20	"	−1.21 (σ), −4.82 ($E_{1/2}$)	0.995, 0.953	528	164

* Triarylverdazyl radicals (X–R) and their salts $(X-R)^+$ substituted in the *p*-position of the $C_{(6)}$-phenyl ring.

** The average isokinetic temperature determined by various methods (from the relation between E_a, on the one hand, and $\Delta S^{\neq}$, $\lg k_2, T_1$, and $\lg k_2, T_2$, on the other, and between ρ and $1/T$, etc.).

*** 3,5-Diethoxycarbonyl-2,6-dimethyl-4(X)-1,4-dihydropyridines.

The influence of the nature of the substituent in (II) and of the polarity of the medium on the kinetics and mechanism of the reaction

$$\dot{V} + C(NO_2)_4 \begin{cases} \longrightarrow \overset{\oplus\ominus}{V}C(NO_2)_3 + NO_2^{\cdot} & \text{(non-polar solvents),} \\ \longrightarrow \overset{\oplus\ominus}{V}C(NO_2)_3 + \overset{\oplus\ominus}{V}NO_2 & \text{(polar solvents)} \end{cases}$$

has been studied[107] in relation to the model reaction involving electron transfer from triarylverdazyl to tetranitromethane (TNM). In polar solvents radicals (II) react with $NO_2^{\cdot}$ in a solvent cage {the stoichiometry corresponds to $[(II)]/[TNM] > 1$}. The reaction is characterised by relatively small activation parameters $E_a = 3-5$ kcal mole^{-1} and $\Delta S^{\neq} = -35-20$ e.u. The rate of reaction $v = k_2[V^{\cdot}][TNM]$ depends significantly on the polarity and solvating capacity of the solvent (on passing from cyclohexane to propylene carbonate, k_2 increases by a factor greater than 10^3). The effect of the substituent in the *p*-position relative to the $C_{(6)}$ -phenyl ring of (II) can be described satisfactorily in terms of the Hammett equation (Table 4). The solvation of (II) by tetrahydrofuran molecules[109] leads to an appreciable decrease of the influence of the polar properties of substituents (Table 4). The rates of reaction of (II) with TNM are also satisfactorily correlated with the polarographic oxidation potentials of (II) (Dimroth's equation) (Table 4). This type of relation between the kinetic and thermodynamic parameters of the reaction with high proportionality coefficients is regarded as evidence for electron transfer in the rate-determining stage[110].

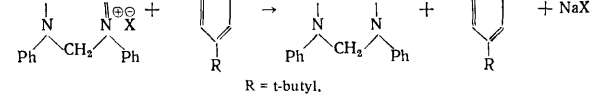
When (I) interacts with tetracyanoethylene and chloranil, which gives rise to stable radical-anions on reduction, the EPR spectra of (I) and the oxidant radical-anion are superimposed, the intensity of the former decreasing with time and that of the latter increasing; the electronic spectra show clearly the absorption band due to the verdazyl salt[108,111]. When the difference between the donor–acceptor properties of the free radicals is fairly large, their interaction may occur via the transfer of one electron and may lead to the formation of a corresponding cation and anion. We observed this in the reaction of (II) with acyloxy-radicals formed in the decomposition of diacyl peroxides[112,113] ($PhCOO^{\cdot}$, $C_6H_{13}COO^{\cdot}$, $C_{11}H_{23}COO^{\cdot}$), NO_2,[107] and acetyl radicals formed in decomposition of lead tetraacetate[108]. Radical (I) recombines with active radicals such as $^{\cdot}CH_2Ph$, $(CH_3)_2\dot{C}COCH_3$, radicals derived from monomers[114–117], $(CH_3)_2\dot{C}CN$,[118], and $^{\cdot}CH_3$,[119] forming addition products (tetrazines). Such recombination makes it possible to classify $^{\cdot}CH_3$ and 1-cyano-1-methylethyl radicals as nucleophiles, which agrees with the view of Ingold and Roberts[120]—halogen-containing free radicals and the majority of radicals with the free electron centred on O or S atoms are classified by these workers as electrophiles, while triethylstannyl, methyl, cyclohexyl, and 1-cyano-1-ethyl radicals are classified as nucleophiles.

In 1973 we attempted[93] to carry out a similar classification for stable radicals and discussed the problem of one-electron transfer in a pair of verdazyl radicals differing greatly in their donor–acceptor properties.

Verdazyls do not react with trityl radicals (but they do react with Ph_3COO), DPPH, and the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical, apparently owing to the presence of bulky substituents in the region of the reaction centres[65,116]. However, (I) reacts with phenoxy-radicals via one-electron transfer with the formation of the corresponding salt[108,111,121,122]. The rate of reaction of substituted phenoxy-radicals with (I) increases with increase of the electron-accepting capacity of the substituent in the *p*-position of the benzene ring, with decrease of $E_{1/2}$ for the polarographic reduction of phenoxy-radicals, and with increase of electron density in the *p*-position of the phenoxy-radical[111].

Like verdazyl monoradicals, the biradicals are readily oxidised by Lewis acids and peroxy-compounds, being converted into diamagnetic salts. It has been shown[123] that the polarographic oxidation of (VI) is reversible, with successive transfer of two electrons. Presumably the oxidation of verdazyl biradicals by strong oxidants also takes place via consecutive one-electron transfer.

In contrast to the radicals, verdazyl salts exhibit pronounced electron-accepting properties. One-electron reduction of verdazyl salts is one of their characteristic reactions and, in view of the high stability of verdazyls, the reaction frequently stops at this stage. Verdazyl salts are used as electrophilic components in order to confirm the hypothesis of one-electron transfer in the interaction of two diamagnetic substances (reactions with tetramethyl-*p*-phenylenediamine and with sodium tri-t-butylphenoxide)[79,108,124]



The resulting EPR spectrum corresponds to the superposition of the spectra of two radicals: (I) and tri-t-butylphenoxyl. When verdazyl salts interact with leucoverdazyls, two verdazyl radicals are also formed[79,90]. If metallic potassium or sodium, an alkali metal alkoxide, or an alkali metal phenoxide is used as the donor, the reaction with verdazyl salts proceeds almost instantaneously[108]. In the reaction with alcohols the verdazyl salt is reduced to the initial radical (methanol is then oxidised to formaldehyde)[125].

Reactions involving one-electron transfer to verdazyl salts occur readily when aromatic and aliphatic amines are used as the donors[81,124,126,127]. The rate of oxidation of amines by verdazyl salts is almost independent of the nature of the salt counterion and of the replacement of H by D in the amino-group[126]. The activity of amines is determined by both electronic and steric effects; they depend to a large extent on the nucleophilic properties of the amine. On passing to aliphatic amines[127], the rate of oxidation of verdazyl salts increases by 2–4 orders of magnitude compared with aromatic amines due to the decrease of E_a (aliphatic amines are much stronger nucleophiles). It is noteworthy that in the reactions with amines the yield of radical (II) is approximately 70–80% for $PhNR_2'$ and aliphatic amines, approximately 60–70% for PhNR'H, and approximately 10–15% for $PhNH_2$ (this is apparently due to side reactions of verdazyl salts[2,118]). The amine radical-cation formed in the elementary electron transfer step readily splits off a proton and is converted into an amine radical, which then either reacts with (II) in the solvent cage or emerges from the latter, which entails the accumulation of (II). The rate of oxidation of anilines is relatively insensitive to the electronic effects of the substituent in the salt (Table 4). In the oxidation of *p*-substituted anilines by verdazyl salts Hammett's, Dimroth's, and Brønsted's correlation equations are found to hold (Table 4). The occurrence of such correlations shows that the mechanisms of all the reactions have a feature in common, believed nowadays to be one-electron oxidation-reduction (*SET* mechanism)[103,110].

The foregoing considerations show that verdazyl radicals may be used in chemistry as one-electron reductants, while verdazyl salts can be used as one-electron oxidants.

3. Reactions of Verdazyls with Acids

The majority of stable radicals react with protic acids; the possibility of such reactions is determined to a large extent by the nucleophilic properties of the radicals. This can explain the high stability of perfluorodimethylnitroxide, di-(4-nitrophenylaminoxyl), 3-imidazolinyl, and porphyrexide in relation to inorganic acids[128]. Being strong nucleophiles, verdazyls are readily oxidised by various acids and, depending on the proton-donating properties of the acid, there is a gradual transition from proton and electron transfer to homolytic substitution reactions[90].

The reaction of (II) with carboxylic acids involves the reversible formation of the cation and the verdazyl leuco-base[2]:

$$2V^{\cdot} + R'CO_2H \overset{K_p}{\rightleftarrows} VH + V^{+}R'COO^{\ominus}$$

The state of equilibrium in the acid–base interaction depends on the donor–acceptor properties of the reactants, their structure and concentration, the nature of the solvent, and temperature[90,129]. When (I) interacts with inorganic (H_2SO_4, HBr, HNO_3) and strong organic acids (CF_3CO_2H, CCl_3CO_2H), the equilibrium is greatly displaced towards the formation of the products, VH being oxidised to the radical and being thus gradually converted into a salt[2]. A study of the equilibrium between (II) and $ClCH_2CO_2H$ showed[130] that, depending on the nature of the solvent, the effective equilibrium constant depends on the concentration of the acid (in alcohol) or on its square (in DMF), or on the concentration of the acid dimer (in benzene), and, depending on the substituent in the *p*-position of the $C_{(6)}$-phenyl ring of (II), the equilibrium constant changes by several orders of magnitude[131,217]. In alcohol and DMF the equilibrium constants are satisfactorily correlated with Hammett's σ constants of the substituents and the polarographic oxidation potentials of verdazyls (Table 4). Verdazyls enter into this reaction as electron donors and the high coefficients in the correlation equations indicate an appreciable charge separation in the activated complex of the reaction. The solvent effect is associated mainly with the change in the proton-donating properties of the acid[129]. There is a linear relation between the disproportionation constants of (II) and the pK_a of the acids (Brønsted's equation) (Table 4). Since the ionisation of acids reduces to proton transfer from the acid to the solvent and the reaction of HX with triarylverdazyls apparently involves partial proton transfer from HX to (II), it is clear that the free energies of the two processes are related. The proportionality coefficient in Brønsted's equations indicates the decisive role of proton transfer[132] in the reaction of (II) with protic acids.

The reaction of (II) with protic acids is believed to proceed via a series of consecutive equilibria[90,217]. The formation of hydrogen-bonded complexes (*a*), proton transfer via the hydrogen bond with formation of a close ion pair (*b*), the dissociation of ion pairs (*c*), electron transfer from the free verdazyl radical to the protonated radical (*d*), and protonation of the resulting leuco-base (*e*):

$$V^{\cdot} + HX \underset{a}{\rightleftarrows} V^{\cdot} \ldots HX \underset{b}{\rightleftarrows} VH^{\oplus\cdot} \ldots X^{\ominus} \underset{c}{\rightleftarrows} VH^{\oplus\cdot} + X^{\ominus} \overset{V^{\cdot}}{\underset{d}{\rightleftarrows}} VH + V^{\oplus}X^{\ominus} \underset{e}{\rightleftarrows} VH_2^{\oplus}X^{\ominus} + V^{\oplus}X^{\ominus}$$

The equilibrium constant for stage *b* depends on the strength of the acid HX and the base $VH^{\oplus}$ and can be estimated approximately in terms of the quantity $\Delta pK_a = pK_{VH^{\oplus}} - pK_{HX}$. The solvent participates in processes *a*–*e* as an active proton donor. Electron-accepting substituents in verdazyls reduce the basicity of both $V^{\cdot}$ and VH, the equilibria in processes *b*, *c*, and *d* being displaced to the left in the direction of the initial reactants. The thermodynamic parameters of the reaction of (II) with acids ($\Delta H^{\circ} = -2$–5 kcal mole^{-1}, $\Delta S^{\circ} = -5$–20 e.u.)[90,129] are consistent with the parameters of the proton transfer reaction in the interaction of amines with carboxylic acids. In DMF, chloroacetic acids apparently form 1 : 2 ion pair complexes i.e. $[VH^{\oplus}][HX(X^{\ominus})]$ [in the reaction of (II) with carboxylic acids the equilibrium in process *e* is apparently fully displaced to the left]. Comparison of the pK values for free radicals shows that verdazyls are the most basic species: $pK \simeq 1$ for triphenylphenoxyl, $pK = 5.5 \pm 2$ for 2,2,6,6-tetramethylpiperidin-1-yloxyl[133], and $pK \simeq 6.2$ for (XIII).[26]

An experimental study of the kinetics of the disproportionation of (II) in the presence of carboxylic acids showed[134] that the rate of reaction is determined by the stage involving electron transfer from free $V^{\cdot}$ to the solvated species: $v = k_3[V^{\cdot}]^2[R'CO_2H]$. The reaction with hydrogen halides may be used for the potentiometric determination of verdazyl[65]. The use of triarylverdazyls in the study of the kinetics of the ionisation of t-butyl halides in organic solvents is based on this factor[135–140]:

$$(CH_3)_3CX \rightarrow (CH_3)_3C^{\oplus}X^{\ominus} \rightarrow (CH_3)_2{=}CH_2 + HX \quad .$$

The hydrogen halide formed reacts rapidly and quantitatively with (II).

The presence of protonated silanol groups on the surface of dispersed silica induces the reverse transition from the radical to the verdazyl cation[141].

The interaction of triarylverdazyls with thio-acids (dehydrogenation of the S–H bond) has been studied in relation to thiophenols. In polar solvents the reaction proceeds via the mechanism[142]:

$$V^{\cdot} + H{-}S{-}Ph \rightarrow VH + \dot{S}Ph \quad ,$$
$$\dot{S}Ph + \dot{S}Ph \rightarrow Ph{-}S{-}S{-}Ph \quad .$$

In non-polar solvents the reaction is reversible:

$$2V^{\cdot} + H{-}S{-}Ph \overset{K_p}{\rightleftarrows} VH + V{-}S{-}Ph \quad .$$

In the reaction with thiophenols triarylverdazyls behave as dehydrogenating agents in polar solvents and also as acceptors of the $PhS^{\cdot}$ free radicals in non-polar solvents[90,142]. The rate of dehydrogenation of thiophenols $v = k_2[V^{\cdot}][PhSH]$ depends on the nature of the substituent in the *p*-position of thiophenol and increases on passing from unsubstituted to substituted thiophenols, which is apparently due to the increase of stability after the introduction of substituents into the intermediate thiol radicals. In the reaction with thiophenols verdazyls behave as electron donors, and the effect of the substituent in the radical is satisfactorily described by the Hammett equation (Table 4)[218].

4. Dehydrogenation by Verdazyl Radicals and Cations

Verdazyls are readily reduced either in an acid medium[26,130] or when compounds with mobile hydrogen, for example hydrazine and phenylhydrazine, are used[2,80,90,143]. A characteristic feature of the reduction of triarylverdazyls as well as iminoxyls[25] is that their occurrence

requires the presence of not only an electron donor, but also a proton donor[80,90]. Leucoverdazyls are readily oxidised by atmospheric oxygen to radicals and in the presence of alkalis the rate of oxidation increases sharply; thus verdazyls may be regarded as dehydrogenation catalysts:

$$V^{\cdot} + BH \rightarrow VH + B^{\cdot};\ VH \xrightarrow[O_2]{KOH} V^{\cdot}$$

Hydrazobenzene (HB) is a powerful reductant in relation to (II). The reaction kinetics have been studied in detail[144]. The rate of reaction is described by the equation $v = k_2[V^{\cdot}][HB]$ and depends little on the nature of the solvent§; as the electron-donating properties of the radical become more pronounced, the rate increases and there is a correlation of the rate constants both with σ constants and with the electrophilic σ^+ constants[147] (Table 4). There is also a correlation between $\lg k_2$ and the polarographic oxidation potentials of verdazyls (Table 4). The excellent correlation between the HB dehydrogenation rate constants and the electrophilic constants of substituents and the negative reaction constants ρ and α in Dimroth's equation shows that the structure $X^{\delta-}-H\ldots{}^{\delta+}V^{\cdot}$ makes a significant contribution to the transition state. It has been shown[90,129] that radicals (II) readily dehydrogenate compounds with acid or weakly basic properties.

The radical mobility of the hydrogen atom in the C–H bond has been studied in relation to the reaction of (II) with 1,4-dihydropyridines (DP), which are weak bases[148]. DP are analogues of biologically active compounds—coenzymes and dihydrocoenzymes. They exhibit striking electron- and hydrogen-donating properties and behave as hydrogen transferring agents in biological oxidation-reduction processes[148]. The kinetics of the reaction of (II) with *N*-benzyl-1,4-dihydronicotinamide (BDN) and 3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine (Hantzsch ester, HE) have been studied in detail[90,129,149–156]. The rate of reaction is described by the equation $v = k_2[V^{\cdot}][DP]$ and depends significantly on the nature of the substituent in the 4-position of DP. For triarylverdazyls substituted in the *p*-position of the $C_{(6)}$-phenyl ring, a complete inversion of the activity series is observed on passing from DMF to C_2H_5OH [the values of k_2(rel.) are listed below]:

	bis-CH_3O*	CH_3O	H	Cl	NO_2
		DMF, 25°			
BDN	1	1.6	1.8	2.2	2.8
HE	1	1.9	2.0	2.2	2.7
		Alcohol, 25°			
BDN	2.9	1.7	1.4	1.1	1
HE	5.1	4.3	1.8	1.6	1

* 2,6-bis-(4-methoxyphenyl)-4-phenylverdazyl.

Such unusual behaviour of verdazyl radicals is associated with the enhancement of their nucleophilic properties on passing from DMF to alcohol[90]. The rate constants for the reactions in DMF and alcohol are correlated respectively with the σ and σ^+ constants of the substituents and the polarographic reduction and oxidation potentials of radicals (II) (Table 4). In DMF the verdazyls (II) behave as electron acceptors, while in alcohol they behave as electron donors. Variation of ρ and the zero value of the latter have been observed recently for reactions involving the abstraction of hydrogen from substituted toluenes on passing from methyl to t-butyl and heptyl radicals, which the authors also explained by the enhancement of the nucleophilic properties of the radicals[157].

§ This was also observed in the dehydrogenation of the tetrazines (II).[145,146]

The observed small effects of the substituents in the verdazyls can be explained by the closeness of the experimental temperature to the isokinetic temperature β [158] [when β is traversed, the activity of (II) is reversed[90] (Table 4)]. It must be emphasised that the isokinetic or isoequilibrium relations are some of the most important characteristics of reactions, being particularly necessary for the interpretation of the polar effects of substituents, whose influence on the rate of reaction depends significantly on the experimental temperature and on β.

Data for the dehydrogenation of the C–H bonds of DP by verdazyls show that the rate of abstraction of hydrogen is in this case lower than in the reaction with O–H and S–H acids and also with HB (N–H bonds). It appears that the polarity of the dissociated bond is important for hydrogen transfer reactions involving (II). Presumably in the first stages of the dehydrogenation reaction, radical (II) is solvated (a hydrogen bond is formed) by the molecule with which it subsequently reacts. In this case the formation of the hydrogen bond precedes the formation of the activated complex and such association facilitates the reaction to a large extent[5,159]. When hydrogen is abstracted from polar X–H bonds, the increasing contribution of the Coulombic interaction between V$^{\cdot}$ and X–H leads to a decrease of the barrier¶. In the transition state of the dehydrogenation reaction there is a possibility of a shift of electron density and of proton migration via the hydrogen bond, depending on the donor–acceptor properties of the reactions[160]. The rate of dehydrogenation of (II) is influenced mainly by the specific solvation of radicals, which thus exerts the principal influence on the initial state. The solvation of the activated complex is apparently slight[90]. For verdazyls, which are some of the most stable free radicals, the main role should be played by the polar effects of the reactants and the polarisability of the hydrogen donor molecule, in conformity with Hammond's postulate.

Examination of data for reactions involving the abstraction of hydrogen by stable radicals makes it possible to represent these reactions by the following schemes[5,90,129,159]:

$$R^{\cdot} + HX - \begin{cases} \xrightarrow{a} (R^{\cdot}\ldots H\ldots X) \rightarrow RH + X^{\cdot} - \begin{cases} \longrightarrow X-X \\ \longrightarrow X-R \end{cases} \\ \xrightarrow{b} (R^{\cdot}\ldots \overset{\delta-}{H}\overset{\delta+}{X}) \rightarrow R^{\ominus} + HX^{\oplus\cdot} \rightarrow RH + X^{\cdot} \\ \xrightarrow{c} (R^{\cdot}\ldots \overset{\delta+}{H}\overset{\delta-}{X}) \rightarrow R^{\oplus} + HX^{\ominus\cdot} \xrightarrow{R^{\cdot}} RH + R^{\oplus}X^{\ominus} \\ \xrightarrow{d} (R^{\cdot}\ldots \overset{\delta+}{H}-\overset{\delta-}{X}) \rightarrow RH^{\oplus} + X^{\ominus} \xrightarrow{R^{\cdot}} RH + R^{\oplus}X^{\ominus} \end{cases}$$

They describe the possible pathways in free-radical substitution. Pathway *a* presupposes radical abstraction of hydrogen via the intermediate formation of a symmetrical activated complex. The interaction of R$^{\cdot}$ with hydrogen donors can proceed with appreciable charge separation in the transition state (*b*, *c*, and *d*). The radical behaves as an electron acceptor (*b*), an electron donor (*c*), and a proton acceptor (*d*) (*c* and *d* differ little). The choice of reaction pathway depends on the donor–acceptor properties of the reactants, the polarity of the medium, and other reaction conditions. The structure $X^{\delta-}-H^{\delta+}\ldots R^{\cdot} \rightleftharpoons X^{\delta-}\ldots HR^{\cdot\delta+}$ may contribute significantly to the transition states of the (II) dehydrogenation reactions. However, it is not clear how to reconcile the low reaction constants (Table 4) and the correlation with the σ^+ constants, indicating the localisation of a large positive charge at the reaction centre[161].

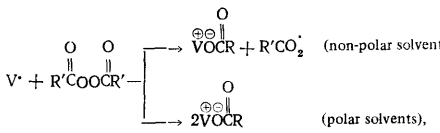
¶ In this case E_a increases in the following sequence of bonds: O–H < N–H < S–H < C–H.

In the excited state (I) readily dehydrogenates various hydrocarbons with which it does not react under the usual conditions[29].

The possibility of acid catalysis of radical reactions was demonstrated for the reactions of nitrogen oxides with amines and diamines[5]. Acid catalysis of reactions involving verdazyls takes place particularly readily because of the high rate of reaction of (II) with acids. The radical reaction pathway then changes to an ionic pathway, and the rate of reaction increases markedly[129,162]. The rate of dehydrogenation of DP on passing from (II) to verdazyl salts increases by a factor of 10^6–10^7.[90,129,155,163] The substituent in the 4-position of HE has a significant influence on the rate of reaction, which changes by a factor of 10^5 when R=H is replaced by R = C_6H_5.[164] In the reaction with a verdazyl salt the effect of the substituent in the *p*-position of the phenyl ring in the 4-position in HE is described by the Hammett and Dimroth equations (Table 4). The ease of the hydride shift reaction is due to the conversion of DP into a stable pyridinium salt[148]. The data obtained for the influence of the substituent in the 4-position in DP on the rate of reaction with (II) and verdazyl salts are in good agreement with quantum-chemical calculations, showing that the most reactive atom in the pyridine ring is the carbon atom in the 4-position[148]. Different catalytic processes occurring with participation of coenzyme models are also determined by the presence of this carbon atom. It appears that the rest of the molecule—the adenine ring and the phosphate chain—merely facilitates fixation on the protein. The use of verdazyls in the study of electron and hydride transfer with participation of DP may be of interest for the elucidation of the causes of the catalytic action of enzymes incorporating various coenzymes[148].

5. Reactions of Verdazyls with Peroxy-Compounds

The reaction of verdazyl radicals with peroxy-compounds is regarded as bimolecular homolytic substitution S_H2 at the oxygen atom[125]. It has been shown[109,112,113,125,165–169] that verdazyls readily induce the decomposition of diacyl peroxides:



where R′ = Ph, C_6H_{13}, or $C_{11}H_{23}$. The benzoyloxy-radical $PhCO_2^{\cdot}$, formed in non-polar solvents, has been identified on the basis of its decomposition products[125]. The verdazyl salts $V^{\oplus}O_2CR'^{\ominus}$ are relatively unstable and undergo further reactions associated with the opening of the verdazyl ring and the formation of formazans[125]. The rate of reaction of (II) with diacyl peroxides is described by the second-order equation $v = k_2[V^{\cdot}][\text{peroxide}]$, the stoichiometry of the reaction being represented by [(II)]/[peroxide] = 1 : 1 in non-polar solvents [this made it possible to recommend (I) as an analytical reagent for the determination of low concentrations of benzoyl peroxide (BP)][170] and ~2 : 1 in polar solvents[165,166], which is due to the stability of the radical $R'CO_2^{\cdot}$. Thermal decomposition of diacyl peroxides takes place at an appreciable rate only at elevated temperatures (70–80°C). Thus $k_1 = 4.8\times10^{-8}$ s^{-1} and E_a = 30 kcal $mole^{-1}$ for BP in benzene at 30°C;[171] the decomposition of BP induced by (II) is approximately 10^9 faster, which is due to the sharp decrease of E_a to 5–8 kcal $mole^{-1}$.

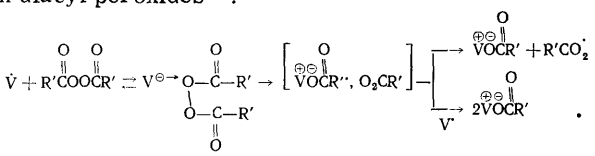
The rate of oxidation of verdazyls by BP depends little on the nature of the solvent, and the changes in the rate are not associated with the influence of the polarity of the medium, but are due to the specific solvation of (II). The relatively low activation entropy $\Delta S^{\neq} = -(29–33)$ e.u. indicates the formation of a fairly ordered transition state. In an alcoholic medium the reaction with BP leads to the regeneration of (I),[172] which is associated with the interaction of the reaction products (verdazyl salts) with alcohol molecules, the process being strongly accelerated by alkali (KOH).[125]

The rate of reaction of (II) with diacyl peroxides depends little on the nature of the substituent in the $C_{(6)}$-phenyl ring of (II) and increases as the electron-donating properties of the substituents become enhanced. The validity of the Hammett and Dimroth correlation equations and the isokinetic relation (Table 4) indicates a unique oxidation mechanism for all verdazyl radicals.

As the electron-accepting properties of substituents in BP become more marked (i.e. as the peroxy-oxygen becomes more electrophilic), the rate of reaction rises and the effect of the substituent is described by the Taft equation (which is probably associated with attack on the peroxy- and not the carbonyl oxygen atom) (Table 4). The rates of reaction of substituted BP with radicals (II) are satisfactorily correlated with the potentials $E_{1/2}$ for the reduction of peroxides[173]. The high values of α in the Dimroth equation, amounting to approximately 30, are striking (Table 4).

Special experiments established that the molecular rearrangement of the peroxide (carboxy-inversion) takes place very slowly and does not affect the rate of the reaction with verdazyls considered here[174].

On the basis of the results, the following mechanism has been proposed for the interaction of verdazyl radicals with diacyl peroxides[125]:



In the rate-determining stage of the reaction (II) attacks the peroxy-oxygen. Experiments using BP labelled with ^{18}O in the carbonyl group have shown that attack by trialkylstannyl and triphenylmethyl radicals also takes place at the peroxy-oxygen[120]. Quantum-chemical calculations, indicating a deficiency of electron density in the peroxy-linkage, are consistent with this finding[175]. The weak influence of the polarity of the medium and the low reaction constants ρ in the Hammett and Taft equations may indicate the formation of a weakly polar transition state in this reaction, i.e. the rate-limiting stage is the formation of a complex and electron transfer takes place in subsequent rapid stages. In weakly polar solvents the radical-ion pair formed is unstable and undergoes further transformations, while in polar and $R'CO_2^{\cdot}$ stabilising solvents, $R'CO_2^{\cdot}$ reacts with a second verdazyl radical.

It is noteworthy that the mechanism involving electron transfer in the rate-limiting stage (*SET*) has been quite adequately demonstrated for reactions involving the oxidation of amines by organic peroxides[171,176]. According to the authors, the validity of this mechanism is proved by correlations of the Hammett, Taft, and Dimroth types, as well as correlations between the rate constants and the

ionisation potentials and electron affinities. Furthermore, the reactions of free radicals and peroxides may involve either homolytic substitution or electron transfer, but one cannot draw a sharp boundary between them. When a complex is formed, a structure with charge separation, the extent of which is determined by the donor–acceptor properties of the reactants and other reaction conditions, may make a considerable contribution to the transition state. In many cases, the reaction is preceded by the formation of a loose complex between the reactants, and electron transfer is the rate-limiting stage[177]. A weak influence of the dielectric constant ϵ of the medium may be observed when the energy of the transition state is closer to the initial state on the reaction coordinate than to the final state. The structure of the transition state then resembles that of the initial compounds and the polar effects of the medium play a small role according to Hammond's postulate.

It is noteworthy that neither the reaction products, nor the effect of solvent polarity[177], nor the existence of various correlation equations, nor the coefficients in these equations[167] can serve as exclusive evidence for reactions involving a one-electron transfer mechanism and do not allow a choice of a particular mechanism.

6. Complex Formation

The solvent is known[5,178] to be capable of influencing significantly the kinetics and mechanism of radical liquid-phase reactions, which is attributed mainly to its ability to form hydrogen-bonded and π- or n-complexes. The formation of complexes of stable radicals with solvent molecules† as a rule leads to an appreciable decrease of their reactivity. The experimentally observed effective rate constant is expressed by a complex combination of the rate constants for the reactions of non-solvated and solvated molecules, the equilibrium constants for the complex formation reactions, and the coordination numbers of the solvate[5,178]. The formation of π-complexes is well known for many stable radicals[5]. The rates of dehydrogenation of HB [144] and dihydropyridines[90,156] and of the reactions with BP [165] and with lauroyl peroxide[109], involving triarylverdazyls, decrease appreciably on passing from hydrocarbons to π- and n-donor solvents.

The formation of π- and n-complexes of triphenylverdazyl and the kinetic manifestations of such complex formation have been investigated by spectroscopic and kinetic methods for reactions carried out in mixed solvents[109,156,169,179]. As for other stable radicals[5,178], association with only one molecule of the complex-forming solvent is significant for (I). The rate constants for the solvated radicals (I) are smaller by 1–2 orders of magnitude than those for the non-solvated radicals[109,156,169]. With increase of the concentration of the π- and n-donor solvents in the mixture, there is a parallel increase of E_a [90,109] (which may be attributed to the necessity for the dissociation of the radical–solvent complexes) and of $\Delta S^{\neq}$ (desolvation preceding the formation of the transition state leads to disordering of the system[5,178]). The formation of π-complexes of (I) in aromatic solvents is accompanied by a bathochromic shift of the $\pi \rightarrow \pi^*$ absorption band, and a decrease of the molar extinction coefficients at λ_{max} compared with spectra recorded in hexane[156,169]. The thermodynamic constants for the formation of the complexes as well as the difference between the bond energies of the complex in the ground and excited states[108],,i.e. $\Delta H_g - \Delta H_e = h(\nu_0 - \nu_S)$, where ν_0 and ν_S are the frequencies at the electronic band maxima of (I) in hexane and in a solvating solvent, as well as the equilibrium constants for the solvation of (I) in the ground and excited states, i.e.

$$V^{\cdot} + S \overset{K_g}{\rightleftarrows} V_s^{\cdot} \quad ,$$

$$V^{\cdot *} + S \overset{K_e}{\rightleftarrows} V_s^{\cdot *} \quad ,$$

where K_g and K_e are the equilibrium constants for the solvation of (I) in the ground and excited states and S is the solvent, may be determined from the absorption spectra of (I) in mixed solvents. The formation of π-complexes by (I) with benzene and pyridine causes a bathochromic shift; $\Delta H_e - \Delta H_g$ is 2.4 kcal mole^{-1} in benzene and 4.0 kcal mole^{-1} in pyridine[156,169], i.e. the stabilities of the π-complex of the excited (I) in benzene and pyridine exceed by 2.4 and 4.0 kcal mole^{-1} respectively the stability of the π-complex in the ground state. There is an increase in the equilibrium constants for solvation in the excited state [$\ln K_e/K_g = (\Delta H_e - \Delta H_g)/RT$][180] and the dipole moment (~9 D) [29] on photoexcitation of (I).[29]

Table 5. Thermodynamic parameters of the complexes of stable radicals with organic solvents[219].

Solvent	$K_{25°}$*, litre mole^{-1}	$-\Delta H°$, kcal mole^{-1}	$-\Delta S°$, e.u.	$\Delta G°$, kcal mole^{-1}
	t-Butyl mesityl nitroxide (Ref.181)			
Benzene	0.14	5.8	23.6	1.2
Chlorobenzene	0.18	3.5	15.2	1.0
Bromobenzene	0.22	2.2	10.5	0.9
Styrene	0.15	1.5	8.7	1.1
Methyl methacrylate	0.18	4.4	18.1	1.0
Methyl acrylate	0.45	10.9	38.1	0.5
Methylacrylonitrile	0.15	7.1	27.6	1.1
	Triphenylverdazyl (Refs. 155 and 169)			
Benzene	0.26	1.5	7.7	0.8
Anisole	0.45	0.9	4.7	0.5
Pyridine	0.41	2.6	10.7	0.6
	Phenoxyls (Ref.182)			
Nitrobenzene**	0.37	1.6	7.3	0.6
Nitrobenzene ***	0.81	1.4	5.0	0.1
Nitrobenzene****	1.0	2.5	8.3	0
	Dianisyl nitroxide (Ref.183)			
Benzene	0.15	6.2	24.6	1.1

* At the isoequilibrium temperature β = 283 K, we have $\ln K_p = 1.0 \pm 0.4$, which does not allow sufficiently rigorous inferences concerning the isoequilibrium conditions[158].

** 2,4,6-Tri-t-butylphenoxyl.

*** 2,6-Di-t-butyl-4-phenylphenoxyl.

**** Galvinoxyl

Since the initial state in radical reactions frequently involves a higher degree of solvation than the transition state, an increase of solvation causes an increase of E_a and makes the process less exothermic[109,156,169]. Solvation also leads to a weakening of the electrophilic or nucleophilic properties of the radicals and to a diminution of the role of polar influences[90,107,178].

† The dissolution of any substance B is accompanied, in principle, by solvation and the formation of a solvate complex having the average composition $B_{solid} + nS \rightleftharpoons BS_n$.

Table 5 presents the thermodynamic parameters for the formation of complexes by (I) and other stable radicals in π-donor solvents (the solvation equilibrium constants were determined from chromatographic[181], kinetic[182], and spectroscopic data[183]). The enthalpies and entropies of the complex formation reactions vary in parallel—the higher the heat of formation of the complex the lower the value of ΔS°. The most stable complex is that of t-butyl mesityl nitroxide with methyl acrylate. The relation between ΔH° and ΔS° for the π-complex formation reactions of stable radicals (14 complexes) is satisfactorily described by the equation[219]

$$\Delta H^0 = 0.283\Delta S^0 - 0.535 \ (r = 0.992, \ s_0 = 0.377).$$

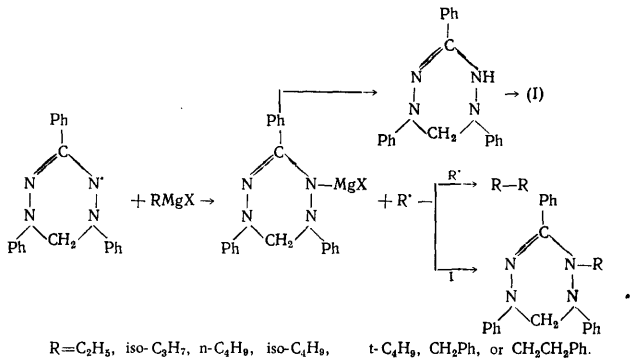
The isoequilibrium temperature β = 283 K. The free energies of formation of the complexes change comparatively little (ΔG° = 0.8 ± 0.4 kcal mole^{-1}), which is due to the closeness of the experimental temperature to β. Presumably the linear relation between ΔH° and ΔS° is a characteristic feature of the thermodynamics of the formation not only of complexes of the donor–acceptor type[184] but also of other complexes having similar structures and compositions.

The elucidation of the nature of the complexes formed by radicals with the molecules of organic solvents is important for the theory of reactivity. It has been observed for certain radicals, particularly DPPH and phenoxyls[178], that the hyperfine interaction in the EPR spectra depends on the nature of the solvent. This indicates partial electron transfer on complex formation. Virtually no changes in the hyperfine interaction constants in electron-donating solvents have been observed for (I).[90,109,156] Specific intermolecular interactions (van der Waals and dipole–dipole interactions as well as interactions involving polarisation forces) may play a significant role in the formation of complexes by radicals with solvent molecules[185]. When a π-complex of the radical and solvent molecules is formed, the π orbitals of the radical and the ligand overlap, which leads to paramagnetic shifts of the NMR lines and a change in the T_1 and T_2 relaxation times of the ligand nuclei, and is responsible for dynamic nuclear polarisation (DNP).[5] DNP studies on many radicals in electron-donating solvents have shown that the degree of transfer of the unpaired electron in the π-complex is small[5,178]. A DNP study on verdazyls led to the discovery of a large contribution of the contact interaction to nuclear polarisation, which is associated with the high spin density in the verdazyl ring[63,64]. The presence of a spin density in the ligand causes either spin polarisation of the C–H bonds or the density spreads via a hyperconjugation mechanism.

The steric orientations of the radical and the ligand are very important in the delocalisation of the unpaired electron. The orientations of the complexes of radicals with solvent molecules obey a statistical distribution[186]. The most stable configuration in this distribution is not optimal either from the standpoint of charge transfer or the pre-reaction complex. There is no reaction within the π-complex, as shown by Russell in chlorination reactions and by Buchachenko and Sukhanova[187] in the reaction involving the abstraction of hydrogen from ethylbenzene by an N-oxide radical.

7. Reactions of Verdazyls with Organometallic Compounds

Kinoshita and coworkers[40,43] showed that polymers incorporating the tetrazine structure are formed in the initiation of the anionic polymerisation of vinyl monomers incorporating the verdazyl structure by Grignard reagents, alkyl-lithium compounds, and sodionaphthalene. It is suggested that the reactions of triarylverdazyls with organolithium compounds (EtLi, BuLi), organoaluminium compounds [$Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al(t\text{-}C_4H_9)_3$, or Grignard reagents (ethyl-, isopropyl-, or butyl-magnesium bromides, benzylmagnesium chloride) proceed via the intermediate formation of a metallic salt of the verdazyl and be treated as free-radical substitution at the nitrogen atom[188–191]. The following mechanism of the reaction with (I) has been proposed for organomagnesium compounds, for example on the basis of the analysis of the reaction products:

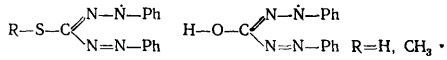


R=C_2H_5, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, t-C_4H_9, CH_2Ph, or CH_2CH_2Ph.

Metal salts of the verdazyl (I) are unstable and readily hydrolyse with formation of leuco-bases, which are oxidised to (I).

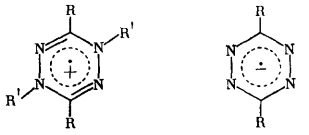
V. TETRAZINYL RADICAL-IONS AND TETRA-AZA-PENTENYL, TETRAZOLINYL, AND PHOTOTETRA-ZOLINYL RADICALS

Cyclic compounds with four nitrogen atoms (tetrazines and tetrazolium salts) as well as their linear analogues (formazans and tetra-azapentenyls) show a very high tendency towards the formation of radical structures, because of the possibility of a marked delocalisation of the unpaired electron, which lowers the energy of the ground state of the system. Thus stable (withstanding boiling) radicals are formed readily in dioxan solutions of copper dithizonate and diphenylcarbazonate complexes. The EPR spectra indicate interaction (aN ≃ 6 G) with the four equivalent nitrogen atoms[192]:



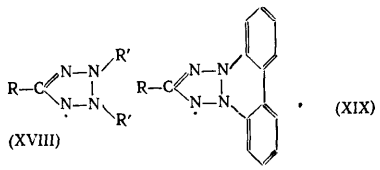
The *sym*-tetrazine/1,4-dihydro-*sym*-tetrazine system is of the oxidation-reduction type (like the quinone/hydroquinone system) and readily forms radicals[193–195]. The one-electron oxidation of 1,4-dihydro-*sym*-tetrazines leads to relatively stable radical-cations. The hyperfine interaction constants are $a^{N}_{1,5}$ = 7.4–8.0 G and $a^{N}_{2,4}$ = 3.4–4.5 G depending on the substituents. When *sym*-tetrazines are reduced by alkali metals, fairly stable radical-anions

are formed:



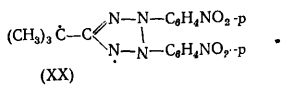
R = CH_3, or Ph, R' = H; R = Me, Et, iso-Pr, or
R, R' = Ph; $(Ph)_2CH$.

The first stable tetrazolinyl and phototetrazolinyl radicals [(XVIII) and XIX) respectively] were synthesised by Kuhn and coworkers[196]:



(XVIII) (XIX)

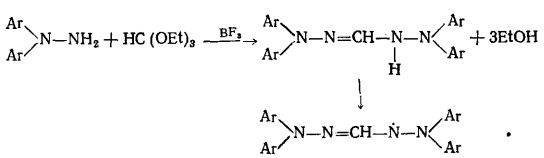
The triphenyltetrazolinyl radical is stable in air and its EPR spectrum indicates the interaction of the unpaired electron with the two pairs of equivalent nitrogen atoms ($a^N_{2,3}$ = 7.5 G, $a^N_{1,4}$ = 5.6 G). The radicals are readily obtained on reduction of tetrazolium and phototetrazolium salts or on homolytic abstraction of hydrogen from formazans, or on their oxidation to tetrazolium salts[197-199]. Intramolecular electrochemical cyclisation of formazans to tetrazolium salts proceeds via the intermediate formation of radical-cations[200]. It has been shown that the tetrazolium radicals formed on oxidation of formazans, on reduction of tetrazolium salts, on disproportionation of a mixture of a formazan and a salt, and on homolytic abstraction of hydrogen from formazan have cyclic structures[201]. Only one stable tetrazolinyl radical, namely radical (XX), has been isolated in a crystalline state[202]:



(XX)

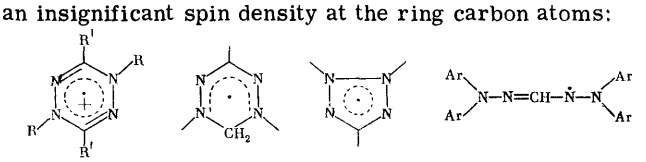
A study of the magnetic susceptibility of (XX) showed that[198] it is monomeric in solution. The stability of tetrazolinyl radicals increases as the electron-accepting properties of the substituents in the N-phenyl rings become more pronounced and $a^N_{2,3} > a^N_{1,4}$ for both tetrazolinyl and phototetrazolinyl radicals.

Apart from cyclic radicals with four nitrogen atoms, their linear analogues (tetra-azapentenyl radicals) are also known[203-205]. They are obtained by oxidising with oxygen, silver oxide, or lead dioxide the products of the condensation of orthoformic ester with an asymmetric hydrazine:



These radicals have a bluish-green colour (λ_{max} = 600–700 nm) and are much less stable than their cyclic analogues. Some of them, for example 1,1,5,5-tetraphenyl-1,2,4,5-tetra-azapentenyl, are stable and can exist for weeks in a crystalline form. In solution tetra-azapentenyls are monomeric and obey the Beer–Lambert law.

Comparison of the EPR spectra of verdazyls, tetrazinyl radical-ions, tetrazolinyl radicals, and tetra-azapentenyls illustrates the significant influence of the delocalisation of the unpaired electron on the stability of the radicals. All the radicals and radical-ions have seven π electrons and an insignificant spin density at the ring carbon atoms:



Most of the spin density is located at the terminal nitrogen atoms of the hydrazidinyl system[6]: $a^N_{1,5}/a^N_{2,4}$ is ~1 for verdazyls, ~1.7 for tetra-azapentenyls, and ~2 for tetrazinyl radical-cations; $a^N_{2,3}/a^N_{1,4}$ is ~1.3 for tetrazolinyls and ~2 for phototetrazolinyls. Electron-accepting substituents in the benzene ring cause a partial withdrawal of electron density from the central ring and tend to make the nitrogen atoms equivalent; the stability of tetrazolinyls and phototetrazolinyls then increases.

VI. PRACTICAL ASPECTS OF THE CHEMISTRY OF VERDAZYL RADICALS

The vigorous development of the chemistry of verdazyls is associated with the important role which they play in the solution of various theoretical and practical problems.

Verdazyls proved to be convenient objects for the solution of many problems in theoretical chemistry (the determination of the mechanisms of elementary chemical reactions, the determination of the relation between the reactivity and structure of reagents, and the study of the propagation of π- and σ-electron spin density, intermolecular interactions, weak exchange interactions of electrons, ferromagnetic interactions, etc.). In many cases it has been possible to elucidate in relation to verdazyls the influence of solvent polarity, π- and n-complex formation, and hydrogen bonds on the kinetics of liquid-phase radical reactions. The important role of polar factors (and of the isokinetic temperature in their interpretation) in the kinetics and mechanisms of homolytic reactions has been demonstrated. Verdazyls are convenient spin labels for the study of the dynamic structures of polymers in solutions; verdazyl bi- and tri-radicals are used to study the structures and molecular motions in isotropic and liquid-crystal solutions[206,207], which is of interest for structural chemistry, because it makes it possible to determine the number of unpaired electrons and the average distance between them.

As a result of the discovery of methods for the synthesis of verdazyls without affecting the free valence, it is possible to obtain spin-labelled compounds, so that verdazyls are likely to be useful in molecular biology, biophysics, the physical chemistry of polymers, the synthesis of spin-labelled drugs, and models of physiologically active compounds, and in the study of the mechanism of the action by EPR.

Verdazyls can be used in analytical chemistry as indicators[217]. In view of their very high stability, ready availability, and the possibility of obtaining them as 100% pure preparations, verdazyls are likely to be useful as standards in quantitative measurements by EPR (the percentage content of DPPH, for example, varies markedly with time[208]). The possibility of using verdazyls in laser engineering has been investigated[209]. Being stable over a wide range of potentials (~1 V), triphenylverdazyl may be used as a "trap" for short-lived radicals obtained in electrode reactions (DPPH, for example, is electrochemically stable only in the region of ~0.3 V).[97]

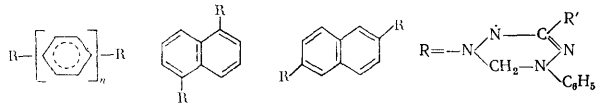
Pokhodenko et al.[210] showed recently that, in the electron transfer reaction between two stable radicals one of which is triphenylverdazyl, an e.m.f. ranging from several tenths of a volt to several volts is generated. The formation of reversible galvanic cells based on stable radicals or radical-ions[211] is of considerable theoretical and practical interest.

The use of verdazyls as dyes is promising. In contrast to DPPH, verdazyls dye fabrics uniformly, which permitted their employment for the study of the wear of knitted materials[212]. The ability of verdazyls to dye polymeric materials may prove useful in the study of the mechanical degradation of polymers by EPR.

Verdazyls react with many compounds which are sources of free radicals: peroxides, hydroperoxides, and transition metal compounds. The properties of verdazyls as free radical acceptors permit the study of cell effects in the decomposition of initiators of radical polymerisation and the dependence of the yield of radicals on the nature of the solvent. The ability of verdazyls to terminate kinetic chains by reacting with active radicals makes it possible to use them as inhibitors of autoxidation and radical polymerisation. Thus the polymerisation of styrene in the presence of triphenylverdazyl (1 : 30 000) is strongly inhibited and the autoxidation of benzaldehyde at 20°C is fully suppressed[2]. Water-soluble verdazyls inhibit the decomposition of H_2O_2 initiated by catalase or platinum black[26]. Verdazyls inhibit effectively the polymerisation not only of styrene but also of other monomers—methyl methacrylate, acrylonitrile, vinyl chloride, and vinyl acetate. In the presence of (I) polarisation is fully suppressed and after its consumption takes place at the same rate as in the absence of added inhibitor. The induction period increases linearly with increasing concentration of (I) for the same initiator concentration, which shows that, in contrast to aliphatic nitroxides, (I) does not undergo side reactions. The linear dependence of the induction period on the verdazyl concentration shows that these radicals initiate the formation of kinetic chains to only a slight extent[115]. The period corresponding to inhibition by verdazyls may be measured spectroscopically and verdazyls can thus be used to determine the rate of initiation. In contrast to hydroxylamines, leucoverdazyls do not affect the induction period but inhibit polymerisation effectively. The activities of various inhibitors of radical polymerisation have been compared in relation to the polymerisation of oligourethane-acrylate initiated by azobisisobutyronitrile. Verdazyl mono- and bi-radicals are powerful inhibitors[213,214]. Its high effectiveness, the simplicity of its synthesis, its ready availability, and the possibility of the visual monitoring of its concentration made it possible to recommend triphenylverdazyl as a promising stabiliser in the manufacture, storage, and processing of many oligomeric and monomeric compounds[214].

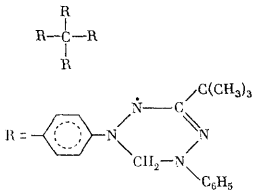
The development of research into polymers with stable radicals in the main or side chains was stimulated by the great interest in new semiconducting materials. Polymers with verdazyl radicals (molecular weight 2300–4800) as well as oligomers containing verdazyls in the polymer matrix are of interest from the standpoint of their electrical properties, radical reactions, and practical employment as antioxidants, redox indicators, and catalysts of certain oxidation-reduction reactions[36-45,115-117,215].

During the preparation of the manuscript for the press, a number of studies devoted to the chemistry of verdazyl radicals were published. New verdazyls containing heteroaromatic substituents in the 1-position of the formazan group[220,221] and triarylverdazyl radicals with perfluorophenyl substituents[222] were synthesised. New verdazyl biradicals have been obtained from the corresponding diformazans or monoverdazyls using a 1-cyano-1-methylethyl protecting group[223]:



$R' = C_6H_5$, or $C(CH_3)_3$.

Neugebauer et al.[224] recently obtained the tetraverdazyl (XXI), which is readily soluble in organic solvents:



4-Verdazyl[2,2]paracyclophanes have been obtained in order to study the characteristics of the distribution of spin density and interactions involving charge transfer[225]. The magnetic properties, ENDOR spectra, and characteristics of the intermolecular interactions of verdazyls with C_6H_6 and CCl_4 have been investigated[226-228].

Studies on the chemical properties of verdazyls have been developed further. It has been observed[229] that triphenylverdazyl catalyses the dark PI_3 polymerisation reaction in hexane, forms complexes with molecular oxygen[230], and decomposes peracids[231]. Triphenylverdazyl reacts reversibly with hydroquinone[232] and forms dicyanodiaziridine in the reaction with bromodicyanomethane[233]. The regeneration of verdazyls in reactions with peroxy-compounds, discovered by Yarmolyuk[125], has been investigated[234,235]. A study has been made of the influence of the composition of binary solvents on the kinetics of chemical reactions with participation of verdazyls[236-238]. The oxidation-reduction reactions of verdazyls have been investigated[239,240]. Quantum-chemical calculations on verdazyl radicals, ions, and leuco-compounds by the INDO method with total optimisation of the geometry, which made it possible to calculate their electronic and steric structures, can serve as a basis for the understanding and prediction of the chemical properties and reactivities of these species[241,242].

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