Aromatic polyazides and high-spin nitrenes

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Aromatic polyazides are widely used as starting compounds in organic synthesis and for preparation of nitrogen—carbon nanomaterials and high-spin nitrenes. The latter have the strongest magnetic properties among organic polyradicals and are of considerable interest for studying molecular magnetism. The review summarizes the results of recent studies of aromatic polyazides and high-spin nitrenes carried out at the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

Key words: azides, nitrenes, high-spin states, molecular magnetism, energetic materials, nanomaterials.

Introduction

Aromatic azides are widely used as starting compounds in organic synthesis, as photoaffinity and cross-coupling reagents in molecular biology and polymer chemistry and as photoresists in microelectronics.[1—4] When molecules contain several nonequivalent azido groups, these groups can selectively undergo 1,3-dipolar cycloadditions, reduction, phosphorylation, and decomposition upon photolysis and thermolysis.[5] The use of selective reactions of the azido groups opens up new in principle prospects in the targeted synthesis of organic compounds. Yet another new trend in the application of aromatic polyazides is as the starting compounds to prepare various nitrogen—carbon nanomaterials possessing a number of useful chemical, physical, and biological properties.[6—10] The mechanism of decomposition of aromatic polyazides and the key steps of formation of nitrogen—carbon nanomaterials are studied by photolysis of the starting polyazides in cryogenic matrices.[11,12] The reaction intermediates are high-spin nitrenes, which are themselves of considerable interest as objects for investigating the molecular magnetism in organic compounds.

This review summarizes the results of recent studies of aromatic polyazides and high-spin nitrenes carried out at the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

Synthesis and properties of aromatic polyazides

The synthesis of only 22 monocyclic aromatic compounds with three or more azide groups in the aromatic ring has been described to date (compounds **1**—**22**). The first synthesized polyazide, 2,4,6-triazido-1,3,5-triazine (**1**) was obtained by the reaction of 2,4,6-trichloro-1,3,5-triazine with NaN_3.[13] This triazide immediately attracted considerable attention as an energetic compound easily exploding on mechanical action (impact, friction, pressure). The high sensitivity of triazide **1** to mechanical action is due to the high content of nitrogen in its molecule (82.35%) and great positive enthalpy of formation (5162 kJ kg^{-1})[6]. The repeated attempts to use this triazide for photochemical generation of high-spin nitrenes have long been unsuccessful due to low kinetic stability of these nitrenes in crystals of the starting triazide or frozen organic solutions.[14—16] Pyrolysis of triazide **1** results in the formation of nitrogen—carbon nanomaterials, C_3N_4 and C_3N_5, having very high mechanical strength and chemical inertness.[10] Using IR and ESR spectroscopy, the mechanism of photochemical decomposition of triazide **1** in argon matrices was studied and it was established that nitrogen—carbon nanomaterials C_3N_4 are formed from the NCN=C=NCN molecules, which are decomposition products of the septet 2,4,6-trinitreno-1,3,5-triazine.[11,12]

The closest analog of triazide **1** is 2,4,6-triazidopyrimidine (**2**) obtained by the reaction of 2,4,6-trichloropyrimidine with NaN_3.[17] Biological testing demonstrated that this triazide has a very high antitumor activity with respect to many forms of sarcoma and leukosis.[18] Like triazide **1**, triazide **2** is also very explosive. The catalytic detonation of triazide **2** in the presence of $Ni(ClO_4)_2$ produces nitrogen—carbon nanotubes in a more than 90% yield.[6] The mechanism of photochemical decomposition of triazide **2** in cryogenic matrices was studied by IR and ESR spectroscopy, and it was found that nitrogen—carbon nanotubes are formed from the NCN, NNC, and NCN=C=NCN molecules, resulting from decomposition

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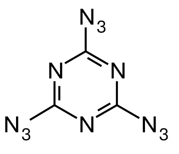
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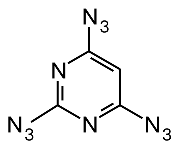
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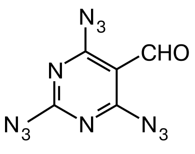
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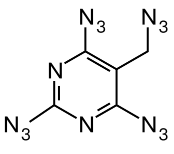
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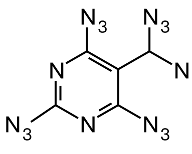
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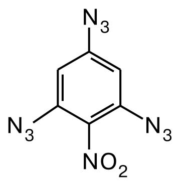
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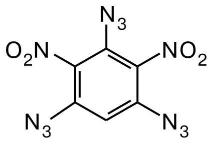
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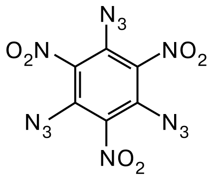
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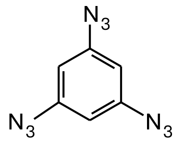
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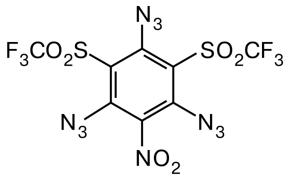
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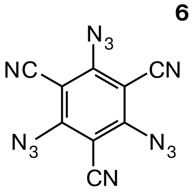
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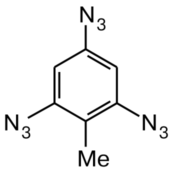
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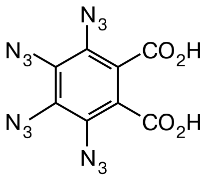
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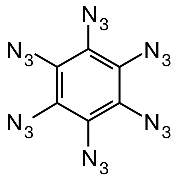
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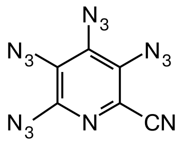
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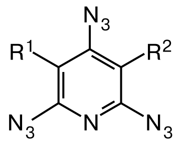

16—22

16: $R^1 = R^2 = F$
17: $R^1 = R^2 = Cl$
18: $R^1 = R^2 = Br$
19: $R^1 = R^2 = CN$
20: $R^1 = Cl, R^2 = CN$
21: $R^1 = Cl, R^2 = CF_3$
22: $R^1 = F, R^2 = CN$

of the septet 2,4,6-trinitrenopyrimidine.[19] As potential energetic polyazides with relatively low impact sensitivity, azidopyrimidines **3—5** were prepared.[6] In relation to these compounds, it was shown that a decrease in the melting point of polyazides substantially decreases their impact sensitivity. Especially low sensitivity is inherent in liquid pentaazide **3**, despite the presence of five explosion-hazardous azide groups in its molecule.

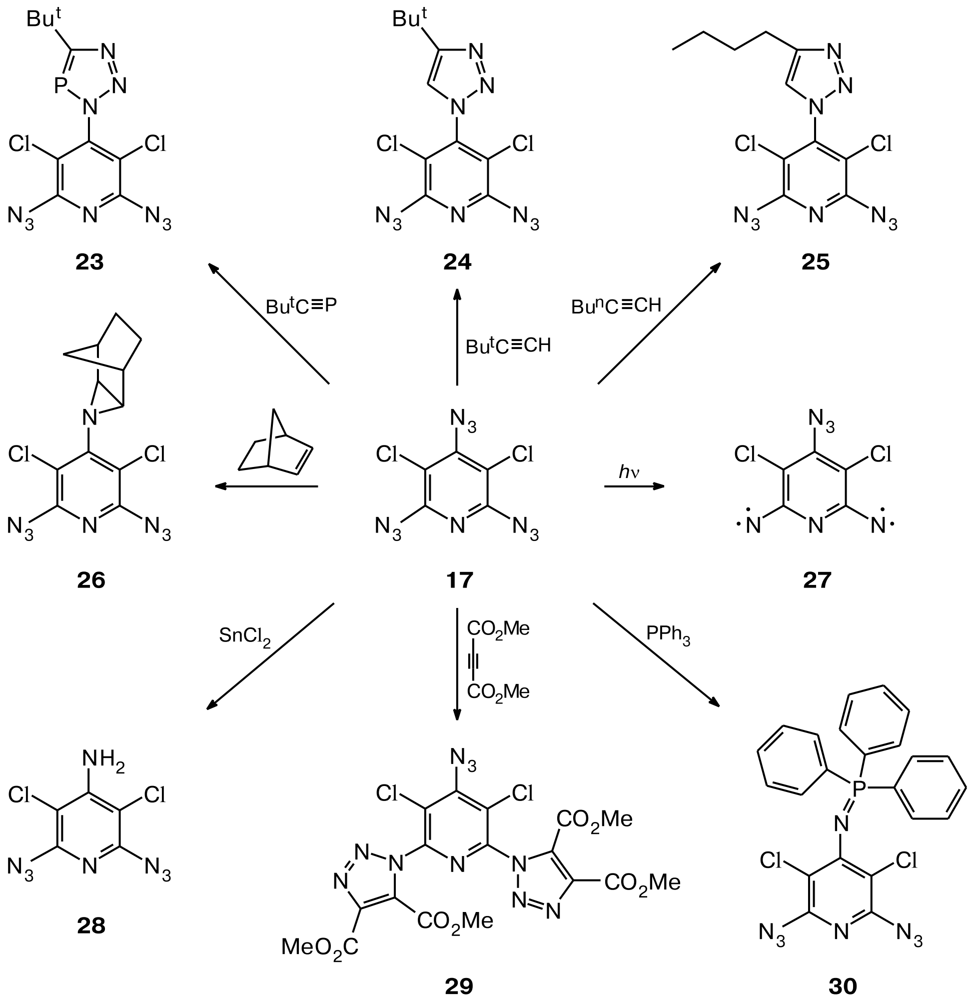
Triazidobenzenes **6—12** were synthesized by the diazotization—azidation reaction of the corresponding triamines.[20—24] Triazides **6—8** were studied only as regards their possible use as explosives combining useful properties of nitrobenzenes and azides.[20] Triazides **9** and **10** were considered as potential cross-coupling reagents for polymer chemistry, although subsequently they did not find wide practical use.[21,22] The most notable role in the development of chemistry was played by triazides **11** and **12**, from which the first septet trinitrenobenzenes were obtained by low-temperature solid-state photolysis.[23,24] The synthesis of tetraazidophthalic acid **13** by the reaction of tetrachlorophthalic anhydride with NaN_3 and the preparation of hexaazidobenzene **14** in a very low yield by the reaction of hexafluorobenzene with NaN_3 were also reported.[25,26] However, no physicochemical studies of these compounds were carried out and the compounds were not used for any purpose. The only monocyclic aromatic compound with four azide groups in the ring whose structure was studied in detail by physicochemical methods is tetraazidopyridine **15** obtained by the reaction of tetrachloro-2-cyanopyridine with NaN_3.[27] This tetraazide is highly sensitive to mechanical action, it explodes on fast heating to 23 °C. On very slow heating, tetraazide **15** melts at 103 °C and then decomposes to give the black product C_3N_3 similar to the product obtained upon pyrolysis of triazides **1** and **2**.

2,4,6-Triazidopyridines **16—22** obtained by the reactions of the corresponding perhalogenated pyridines with NaN_3 are the best studied aromatic triazides.[28—34] The ease of replacement of halogen atoms in the pyridine ring by the azido groups considerably decreases in the series Br > Cl > F and increases upon the introduction of electron-withdrawing groups such as CN and CF_3 into the β-position of the pyridine ring. Since the nitrogen content in the molecules of triazides **16—22** is relatively low (<69%), they are slightly impact- or friction-sensitive. The most interesting energy characteristics were found for triazide **19**, which considerably surpasses triazide **1** in the enthalpy of formation (5740 kJ kg^{-1}) but is much less explosive.[27]

Selective reactions of azide groups

The reactions of azides used most often in organic chemistry include 1,3-dipolar cycloaddition, reduction of azides to amines, and Staudinger phosphorylation of azides. For long, aromatic monoazides or di- and triazides with equivalent azide groups have been used in these reactions.[1—4] Then 2,4,6-triazido-3,5-dibromopyridine (**18**) containing non-equivalent azide groups in the α- and

Scheme 1



γ-positions of the pyridine ring was synthesized.[28] The reaction of this triazide with an equimolar amount of PPh$_3$ was found to occur selectively to give only one of the two possible isomeric iminophosphoranes NC$_5$(Br)$_2$(N$_3$)$_2$—N=PPh$_3$. Unfortunately, due to the absence of ^{13}C NMR data, the structure of the obtained product was not determined. Later, triazidopyridines **16**, **17**, **19**, and **20** were prepared and studied in the 1,3-dipolar cycloaddition, reduction, phosphorylation, nucleophilic substitution, thermolysis, photolysis, and γ-radiolysis.[29—52] Scheme 1 presents some reactions of triazide **17** to produce compounds **23—30**.

Quantum chemical and X-ray diffraction studies showed that the γ-azide groups of triazides **16—20** located in the nodal symmetry line have lower electron density than the α-azide groups and, as a consequence, they are electron-deficient and are characterized by weaker N—N$_2$ bonds, more curved N$_\alpha$—N$_\beta$—N$_\gamma$ chains of atoms, more electrophilic terminal N$_\gamma$ atoms, lower HOMO density, and higher LUMO density.[39,40,50—53] As a consequence, the γ-azide groups of triazides **16—20** selectively add electron-rich dipolarophiles (norbornenes, Bu^{t}C≡CH, Bu^{n}C≡CH, Bu^{t}C≡P) and PPh$_3$, can be selectively reduced to amines and selectively thermolyzed. Conversely, α-azide groups of triazides **16—20** selectively add electron-deficient dipolarophiles (MeO$_2$CC≡CCO$_2$Me) and selectively dissociate on exposure to electron impact, UV light, or γ-radiation.[29—52]

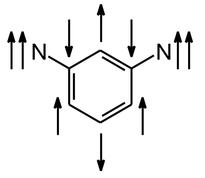
Currently, selective reactions of the azide groups of organic polyazides are successfully used in the synthesis of complex biologically active compounds.[54—57]

Topology of high-spin nitrenes

The vast majority of organic compounds exist in the singlet spin state. This means that the molecules of these compounds have one energy minimum irrespective of the external magnetic field. When molecules having one unpaired electron get into an external magnetic field, the lower energy level is split into two sublevels due to orientation of the electron spin parallel and antiparallel to the external magnetic field. Such molecules are called doublet molecules ($S = 1/2$). When the molecule has two unpaired electrons, each unpaired electron occurs in the magnetic field induced by the adjacent electron. Therefore, splitting of the lower energy level in these molecules into three sublevels, W_1 (both spins are along the field), W_{-1} (both spins are against the field), and W_0 (the spins are opposite to each other) occurs without the external magnetic field and is called zero-field splitting and the molecules themselves are called triplet molecules ($S = 1$).

The energy gaps between the three sublevels are described by two magnetic parameters, D and E. The parameter D is often called internal magnetic anisotropy. This parameter characterizes the strength of dipole—dipole interactions between the unpaired electrons, it is directly proportional to the spin density on the radical centers and inversely proportional to the distance between the spins cubed.[58] The larger the parameter D, the stronger the magnetic properties of the molecule, because the energy barrier between two magnetic states, W_1 and W_{-1}, is directly proportional to the parameter D and to the system spin state squared S^2.[59] The parameter E characterizes the symmetry of the magnetic system, it is equal to zero if the magnetic axes X and Y are equivalent (axial symmetry). The molecules with four unpaired electrons have five energy sublevels and are called quintet molecules ($S = 2$), and molecules with six unpaired electrons have seven sublevels and are called septet molecules ($S = 3$). The magnetic parameters D and E can be measured from the ESR spectra of high-spin molecules where these parameters describe line splitting in the spectrum. Now researchers are able to record and analyze the ESR spectra of nitrenes having quartet, quintet, and septet spin states.

Among all organic polyradicals, high-spin nitrenes have the highest D values and exhibit the strongest magnetic properties.[60] The active research of high-spin nitrenes started after the publication[61] of the first ESR spectra of quintet dinitrenes **31** and **32**. Then the ESR spectra of more than 50 structurally different quintet dinitrenes were recorded.[60] The key outcome of these studies is clear-cut understanding of what dinitrene structures can have the quintet ground spin state and what ESR spectra are observed for different dinitrenes. For a large number of examples, it was demonstrated that dinitrenes of types **31**—**33** with spin density of the same sign on the nitrene centers always have a quintet ground state. In the case of dinitrenes like **34** with different signs of spin density on the nitrene centers, the molecules have a singlet ground state located 100—200 cal mol^{-1} below the quintet excited state.[61] For these systems, it is possible to observe the ESR spectra of the excited quintet dinitrenes, which differ considerably from the spectra of dinitrenes with a quintet ground state. The singlet dinitrenes of type **35**—**38** whose molecules contain linker atoms or fragments with a lone electron pair, which changes the electron density sign in



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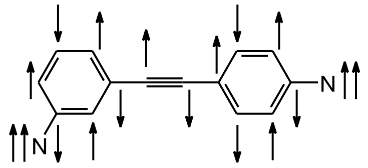

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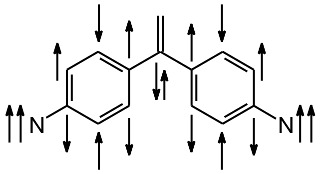

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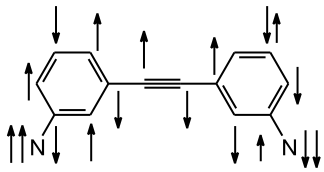

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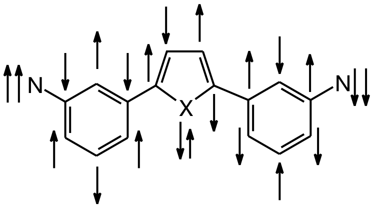
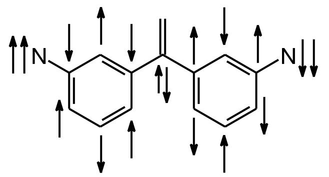


35—37



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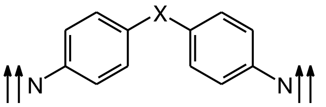

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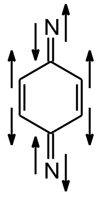
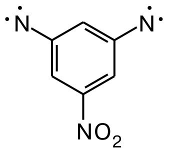


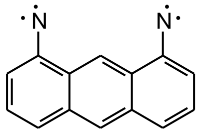
41

X = O (**35**, **39**), S (**36**, **40**), NH (**37**)



42

$|D|$ = 0.224
$|E|$ = 0.038



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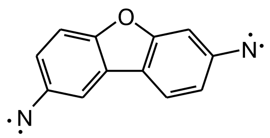
$|D|$ = 0.243
$|E|$ = 0.003



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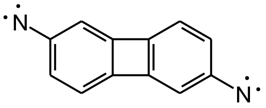
$|D|$ = 0.292
$|E|$ = 0.009



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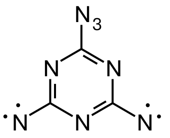
$|D|$ = 0.260
$|E|$ = 0.000



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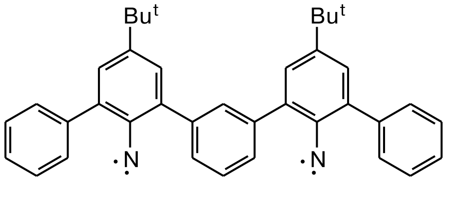
$|D|$ = 0.280
$|E|$ = 0.058



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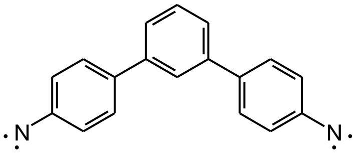
$|D|$ = 0.340
$|E|$ = 0.011



48

$|D|$ = 0.201
$|E|$ = 0.036

Note. The $|D|$ and $|E|$ values are given (cm^{-1}).

the neighboring ring, can be conventionally assigned to this group of compounds.[60] The oxygen atom in dinitrenes such as **39** blocks the ferromagnetic interactions between the nitrene centers, while the sulfur atom in dinitrene **40**, conversely, does not hamper these interactions. The dinitrene molecules of type **41** have a quinoid structure and a singlet ground spin state. The ESR spectra of triplet excited molecules recorded for these systems almost do not differ from the ESR spectra of most triplet biradicals.[60]

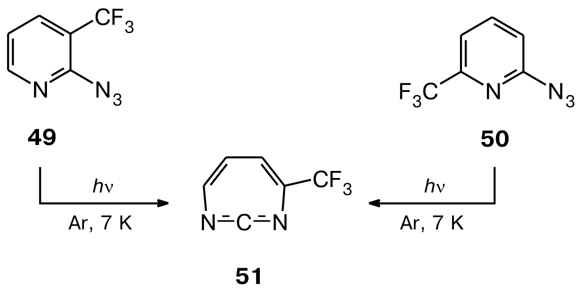
With the advent of programs for computer simulation of the ESR spectra of high-spin nitrenes, precise measurements of the magnetic parameters became possible. The magnetic parameters of quintet dinitrenes **42**—**48** were determined; for dinitrene **42**, all ESR signals were also assigned.[16,62—66]

High-spin nitrenes are studied at the Institute of Problems of Chemical Physics, Russian Academy of Sciences. The initial task was to study the photolysis of triazides **16**—**20** and to record the first ESR spectra of septet trinitrenes. Subsequently the works became more extensive and covered not only magnetic and structural ESR studies of quintet and septet nitrenes but also studies of photochemical reactions of high-spin nitrenes by matrix IR and UV spectroscopy. The results of these works are discussed below.

Matrix IR spectroscopy of high-spin nitrenes

Not a single IR spectrum of a triplet pyridylnitrene was recorded before 2000. Extensive studies of the photolysis of many azidopyridines (*e.g.* **49** and **50**) in argon at 7 K showed that pyridylnitrenes formed in the first step of photolysis immediately rearrange to diazacycloheptatetraenes (*e.g.* **51**), which can be detected by IR spectroscopy (Scheme 2).[67] These data cast doubt on the possibility of photochemical synthesis of high-spin pyridylnitrenes in amounts sufficient at least for their detection by IR spectroscopy.

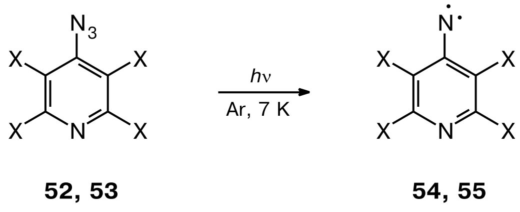
Scheme 2



In order to elucidate the factors preventing the undesirable rearrangements of pyridylnitrenes to low-spin products, we studied photolysis of azides **52** and **53** in argon at 7 K (Scheme 3).[68,69] It was found that the only products of photolysis of azidopyridines with protecting Cl and F atoms located in the *ortho*-positions to the azide group are photochemically highly stable triplet nitrenes **54** and **55**.

Attempted insertion of nitrenes into the aromatic ring from the side of endocyclic nitrogen by photolysis of azides

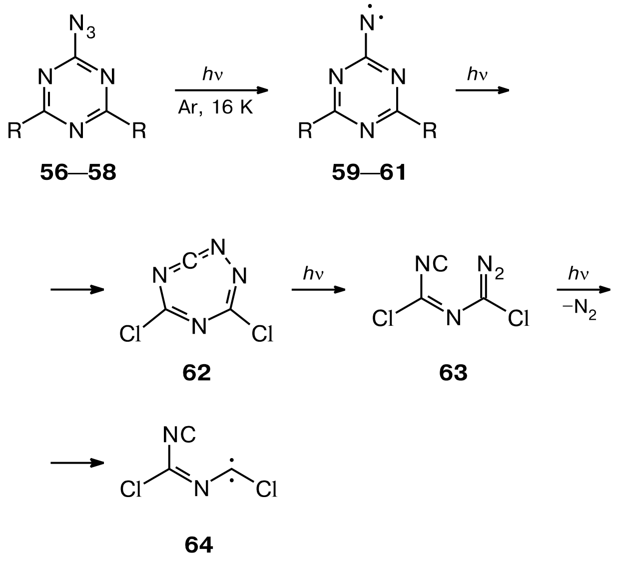
Scheme 3



X = F (**52**, **54**), Cl (**53**, **55**)

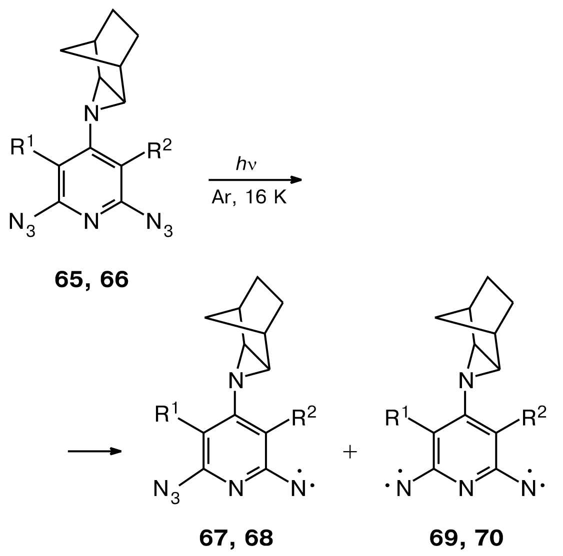
56—58 demonstrated that this reaction takes place only for nitrene **59** ($D = 1.377$ cm^{-1}, $E = 0.011$ cm^{-1}) having a moderate spin density on the nitrene center (Scheme 4).[70,71] Triplet nitrenes **60** ($D = 1.427$ cm^{-1}, $E = 0.013$ cm^{-1}) and **61** ($D = 1.465$ cm^{-1}, $E = 0.011$ cm^{-1}) having very high spin density are photochemically stable and are formed upon photolysis of azides **57** and **58** in a quantitative yield.[70,71] In this study, it was found that the photochemical insertion of nitrene centers into the aromatic ring is possible only for triplet nitrenes with 0.9 cm^{-1} $< D <$ 1.4 cm^{-1}.

Scheme 4



Photolysis of diazides **65** and **66** produced quintet dinitrenes **69** and **70** containing some triplet nitrenes **67** and **68** that were not completely photolyzed (Scheme 5).[68] Photolysis of triazide **17** gave even a more complex mixture of products consisting of isomeric triplet nitrenes **71** and **72**, quintet dinitrenes **73** and **74**, and septet trinitrene **75** (Scheme 6).[68] Attempts to perform complete photolysis of the intermediate azidonitrenes to pure di- and trinitrenes were unsuccessful. However, no products of nitrene insertion into the pyridine ring or products of decomposition of high-spin nitrenes were found. Quintet dinitrenes **69**, **70**, **73**, and **74** and septet trinitrene **75** were the first organic compounds having quintet and septet ground spin states to be detected by IR spectroscopy. In the studies, it was found that increase in the spin state of organic molecules by unity decreases the intensity of IR bands by an order of magnitude. To enable recording of the IR bands of septet trinitrenes, the yield of trinitrenes upon photolysis of triazides should be nearly quantitative.

Scheme 5

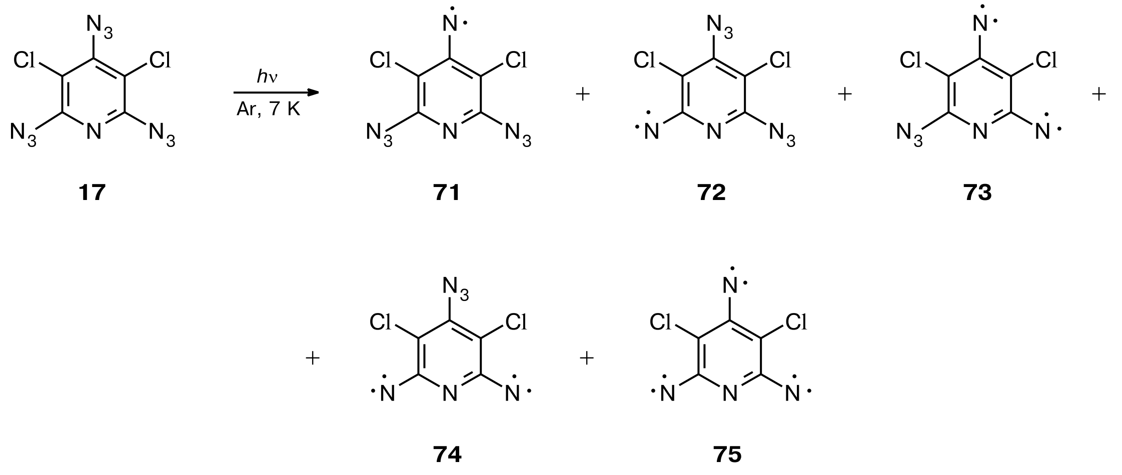


R^1 = R^2 = Cl (**65**, **67**, **69**); R^1 = Cl, R^2 = CN (**66**, **68**, **70**)

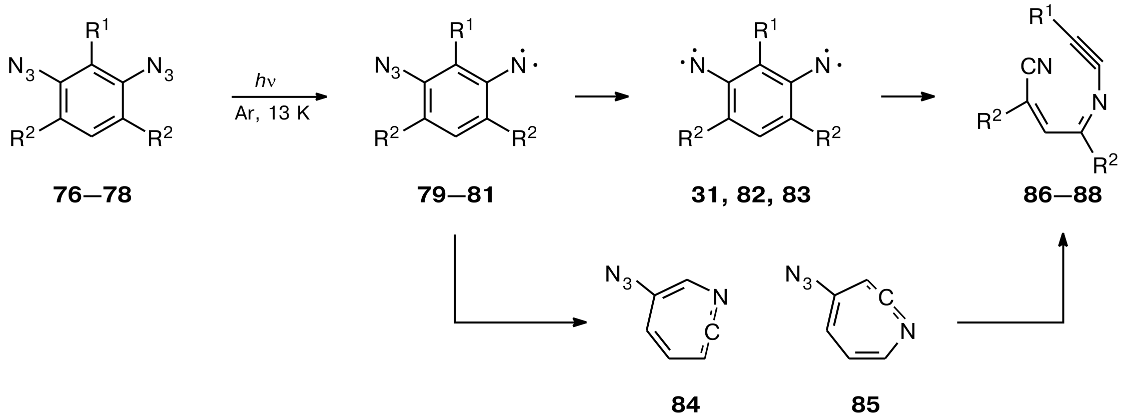
It has long been unknown what is the yield of quintet dinitrene **31** upon the photolysis of diazide **76** (Scheme 7). To clarify this issue, we studied the photolysis of diazide **76** and its methylated derivatives **77** and **78** in argon at 13 K, which occurs *via* nitrenes **79—81** and dinitrenes **31**, **82**, **83**.[72,73]

It turned out that the maximum yield of dinitrene **31** (34%) as a mixture with triplet nitrene **79** (45%) and ring expansion by-products **84** (7%) and **85** (14%) is achieved after 1 min of photolysis. Then all of these compounds decompose under the action of light mainly to acetylenes **86—88**. The presence of protecting methyl groups in the benzene ring completely suppresses the undesirable rearrangements of triplet nitrenes, thus markedly increasing the yield of dinitrenes **82** (50% after photolysis for 2 min) and **83** (95% after photolysis for 30 min). Other products formed in these steps of photolysis were triplet nitrenes **80** (50%) and **81** (5%). In the case of photolysis of diazide **78**, the first pure IR spectrum of quintet dinitrene was recorded.[72] Recently, together with researchers from the Bochum University, we also recorded the pure IR spectrum of the septet trinitrene obtained by photolysis of 2,4,6-triazidotoluene in argon at 4 K.[74]

Scheme 6



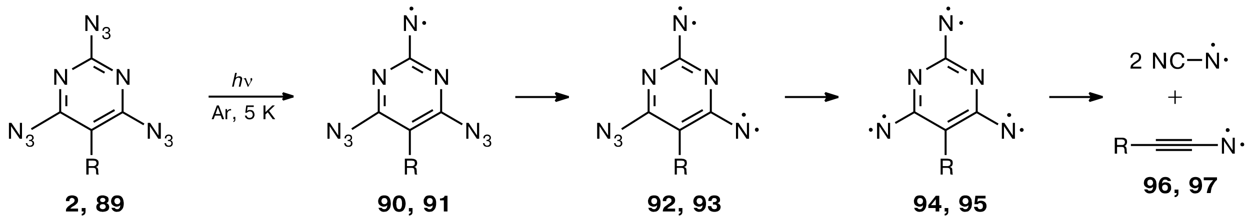
Scheme 7



$R^1 = R^2 = H$ (**31**, **76**, **79**, **86**), Me (**78**, **81**, **83**, **88**); R^1 = Me, R^2 = H (**77**, **80**, **82**, **87**)

Interesting results were obtained for photolysis of 2,4,6-triazido-3,5-difluoropyridine in neon at 4 K studied by matrix IR spectroscopy.[74] Under these conditions, photolysis of the triazide occurs selectively to give successively the corresponding triplet 2-nitrenopyridine, quintet 2,6-dinitrenopyridine, and then almost pure septet 2,4,6-trinitrenopyridine. The photolysis of triazides **2** and **89** also occurs selectively to give triplet nitrenes **90** and **91**, quintet dinitrenes **92** and **93**, and septet trinitrenes **94** and **95** (Scheme 8).[75] The latter are formed in a 10—15% maxi-

Scheme 8



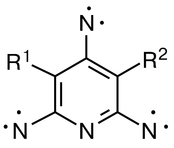
R = H (**2**, **90**, **92**, **94**, **96**), Cl (**89**, **91**, **93**, **95**, **97**) mum yield upon photolysis for 1 min and then decompose to triplet cyanonitrenes and acetylenylnitrenes **96** and **97** (see Scheme 8).

ESR spectroscopy of high-spin nitrenes

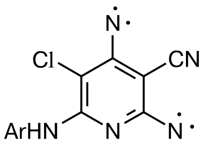
Before 2000, no ESR spectra of septet trinitrenes were reported. Our study of the photolysis of triazides **16**, **17**, **19**, and **20** in 2-methyltetrahydrofuran (2MTHF) solutions frozen at 77 K aimed at detecting trinitrenes **75** and **98—102**, which was carried out in cooperation with researchers of the University of Massachusetts, allowed us to record the ESR signals of septet trinitrenes **75** and **98** and to determine for the first time the magnetic parameters of such molecules ($D = 0.100$ cm^{-1}, $E = 0.0005$ cm^{-1} and $D = 0.098$ cm^{-1}, $E = 0.000$ cm^{-1} for **75** and **98**, respectively).[76] The ESR spectra of a large series of quintet dinitrenes, in particular, **69**, **70** and **103—110** were also studied (see Refs 77—82).

The studies showed that the ESR spectra of quintet dinitrenes **103—107** ($D = 0.21$—0.22 cm^{-1} and $E = 0.043$—0.044 cm^{-1}) differ little from the spectra of other dinitrenes with *meta*-orientation of the nitrene centers in the aromatic ring, for example, **31** and **42**. Conversely, the ESR spectra of dinitrenes **69** and **109** did not resemble any known spectra of quintet molecules and could not be computer simulated for a long time.[78—80] Only recently,[81,82] were we able to find out that dinitrenes **69** and **109** refer to a special group of quintet molecules with extremely high ($E/D \approx 0.33$) magnetic parameters E. It was also found that by no means all high-spin nitrenes can be detected by ESR in frozen solutions of 2MTHF even at 4 K. For example, we were unable to record the ESR signals of the septet trinitrenes **99** and **100** or quintet dinitrenes **108** and **110** (see Refs 76,78,80). All these molecules had a high spin density on nitrene centers ($D_T > 1.1$ cm^{-1}) and, possibly, readily reacted with 2MTHF.

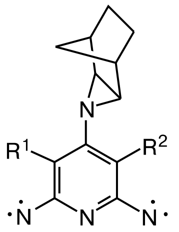
In order to elucidate the relationship between the structure and the magnetic properties of high-spin nitrenes, we studied the ESR spectra of quintet dinitrene **109** and septet trinitrenes **75**, **98—102**, and **111—113** in solid argon at 4—15 K.[24,75,83—87] Unlike studies in frozen 2MTHF solutions, in the argon matrices we recorded high-resolution ESR spectra not only for known septet trinitrenes **75** and **98** but also for previously elusive septet trinitrenes **99** and **100** and for trinitrenes **101**, **102** and **111—113**. The key result of these works was the strict description of the relationship between the molecular structure and magnetic parameters for the quintet dinitrenes and septet trinitrenes within the framework of theory of the one-center spin-spin interaction between two and three nitrene centers with triplet splitting tensors D_T. It was shown that the dependence of the magnetic parameters D_q and E_q of quintet dinitrenes on D_T and on the dipole angle $\theta = 2\alpha$ be-



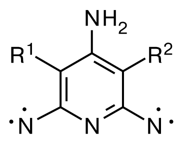
75, 98—102



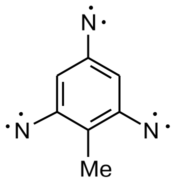
103—107



69, 70, 108



109, 110



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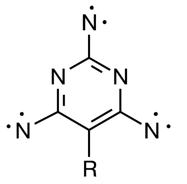
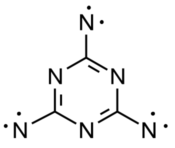


112, 113



114

Compound	R^1	R^2
69	Cl	Cl
70	Cl	CN
75	Cl	Cl
98	Cl	CN
99	F	F
100	CN	CN

Compound	R^1	R^2
101	Cl	CF$_3$
102	F	CN
108	CN	CN
109	Cl	Cl
110	CN	CN

Compound	Ar
103	p-OMeC$_6$H$_4$
104	p-MeC$_6$H$_4$
105	Ph
106	p-BrC$_6$H$_4$
107	p-NO$_2$C$_6$H$_4$

tween the C—N bonds of two nitrene centers is described[73,82,85,88] by the equations

$$D_q = D_T(3\sin^2\alpha - 1)/6, \quad (1)$$

$$E_q = D_T(\cos^2\alpha)/6. \quad (2)$$

These functions are plotted in Fig. 1, *a*. It can be seen that the quintet dinitrenes with $\theta < 112°$ have $D_q \approx D_T/6$, $E_q \approx D_T/18$, and $E_q/D_q \approx 1/3$. These molecules are exemplified by quintet dinitrenes **69** and **109**. The parameter D_T is usually very close to the parameter D_t of triplet azidonitrene, which is an intermediate formed in the photolysis of the starting diazide. Therefore, having measured the parameter D_t of the triplet azidonitrene at early stage of diazide photolysis and having calculated the θ angle by quantum chemical methods, one can solve Eqs. (1) and (2) to predict rather accurately the magnetic parameters of the quintet dinitrene. Meanwhile, determination of the magnetic parameters D_q and E_q from the ESR spectra provides rather accurate estimation of the θ angle. Solution of such problems is especially topical for the study of selective photolysis of the azide groups of aromatic polyazides if reliable spectral identification of isomeric high-spin nitrenes is required.[24,76,83–87]

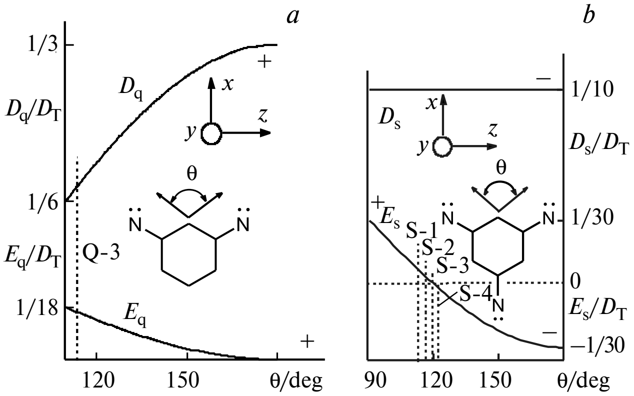


Fig. 1. Magnetic parameters *D* and *E* of quintet dinitrenes (*a*) and septet trinitrenes (*b*) *vs.* parameter D_T and angle θ.

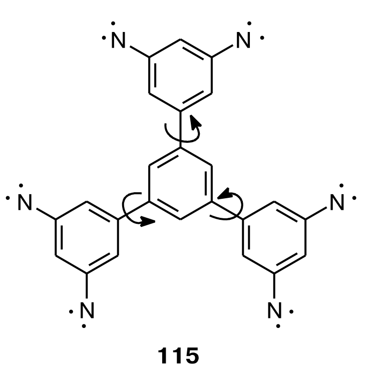
In the C_{2v}-symmetric molecules of septet trinitrenes **75**, **98—102** and **111—113**, two symmetric nitrene centers have the same spin density, $\rho_1 = \rho_2 = \rho$, and equal parameters $D_{T1} = D_{T2} = D_T$, while the third nitrene center has a somewhat different spin density ρ_3 and the parameter $D_{T3} = D_T(1 + \lambda)$, where $\lambda = (\rho_3 - \rho)/\rho$. The dependence of the magnetic parameters D_S and E_S of these septet trinitrenes on parameters D_T, λ, and $\theta = 2\alpha$ is described[24,86,89,90] by the equations

$$D_S = -D_T(1 + \lambda/3)/10, \quad (3)$$

$$E_S = D_T(4\cos^2\alpha - 1 + \lambda)/30. \quad (4)$$

These functions are plotted in Fig. 1, *b*. The D_{3h}-symmetric septet trinitrene **114** is a special case of the axially symmetric septet molecules with $\alpha = 60°$, $\lambda = 0$, and $E_S = 0$. This trinitrene has the highest spin density per atom of the molecule among all of the organic polyradicals and the highest magnetic anisotropy ($D_S = -0.123$ cm^{-1}).[12] The removal of one endocyclic nitrogen atom from the aromatic ring of septet trinitrenes decreases the parameter D_S by ~10%. Indeed, the magnetic parameters D_S of septet trinitrenes **112**, **100**, and **111** are –0.112, –0.1011, and –0.0938 cm^{-1}, respectively (see Refs 24, 75, 89).

As noted above, magnetic properties of molecules are directly proportional to their spins squared. High-spin nitrenes with $S > 3$ can be prepared only for polynuclear systems such as hexanitrene **115** and octanitrene **116**. Currently, analysis of the ESR spectra of this type of complex systems has not been ultimately developed. Study of the magnetic properties of the quintet dinitrene **117** formed as a mixture of a large number of rotation isomers was the first step along this route.[91] The experimental ESR spectrum of these isomeric dinitrenes in 2MTHF solutions frozen at 7 K showed a pronounced broadening of many signals in the region of 0 to 5000 G, and it could not be computer simulated by standard adjustment of spin Hamiltonian parameters *g*, D_q, and E_q. The successful simu-



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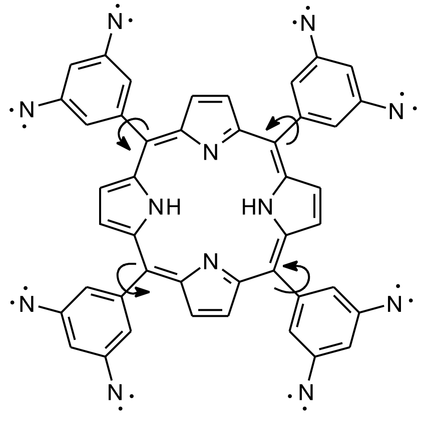

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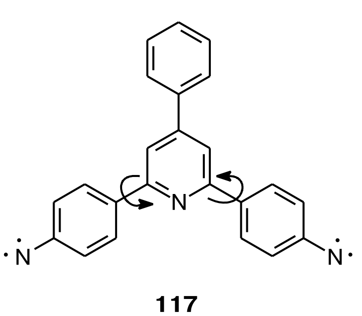

117

lation of the experimental ESR spectrum was carried out owing to the use of the line broadening parameter $\Gamma(E_g)$ = 420 G, indicating the presence of a large number of rotation isomers with markedly differing magnetic parameters E_q in the sample. In addition, it was found that quintet dinitrene **117** forms molecular complexes with 2MTHF, and the magnetic properties of these complexes are not related by Eqs (1) and (2) to the structural parameters of free dinitrene.[91] The same complexes were found in our previous study[24] for septet trinitrene **111** in 2MTHF solutions frozen at 4 K.

ESR spectroscopy is also an informative method for investigation of nitrenes in the crystals of the starting azides. At the macroscopic level, the magnetic characteristics of the light-irradiated crystalline azides are usually studied by magnetic measurements by a SQUID magnetometer.[92] However, the knowledge about particular products of photolysis of crystalline azides can be gained only by ESR spectroscopy.[47—51,93—95] Thus we showed that γ-radiolysis of crystalline triazides **17** and **19** yields mainly the corresponding quintet 2,6-dinitrenopyridines, which start to decay only as crystals are warmed up above 240 K.[47—51] The major products of photolysis of crystalline polyazides are the corresponding triplet nitrenes, which can undergo exchange interactions with one another to give quintet dimers.[94] The key condition for the formation of such magnetically active assemblies of triplet nitrenes is a non-coplanar arrangement of molecules of the starting azides in the neighboring stacks of the crystal.

Study of high-spin nitrenes by UV spectroscopy

The first UV spectrum of high-spin nitrenes in argon matrices was recorded[72] in 2003. Photolysis of diazide **77** in argon at 13 K gave rise to an UV spectrum of triplet nitrene **80** (absorption bands at 309, 324, 401, 408, 418, 422, and 434 nm) at an initial stage of the reaction, and subsequently it was transformed to the UV spectrum of quintet dinitrene **82** (absorption bands at 307, 326, 395, 418, and 422 nm). The theoretical analysis of these spectra including full assignment of all of the observed bands was performed in terms of the second-order multiconfigurational quasidegenerate perturbation theory (MCQDPT2).[96]

The calculations showed that the two longest-wavelength absorption bands of quintet dinitrene **82** have the character of π→SOMO transitions between the electron levels 4a″→6a″ and 4a″→5a″ (Fig. 2).[96]

We described[97] the UV/Vis spectra of quintet dinitrene **109** and septet trinitrene **75** in 2MTHF solutions frozen at 77 K. Dinitrene **109** exhibited a strong long-wavelength absorption band with a maximum at 638 nm, while trinitrene **75** showed a long-wavelength absorption band with a maximum at 709 nm. In view of the currently available data, these absorption bands of the quintet and septet nitrenes should be assigned to complexes of high-spin nitrenes with 2MTHF molecules. This assignment is supported by the results of a comparative study of the ESR spectra of high-spin nitrenes in the solid argon and frozen 2MTHF solutions and quantum chemical calculations of the UV spectrum of quintet dinitrene **82** (see Refs 24, 85, and 96).

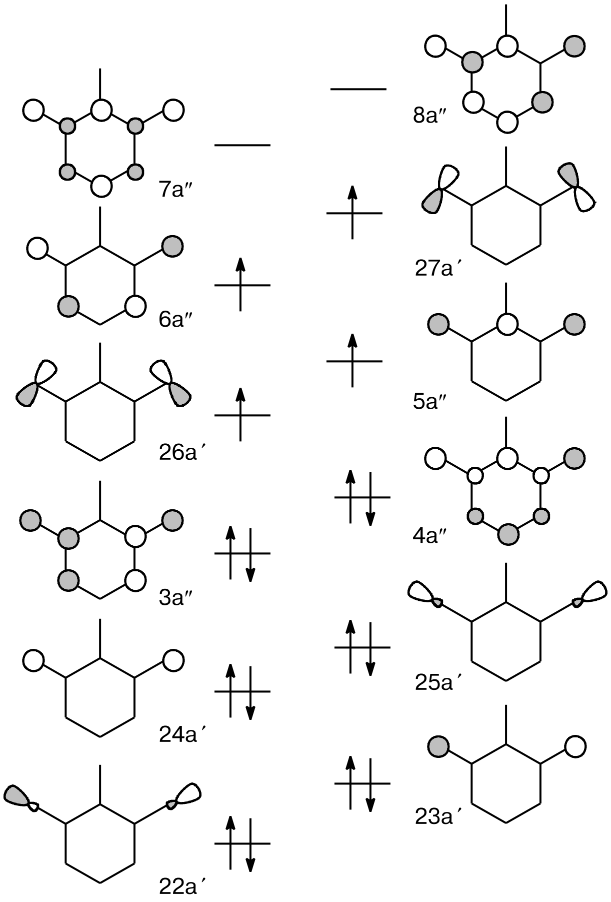

Fig. 2. Active field molecular orbitals in the calculation of dinitrene **82**.

The studies of aromatic polyazides and high-spin nitrenes carried out during the last decade provided lots of new data on the synthesis, stability, reactivity, and physicochemical properties of these unique compounds. The experience accumulated in the synthesis and investigation of monocyclic aromatic triazides and septet trinitrenes is now used to study much more complex subjects such as polynuclear polyazides, polyazidoporphyrins, and high-spin polynitrenes with $S > 4$ prepared by photolysis of these azides.

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References

1. *Organic Azides: Synthesis and Applications*, Eds S. Brase, K. Banert, Wiley, Chichester, 2010.
2. *Azides and Nitrenes, Reactivity, and Utility*, Ed. E. F. V. Scriven, Academic Press, New York, 1984.
3. S. Brase, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem., Int. Ed.*, 2005, **44**, 5188.
4. E. F. V. Scriven, K. Turnbull, *Chem. Rev.*, 1988, **88**, 297.
5. S. V. Chapyshev, *Synlett*, 2009, 1.
6. C. Ye, H. Gao, J. A. Boatz, G. W. Drake, B. Twamley, J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2006, **45**, 7262.
7. M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, *Angew. Chem., Int. Ed.*, 2005, **44**, 737.
8. M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. D. Gillard, *Angew. Chem., Int. Ed.*, 2004, **43**, 5658.
9. E. G. Gillan, *Chem. Mater.*, 2000, **12**, 3906.
10. E. Kroke, M. Schwarz, *Adv. Mater.*, 1999, **11**, 158.
11. T. Sato, A. Narazaki, Y. Kawaguchi, H. Niino, G. Bucher, *Angew. Chem., Int. Ed.*, 2003, **42**, 5206.
12. T. Sato, A. Narazaki, Y. Kawaguchi, H. Niino, G. Bucher, D. Grote, J. J. Wolff, H. H. Wenk, W. Sander, *J. Am. Chem. Soc.*, 2004, **126**, 7846.
13. H. Finger, *J. Prakt. Chem.*, 1907, **75**, 103.
14. R. M. Moriarty, M. Rahman, G. J. King, *J. Am. Chem. Soc.*, 1966, **88**, 842.
15. A. V. Pochinok, V. A. Smirnov, S. B. Brichkin, V. Ya. Pochinok, L. F. Avramenko, T. F. Grigorenko, *Khim. Vysokikh Energii*, 1982, **16**, 151 [*High Energy Chem.* (*Engl. Transl.*), 1982, **16**].
16. T. Nakai, K. Sato, D. Shiomi, T. Takui, K. Itoh, M. Kozaki, K. Okada, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 157.
17. V. Ya. Pochinok, L. F. Avramenko, T. F. Grigorenko, A. V. Pochinok, I. A. Sidorenko, L. N. Bovchalyuk, *Ukr. Khim. Zh.* (*Ukr. Chem. J.*) 1979, **45**, 975 (in Russian).
18. A. V. Pochinok, N. I. Sharykina, T. A. Bukhtiyarova, *Fiziolog. Aktiv. Veshchestva* (*Physiologically Active Substances*), 1990, **22**, 76 (in Russian).
19. S. V. Chapyshev, *V Vseross. nauchn. konf. "Energeticheskie kondensirovannye sistemy" (The V All-Russian Scientific Conf. "Energetic Condensed Systems") (Chernogolovka, October 26—28, 2010*), *Abstr.*, Moscow, 2010, p. 68 (in Russian).
20. D. Adam, K.Karaghiosoff, T. M. Klapotke, G. Holl, V. Kaiser, *Propellants, Explosives, Pyrotechnics*, 2002, **27**, 7.
21. D. S. Breslow, A. F. Marcantonio, US Pat. 3297674; *Chem. Abstrs*, 1967, **66**, 56182.
22. V. N. Boiko, I. V. Gogoman, G. M. Shchupak, L. M. Yagupol´skii, *Zh. Org. Khim.*, 1987, **23**, 2586 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1987, **23**].
23. T. Wasserman, R. Schueller, W. A. Yager, *Chem. Phys. Lett.*, 1968, **2**, 259.
24. S. V. Chapyshev, E. Ya. Misochko, A. V. Akimov, V. G. Dorokhov, P. Neuhaus, D. Grote, W. Sander, *J. Org. Chem.*, 2009, **74**, 7238.
25. S. Marburg, P. A. Crieco, *Tetrahedron Lett.*, 1966, 1305.
26. J. G. Morse, L. P. Kuhn, US Clearinghouse Fed. Sci. Tech. Inform. AD, 1970, No. 713665, 20 p.; *Chem. Abstrs*, 1971, **75**, 19826.
27. Yu. M. Mikhailov, S. V. Chapyshev, V. V. Nedel´ko, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 2034 [*Russ. Chem. Bull.*, *Int. Ed.*, 2009, **58**, 2097].
28. S. D. Moshchitskii, F. F. Zeikan´, A. F. Pavlenko, V. P. Kukhar´, *Khim. Geterotsikl. Soedin.*, 1979, 1492 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1979, **15**, 1197].
29. S. V. Chapyshev, *Khim. Geterotsikl. Soedin.*, 1993, 1650 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1993, **29**, 1426].
30. S. V. Chapyshev, T. Ibata, *Heterocycles*, 1993, **36**, 2185.
31. S. V. Chapyshev, U. Bergstrasser, M. Regitz, *Khim. Geterotsikl. Soedin.*, 1996, 67 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1996, **32**, 59].
32. S. V. Chapyshev, *Khim. Geterotsikl. Soedin.*, 2001, 1056 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2001, **37**, 968].
33. S. V. Chapyshev, *Mendeleev Commun.*, 1999, **9**, 164.
34. S. V. Chapyshev, N. V. Chapysheva, D. V. Korchagin, G. V. Shilov, Yu. M. Mikhailov, *III Vseross. nauchn. konf. "Energeticheskie kondensirovannye sistemy" (The III All-Russian Scientific Conf. "Energetic Condensed Systems") (Chernogolovka, October 31— November 2, 2006)*, *Abstr.*, Moscow, 2006, p. 208 (in Russian).
35. S. V. Chapyshev, U. Bergstrasser, M. Regitz, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 252 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1996, **45**, 242].
36. S. V. Chapyshev, V. M. Anisimov, *Khim. Geterotsikl. Soedin.*, 1997, 676 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1997, **33**, 587].
37. S. V. Chapyshev, V. M. Anisimov, *Khim. Geterotsikl. Soedin.*, 1997, 1521 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1997, **33**, 1315].
38. S. V. Chapyshev, *Khim. Geterotsikl. Soedin.*, 1999, 702 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1999, **35**, 632].
39. S. V. Chapyshev, *Mendeleev Commun.*, 1999, 166.
40. S. V. Chapyshev, *Khim. Geterotsikl. Soedin.*, 2000, 1497 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2000, **36**, 1289].
41. S. V. Chapyshev, R. Walton, P. M. Lahti, *Mendeleev Commun.*, 2000, 7.
42. S. V. Chapyshev, R. Walton, P. M. Lahti, *Mendeleev Commun.*, 2000, 187.
43. S. V. Chapyshev, M. S. Platz, *Mendeleev Commun.*, 2001, 56.
44. S. V. Chapyshev, *Khim. Geterotsikl. Soedin.*, 2001, 935 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2001, **37**, 861].
45. S. V. Chapyshev, *Khim. Geterotsikl. Soedin.*, 2003, 87 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2003, **39**, 83].
46. S. V. Chapyshev, *Mendeleev Commun.*, 2007, 287.
47. S. V. Chapyshev, S. I. Kuzina, A. I. Mikhailov, *Mendeleev Commun.*, 2007, 207.
48. S. I. Kuzina, A. I. Mikhailov, S. V. Chapyshev, *Dokl. Akad. Nauk*, 2007, **418**, 341 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 2007, **412**, 34].
49. S. I. Kuzina, A. I. Mikhailov, S. V. Chapyshev, *Khim. Vysokikh Energii*, 2007, **41**, 245 [*High Energy Chem.* (*Engl. Transl.*), 2007, **41**, 245].
50. S. I. Kuzina, D. V. Korchagin, G. V. Shilov, S. V. Chapyshev, A. I. Mikhailov, S. M. Aldoshin, *Dokl. Akad. Nauk*, 2008, **418**, 341 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 2008, **418**, 7].
51. S. I. Kuzina, A. I. Mikhailov, S. V. Chapyshev, D. V. Korchagin, G. V. Shilov, S. M. Aldoshin, *Zh. Fiz. Khim.*, 2008, **82**, 2081 [*Russ. J. Phys. Chem. A* (*Engl. Transl.*), 2008, **82**, 1870].
52. S. M. Aldoshin, D. V. Korchagin, K. V. Bozhenko, G. V. Shilov, S. V. Chapyshev, *Izv. Akad. Nauk, Ser. Fiz.*, 2008, **72**, 1254 [*Bull. Russ. Acad. Sci. Physics* (*Engl. Transl.*), 2008, **72**, 1556].

53. D. V. Korchagin, K. V. Bozhenko, S. V. Chapyshev, S. M. Aldoshin, *Khim. Vysokikh Energii*, 2009, **43**, 341 [*High Energy Chem.* (*Engl. Transl.*), 2009, **43**, 289].
54. Q. Li, Q.-H. Fan, L.-H. Zhang, X.-S. Ye, *Synlett*, 2006, 2464.
55. L. C. Campeau, P. D. O'Shea, *Synlett*, 2011, 57.
56. P. T. Nyffeler, C.-H. Liang, K. M. Koeller, *J. Am. Chem. Soc.*, 2002, **124**, 10773.
57. P. R. Sridhar, K. R. Prabhu, S. Chandrasekaran, *J. Org. Chem.*, 2003, **68**, 5261.
58. W. Weltner, Jr., *Magnetic Atoms and Molecules*, Dover Publications, New York, 1989.
59. A. Rajca, *Chem. Rev.*, 1994, **94**, 871.
60. *Magnetic Properties of Organic Materials*, Ed. P. M. Lahti, Marcel Dekker, New York, 1999.
61. S. Murata, H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 5547.
62. T. A. Fukuzawa, K. Sato, A. S. Ichimura, T. Kinoshita, T. Takui, K. Itoh, P. M. Lahti, *Mol. Cryst. Liq. Cryst.*, 1996, **278**, 253.
63. R. S. Kalgutkar, P. M. Lahti, *J. Am. Chem. Soc.*, 1997, **119**, 8784.
64. Y. Miura, H. Oka, Y. Teki, *Bull. Chem. Soc. Jpn*, 2001, **74**, 385.
65. N. Oda, T. Nakai, K. Sato, D. Shiomi, M. Kozaki, K. Okada, T. Takui, *Mol. Cryst. Liq. Cryst.*, 2002, **376**, 501.
66. R. S. Kalgutkar, P. M. Lahti, *Tetrahedron Lett.*, 2003, **44**, 2625.
67. R. A. Evans, M. W. Wong, C. Wentrup, *J. Am. Chem. Soc.*, 1996, **118**, 4009.
68. S. V. Chapyshev, A. Kuhn, M. W. Wong, C. Wentrup, *J. Am. Chem. Soc.*, 2000, **122**, 1572.
69. S. V. Chapyshev, C. Wentrup, *Khim. Geterotsikl. Soedin.*, 2001, 1219 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2001, **37**, 1119].
70. S. V. Chapyshev, *Mendeleev Commun.*, 2002, 227.
71. S. V. Chapyshev, *Mendeleev Commun.*, 2003, 53.
72. S. V. Chapyshev, H. Tomioka, *Bull. Chem. Soc. Jpn*, 2003, **76**, 2075.
73. S. V. Chapyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1085 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1126].
74. J. C. Finke, Ph.D. Thesis, Ruhr-University of Bochum, Bochum, 2010, 286 pp.
75. S. V. Chapyshev, *Abstrs V Intern. Conf. "High-Spin Molecules and Molecular Magnets" (N. Novgorod, 31 August—2 September, 2010)*, N. Novgorod, 2010, O-7.
76. S. V. Chapyshev, R. Walton, J. A. Sanborn, P. M. Lahti, *J. Am. Chem. Soc.*, 2000, **122**, 1580.
77. S. V. Chapyshev, R. Walton, P. M. Lahti, *Mendeleev Commun.*, 2000, 138.
78. S. V. Chapyshev, R. Walton, P. M. Lahti, *Mendeleev Commun.*, 2000, 114.
79. S. V. Chapyshev, P. R. Serwinski, *Mendeleev Commun.*, 2001, 92.
80. S. V. Chapyshev, R. Walton, P. R. Serwinski, P. M. Lahti, *J. Phys. Chem. A.*, 2004, **108**, 6643.
81. S. V. Chapyshev, P. M. Lahti, *J. Phys. Org. Chem.*, 2006, **19**, 637.
82. S. V. Chapyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1536 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1593].
83. S. V. Chapyshev, P. Neuhaus, D. Grote, W. Sander, *Abstrs of 30th Intern. Symp. on Free Radicals (Savonlinna, 25—30 July, 2009)*, Helsinki, 2009, 103.
84. E. Ya. Misochko, A. V. Akimov, V. F. Lavitskii, S. V. Chapyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 2284 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 2364].
85. E. Ya. Misochko, A. V. Akimov, S. V. Chapyshev, *J. Chem. Phys.*, 2008, **128**, 124504.
86. E. Ya. Misochko, A. V. Akimov, S. V. Chapyshev, *J. Chem. Phys.*, 2008, **129**, 174510.
87. S. V. Chapyshev, D. Grote, C. Finke, W. Sander, *J. Org. Chem.*, 2008, **73**, 7045.
88. S. V. Chapyshev, *Zh. Fiz. Khim.*, 2009, **83**, 322 [*Russ. J. Phys. Chem. A* (*Engl. Transl.*), 2009, **83**, 254].
89. S. V. Chapyshev, P. Neuhaus, D. Grote, W. Sander, *J. Phys. Org. Chem.*, 2010, **23**, 340.
90. E. Ya. Misochko, D. V. Korchagin, K. V. Bozhenko, S. V. Chapyshev, S. M. Aldoshin, *J. Chem. Phys.*, 2010, **133**, 064101.
91. S. V. Chapyshev, D. V. Korchagin, *V Vseross. nauchn. konf.-shkoly "Vysokoreaktsionnye intermediaty khimicheskikh reaktsii"* [*V All-Russian Scientific Workshop Conf. "Highly Reactive Intermediates of Chemical Reactions"*] *(Moscow Region, October 11—14, 2010*), Moscow, 2010, p. 78 (in Russian).
92. R. B. Morgunov, V. L. Berdinskii, M. V. Kirman, I. Tanimoto, S. V. Chapyshev, *Khim. Vysokikh Energii*, 2007, **41**, 37 [*High Energy Chem.* (*Engl. Transl.*), 2007, **41**, 33].
93. L. Mahe, A. Izuoka, T. Sugawara, *Bull. Chem. Soc. Jpn*, 1998, **71**, 1259.
94. S. V. Chapyshev, V. F. Lavitskii, A. V. Akimov, E. Ya. Misochko, A. V. Shastin, D. V. Korchagin, G. V. Shilov, S. M. Aldoshin, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 513 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 524].
95. S. V. Chapyshev, *Sovremennye Problemy Organicheskoi Khimii* (*Modern Problems of Organic Chemistry*), Ed. R. R. Kostikov, M. A. Kuznetsov, M. S. Berd, Lem, St.-Petersburg, 2010, issue 15, 121 (in Russian).
96. K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, T. Takui, *Angew. Chem., Int. Ed.*, 2006, **45**, 2257.
97. S. V. Chapyshev, *Mendeleev Commun.*, 2002, 168.

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