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1 AUTHOR:

Sergei Victorovich Chapyshev

Russian Academy of Sciences

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Photochemical synthesis and properties of quintet pyridyl-2,6-dinitrenes

S. V. Chapyshev

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: chap@icp.ac.ru; chapyshevs@mail.ru

The structures and properties of quintet pyridyl-2,6-dinitrenes formed by low-temperature photolysis of 2,6-diazidopyridines were studied by ESR and quantum chemical (B3LYP/6-31G*) methods. The synthesized dinitrenes represent a new type of quintet tetraradicals for which the ratio of zero-field splitting parameters is $|E_q|/|D_q| = 1/3$. This ratio is characteristic of quintet molecules in which the vector angle between two biradical centers is close to 114.5°.

Key words: azides, nitrenes, photolysis, ESR, high-spin states.

In the present time, works on minimization of the dimensionality of magnetic information carriers have reached a level after which the creation of basically novel magnetic materials with the size of one molecule will be necessary.[1—3] Therefore, studies of high-spin molecules, using which one can reveal regularities of magnetic interactions between several unpaired electrons in one molecule and thus obtain valuable information on magnetism at the molecular level, become more urgent.[4,5] Among all classes of organic tetraradicals, quintet dinitrenes prepared by the low-temperature solid-phase photolysis of aromatic diazides[6] are the strongest magnetics. Due to strong exchange interactions between four unpaired electrons, the five energy sublevels W_{-2}, W_{-1}, W_0, W_{+1}, and W_{+2} in the ground quintet spin state of dinitrenes are considerably split. The zero-field splitting parameters are determined from the ESR spectra, which are rather simple (Fig. 1) only for quintet molecules with $|D_q| \ll 0.33$ cm^{-1} (see Ref. 7). Since quintet dinitrenes have the D_q parameters comparable with a quantum of microwave energy (0.33 cm^{-1}) of standard X-band ESR spectrometers, their ESR spectra differ strongly from the first-order spectra and are very difficult for analysis.

Three types of quintet dinitrenes have been known to the present time. The first type is presented by quintet dinitrenes in molecules of which the vector angle Θ between two C—N nitrene bond is ~0° (see Refs 8—10). These dinitrenes have the highest D_q parameters (0.34 cm^{-1}),[8,9] and their E_q parameters are close to zero. In quintet dinitrenes of the second type the Θ vector angle is close to 180° (see Refs 10 and 11). The ESR spectra of these dinitrenes also correspond to molecules with very high D_q parameters and almost zero E_q parameters and
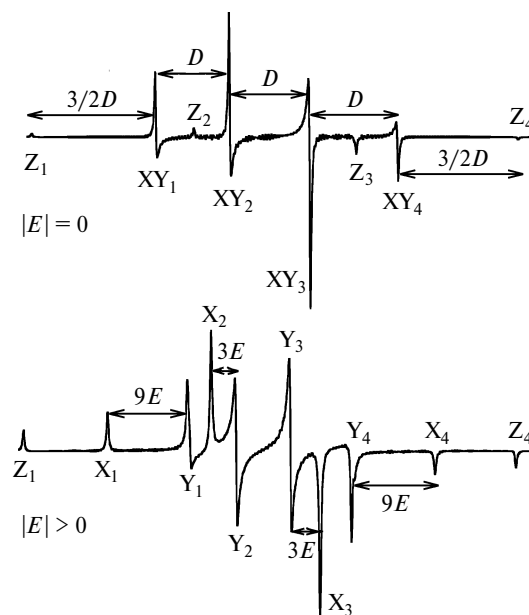
Fig. 1. First-order ESR spectra of quintet molecules with $E_q = 0$ and $E_q > 0$.

does not virtually differ from the ESR spectra of quintet dinitrenes of the first type.[10,11] The third type covers the most plentiful group of quintet dinitrenes for which the Θ vector angle is ~118—125° (see Refs 12—20). Quintet dinitrenes of this type are characterized by the D_q parameters about 0.18—0.24 cm^{-1} and high E_q parameters, being ~20% of the D_q parameters. Due to this, the ESR spectra of these dinitrenes contain all the 12 lines of the X-, Y-, and Z-transitions and are most difficult for analysis.[20] In the general form the dependence of the D_q and

E_q parameters of the Θ value (when it varies from 118 to 180°) is described rather exactly by the equations

$$D_q = D_t(3\sin^2\alpha - 1)/6, \tag{1}$$

$$E_q = D_t(\cos^2\alpha)/6, \tag{2}$$

where $\alpha = \Theta/2$, and the D_t parameters of the triplet center in quintet dinitrene is approximately equal to the D_T parameter of intermediate triplet azidonitrene.[11]

Quintet dinitrenes for which the Θ vector angle is less than 118° are of interest from the theoretical point of view. According to Eqs (1) and (2), these dinitrenes should have very high E_q parameters, whose values at $\alpha = 45°$ become comparable with the D_q parameters. In this case, the quintet spin state with $E_q' = D_q'$ will degenerate to another quintet spin state with $D_q'' = 2D_q'$ and $E_q'' = 0$, because splitting between the utmost sublevels W_{-2} and W_{+2} of the first quintet state to $6(D_q' + E_q')$ will be equal to $6(2D_q' + 0)$. The solutions of Eqs (1) and (2) for $D_q' = 1$ cm^{-1} and $D_q'' = 0.5$ cm^{-1} show that this mutual transformation of the quintet states should be observed for dinitrenes, whose E_q parameters achieve 1/3 of the D_q parameters. Hund's rule that forbids high-spin molecules to have very high E parameters is true for this ratio of the two parameters.

To investigate quintet dinitrenes with extremely high E_q parameters, in the present work we studied the paramagnetic photolysis products of diazides **1a,b** (Scheme 1) using ESR and quantum chemical methods.

Scheme 1
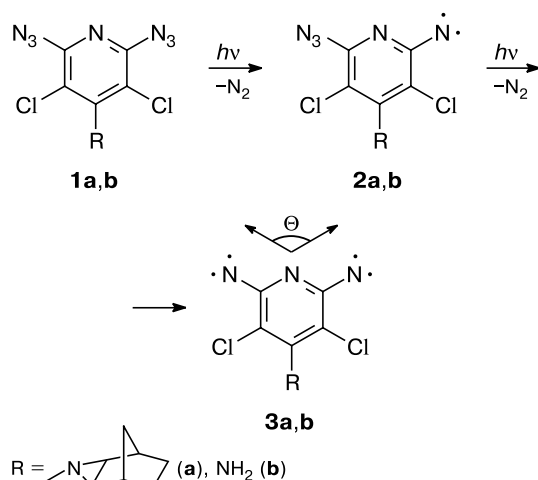
Experimental

Diazides **1a,b** were synthesized using known procedures.[21,22]
ESR spectra were recorded on a Bruker ESP-300 instrument with the working region from 0 to 10000 G in solutions of 2-methyltetrahydrofuran (MTHF) frozen at 77 K. The micro-

wave radiation frequency during measurements of ESR spectra of the photolysis products of diazides **1a,b** was 9.562 and 9.607 GHz, respectively. The experimental procedure was the following. A weighed sample of diazide (1 mg) was dissolved in 1 mL of MTHF freshly distilled above LiAlH$_4$ and placed into a standard 4-mm quartz tube designed for ESR spectra recording. The solution was deaerated by three cycles of freezing at 77 K, air evacuation at $5 \cdot 10^{-6}$ atm, and thawing out. The tube with the deaerated solution was sealed and placed into a spectrometer cell cooled to 77 K. The light source was a high-pressure xenon lamp with a power of 1000 W equipped with a 150-mm water filter. The sample was placed at a distance of 20 cm from the light source and irradiated with the light with $\lambda > 300$ nm for 5 min, and then ESR spectra were recorded.

Theoretical ESR spectra were calculated using the SIM ESR nonempirical program designed for simulation of ESR spectra of high-spin molecules randomly oriented in the solid phase.[23] It was conventionally accepted for spectra calculation that the g factor for all nitrenes is 2.0023. The D and E zero-field splitting parameters for triplet and quintet nitrenes were determined from calculated spectra that completely coincide with the experimentally obtained ESR spectra.

Quantum chemical calculations of molecules of triplet and quintet nitrenes were performed by the B3LYP/6-31G* method from the GAUSSIAN-94 program package.[24]

Results and Discussion

Photolysis of diazide **1a** for 5 min resulted in the appearance in the ESR spectrum of the characteristic signal of the X,Y_2-transition of triplet azidonitrene **2a** at 6990 G and groups of signals of quintet dinitrene **3a** at magnetic field strengths H of 420, 3320, 3420, 3670, 6740, and 9480 G (Fig. 2, *a*). A similar ESR spectrum appears also after photolysis of diazide **1b** (Fig. 3, *a*). The characteristic signal of the X,Y_2-transition of triplet azidonitrene **2b** was manifested at 7300 G, and the signals of quintet dinitrene **3b** were observed at 320, 3390, 3470, 3760, 7000, and 9900 G.

Simulation of signals of the X,Y_2-transitions of triplet azidonitrenes **2a** and **2b** showed that the D_T and E_T parameters of these biradicals are $|D_T| = 1.029$ cm^{-1}, $|E_T| < 0.003$ cm^{-1} and $|D_T| = 1.068$ cm^{-1}, $|E_T| < 0.002$ cm^{-1}, respectively. The higher D_T parameters of triplet nitrenes indicate a higher spin density on their nitrene centers.[7] The B3LYP/6-31G* quantum chemical calculations confirm that of the two quintet dinitrenes **2a** and **2b** the latter has the higher spin density on the nitrene center (Table 1).

The ESR spectra recorded for quintet dinitrenes **3a,b** differ basically from those of all earlier studied quintet molecules.[8−20] First, the number of signals is surprisingly small, and they are absent in the region from 500 to 3100 G. ESR spectra of this type are theoretically possible only for quintet molecules, whose E_q parameters are ~1/3 of the D_q parameters. For this ratio of the two parameters, the signals of four X-transitions will be superposed with the signals of four Z-transitions, and the signals of the
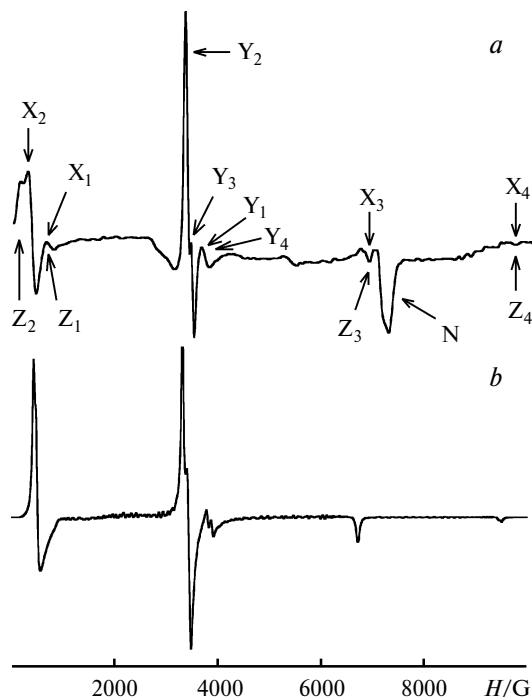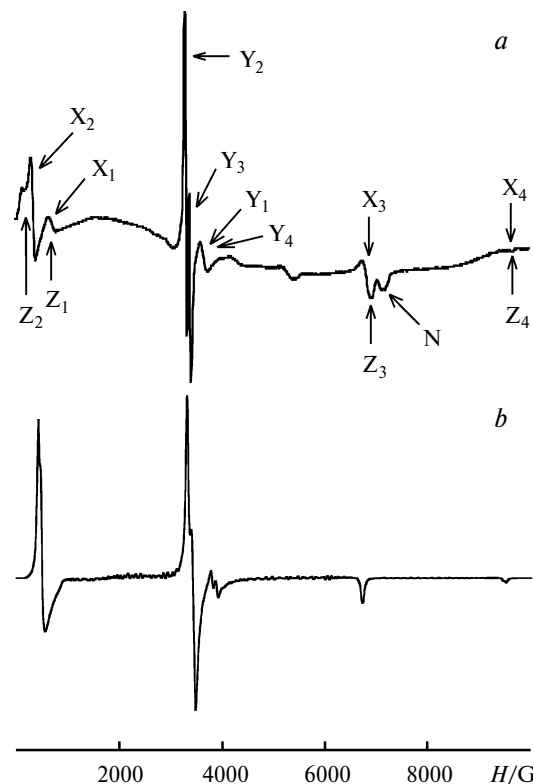
Fig. 2. ESR spectra of the photolysis products of diazide **1a** (*a*) and the quintet spin state with g = 2.0023, $|D|$ = 0.191 cm^{-1}, and $|E|$ = 0.0625 cm^{-1} (*b*).

Y-transitions will come together in the central part of the spectrum at g = 2.0023 (see Fig. 1). As a result, the region from 500 to 3100 G will be free from signals of the X_1-, X_2-, and Y_2-transitions, and the total number of signals in the first-order ESR spectrum will decrease from 12 to 5.

The B3LYP/6-31G* quantum chemical calculations showed that the Θ vector angles in molecules of quintet dinitrenes **3a** and **3b** are 114.7 and 114.5°, respectively (see Table 1). It can be found from the solutions of Eqs (1) and (2) for α = 57.35° and D_t = 1.029 cm^{-1} that quintet dinitrene **3a** tentatively has $|D_q|$ = 0.193 cm^{-1} and $|E_q|$ = 0.050 cm^{-1}. The solutions of the same equations for α = 57.25° and D_t = 1.068 cm^{-1} predict that quintet dinitrene **3b** has the parameters $|D_q|$ = 0.200 cm^{-1} and $|E_q|$ = 0.052 cm^{-1}. These estimates of the D_q and E_q parameters served as the initial data for the precise calcula-

Table 1. Zero-field splitting parameters (D_T, E_T, D_q, and E_q), spin densities on the nitrene centers (ρ_N), and vector angles (Θ) for nitrenes **2a,b** and **3a,b**

Nitrene	D_T	E_T	D_q	E_q	ρ_N	Θ
	cm^{-1}					/deg
2a	1.029	0.003	—	—	1.5957	—
2b	1.068	0.002	—	—	1.6079	—
3a	—	—	0.1910	0.0625	1.6440	114.7
3b	—	—	0.2020	0.0664	1.6583	114.5

Fig. 3. ESR spectra of the photolysis products of diazide **1b** (*a*) and the quintet spin state with g = 2.0023, $|D|$ = 0.202 cm^{-1} and $|E|$ = 0.0664 cm^{-1} (*b*).

tion of the ESR spectra of quintet dinitrenes **3a,b** using the SIM ESR program.[23]

The simulated ESR spectra of quintet dinitrenes **3a,b** are presented in Figs 2, *b* and 3, *b*. According to the results of calculations, quintet dinitrenes **3a** and **3b** have $|D_q|$ = 0.191 cm^{-1}, $|E_q|$ = 0.0625 cm^{-1} and $|D_q|$ = 0.202 cm^{-1}, $|E_q|$ = 0.0664 cm^{-1}, which only insignificantly differs from the values obtained by the solution of Eqs (1) and (2). The higher D_q parameter of quintet dinitrene **3b** is due to the higher spin density on the nitrene centers (see Table 1). Evidently, the stronger electron-releasing substituents in position 4 of the pyridine ring of pyridyl-2,6-dinitrenes stronger push out the spin density from the aromatic ring to the nitrene centers. A similar effect has been observed previously for molecules of triplet nitreno-*sym*-triazines.[25,26] Another interesting effect is a considerable increase in the spin density on the nitrene centers upon the transformation of triplet azidonitrenes **2a,b** into quintet dinitrenes **3a,b** (see Table 1). This effect shows that the D_t parameters of the triplet centers in molecules of quintet dinitrenes **3a,b** should substantially exceed the D_T parameters of triplet azidonitrenes **2a,b**. Therefore, substitution of the latter into Eqs (1) and (2) for calculation of the D_q and E_q parameters of quintet dinitrenes **3a,b** is incorrect. Comparison of the spin den-

sity on the nitrene centers and D_T parameters of azido-nitrenes **2a** and **2b** (see Table 1) shows that an increase in the spin density on the nitrene centers by 0.01 induces an increase in the D_T parameters by 0.04 cm^{-1}. If this dependence is retained, the D_t parameters of the triplet centers in molecules of dinitrenes **3a** and **3b** should be ~1.23 and 1.27 cm^{-1}, respectively.

The E_q parameters of quintet dinitrenes **3a,b** exactly calculated using the SIM ESR program reach ~1/3 of their D_q parameters and are ultimately acceptable for quintet spin states. According to the B3LYP/6-31G* quantum chemical calculations, such E_q parameters are inherent in quintet dinitrenes in molecules of which the Θ vector angle between two C—N nitrene bonds is ~114.5°. These can be various heterocyclic dinitrenes in molecules of which two nitrene centers are in the *ortho*-positions to the endocyclic heteroatom (2,6-dinitrenopyridines, 2,6-dinitrenopyrimidines, 2,6-dinitrenopyrazines, *etc.*). Despite relatively low D_q parameters, these dinitrenes always have very high spin density on the nitrene centers and are characterized by considerable splitting of the W_{-2} and W_{+2} sublevels. For instance, the splitting of the W_{-2} and W_{+2} sublevels for a molecule of quintet dinitrene **3b** is 1.61 cm^{-1}, which is comparable with the splitting of the same sublevels in quintet dinitrenes for which the Θ vector is equal to 0 (see Ref. 10) or 180° (see Ref. 11).

For unambiguous assignment of all signals in the ESR spectra of quintet dinitrenes **3a,b**, we simulated the signals of the transitions between the sublevels $W_{\pm2}$ and $W_{\pm1}$, as well as $W_{\pm1}$ and W_0 in a molecule of quintet dinitrene **3a** (Fig. 4). The results of simulation showed that the signals at 420, 800, 6740, and 9480 G are assigned
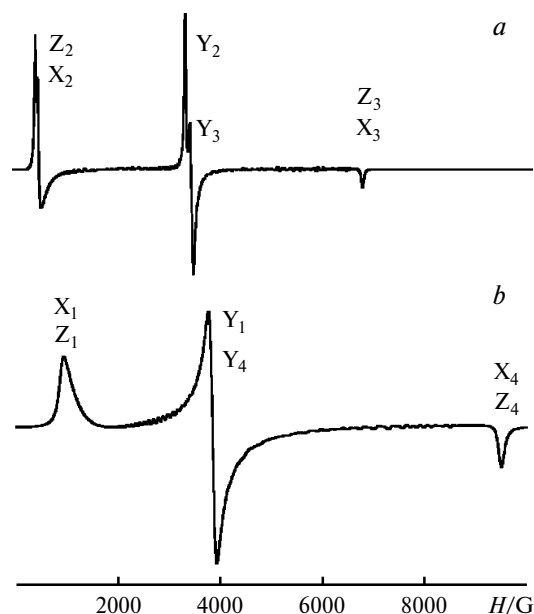
to the overlapped lines of the Z_2/X_2-, Z_1/X_1-, Z_3/X_3-, and Z_4/X_4-transitions, respectively (see Fig. 2, *a*). The high-intensity split signal at 3400 G belongs to lines of the Y_2- and Y_3-transitions, and the weak signal at 3670 G is attributed to lines of the Y_1- and Y_4-transitions. Due to this characteristic arrangement of signals, quintet molecules with $|E_q|/|D_q| = 1/3$ can easily be identified by ESR.

Synthesized dinitrenes **3a,b** are the first representatives of quintet molecules that exist at the frontier of intersection of two different quintet spin states with D_q', E_q' and D_q'', E_q''. The dependences of D_q' and E_q' on the α' angle are described by Eqs (1) and (2). AT $\alpha' = 45°$ and $D_t' = 1$ cm^{-1}, the D_q' and E_q' values become equal to 0.083 cm^{-1} and the quintet spin state completely degenerates to another quintet spin state with $D_q'' = 0.167$ cm^{-1}, $E_q'' = 0$ cm^{-1}, and $D_t'' = 0.5$ cm^{-1}. The dependences of the D_q'' and E_q'' parameters of this new quintet state on the α'' angle are described by the equations

$$D_q'' = D_t''(3\cos^2\alpha'' - 1)/6, \tag{3}$$

$$E_q'' = D_t''(\sin^2\alpha'')/6, \tag{4}$$

where $\alpha'' = \alpha' - 45°$.

The plots of the D_q and E_q parameters *vs.* α' value for two quintet spin states are presented in Fig. 5. It is seen that the D_q' curve intersects the D_q'' curve at $\alpha' = 54°$. This means that the mutual transformation of two quintet spin states occurs at the α' values equal to 54°. However, it cannot be ruled out that in the region of $\alpha' = (54\pm4)°$ the wave functions of two different quintet spin states are noticeably overlapped due to which the calculation of the D_q and E_q parameters of quintet molecules using Eqs (1)—(4) for this region of α' values becomes not quite precise. The study of dinitrenes **3a,b** shows clearly that the quintet spin states gain maximally acceptable values of the E_q parameters already at $\alpha' = 57.35°$.

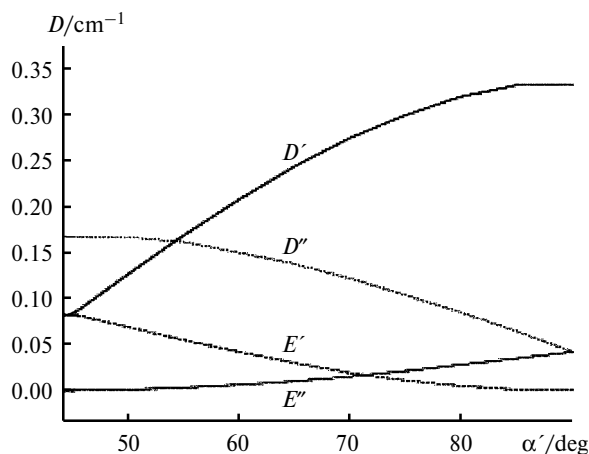**Fig. 4.** Calculated lines of the $W_{\pm1}/W_0$ (*a*) and $W_{\pm2}/W_{\pm1}$ (*b*) transitions in the ESR spectrum of quintet dinitrene **3a**.

Fig. 5. Plots of the D_q' and E_q' parameters of the quintet spin state with $D_t' = 1$ cm^{-1} and the D_q'' and E_q'' parameters of the quintet spin state with $D_t'' = 0.5$ cm^{-1} *vs.* α' angle.

Thus, photolysis of diazides **1a**,**b** generates dinitrenes **3a**,**b**, which represent a new type of quintet molecules for which the ratio of the zero-field splitting parameters $|E_q|/|D_q|$ is approximately equal to 1/3. This type of quintet molecules is characterized by a special arrangement of signals in the ESR spectra for which lines of the X_i- and Z_i-transitions are mutually overlapped, and the lines of four Y-transitions come together in the central part of the spectrum at $g = 2.0023$. These ESR spectra are characteristic of quintet dinitrenes in molecules of which the vector angle between two C—N bonds is close to 114.5°.

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