2364 *Russian Chemical Bulletin, International Edition, Vol. 56, No. 12, pp. 2364—2369, December, 2007*

EPR spectroscopy of quintet 4-amino-3,5-dichloropyridine-2,6-diyldinitrene isolated in solid argon

E. Ya. Misochko,* A. V. Akimov, V. F. Lavitskii, and 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: misochko@icp.ac.ru

An EPR spectrum of solid Ar isolated quintet 4-amino-3,5-dichloropyridin-2,6-diyldinitrene that formed by the photolysis of 4-amino-2,6-diazido-3,5-dichloropyridine at 15 K was recorded. Using computer simulation based on numerical diagonalization of the quintet spin Hamiltonian matrices, it was established that this EPR spectrum corresponds to a quintet spin state with the magnetic parameters $g = 2.0023$, $|D_q| = 0.2100$ cm^{-1}, and $|E_q| = 0.0560$ cm^{-1}. Owing to high resolution of the experimental spectrum, the zero-field splitting parameters of the quintet intermediate were determined to an accuracy of at least $5 \cdot 10^{-4}$ cm^{-1}. Calculations of the fine-structure energy levels in external magnetic field and the dependences of the EPR signal positions and intensities of the quintet dinitrene on the direction of external magnetic field were performed for the first time. This allowed unambiguous assignment of all EPR lines of quintet molecules having both in-principal-axis and off-principal-axis orientations.

Key words: azides, nitrenes, photolysis, matrix isolation, EPR, high-spin states.

Investigations of high-spin organic compounds are carried out as part of a new avenue of research in modern chemistry, namely, design of single-molecule organic magnetic materials.[1—3] The main body of information on the structure and properties of high-spin molecules is extracted from EPR spectroscopy data. The role of this method in chemistry of high-spin compounds is similar to that played by NMR spectroscopy in traditional organic chemistry. Elaboration of modern programs for computer simulation of EPR spectra of high-spin compounds in the late 1990s made it possible to determine the zero-field splitting (ZFS) parameters[4—7] by comparing the experimental and calculated spectra.[8—10] However, some problems concerning the interpretation of the EPR spectra of such systems and the accuracy in determination of the ZFS parameters from experimental spectra are still to be solved.

The first problem is to identify the experimental EPR spectra. The magnetic spin Hamiltonian of a high-spin system includes two terms containing different operators of the total spin, S, of the system:

$$\mathbf{H} = g\beta B\mathrm{S} + S\hat{\mathbf{D}}S. \qquad (1)$$

The first term describes the Zeeman electron interaction while the second term accounts for internal anisotropic magnetic interactions between the unpaired electrons. The tensor, $\hat{\mathbf{D}}$, of internal magnetic interactions in the molecule is characterized by two scalar parameters D and E and determines the fine-structure parameters. Typically, the D parameters of quintet nitrenes lie in the range 0.2—0.3 cm^{-1}, so the energy of the Zeeman term in the Hamiltonian (1) in the case of X-band measurements is comparable (at high fields, 0.3 T $< B <$ 1 T) or lower (at $B <$ 0.3 T) than the energy of intramolecular magnetic interactions.[1] This leads to complex angular dependences of the resonance magnetic fields and probabilities of induced transitions. Therefore, the EPR spectra of high-spin molecules randomly oriented in the solid phase should exhibit extra signals of molecules with off-principal-axis orientations. As a rule, itrs hard to distinguish between the extra EPR lines and the signals of the molecules with in-principal-axis orientations (the latter are usually considered as characteristic points of the spectrum).[4] So comprehensive studies of experimental EPR spectra of high-spin nitrenes have not been carried out so far, although certain features of the EPR spectra of model systems with $S = 2$ were reported earlier.[11,12]

Another problem consists in that the available EPR spectra of quintet dinitrenes were recorded in organic glasses[1,4,5,7—10] or in crystals of the starting azides at T = 77 K.[6] The molecular environment can affect the stabilized intermediates generated under such conditions and thus change their structural and magnetic properties. In addition, at this temperature (T = 77 K), molecules can execute large-amplitude librations, which cause an

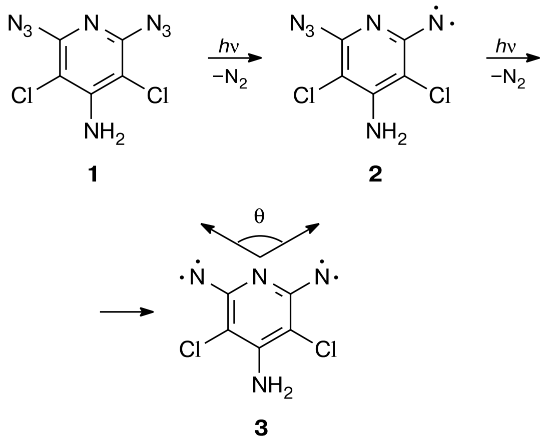
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2284—2289, December, 2007.

effective distortion of the magnetic parameters determined by the analysis of the EPR spectra based on the model of "frozen" particles. Probably, because of this the EPR lines of quintet molecules in organic glasses are rather broad (up to 5—10 mT). The low spectral resolution precludes the identification of closely spaced lines as well as the lineshape and resonance magnetic field calculations during computer simulation of EPR powder spectra.

In this work we used an alternative approach, which makes it possible to significantly reduce the effects of the factors mentioned above. Isolation of intermediates in solid argon (substance of low polarizability containing no magnetic nuclei and weakly interacting with other molecules) at $T < 30$ K provides a unique high spectral resolution of the hyperfine structure of the EPR spectra of doublet radicals (<0.1 mT)[13] and makes it possible to substantially enhance the resolution of the EPR spectra of high-spin nitrenes, as was recently shown taking a septet intermediate as an example.[14]

The aim of this work was to determine the parameters of the $\hat{\mathbf{D}}$ tensor from the EPR spectral parameters of quintet dinitrenes isolated in solid argon, to identify the experimental spectra using computer simulation of EPR powder spectra, and to determine the angular dependences of the resonance magnetic fields and corresponding transition intensities. We studied the paramagnetic products of photolysis of diazide **1** in frozen 2-methyltetrahydrofuran solutions at 77 K (Scheme 1), namely, a triplet nitrene **2** and a quintet dinitrene **3**.[9] The latter has an unusual EPR spectrum characteristic of only the quintet molecules with high asymmetry of the $\hat{\mathbf{D}}$ tensor, $|E_q|/|D_q| \approx 1/3$. A feature of these molecules consists in that even minor changes in the angle q between the nitrene C—N bonds (see Scheme 1) may lead to substantial changes in the $|E_q|/|D_q|$ ratio and, as a consequence, the EPR spectra.[9]

Scheme 1



In this work we for the first time recorded a high-resolution EPR spectrum of quintet intermediate **3** isolated in solid argon. By comparing the experimental EPR spectrum with the calculated EPR powder spectra the parameters of the $\hat{\mathbf{D}}$ tensor were determined with high accuracy. The assignment of spectral components done for the first time revealed a number of extra lines corresponding to off-principal-axis molecular orientations relative to the direction of external magnetic field.

Experimental

The base unit of the experimental setup for cryogenic measurements and the procedure for EPR measurements were described in detail elsewhere.[15,16] Thin argon films were grown by vacuum co-condensation of two gas beams (argon and diazide **1**) on the substrate of a helium cryostate cooled to 15 K. The molecular beams were co-deposited on the lower end of a flat sapphire rod from two spatially separated nozzles. The diazide molecules were generated by sublimation of diazide powder placed in a quartz tube heated to ~110 °C with an external heater. The heating regime of the diazide-containing tube was chosen preliminarily and provided an optimum deposition rate (~10^{12} molecule min^{-1}). The diazide film growth rate was determined from the interferogram of a He—Ne laser bean reflected from the surface of the growing film. The argon flow rate was chosen in such a manner that the Ar : **1** ratio be (1500—3000) : 1. The samples were at most 150 μm thick. After sample preparation the lower end of the sapphire rod was lowered to the center of the EPR spectrometer cavity.

EPR spectra were recorded with an X-band spectrometer (Radiopan). A window in the cavity permitted on-site photolysis of the sample at 15 K. Impurity paramagnetic centers present in the sapphire rod show a number of narrow EPR lines. The EPR spectrum of the pure sapphire rod was recorded preliminarily; the corresponding lines are given in grey in the experimental spectrum (Fig. 1, spectrum *1*).

Samples were UV photolyzed at 266 nm (fourth harmonic of a Nd—YAG laser operating at a repetition frequency of 10 Hz) and at 337 nm (using a N_2 laser operating at a repetition frequency of 1000 Hz). The average laser power was at most 10 mW cm^{-2}.

Diazide **1** was synthesized following a known procedure.[17] Computer simulation of EPR spectra was carried out using the *EasySpin* program package based on the exact numerical diagonalization of the spin Hamiltonian (1).[18]

Results and Discussion

Generation of stabilized quintet 4-amino-3,5-dichloropyridin-2,6-diyldinitrene in solid argon. Quintet radicals **3** are products of two-step photolysis of the starting diazide **1**, which involves generation of trpilet radical **2** as intermediate stage (see Scheme 1). Earlier studies[19] revealed additional channels of photodissociation of quintet radicals and generation of doublet and singlet species during the photolysis of these systems. Based on this, we preliminary chose the photolysis conditions that provided gen-

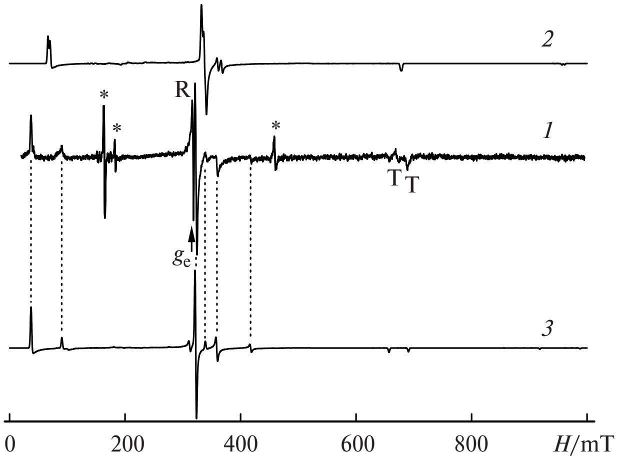


Fig. 1. Experimental EPR spectrum of products of photolysis of diazide **1** in argom matrix at 15 K (*1*) (lines of paramagnetic centers in the sapphire rod used as a substrate are given in grey and asterisked; lines of trpilet intermediate product **2** are denoted by "T"; photolysis also produces a doublet radical (R) having a line centred at the *g*-factor of free electron g_e), and calculated EPR spectra of quintet radical with the ZFS parameters determined for intermediate **3** in frozen organic solvent $D_q = 0.202$ cm^{-1} and $E_q = 0.0664$ cm^{-1} (*2*) and with optimum parameters $D_q = 0.2100$ cm^{-1} and $E_q = -0.0560$ cm^{-1} (*3*). Vertical grey labels show positions of the lines in the experimental spectrum, which were used for optimizatio of the ZFS parameters of the quintet radical (see text). Obtained at a microwave ratiation frequency of 8.910 GHz.

eration of a maximum amount of quintet radicals. First, the sample was irradiated at 266 nm until a maximum intensity of the EPR lines of trpilet radicals and then irradiated again at 337 nm until a maximum intensity of the EPR lines of the quintet radicals. The EPR spectrum of the products of photolysis of diazide **1** is shown in Fig. 1. The signal of the substrate (sapphire rod) is shown in gray. The first stage of photolysis results in (i) trpilet radicals showing two lines at 670 and 688 mT (denoted as "T" in the spectrum) as the major product and (ii) quintet radicals showing very weak signals as the minor product. In the second stage of photolysis the intensities of these lines considerably increase, whereas the line intensities of the trpilet radicals decrease by a factor of 2 to 3. Prolonged photolysis at 337 nm causes a slow decrease in the intensities of the EPR lines of the quintet and trpilet species and a monotonic increase in the intensity of the line denoted by "R" throughout the photolysis. The kinetic behavior of this line differs from the changes in the line intensities in the spectra of the trpilet and quintet radicals. The EPR spectrum of the radicals producing the "R" line exhibits a single line of width 2 mT centred around the *g*-factor of free electron. This is the sole spectral line with this type of kinetic behavior. Therefore, we assume this is a signal of by-products of photolysis of the starting diazide, namely, the doublet radicals with unresolved hyperfine structure. Based on the different kinetic behavior of the EPR lines of the doublet, trpilet, and quintet radicals, we recorded nine lines corresponding to the stabilized quintet intermediate. Owing to high spectral resolution the positions of the main lines were determined to an accuracy of at least 0.5 mT. No significant changes in the shape and positions of the lines corresponding to the triplet and quintet radicals were observed in the temperature range 7—30 K. It follows that these species show no high librational or rotational mobility in solid argon.

Determination of the parameters of the tensor $\hat{\mathbf{D}}$ of quintet intermediate 3. The parameters, D_q and E_q, of the tensor of magnetic interactions were determined by comparing the experimental EPR spectrum with the simulated powder spectra calculated based on the exact solutions of the secular equation for the spin Hamiltonian (1) for the system with $S = 2$.

The values used as the starting approximation, $D_q = 0.202$ cm^{-1} and $E_q = 0.0664$ cm^{-1}, were obtained in a study[9] of the EPR spectrum of radical **3** in frozen solution. Individual lines were assumed to be Gaussians with the widths varied from 0.1 to 1 mT. The EPR spectrum of the quntet species with these fine-structure parameters is shown in Fig. 1. Comparison of this spectrum with the experimental one shows that positions of the resonance lines differ appreciably. The shape of certain lines also differs to such a great extent that these distinctions can not be described by varying individual linewidths. To obtain an optimum theoretical spectrum, we varied the parameters D_q and E_q to minimize the functional, *R*, of the root-mean-square deviation of the experimental resonance magnetic fields from calculated values:

$$R = \sqrt{\frac{1}{n}\sum_{k}^{n}(H_k^{\text{calc}} - H_k^{\text{exp}})^2}, \qquad (2)$$

where $n = 6$ is the number of evaluated lines in the spectrum under study. Positions of these lines are shown in Fig. 1. Three spectral lines at the resonance fields near 310, 658, and 688 mT overlap with the lines of the doublet and trpilet radicals. Therefore, they were not included in the functional (2).

The calculated optimum spectrum (see Fig. 1) corresponds to the minimum value $R = 0.33$ mT attained using the quintet species parameters $D_q = 0.2100$ cm^{-1} and $E_q = -0.0560$ cm^{-1} (negative sign for E_q was chosen with allowance for the known properties of the $\hat{\mathbf{D}}$ tensor of this kind of species[1]). The accuracy in determination of the D_q and E_q values was determined using the plots shown in Fig. 2. The functional value $R = 0.60$ mT was chosen as the critical value at which the positions of the lines in the experimental and calculated spectra differ by more than the corresponding linewidths. The accuracy in determination thus obtained was ±0.0005 for D_q and ±0.0002 cm^{-1} for E_q.

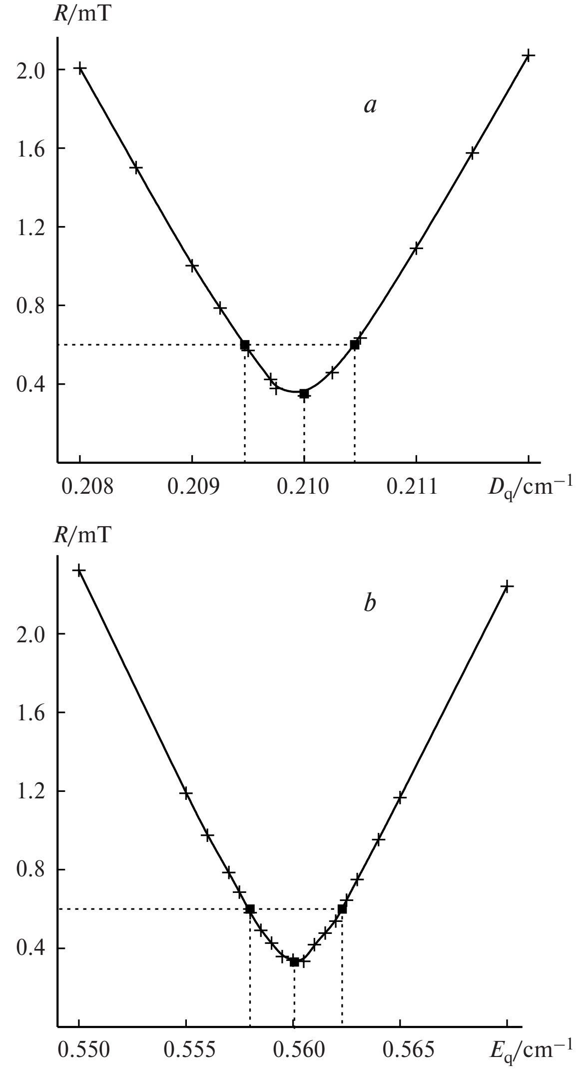


Fig. 2. The functional, $R(D_q)$, of the root-mean-square deviation of the positions of six lines in the calculated EPR spectrum from those of experimental spectral lines near the optimum values of the ZFS parameters at E_q = 0.0560 cm^{-1} and $R(E_q)$ at D_q = 0.02100 cm^{-1}. The horizontal line show the value of the functional R, which exceeds the linewidths in the experimental spectrum.

Analysis of the EPR spectrum of quintet intermediate 3 in solid argon. Identification of lines in the EPR spectrum corresponding to the spin Hamiltonian (1) is a complicated task. This is mainly due to two reasons.

One of them is related to specific features of the resonance magnetic field distribution function for a sample containing randomly oriented species. Assuming a δ-function-like individual lineshape, the distribution density function for a particular transition has the form:

$$\rho(H) = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\delta(H - H(\theta))W(\theta,\phi), \qquad (3)$$

where ϕ and θ are the Euler angles characterizing the mutual arrangement of the principal axes of the tensor **D**^ in the laboratory system of coordinates where the external magnetic field is parallel to the Z' axis, $W(\theta,\phi)$ is the transition probability, and $H(\theta,\phi)$ is the resonance field position. The function $\rho(H)$ differs from zero on a finite segment of H values $[H_{\min}, H_{\max}]$, is discontinuous at the points $H_{\min}$ and $H_{\max}$, and has extra singularities[20,21] at

$$\frac{1}{\sin\theta}\frac{\partial H(\theta,\varphi)}{\partial\theta} = 0, \quad \frac{1}{\sin\theta}\frac{\partial H(\theta,\varphi)}{\partial\varphi} = 0\,. \qquad (4)$$

In the vicinity of these points a small interval of magnetic fields ΔH corresponds to a large solid angle $\Delta\Omega$, which provides a peak intensity in the function $\rho(H)$. The experimental EPR spectrum represents a derivative of the distribution function $d\rho(H)/dH$. Therefore, the EPR lines appear at singular points. Positions of the resonance EPR lines are determined by the conditions (4) where $d\theta/dH \to \infty$ (see Ref. 20). This condition is always met at in-principal-axis orientations of the magnetic field, where the **H** vector is parallel to one of the principal axes X, Y, and Z of the $\hat{\mathbf{D}}$ tensor (EPR lines at $\mathbf{H} \parallel Z$, $\mathbf{H} \parallel X$ and $\mathbf{H} \parallel Y$ are denoted as z_i, x_i, and y_i, respectively). In addition, singularities of the type (4) of the distribution function $\rho(H)$ may appear at other magnetic field orientations relative to the axes of the $\hat{\mathbf{D}}$ tensor. These are the so-called extra lines. The possibility for these lines to appear in the EPR spectra of quintet radicals was predicted in the course of analysis of the spin Hamiltonian (1) for $S = 2$.[12]

The second problem in the identification of the EPR spectra of such species is to calculate the probability, $W(\theta,\phi)$, of the transition between different fine-structure levels in external magnetic field. When the Zeeman term in the spin Hamiltonian (1) is not predominant, the eigenvalue of the electron spin projection (m_s) is not a good characteristic of the energy levels, *i.e.*, the wave function of each state is a superposition of several eigenfunction of the projection m_s. Therefore, even for the allowed transitions with $\Delta m_s = \pm 1$ the transition probability varies over a wide range depending on the resonance field and orientation of the tensor $\hat{\mathbf{D}}$ relative to the direction of the vector **H**. Transition probability calculations require determination of the resonance magnetic field, the eigenfunctions of the Hamiltonian (1), and the squared matrix element of the perturbation induced by the microwave field. Based on the considerations mentioned above, we performed spectral analysis and identification of the observed EPR lines.

Figure 3 shows the calculated energy levels for the in-principal-axis orientations of the $\hat{\mathbf{D}}$ tensor relative to external magnetic field ($\mathbf{H} \parallel X$, $\mathbf{H} \parallel Y$, $\mathbf{H} \parallel Z$) and the resonance magnetic fields determined by diagonalization of the spin Hamiltonian (1). Thick lines correspond to the most probable transitions. Thin lines correspond to the

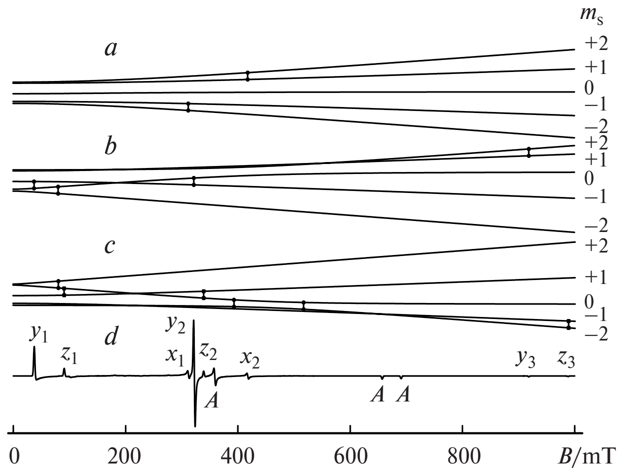


Fig. 3. Fine-structure energy levels of quintet dinitrene **3** plotted *vs.* magnetic field for three in-principal-axis orientations of external magnetic field **H** ‖ *X* (*a*), **H** ‖ *Y* (*b*), and **H** ‖ *Z* (*c*). Vertical lines denote transitions at a microwave ratiation frequency of 8.910 GHz. The forbidden transitions are given in grey; the calculated powder EPR spectrum (see Fig. 1, spectrum *3*) is denoted by "*d*"; the extra lines are denoted by "*A*".

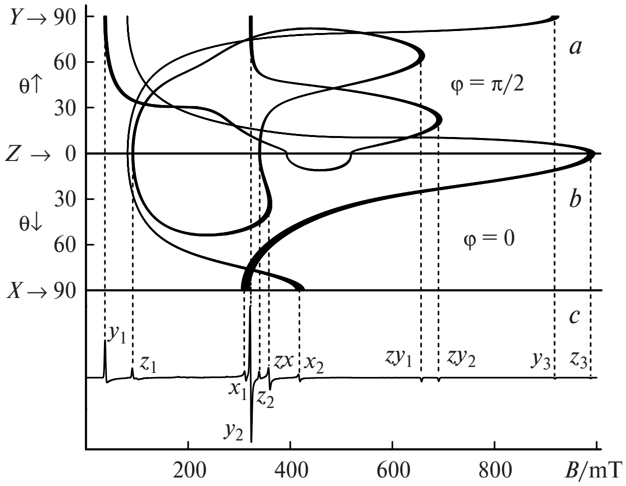


Fig. 4. Positions of resonance magnetic fields plotted *vs.* angle θ at φ = π/2 (in the *zy* plane, *a*) and φ = 0 (in the *zx* plane, *b*) for various transitions, where θ and φ are the Euler angles between the principal axes of the tensor $\hat{\mathbf{D}}$ and the direction of external magnetic field. In the limiting cases (θ = 0 and θ = π/2) this corresponds to the direction of magnetic field along the *X*, *Y*, and *Z* axes of the tensor $\hat{\mathbf{D}}$ (in-principal-axis orientations). Calculated for the spectrum with optimum parameters $D_q = 0.2100$ cm^{-1} and $E_q = -0.0560$ cm^{-1}. The linewidths are proportional to the relative transition probabilities. The calculated powder spectrum (see Fig. 1, spectrum *3*) is denoted by "*c*". Dashed lines denote the resolved transitions for the in-principal-axis orientations, three solid vertical lines denote the extra spectral lines arising at off-principal-axis orientations.

transitions that are five to seven orders of magnitude less probable compared to the former group, thus being almost forbidden. The EPR line assignment based on these considerations demonstrates that only six of the nine experimentally observed lines correspond to the transitions for the in-principal-axis orientations (two EPR lines for each orientation). The transition number for the in-principal-axis orientations increases with an increase in the magnetic field. Since one has $D_q \sim h\nu$ for our experimental conditions, this numbering scheme differs from the commonly accepted one[21] for the quintet molecules characterized by the parameters $D_q << h\nu$. Three lines at 359, 658, and 688 mT should be treated as extra lines. Analysis of the angular dependences of the resonance fields $H(\theta,\phi)$ showed that conditions (4) are met when the **H** vector lies in the *zy* ($\phi = p/2$) and *zx* ($\phi = 0$) planes; the corresponding plots are shown in Fig. 4. For one transition there is a singularity $(d\theta/dH) = \infty$ at θ = 40° in the *zx* plane (see Fig. 4, point zx_1). The other two extra lines are in the *zy* plane at θ = 30 and 60° (denoted as zy_1 and zy_2, respectively). The plots in Fig. 4 also make it possible to understand why the transitions y_1 and y_2 are most intense in the EPR spectrum. For these lines, the condition $dq/dH \to \infty$ is met for a wide range of the angles θ (from 90 to 60°), which corresponds to a large number of molecular orientations corresponding to these resonance magnetic fields. At the same time the allowed transitions y_3 and z_3 (at high magnetic fields of 930 and 990 mT) do not meet this condition, thus having very low intensities and being experimentally undetectable.

The results obtained and analysis of experimental data indicate that the EPR spectrum of quintet dinitrene **3** isolated in solid argon matrix at cryogenic temperatures shows a unique high spectral resolution, which makes it possible to determine the ZFS parameters to an accuracy of at least $5 \cdot 10^{-4}$ cm^{-1}. The simulated EPR spectrum correctly reproduces all lines in the experimental spectrum. The assignment of the spectral components shows that three out of nine observed lines of randomly oriented species are the extra lines corresponding to molecules having off-principal-axis orientations. The parameters of the $\hat{\mathbf{D}}$ tensor determined in this work will be used for analysis of the spin cluster with $S = 2$ containing two spatially separated, magnetically interacting nitrene groups with the total spin $S = 1$, the eigentensors $\hat{\mathbf{D}}_1$ and $\hat{\mathbf{D}}_2$ and the dipole-dipole interaction tensor $\hat{\mathbf{D}}_{1,2}$ (see Ref. 5)

$$\hat{\mathbf{D}} = 1/6[\hat{\mathbf{D}}_1(S = 1) + \hat{\mathbf{D}}_2(S = 1)] + 1/3\hat{\mathbf{D}}_{1,2} \qquad (5)$$

to determine the interrelation between the magnetic and structural parameters of the quintet intermediate.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-32410 and 07-03-00768) and the Chemistry and Materials Science Division of the Russian Academy of Sciences (Program No. 1).

References

1. *Magnetic Properties of Organic Materials*, Ed. P. M. Lahti, Marcel Dekker, New York, 1999.
2. *Molecular Magnets: New Magnetic Materials*, Eds K. Itoh and M. Kinoshita, Kodansha-Godon and Breach, Tokyo, 2000.
3. *Magnetism: Molecules to Materials. Molecular Based Materials*, Eds J. S. Miller and M. Drillon, Wiley, Wein Leim, 2001, Vol. **3**.
4. T. A. Fukuzawa, K. Sato, A. S. Ichimura, T. Kinoshita, T. Takui, K. Itoh, and P. M. Lahti, *Mol. Cryst. Liq. Cryst.*, 1996, **278**, 253.
5. R. S. Kalgutkar and P. M. Lahti, *J. Am. Chem. Soc.*, 1997, **119**, 8784.
6. T. Nakai, K. Sato, D. Shiomi, T. Takui, K. Itoh, M. Kozaki, and K. Okada, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 157.
7. H. Oka, Y. Miura, and Y. Teki, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 41.
8. S. V. Chapyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1085 [*Russ. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 1126].
9. S. V. Chapyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1536 [*Russ. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 1593].
10. S. V. Chapyshev and P. M. Lahti, *J. Phys. Org. Chem.*, 2006, **19**, 637.
11. R. D. Dowsing, *J. Magn. Reson.*, 1970, **2**, 332.
12. J. Baranowski, T. Cukierda, B. Jezowska-Trebiatowska, and H. Kozwski, *J. Magn. Reson.*, 1979, **33**, 585.
13. E. Ya. Misochko, A. V. Akimov, and I. U. Goldshleger, *Usp. Khim.*, 2003, **72**, 262 [*Russ. Chem. Rev.*, 2003, **72**, 233 (Engl. Transl.)].
14. T. Sato, A. Narazaki, Y. Kawaguchi, H. Nino, G. Bucher, D. Grote, J. J. Wolff, H. H. Wenk, and W. Sander, *J. Am. Chem. Soc.*, 2004, **126**, 7846.
15. E. Ya. Misochko, A. V. Akimov, I. U. Goldschleger, D. A. Tyurin, and D. N. Laikov, *J. Chem. Phys.*, 2005, **122**, 34503.
16. E. Ya. Misochko, A. V. Akimov, V. A. Belov, and D. A. Tyurin, *Izv. Akad. Nauk. Ser. Khim.*, 2007, 424 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, **56**, 438].
17. S. V. Chapyshev and M. S. Platz, *Mendeleev Commun.*, 2001, 56.
18. S. Stoll and A. Schweiger, *J. Magn. Reson.,* 2006, **178**, 42.
19. S. V. Chapyshev and H. Tomioka, *Bull. Chem. Soc. Jpn*, 2003, **76**, 2075.
20. G. M. Zhidomirov, Ya. S. Lebedev, S. N. Dobryakov, N. Ya. Shteinshneider, A. K. Chirkov, and V. A. Gubanov, *Interpretatsiya slozhnykh spektrov EPR* [*Interpretation of Complex EPR spectra*], Nauka, Moscow, 1975 (in Russian).
21. W. Weltner, Jr., *Magnetic Atoms and Molecules*, Dover Publications, New York, 1989.

Received June 13, 2007;
in revised form October 4, 2007