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High resolution electron paramagnetic resonance spectroscopy of quintet pyridyl-2,6-dinitrene in solid argon: Magnetic properties and molecular structure

E. Ya. Misochko,[a] A. V. Akimov, and S. V. Chapyshev
Institute of Problems of Chemical Physics of the Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia

The high resolution X-band electron para magnetic resonance (EPR) spectrum of quintet pyridyl-2,6-dinitrene was recorded after the photolysis of 4-amino-2,6-diazido-3,5-dichloropyridine in solid argon matrix at 15 K. This spectrum represents a new type of powder EPR spectra that are characteristic for quintet spin states with zero-field splitting parameters $|E_q/D_q| \approx 1/4$. All EPR lines of the quintet dinitrene were unambiguously assigned based on the eigenfield calculations of the Zeeman energy levels and angular dependencies of resonance magnetic fields. Owing to the high resolution of the experimental EPR spectrum, zero-field splitting parameters of the quintet dinitrene were determined with a high accuracy: $D_q = 0.2100 \pm 0.0005$ cm^{-1} and $E_q = -0.0560 \pm 0.0002$ cm^{-1}. These parameters provide correct information regarding the molecular angle Θ and distance r between two triplet sites in the molecule of quintet dinitrene. The measured molecular angle $\Theta = 114.2° \pm 0.2°$ is in excellent agreement with results of the density functional theory calculations. The analysis of the magnetic parameters shows that the spin population on the nitrene units in the quintet dinitrene is greater than that on the nitrene unit in the triplet nitrene. © 2008 American Institute of Physics. [DOI: 10.1063/1.2840351]

I. INTRODUCTION

Among all organic tetraradicals, quintet dinitrenes have the largest zero-field splitting (zfs) parameters and exhibit the strongest magnetic properties.[1] Such dinitrenes model molecular ferromagnetic domains with four unpaired electrons and are of considerable interest for explorations of molecular magnetism and spin chemistry. For molecules with $\mathbf{S} \geq 1$, the spin Hamiltonian represents a sum of two terms,

$$\mathbf{H} = g\beta HS + S\hat{D}S, \qquad (1)$$

where the first term describes the Zeeman interaction of the total electron spin angular momentum $\mathbf{S}$ with the applied magnetic field, and the second term describes magnetic dipole-dipole interactions between unpaired electrons in the molecule.[2] The traceless tensor $\hat{D}$ is referred to as the zero-field tensor and described by two scalar zfs parameters D and E.

Four prominent features are attributable to quintet molecules:

(1) The high localization of unpaired electrons on the nitrene units, owing to which these units, can be considered as two spatially separated triplet centers,

(2) strong ferromagnetic exchange interactions (~ 10 kcal/mol) between triplet centers and, as a result, large energy gaps between the ground high-spin and excited low-spin states,

(3) very weak spin-orbit interactions, due to which the terms involving higher powers of S_z, S_x, and S_y in the magnetic spin Hamiltonian, are negligibly small,

(4) weak hyperfine interactions on magnetic nuclei.

Based on these features of quintet molecules, Itoh[3] has suggested the model that adequately describes the zero-field term of the quintet spin-state as the product of two interacting triplet centers $\mathbf{S}_1 = 1$ and $\mathbf{S}_2 = 1$. Such an approach gives a simple expression for the quintet zfs tensor $\hat{D}_q$ as follows.

$$\hat{D}_q = \tfrac{1}{6}(\hat{D}_1 + \hat{D}_2) + \tfrac{1}{3}\hat{D}_{12}, \quad \hat{D}_{12} < \hat{D}_1, \hat{D}_2, \qquad (2)$$

where $\hat{D}_1$ and $\hat{D}_2$ are the zero-field tensors of triplets $\mathbf{S}_1$ and $\mathbf{S}_2$, respectively, and the tensor $\hat{D}_{12}$ characterizes magnetic dipole-dipole interactions between triplet sites $\mathbf{S}_1$ and $\mathbf{S}_2$. Expression (2) predicts that quintet zfs parameters D_q and E_q should depend on the molecular angle Θ and the distance r between two triplet sites. Figure 1 demonstrates the angular dependence of these parameters for the case of two equivalent triplet sites when the interaction tensor $\hat{D}_{12}$ in Eq. (2) is negligibly small. Here we use the conventional notations of the zfs parameters: $D_q = \tfrac{3}{2}Z$ and $E_q = \tfrac{1}{2}(X - Y)$, where X, Y, and Z are the eigenvalues of the traceless zfs tensor D_q: $X + Y + Z = 0$ and $|Z| > |X|$ and $|Y|$. Figure 1 also shows that there are two critical points at $\sin^2(\theta_1/2) = \tfrac{1}{3}(\theta_1 = 70.6°)$ and $\sin^2(\theta_2/2) = \tfrac{2}{3}(\theta_2 = 108.8°)$, where the ratio $|E_q/D_q|$ reaches its highest possible value of 1/3. Both parameters D_q and E_q depend strongly on the angle Θ in the regions $\Theta < \theta_1$ and $\Theta > \theta_2$ nearby the critical points θ_1 and θ_2, where $d(D_q)/d\Theta$ amounts to 10^{-2} cm^{-1}/deg (at typical triplet parameter D_t
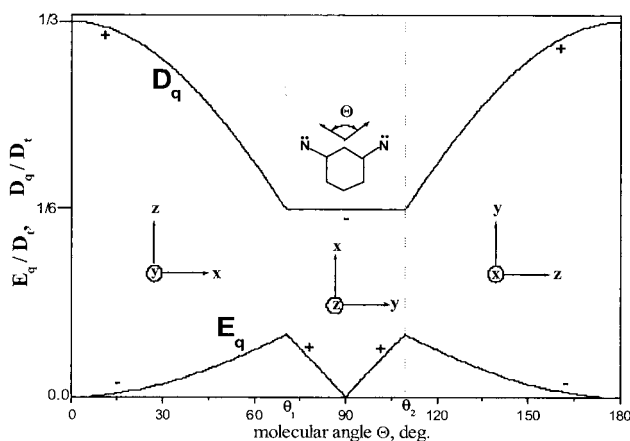
FIG. 1. Quintet zfs parameters D_q and E_q as function of molecular angle Θ for the case of two equivalent triplet sites when the interaction tensor $\hat{D}_{12}$ in Eq. (2) is negligibly small. Orientations of principal axis $\hat{D}_q$ towards the molecular structure are shown.

≈ 1 cm^{-1}). Thus, if the spin Hamiltonian (1) describes the experimentally observable EPR spectrum with an accuracy of $\Delta D \sim 10^{-3}$ cm^{-1}, then the angle Θ can be determined from expression (2) with an accuracy of $\sim 10^{-1}$ deg. However, taking into account the fact that most of quintet dinitrenes have the distance r between two triplet sites of around 0.4–0.5 nm,[1] and magnetic dipole-dipole interactions between these sites may be as great as 10^{-2} cm^{-1}, the interaction tensor $\hat{D}_{12}$ in Eq. (2) can play a noticeable role in estimations of D_q and Θ. Previous EPR studies[1,4–12] of quintet dinitrenes in frozen solutions have demonstrated a validity of Itoh's model and Eq. (2) for geometrically inflexible molecules, even though the interaction tensor $\hat{D}_{12}$ in Eq. (2) was excluded from considerations. In all of these studies, molecules of quintet dinitrenes had the angle Θ between the nitrene C–N bonds close to 0°, 120°, or 180°. Meanwhile, as it follows from Fig. 1, the zfs parameters of quintet dinitrenes are the most sensitive toward Θ in the 109°–120° region. Such a type of quintet molecules, namely, dinitrene 3 with $\Theta = 114.5°$, has recently been obtained during the photolysis of diazide 1 in organic glass at 77 K (Scheme 1).[12,13]
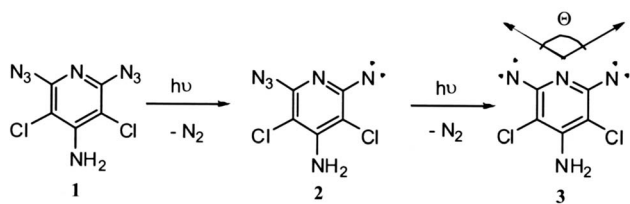
Scheme 1

Unfortunately, a poor spectral resolution of the experimental EPR spectrum of dinitrene 3 in frozen solutions made impossible the very precise determination of its zfs parameters. In order to overcome this problem, in this work, an EPR study of the photolysis of diazide 1 in a solid argon matrix at 15 K has been accomplished. The high resolution EPR spectra of triplet nitrene 2 and quintet dinitrene 3 recorded in an argon matrix allowed us, for the first time, to derive from these spectra the zfs parameters with an accuracy better than

10^{-3} cm^{-1} and completely analyze these spectra, by using calculations of the Zeeman energy levels and angular dependencies of the resonance magnetic fields. Based on the zfs parameters for dinitrene 3 measured, the contribution of the interaction tensor $\hat{D}_{12}$ in Eq. (2) for quintet molecules has also been evaluated.

II. EXPERIMENT

Diazide 1 was synthesized according to the literature procedure.[14]

The experimental technique for matrix isolation used in this study is similar to that described earlier.[15,16] Solid argon films doped with diazide 1 were prepared by vacuum codeposition of two separate molecular beams (Ar and diazide 1 vapor) onto a substrate (sapphire rod) cooled to 15 K. The deposition rate was typically 10 μm/min, and the thickness of the deposited argon films was typically 100 μm. The vapor of 1 was produced by an oven heating the polycrystalline 1 to ~ 107 °C. The oven temperature was regulated by a precise temperature controller and was chosen to obtain the ratio Ar/M$\sim 10^3$–10^4. Temperature stability was ~ 0.1 K over 7–40 K range. EPR spectra were recorded using a standard 9 GHz spectrometer.

For photochemical generations of triplet and quintet nitrenes (Scheme 1), UV light at 266 (fourth harmonic of a Nd:(YAG) yttrium aluminum garnet laser, with ten pulses per second) and 337 nm (pulse N$_2$-laser, with 10^3 pulses per second) were used. The average laser power did not exceed 5 mW/cm^2. In order to obtain quintet dinitrenes in high yields, a series of preliminary measurements varying photolysis conditions were performed. An optimum photolytic procedure developed is described in the next section.

III. RESULTS AND DISCUSSION

A. EPR spectra of nitrenes

The irradiation of diazide 1 isolated in solid argon at 15 K with light at 266 nm leads to the appearance of an intense EPR line lying close to the free electron g-factor and two signals at 670 and 688 mT. The line at $g = 2.0023$ (R) is attributable to the doublet radical species with unresolved hyperfine structure,[4,5] while signals at 670 and 688 mT are assigned to the lines of x_2- and y_2-transitions of triplet nitrene 2 (T). On further irradiation with light at 266 nm, the intensities of signals at 670 and 688 mT reach their maxima and then start to decay. Simultaneously, week EPR lines at 38, 323, and 359 mT of quintet dinitrene 3, appear (see Fig. 2). In order to obtain the most intense signals of quintet dinitrene 3, the photolysis at 266 nm was interrupted when signals T reached their maximum values, and then the sample was irradiated with light at 337 nm. The photolysis at 337 nm leads to slow decay of signals T, further growth in intensity of the signal R, and the appearance of a series of new intense EPR lines of quintet dinitrene 3 (see Fig. 2). The final EPR spectrum obtained is shown in Fig. 3. The different kinetic behavior of the EPR lines from doublet, triplet, and quintet species allowed us to unambiguously select nine EPR lines of quintet dinitrene 3. Owing to a high resolution of the
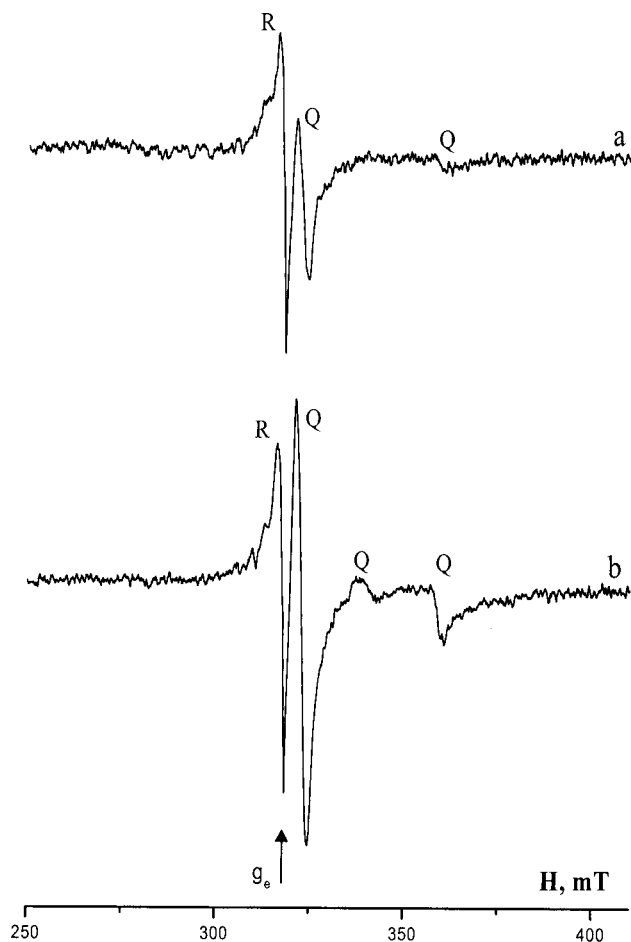
FIG. 2. EPR spectra of the photolyzed sample Ar/diazide 1 ≈2.10³ at 15 K: (a) After photolysis with light at 266 nm and (b) after subsequent photolysis at 337 nm. EPR lines of doublet and quintet species are labeled as R and Q, respectively. The microwave frequency is ν_0=8.910 GHz.

FIG. 3. EPR spectra of the sample shown in Figs. 2(a) and 2(b). Simulated powder spectra of the triplet nitrene with D_T=1.0630 cm⁻¹ and E_T =0.0032 cm⁻¹ (c), and the quintet dinitrene with D_q=0.2100 cm⁻¹ and E_q =−0.0560 cm⁻¹ (d). EPR lines in the spectrum (b) shown by gray color arise from impurities in the sapphire rod and are present in the absence of the sample.

electron spin resonance spectrum obtained, the resonance magnetic fields for all lines were measured with a high accuracy (<0.5 mT). Shape and resonance magnetic fields of all components in the EPR spectrum did not change in the temperature range of 7–30 K. Intensities of the strong EPR lines of dinitrene 3 obey the Curie law, hence confirming the ground quintet spin-state of this dinitrene.

B. Zero-field splitting parameters of nitrenes

The zfs parameters D_q and E_q of the quintet tensor $\hat{D}_q$ for dinitrene 3 were determined from comparison of computer simulated and experimentally recorded EPR spectra. Simulations were performed using the EASYSPIN program package,[17] operating with an exact numerical matrix diagonalization analysis of the spin Hamiltonian (1) for randomly oriented species with **S**=2. As starting parameters, we, at first, choose **S**=2, g=2.0023, D_q=0.202 cm⁻¹, and E_q =0.0664 cm⁻¹, which were derived previously from EPR spectra of dinitrene 3 in 2-methyltetrahydrofuran at 77 K.[12] It was found that this simulated spectrum significantly differs from the experimental one. The zfs parameters D_q and E_q yielding the best approximation to the true values were evaluated by minimization of the functional R, which was defined as a root-mean-square (rms) deviation of calculated
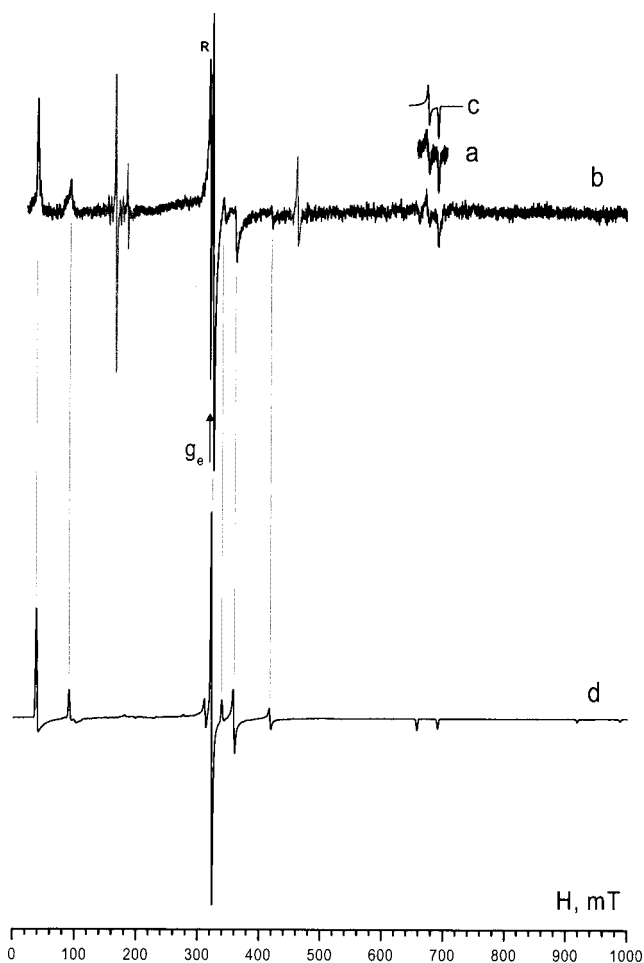
resonance fields H_k (calc) from those measured experimentally H_k (expt),

$$R = \sqrt{\frac{1}{n}\sum_{k}^{n}(H_k(\text{calc}) - H_k(\text{expt}))^2}, \tag{3}$$

where n=6 represents the number of the selected lines in the spectrum of dinitrene 3. These six lines and corresponding to them resonance magnetic fields H_k (expt) are marked in Fig. 3. Other three lines at 310, 658, and 688 mT were excluded from considerations since they are overlapping with EPR patterns of doublet and triplet species. The spectrum optimized (Fig. 3) was obtained at D_q=0.2100 cm⁻¹ and E_q=−0.0560 cm⁻¹ (the negative sign of E_q is taken based on characteristic features of the tensor $\hat{D}$ for such a type of species, see Fig. 1). It corresponds to the rms deviation of R(min)=0.33 mT. To estimate an accuracy of D_q and E_q measurements, the rms deviations were calculated by varying each of the parameters nearby their optimum values (Fig. 4). The rms deviation of R=0.60 mT was chosen as crucial one, if at least one of the tested lines had deviation $|H_{\text{calc}} - H_{\text{expt}}|$ exceeding the line width. This treatment gave the
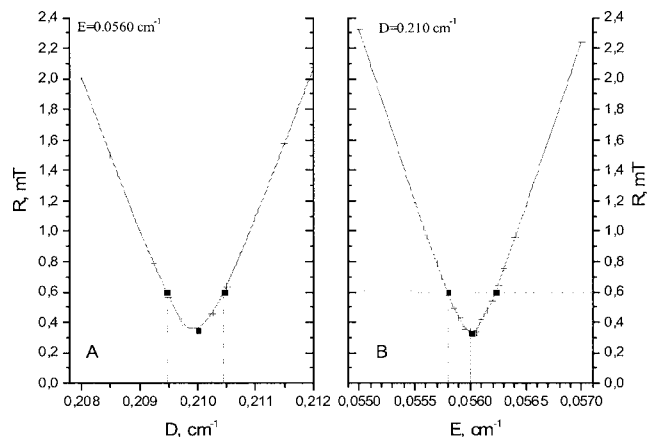
FIG. 4. Dependences of functional R [see Eq. (3) in the text] on the quintet zfs parameters: (A) The parameter E_q is fixed and (B) the parameter D_q is fixed.

experimental errors for D_q and E_q that are not more than ± 0.0005 and ± 0.0002 cm^{-1}, respectively. The same treatment was also applied to evaluate the zfs parameters of triplet nitrene 2. Two resonance magnetic fields at 670 and 688 mT were used for minimizing functional (3). The spectrum optimized [see Fig. 3(b)] corresponds to a singular solution of the spin Hamiltonian (1) for $S=1$ and $R(\min)=0$, because only two parameters, D_T and E_T, were involved in the optimization process. It was found that triplet nitrene 2 has $D_r=1.0630 \pm 0.0005$ cm^{-1} and $E_r=0.0032 \pm 0.0003$ cm^{-1}.

The EPR spectrum of quintet dinitrene 3 in solid argon at 15 K represents a new type of spectra of quintet molecules that have $|E_q/D_q| \approx 1/4$. So far, only quintet dinitrenes with $|E_q/D_q| \approx 0$,[6–8] 1/5,[4,5,9–11] and 1/3 (Ref. 12) have been characterized with X-band EPR spectroscopy. The most indicative feature of EPR spectra of quintet dinitrenes with $|E_q/D_q| \approx 1/4$ is a pattern of three signals at 40, 90, and 323 mT that are absent in EPR spectra of all other quintet dinitrenes.

C. Assignments of the powder EPR spectrum of quintet dinitrene

There are two fundamental problems in complete assignment of the powder EPR spectra of high-spin nitrenes.[2] The first one is related with the presence of two terms in the spin Hamiltonian (1), containing different operators of the total electron spin angular momentum $\hat{S}_z$ and $\hat{S}^2$. At high magnetic fields, when $g\beta H \gg |D|$ and the Zeeman term dominates, the magnetic moment of the molecule processes about the magnetic field axis and each of Zeeman energy level are characterized by a value of m_s, which is a "good" quantum number at this limit. At this region of magnetic fields, only the usual transitions $\Delta m_s = \pm 1$ are allowed. As the applied magnetic field is lowered, the spin functions are mixed, and m_s is no longer a good quantum number. Due to this, at low magnetic fields the transitions $\Delta m_s = \pm 2$ become also allowed. However, some of the transitions $\Delta m_s = \pm 1$ and $\Delta m_s = \pm 2$ will not be observable if $(|D|+|3E|) > h\nu \cong 0.33$ cm^{-1}. The second problem consists in the appearance
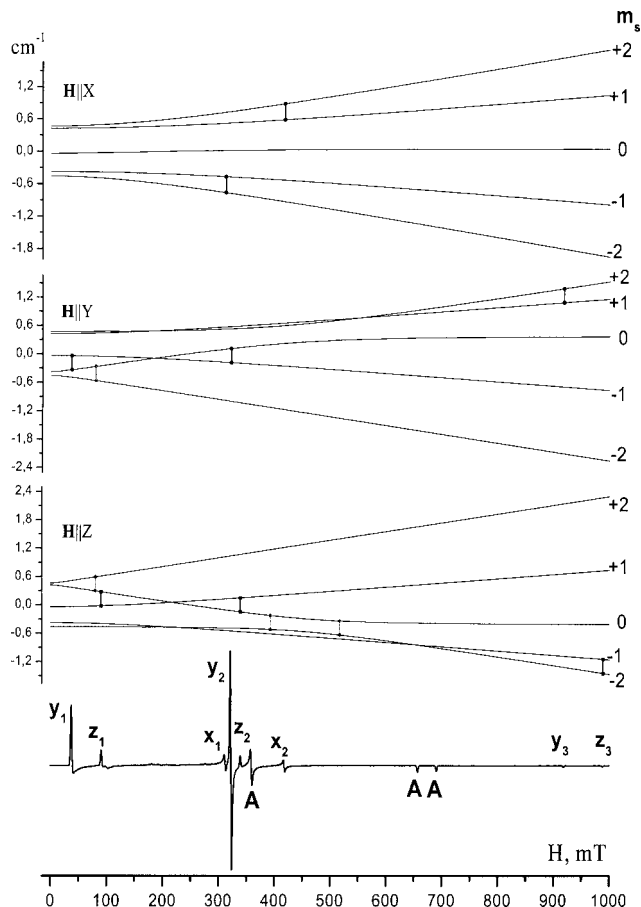

FIG. 5. Calculated Zeeman energy levels, allowed transitions, and simulated powder EPR spectrum of quintet dinitrene with $D_q=0.2100$ cm^{-1} and $E_q=-0.0560$ cm^{-1}. EPR lines in the spectrum are marked according to the notations accepted in the text. The transitions with low probability are gray colored.

of additional "extra lines" in the powder EPR spectra from off-principal-axis oriented molecules. The number and field position of such extra lines can be different, depending on the zfs parameters and molecular symmetry. So far, only a few extra lines have been identified by guess in EPR spectra of quintet dinitrenes with $|E_q/D_q| \approx 0$ and 1/5.[7,4]

To perform a complete assignment of all lines in the spectrum of dinitrene 3, the Zeeman energy levels and angular dependencies of resonance magnetic fields from the direction of the applied magnetic field were calculated. The Zeeman energy levels for canonical orientations of the tensor $\hat{D}$ toward the field axes ($H \| D_X$, $H \| D_Y$, and $H \| D_Z$) are shown in Fig. 5. In strict accord with theory,[2] quintet dinitrene 3 has at zero-field five energy levels: $W_1=-2D_q(1+\alpha)^{1/2}$, $W_2=-D_q-3E_q$, $W_3=-D_q+3E_q$, $W_4=2D_q$, and $W_5=2D_q(1+\alpha)^{1/2}$, where $\alpha=3E_q^2/D_q^2$. Due to large D_q and E_q, only eight transitions $\Delta m_s = \pm 1$ of high probability fall in the 0-1000 mT region, and six of them are well resolved in the experimental spectrum. These are two x_i ($|-2\rangle \leftrightarrow |-1\rangle$ and $|+1\rangle \leftrightarrow |+2\rangle$), two y_i (both $|-1\rangle \leftrightarrow |0\rangle$, due to mixing of the spin functions at low and intermediate magnetic fields), and two z_i $|0\rangle \leftrightarrow |+1\rangle$) transitions. Three other lines at 360, 660, and 680 mT do not fit any of canonical transitions and should be assigned to extra lines. These three lines are

marked as A in Fig. 5. Angular dependencies of resonance magnetic fields (H_{res}) from the polar angle θ are shown in Fig. 6. Due to magnetic nonequivalence of the molecular X and Y axes, the angular dependence of resonance magnetic fields is different in the ZY ($\phi = \pi/2$, upper panel) and ZX planes ($\phi = 0$, lower panel). EPR peaks appear in the powder EPR spectra if $d\theta/dH_{res}$ is turned to infinity. All of allowed transitions for canonical orientations (labeled as x_i, y_i, and z_i) are well-resolved in the spectrum. Three additional extra lines are also clearly seen in Fig. 6. The first one (labeled as zx) at 360 mT appears in the spectrum because the $|0\rangle \leftrightarrow |+1\rangle$ transitions undergo singularity $d\theta/dH_{res} = \infty$ in the ZX plane at $\theta = 40°$. The other two extra lines are the result of

singularities of the $|0\rangle \leftrightarrow |+1\rangle$ and $|-1\rangle \leftrightarrow |0\rangle$ transitions (labeled as zy_1 and zy_2) in the ZY plane at $\theta = 70$ and $20°$, respectively.

D. Fine-structure and molecular parameters of quintet dinitrene

The zfs parameters of triplet nitrene 2 and quintet dinitrene 3 were used for an analysis of expression (2). In the first step, we consider this expression excluding the interaction term $\hat{D}_{12}/3$, as it has been suggested in earlier studies.[4–11] At $\Theta > \theta_2$ (see Fig. 1), the quintet zfs tensor can be written as

$$\hat{D}_q = \begin{vmatrix} -\frac{1}{3}D_q + E_q & 0 & 0 \\ 0 & -\frac{1}{3}D_q - E_q & 0 \\ 0 & 0 & \frac{2}{3}D_q \end{vmatrix}$$

$$= \frac{1}{3}\begin{vmatrix} -\frac{1}{3}D_{Tq} + E_{Tq} & 0 & 0 \\ 0 & \frac{2}{3}D_{Tq} - (D_{Tq} + E_{Tq})\sin^2(\Theta/2) & 0 \\ 0 & 0 & \frac{2}{3}D_{Tq} - (D_{Tq} + E_{Tq}) \times \cos^2(\Theta/2) \end{vmatrix},$$

(4)

where D_{Tq} and E_{Tq} are the zfs parameters of the nitrene units in quintet dinitrene 3. The principal axis D_x is directed perpendicular to the molecular plane, and the eigenvalue X gives the following basic relation between the zfs parameters:

$$D_q - 3E_q = \frac{D_{Tq}}{3} - E_{Tq}. \tag{5}$$

Other two eigenvalues of the tensor $\hat{D}_q$ give an expression for the angle Θ as follows:

$$\sin^2(\Theta/2) = \frac{D_q - E_q + 2/3E_{Tq}}{D_q - 3E_q + 4/3E_{Tq}} \cong \frac{D_q - E_q}{D_q - 3E_q}. \tag{6}$$

where D_q is positive and E_q is negative, as shown in Fig. 1. As it follows from Eq. (6), the zfs parameters D_q and E_q are sensitive tests toward Θ because both these parameters are much greater than E_{Tq} for the given system. One can suggest that the truth of expressions (5) and (6) is determined by strength of the term $\hat{D}_{12}/3$ in Eq. (2), which was previously excluded from considerations. This term can be estimated with the aid of the point dipolar approximation assuming

magnetic dipole-dipole interactions between two dipoles, $S_1 = 1$ and $S_2 = 1$, directed along the corresponding nitrene C–N bonds. The tensor $\hat{D}_{12}$ has the same principal axes as the tensor $\hat{D}_q$,[18]

$$\hat{D}_{12} = U_{dip} \times \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 - 3\cos^2(\Theta/2) & 0 \\ 0 & 0 & 1 - 3\sin^2(\Theta/2) \end{vmatrix},$$

(7)

where $U_{dip} = \mu^2/r^3$, $\mu = 2\mu_e$, and r is the distance between triplet centers in dinitrene 3. If the term $\hat{D}_{12}/3$ is added to the right side of Eq. (4), expression (6) remains in force, and expression (5) transforms to

$$U_{dip} = (D_q - 3E_q) - \left(\frac{D_{Tq}}{3} - E_{Tq}\right). \tag{8}$$

Using Eq. (6) and parameters D_q and E_q derived from the experimental spectrum, we find that $\Theta = 114.2° \pm 0.2°$, which is in perfect agreement with the results ($\Theta = 114.5°$) of the UB3LYP/6-31G* calculations.[12] As stated above, the angular dependence in form (6) is strictly valid if the point-
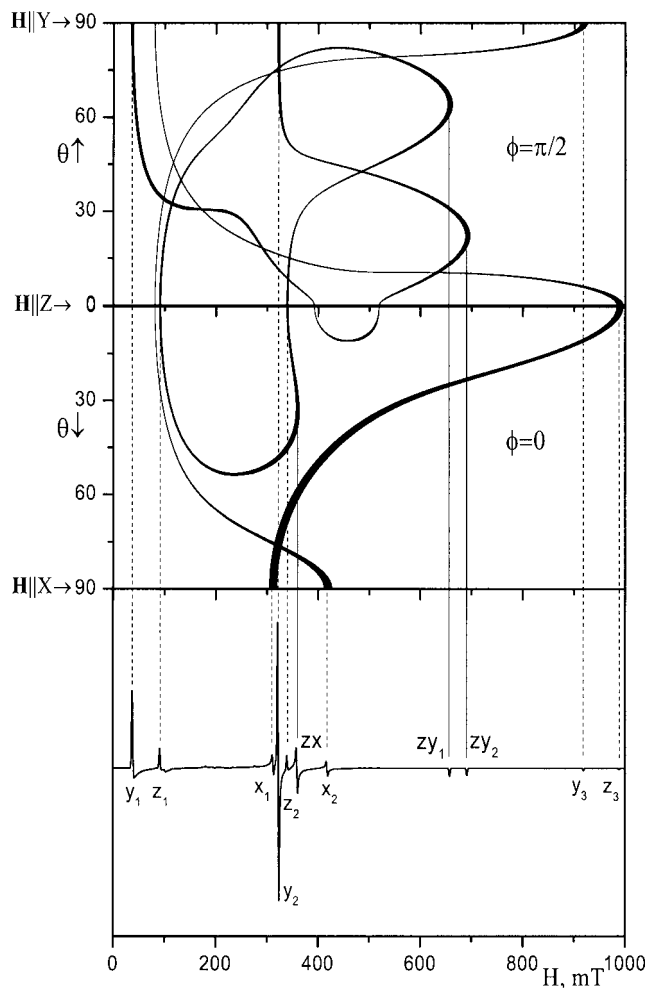
FIG. 6. Calculated resonance magnetic fields for allowed transitions as a function of orientation of the tensor $\hat{D}_q$ relative to the magnetic field H and simulated powder EPR spectrum of quintet dinitrene. The Euler angles θ and ϕ fix the orientation of magnetic field H relative to the axis system of $\hat{D}_q$, X, Y, and Z. Three "extra lines" are marked as zx, zy_1, and zy_2 (see text). The width of curves corresponds to the transition probability.

dipolar approximation for the interacting tensor $\hat{D}_{12}$ is suggested. The obtained good agreement between the measured and theoretically predicted molecular angle Θ testifies that the interaction tensor $\hat{D}_{12}$ in form (7) may be certainly applied for dinitrene molecule. It follows from comparison of Eqs. (8) and (5) that the latter one gives the upper estimation of the parameter $D_{Tq}=1.143\pm0.003$ cm^{-1} for quintet dinitrene 3. This value is essentially larger than the parameter $D_T=1.0630$ cm^{-1} determined for triplet nitrene 2 from the experimental spectrum. However, if we estimate the magnetic dipole-dipole interaction energy U_{dip} in dinitrene 3 using the distance $r=0.458\pm0.010$ nm that was earlier estimated from the UB3LYP/6-31G* calculations[12] (here we assumed an accuracy of calculations as ±0.01 nm), we will find that $U_{dip}=0.018\pm0.001$ cm^{-1}. Using this value of U_{dip} in expression (8), we find that the corrected value D_{Tq} should be equal to 1.089 ± 0.006 cm^{-1}. Because the difference $D_{Tq}-D_T=0.026$ cm^{-1} still exceeds all of our approximations, a conclusion can be made that triplet nitrene 2 and dinitrene 3 have rather differing spin populations on the nitrene units. Indeed, the UB3LYP/6-31G* calculations[12] predict that

electron spin densities on the nitrene units of triplet nitrene 2 and quintet dinitrene 3 are $\rho_N(2)=1.608$ and $\rho_N(3)=1.658$, respectively. This means that quintet dinitrene 3 should have $D_{Tq}\cong[\rho_N(3)/\rho_N(2)]\ D_T=1.096$ cm^{-1}, which is in good agreement with $D_{Tq}=1.089\pm0.006$ cm^{-1} obtained from expression (2).

IV. CONCLUSIONS

The high resolution EPR spectrum of quintet dinitrene 3 with $D_q=0.2100$ cm^{-1} and $E_q=-0.0560$ cm^{-1} has been recorded after the photolysis of diazide 1 in an argon matrix at 15 K. This spectrum represents a new type of X-band EPR spectra that are characteristic for quintet molecules with $|E_q/D_q|\approx1/4$. All EPR lines of quintet dinitrene 3 were unambiguously assigned based on the eigenfield calculations of the Zeeman energy levels and angular dependencies of resonance fields. It was established that the powder X-band EPR spectrum of quintet dinitrene 3 contains eight transitions $\Delta m_s=\pm1$ of high probability and three "extra lines" from molecules with off-principal-axis orientations.

Owing to the high resolution of the experimental EPR spectrum, the zfs parameters D_q and E_q of dinitrene 3 were determined with an accuracy better than 10^{-3} cm^{-1}. This allowed us to precisely estimate D_{Tq} and U_{dip} for quintet dinitrene 3 and then to determine the molecular angle $\Theta=114.2°\pm0.2°$ between two triplet sites in this dinitrene. A unique high precision of the measured molecular parameter Θ is obtained due to high localization of unpaired electrons on the nitrene units providing a validity of expression (2) and the point dipolar approximation for the interaction tensor $\hat{D}_{12}$. The analysis of the magnetic parameters shows that the spin population on the nitrene units in the quintet dinitrene is greater than that on the nitrene unit in the triplet nitrene. This is in good agreement with calculated (DFT) spin densities on the nitrene units of triplet nitrene 2 and quintet dinitrene 3.

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