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# High resolution electron paramagnetic resonance spectroscopy of septet pyridyl-2,4,6-trinitrene in solid argon: Fine-structure parameters of six electron-spin cluster

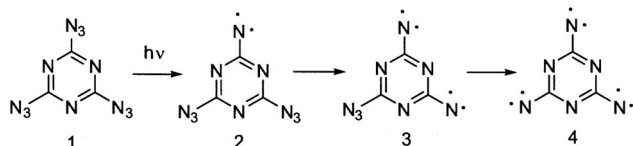
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(Received 24 June 2008; accepted 29 September 2008; published online 6 November 2008)

The high resolution 9 GHz electron paramagnetic resonance (EPR) spectrum of septet pyridyl-2,4,6-trinitrene was recorded after the photolysis of 2,4,6-triazido-3,5-dichloropyridine in solid argon matrix at 15 K. Owing to the high resolution of the experimental EPR spectrum, the zero-field splitting parameters of the septet trinitrene were determined with a high accuracy:  $D_s = -0.1019 \pm 0.0004 \text{ cm}^{-1}$  and  $E_s = 0.00325 \pm 0.00015 \text{ cm}^{-1}$ . All EPR transitions of the septet trinitrene were, for the first, unambiguously assigned based on the eigenfield calculations of the Zeeman energy levels. The spectrum of the septet trinitrene represents a new type of EPR spectra of septet spin states with nonzero zero-field splitting parameter  $E_s$ . The nonvanishing parameter  $E_s$  of the septet trinitrene arises due to magnetic nonequivalence of three triplet centers in the molecule and is manifested in the appearance in the spectrum of separate  $x$  and  $y$  transitions. The septet spin states of this type display at very low magnetic fields two intense  $z$  transitions since the  $|3D_s|$  energy gap between zero-field energy levels  $W_{\pm 1}$  and  $W_{\pm 2}$  fits the quantum of microwave irradiation of a 9 GHz EPR spectrometer. Analysis of the magnetic parameters shows that semiempirical description of the fine-structure tensor for six electron-spin cluster in the septet trinitrene is appropriate for precise estimations of the parameter  $D_s$  but it is too crude to estimate small value of the parameter  $E_s$ . © 2008 American Institute of Physics. [DOI: 10.1063/1.3005378]

## I. INTRODUCTION

Among all organic polyradicals, high-spin nitrenes have the largest zero-field splitting (ZFS) parameters and exhibit the strongest magnetic properties.<sup>1</sup> Such nitrenes model molecular ferromagnetic domains and are of considerable interest for explorations of molecular magnetism and spin chemistry. During the last decade, dozens of quintet dinitrenes<sup>1–8</sup> and several septet trinitrenes<sup>9–11</sup> have been characterized with electron paramagnetic resonance (EPR) spectroscopy, and some of them have been studied by using Fourier transform infrared (FTIR) (Refs. 5 and 11–13) and UV-visible spectroscopy.<sup>5,14,15</sup> Almost all EPR spectra of septet trinitrenes reported to date were recorded in frozen organic solutions and had therefore rather poor spectral resolution.<sup>9,10</sup> The only exception was the high resolution EPR spectrum of septet trinitrene 4 obtained after the photolysis of triazide 1 in an argon matrix at 13 K,<sup>11</sup>



Owing to the formation of only three different nitrenes in the reaction, triplet mononitrene 2, quintet dinitrene 3, and septet trinitrene 4, the EPR transitions of all nitrenes were well resolved. Moreover, since septet trinitrene 4 has the  $D_{3h}$

molecular symmetry, its EPR spectrum was relatively simple for the analysis. The eigenfield spectral simulations showed that this trinitrene had the ZFS parameters  $|D_s| = 0.123 \text{ cm}^{-1}$  and  $E_s = 0.000 \text{ cm}^{-1}$ .

Much more complicated mixture of high-spin nitrenes was formed during the photolysis of triazide 5 (Fig. 1). Previous EPR studies have shown that the photolysis of this triazide frozen at 77 K organic solutions gave isomeric triplet mononitrenes 6 ( $|D_t| = 0.999 \text{ cm}^{-1}$ ,  $|E_t| = 0.003 \text{ cm}^{-1}$ ) and 7 ( $|D_t| = 1.130 \text{ cm}^{-1}$ ,  $|E_t| \sim 0.002 \text{ cm}^{-1}$ ), quintet dinitrenes 8 ( $|D_q| = 0.283 \text{ cm}^{-1}$ ,  $|E_q| = 0.036 \text{ cm}^{-1}$ ) and 9 ( $|D_q| = 0.231 \text{ cm}^{-1}$ ,  $|E_q| = 0.031 \text{ cm}^{-1}$ ), and septet trinitrene 10 ( $|D_s| = 0.100 \text{ cm}^{-1}$ ,  $|E_s| = 0.0005 \text{ cm}^{-1}$ ).<sup>9</sup> Unfortunately, a poor spectral resolution of the experimental EPR spectrum in frozen organic solutions made the very precise determination of the ZFS parameters of nitrenes 6–10 impossible. In order to overcome this problem, in the present work, an EPR study of the photolysis of triazide 5 in a solid argon matrix at 15 K has been accomplished. The high resolution EPR spectrum of a mixture of triplet mononitrenes 6 and 7, quintet dinitrenes 8 and 9, and septet trinitrene 10 recorded in an argon matrix allowed us to derive from this spectrum the ZFS parameters of all nitrenes with an accuracy better than  $10^{-3} \text{ cm}^{-1}$  and, for the first time, completely analyze the spectrum of septet trinitrene 10, by using the eigenfield calculations of the Zeeman energy levels and density functional theory (DFT) calculations of the spin densities and geometry parameters.

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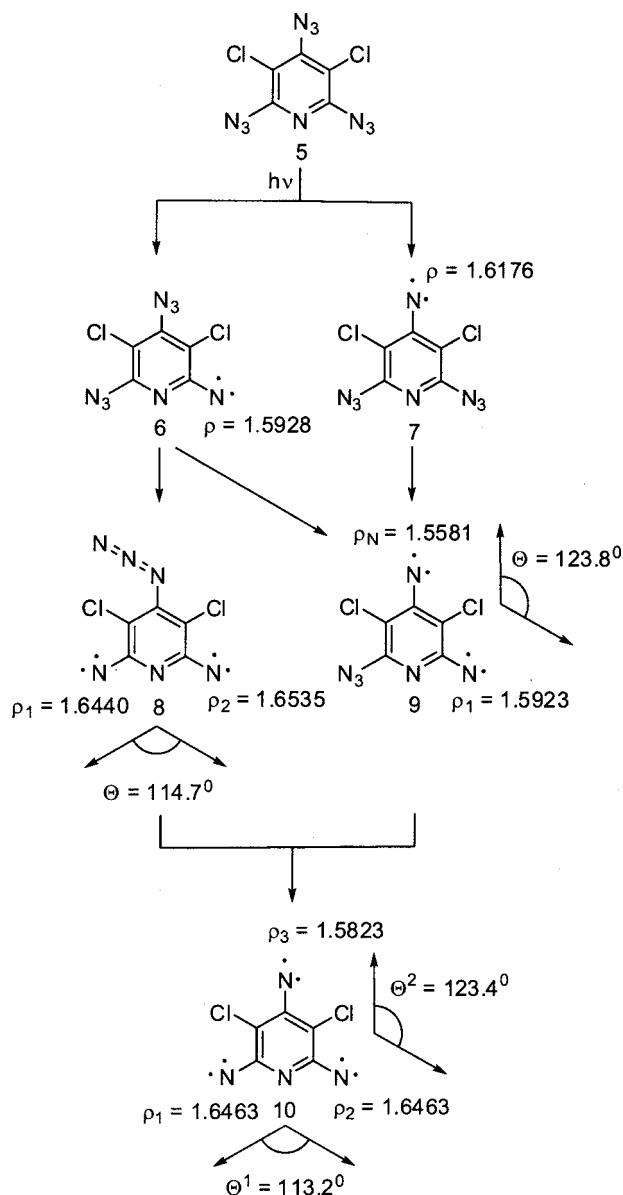


FIG. 1. Photolysis of triazide 5 and selected data of UB3LYP/6-31G\* calculations of nitrenes 6–10 from Ref. 9.

## II. EXPERIMENT

Triazide 5 was synthesized according to the literature procedure.<sup>16</sup>

Experimental technique for matrix isolation used in this study was similar to that described earlier.<sup>8,17</sup> Solid argon films doped with triazide 5 were prepared by vacuum co-deposition of two separate molecular beams (Ar and triazide 5 vapor) onto a substrate (sapphire rod) cooled to 15 K. The deposition rate was typically 10  $\mu\text{mol}/\text{min}$ , and the thickness of the deposited argon films was typically 100  $\mu\text{m}$ . The vapor of triazide 5 was produced by an oven heating the polycrystalline 5 to  $\sim 60^\circ\text{C}$ . The oven temperature was regulated by a precise temperature controller and was chosen to obtain the ratio  $\text{Ar}/\text{M} \sim 10^3\text{--}10^4$ . Temperature stability was  $\sim 0.1$  K over 7–40 K range. EPR spectra were recorded using a standard 9 GHz spectrometer. EPR spectra were recorded at sufficiently low microwave power to avoid the

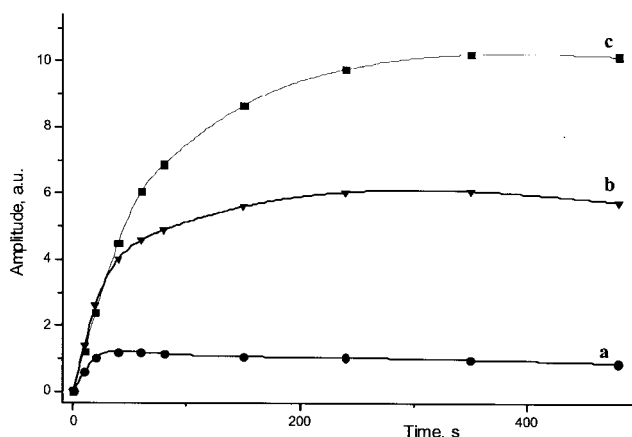


FIG. 2. Kinetics behavior of EPR transitions during the photolysis ( $\lambda = 355$  nm) of the sample Ar/triazide 5 at 15 K: (a) EPR transition at 657 mT (triplet), (b) EPR transition at 297.2 mT (quintet), and (c) EPR transition at 17.7 mT (septet).

saturation effects. Shape and resonance magnetic fields of all components in the EPR spectra did not change in the temperature range of 7–30 K. Intensities of the strong EPR lines in the spectra obey the Curie law in this temperature range.

High-spin nitrenes were generated by the photolysis of triazide 5 with a pulsed  $\text{N}_2$  laser at 337 nm ( $10^3$  pulses per second). The average laser power did not exceed 10  $\text{mW}/\text{cm}^2$ .

## III. RESULTS AND DISCUSSION

### A. EPR spectra of nitrenes

The irradiation of triazide 5 isolated in solid argon at 15 K lead to the appearance of intense EPR transitions at 5.4, 17.7, 297.2, 318.5, 657, and 670 mT. Figure 2 demonstrates different kinetic behaviors of these transitions during the photolysis. The resonances at 657 and 670 mT reached their maximum values at the initial stage of the photolysis and then gradually decayed on further irradiation. These resonances, labeled as T in Fig. 3, were assigned<sup>9</sup> to the  $x_2$  and  $y_2$  transitions of isomeric triplet mononitrenes 6 and 7 formed after photodecomposition of one azido group in triazide 5. Two other intense transitions at 297.2 and 318.5 mT (labeled as  $Q_1$  and  $Q_2$  in Fig. 3) reached their maximum values after more prolonged irradiation. These two resonances were assigned<sup>9</sup> to the most intense  $y_2$  transitions of isomeric quintet dinitrenes 8 and 9 formed after photodecomposition of two azido groups in triazide 5. The detailed analysis of EPR spectra of quintet dinitrenes 8 and 9 will be given below in Sec. III E. Finally, yet two EPR transitions at very low magnetic fields (5.4 and 17.7 mT) showed absolutely different from spectra of nitrenes 6–9 kinetic behavior, becoming the most intense pattern in the spectrum after 80 s of irradiation. Simultaneously with the growth of resonances at 5.4 and 17.7 mT, a series of new intense resonances at 178.5, 186.3, 217.7, and 230.3 mT appeared in the spectrum. The same kinetic behavior of these resonances suggested that all six EPR transitions could safely be assigned to septet trinitrene 10 arising after photodecomposition of all three azido groups in triazide 5. Figure 3 shows the final EPR

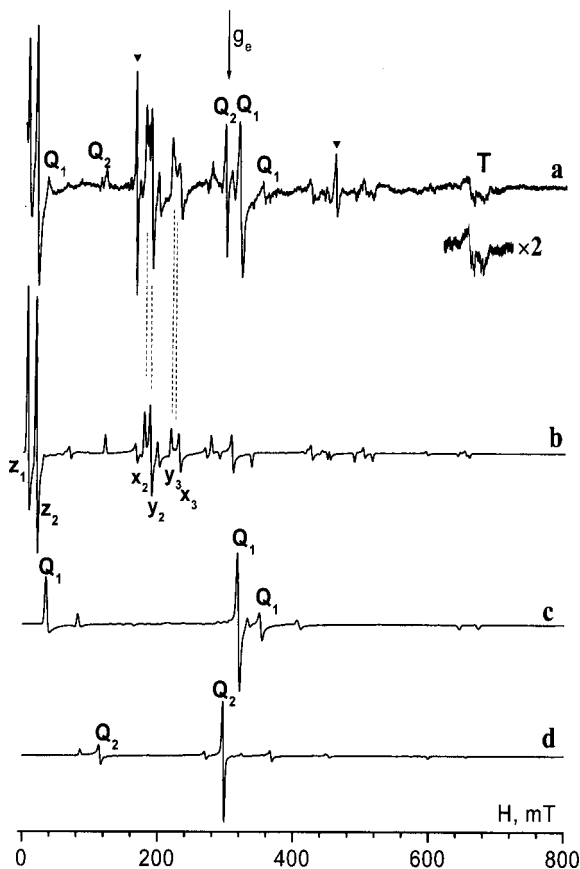


FIG. 3. (a) EPR spectrum of the photolyzed sample Ar/triazide 5  $\approx$  2000 at 15 K. Simulated powder spectra of (b) septet trinitrene 10 with  $D_s = -0.1019$   $\text{cm}^{-1}$  and  $E_s = 0.00325$   $\text{cm}^{-1}$ , (c) quintet dinitrene 8 with  $D_q = 0.2024$   $\text{cm}^{-1}$  and  $E_q = -0.0554$   $\text{cm}^{-1}$ , (d) quintet dinitrene 9 with  $D_q = 0.1970$   $\text{cm}^{-1}$  and  $E_q = -0.0421$   $\text{cm}^{-1}$ . EPR transitions in the experimental spectrum (a) marked as ( $\blacktriangledown$ ) arise from impurities in the sapphire rod and are present in the absence of the sample.

spectrum recorded at 8.91 GHz. This spectrum demonstrates that, besides strong EPR resonances mentioned above, a series of less intense EPR transitions at 120, 170, 199, 268, 275, 308, 337, 353, 424, 488, 503, and 514 mT are also present in the spectrum. Due to low intensities of these resonances, we were unable to follow their kinetic behaviors at our experimental conditions.

### B. Zero-field splitting parameters of septet trinitrene

The ZFS parameters  $D_s$  and  $E_s$  of trinitrene 10 were determined by comparing the computer simulated and experimentally recorded EPR spectra. We have fitted the experimental spectrum to the effective spin Hamiltonian:

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

with  $\mathbf{S}=3$  and zero-field tensor  $\hat{D}_s$ . The powder EPR spectra were simulated using the EASYPIN program package,<sup>18</sup> operating with an exact numerical matrix diagonalization analysis of the spin Hamiltonian (1) for randomly oriented species. We used below a methodology developed in our preceding paper<sup>8</sup> for the analysis of EPR spectra of quintet dinitrenes. According to simple considerations (see discussion in Sec. III C below), the ZFS parameters  $D_s$  of septet

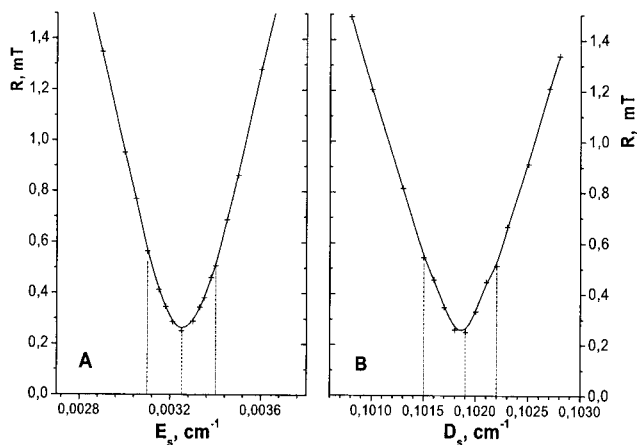


FIG. 4. Dependences of functional  $R$  [see Eq. (3) in the text] on the septet ZFS parameters (a) the parameter  $D_s = -0.1019$   $\text{cm}^{-1}$  is fixed and (b) the parameter  $E_s = 0.00325$   $\text{cm}^{-1}$  is fixed.

trinitrenes should be close to  $-D_t/10$ . As follows from previous EPR studies,<sup>6–8</sup> the characteristic values of  $D_t$  of triplet pyridyltrinitrenes are around 0.97–1.05  $\text{cm}^{-1}$ . Therefore we chose the values  $D_s = -0.100$   $\text{cm}^{-1}$  and  $E_s = 0.002$   $\text{cm}^{-1}$  as starting parameters in our computer simulations of the spectrum. The ZFS parameters  $D_s$  and  $E_s$  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,  $H_k(\text{calc})$ , from those measured experimentally,  $H_k(\text{exp})$ ,

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

where  $n=6$  represents the number of the selected transitions in the spectrum of trinitrene 10. These six intense transitions are marked in Fig. 3 as  $z_1$ ,  $z_2$ ,  $x_2$ ,  $y_2$ ,  $y_3$ , and  $x_3$  at magnetic fields 5.4, 17.7, 178.5, 186.3, 217.7, and 230.3 mT, respectively. The high resolution of such an EPR spectrum allows one to measure resonance fields with accuracy  $\pm 0.3$  mT.

The spectrum optimized (Fig. 3) was obtained at  $D_s = -0.1019$   $\text{cm}^{-1}$  and  $E_s = 0.00325$   $\text{cm}^{-1}$ . It corresponds to the rms deviation of  $R(\text{min}) = 0.26$  mT, and it is close to the experimental spectral resolution. To estimate an accuracy of  $D_s$  and  $E_s$  measurements, the rms deviations were calculated by varying each of the parameters nearby their optimum values, see 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  $|H_{\text{calc}} - H_{\text{exp}}|$  exceeding the line width. This treatment gave the experimental errors for  $D_s$  and  $E_s$  that were not more than  $\pm 0.0004$  and  $\pm 0.00015$   $\text{cm}^{-1}$ , respectively. The same high precision of the fine-structure parameter determination has recently been achieved during our matrix EPR studies of quintet dinitrenes.<sup>8</sup> Such a uniquely high precision of the fine-structure parameter determination for quintet and septet molecules is possible mostly owing to the high resolution of the experimental EPR spectra in argon matrices.

Comparison of simulated and experimentally recorded EPR spectra, see Fig. 3, demonstrates that the simulated spectrum reproduces well the resonance fields, relative intensities, and shapes of all six tested EPR transitions in the

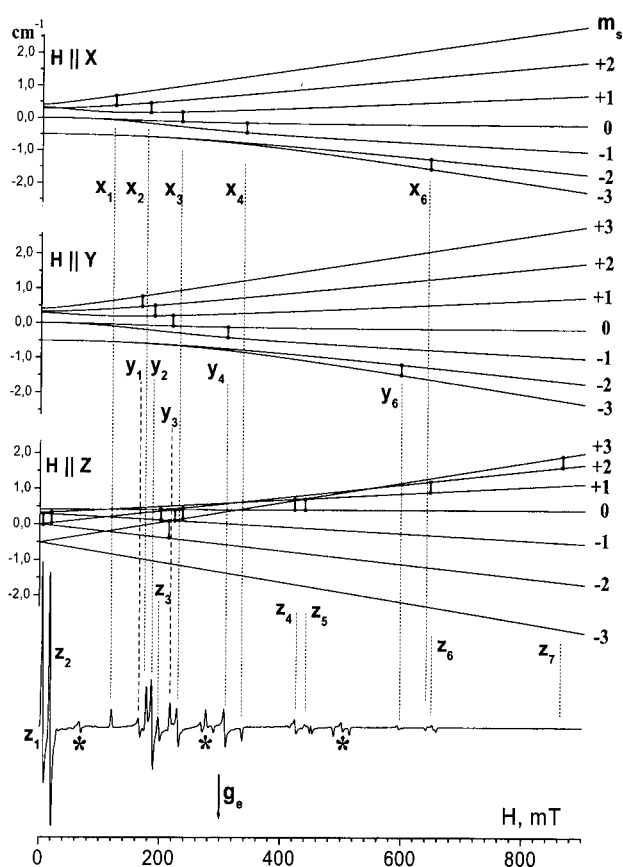


FIG. 5. Calculated Zeeman energy levels, allowed transitions, and simulated powder EPR spectrum of septet trinitrene with  $D_s = -0.1019 \text{ cm}^{-1}$  and  $E_s = 0.00325 \text{ cm}^{-1}$ . EPR transitions are marked according to the notations accepted in the text. The “extra lines” marked as asterisks.

experimental spectrum. Moreover, a number of weak EPR transitions are observed at the same magnetic fields in both the simulated and experimental spectra. This indicates that most of spectral patterns that are clearly seen in the experimental spectrum can definitely be assigned to septet trinitrene 10.

### C. Assignments of the powder EPR spectrum of septet trinitrene

To perform a complete assignment of EPR transitions in the spectrum of trinitrene 10, the Zeeman energy levels for canonical orientations of the tensor  $\hat{D}$  toward the fixed field axes were calculated, see Fig. 5. Three orientations of the magnetic field relatively to the molecular axis  $Z$  were considered, parallel  $\mathbf{H} \parallel \mathbf{D}_z$  and two perpendicular  $\mathbf{H} \parallel \mathbf{D}_x$  and  $\mathbf{H} \parallel \mathbf{D}_y$ . In strict accord with theory,<sup>19</sup> trinitrene 10 has seven energy levels at zero field. Since the parameter  $|D_s|$  is much greater than  $|E_s|$ , the gaps between the energy levels are approximately equal to  $|D_s|$ ,  $|3D_s|$ , and  $|5D_s|$ . One of these gaps,  $|3D_s| \approx 0.31 \text{ cm}^{-1}$ , fits the quantum of microwave irradiation  $h\nu_0 \approx 0.33 \text{ cm}^{-1}$ , hence allowing the transitions for  $z$  components at very low magnetic fields. The appearance of such  $z$  transitions in EPR spectra of septet molecules has earlier been predicted from theoretical analysis of the spin Hamiltonian (1).<sup>19</sup> In our study, we observe two very strong  $z$  transitions at 5.4 and 17.7 mT (marked as  $z_1$  and  $z_2$  in Figs.

TABLE I. Calculated and observed resonance magnetic fields for perpendicular components ( $x_i$  and  $y_i$ ) of allowed transitions in the powder EPR spectrum of septet trinitrene 10.

Transition	Number	Resonance magnetic field (mT)	
		$x_i$ Calc./Observ.	$y_i$ Calc./Observ.
$ +2\rangle \leftrightarrow  +3\rangle$	1	120.0/120.1 $\pm$ 0.3	166.9/170.3 $\pm$ 0.6 <sup>a</sup>
$ +1\rangle \leftrightarrow  +2\rangle$	2	178.2/178.5 $\pm$ 0.3	186.2/186.3 $\pm$ 0.3
$ 0\rangle \leftrightarrow  +1\rangle$	3	230.3/230.3 $\pm$ 0.3	217.7/217.7 $\pm$ 0.3
$ -1\rangle \leftrightarrow  0\rangle$	4	336.6/336.8 $\pm$ 0.3	308.1/307.9 $\pm$ 0.3
$ -2\rangle \leftrightarrow  -1\rangle$	5	...	...
$ -3\rangle \leftrightarrow  -2\rangle$	6	641.0/641.6 $\pm$ 0.6 <sup>b</sup>	595.7/597.0 $\pm$ 0.6 <sup>b</sup>

<sup>a</sup>Overlapped.

<sup>b</sup>Very weak.

3 and 5) due to nonvanishing value of the parameter  $E_s$ . The Zeeman energy level diagram shown in Fig. 5 demonstrates that five couples of perpendicular components ( $x_i$  and  $y_i$ ) corresponding to allowed  $\Delta m_s = \pm 1$  transitions should be realized in the spectrum, and four of them are clearly seen in the experimental spectrum in Fig. 3. Resonance magnetic fields of these lines are given in Table I. There is a perfect agreement between calculated and observed transitions. Since the energy gap between the levels  $m_s = -2$  and  $m_s = -1$  for perpendicular orientations exceeds  $h\nu_0$  at any external magnetic fields in accord with theoretical predictions for septet molecules with  $|D_s| > h\nu_0/5$ ,<sup>19</sup> the  $x_5$ - and  $y_5$  transitions between these levels cannot be observed in EPR spectra. Except of two intense parallel components  $z_1$  and  $z_2$ , the relative intensities of other parallel components  $z_i$  are weak, and some of them are not observable in the experimental spectrum. On the other hand, many of relatively weak lines appear in the spectrum due to off-principal axis transitions (extra lines). These lines are marked in Fig. 5 by asterisks. The appearance of such extra lines in EPR spectra of septet molecules with  $|D_s| \approx 0.1 \text{ cm}^{-1}$  has been discussed in great detail earlier, including illustrations of the calculated angular dependences of the resonance magnetic field for all allowed transitions.<sup>19</sup> Some typical singularities  $d\theta/dH_{\text{res}} = \infty$  in the angular dependences of the resonance magnetic field for EPR transitions in the powder spectra of quintet dinitrenes with  $|E_q/D_q| \sim \frac{1}{4}$  were also demonstrated and discussed in our preceding study.<sup>8</sup>

### D. Fine-structure and molecular parameters of septet trinitrene

Below, we analyzed the ZFS parameters of septet trinitrene 10 in terms of the widely used semiempirical approach<sup>20</sup> that is based on modeling the ZFS tensor  $\hat{D}_s$  as a function of the tensor interactions between three triplet sites in six electron-spin ferromagnetic clusters,

$$\hat{D}_s = \frac{1}{15}(\hat{D}_{t1} + \hat{D}_{t2} + \hat{D}_{t3}). \quad (3)$$

This expression allows one to calculate the tensor  $\hat{D}_s$  for a septet molecule with known molecular geometry and values of  $D_t$  for triplet centers. In a simple case, when a septet



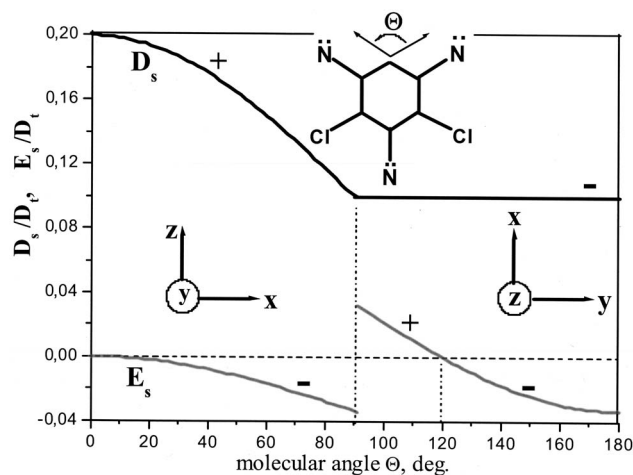


FIG. 6. Septet ZFS parameters  $D_s$  and  $E_s$  as a function of angle  $\Theta$  for the case of three triplet sites with the parameter  $D_t$ . Orientations of the principal axis  $\hat{D}_s$  towards the molecular structure are shown.

molecule has the point symmetry  $D_{3h}$  (three nitrene units are magnetically equivalent and all three angles between the C–N bonds are of  $\Theta=120^\circ$ ), Eq. (3) gives the ZFS parameters  $D_s=-D_t/10$  and  $E_s=0$ . If a septet molecule is axially asymmetrical, as trinitrene 10 with the  $C_{2v}$  symmetry, the nonvanishing parameter  $E_s$  appears in the tensor  $\hat{D}_s$ . In this case, the parameters  $D_s$  and  $E_s$  depend on the parameter  $D_t$  and the angle  $\Theta$  between the C–N bonds of two symmetrical triplet sites, as shown in Fig. 6. One can see that, for all septet molecules with  $\Theta>90^\circ$  the Z axis of the ZFS tensor  $\hat{D}_s$  is perpendicular to the molecular plane, the parameter  $D_s$  equals to  $-D_t/10$ , and the parameter  $E_s$  is a function of the angle  $\Theta$ . When a septet trinitrene has two equivalent nitrene units with  $D_{t1}=D_{t2}=D_t$  and differing from them by  $\lambda$  the third nitrene unit with  $D_{t3}=D_t(1+\lambda)$ , the Eq. (3) is transformed into

$$D_s = -\frac{D_t}{10} \times (1 + \lambda) \quad \text{and} \quad (4)$$

$$E_s = \frac{D_t}{30} \times (4 \times \cos^2(\Theta/2) - 1 + \lambda).$$

In this case, the ratio  $E_s/D_s$  is a function of both the angle  $\Theta$  and the parameter  $\lambda$ ,

$$\left| \frac{E_s}{D_s} \right| \cong \frac{1}{3} \times |\sqrt{3}\Delta\theta + \lambda|, \quad (5)$$

where  $\Delta\theta=(2\pi/3-\Theta)$  and  $|\Delta\theta|\ll 1$ . The first term in Eq. (5) appears due to deviation of  $\Theta$  from  $120^\circ$ , and the second term, due to nonequivalence of triplet units in  $C_{2v}$  symmetrical septet molecules. Thus, knowing the values of  $\Delta\theta$  and  $\lambda$  from quantum-chemical calculations, one can theoretically estimate the ratio  $E_s/D_s$  for septet trinitrenes, by using Eq. (5). As shown previous UB3LYP/6-31G\* calculations (Fig. 1), septet trinitrene 10 has  $\Theta=113.2^\circ$  and spin populations on the  $\alpha$ - and  $\gamma$ -nitrene units of  $\rho_1=\rho_2=1.6463$  and  $\rho_3=1.5823$ , respectively. From this we find that  $\Delta\theta=6.8^\circ$  and  $\lambda\approx(\rho_3-\rho_1)/\rho_1=-0.040$ . The use of these values in Eq. (5)

gives the ratio  $|E_s/D_s|=|0.067-0.013|=0.054$ , which is by 70% larger of  $|E_s/D_s|=0.032$  obtained from the experimental spectrum. In order to clear up which of two values,  $D_s$  or  $E_s$ , is responsible for discrepancy between calculated and measured ratio  $|E_s/D_s|$ , we estimated the values of  $D_s$  and  $E_s$  from DFT calculated spin densities on the  $\alpha$ -nitrene units of trinitrene 10 and mononitrene 6 (Fig. 6). Since mononitrene 6 has  $D_t\approx 1.005\text{ cm}^{-1}$  (see below Sec. III E), the expected parameter  $D_t$  for the  $\alpha$ -nitrene units of trinitrene 10 should be equal to  $D_t\approx(\rho_1/\rho_T)D_T=1.03\text{ cm}^{-1}$ . The use of this  $D_t$  in Eq. (4) yields  $D_s=-0.099\text{ cm}^{-1}$  and  $E_s=0.0053\text{ cm}^{-1}$ . These parameters are valid for the case when the interaction tensor describing magnetic dipole-dipole interactions between the nitrene units is negligibly small. Meanwhile, our previous EPR studies<sup>8</sup> have shown that such magnetic interactions in high-spin nitrenes can be rather strong. If to take into account these interactions in septet trinitrenes, the interaction term  $\hat{D}_{\text{int}}=\hat{D}_{12}+\hat{D}_{13}+\hat{D}_{23}$  describing magnetic dipole-dipole interactions between three nitrene units should be added as a second term in Eq. (3). In the case of the point dipolar approximation for three interacting dipoles with  $S_1=1$ ,  $S_2=1$ , and  $S_3=1$ , the expressions (4) are transformed into  $D_s^*\approx D_s \times (1+3u)$  and  $E_s^*\approx E_s \times (1+3u)$ , where  $u=U_{\text{dip}}/D_t\ll 1$ , and  $U_{\text{dip}}\approx 2 \times 10^{-2}\text{ cm}^{-1}$  is the energy of magnetic dipole-dipole interactions between two nitrene units.<sup>8</sup> The solutions of such equations yield  $D_s^*\approx -0.105\text{ cm}^{-1}$  and  $E_s^*\approx 0.0055\text{ cm}^{-1}$ . These values show that a scale of discrepancy between semiempirical calculations and experimental measurements of the fine-structure parameters  $D_s$  and  $E_s$  amounts to  $\sim 0.002\text{ cm}^{-1}$ , what is less than 2% of  $D_s=-0.1019\text{ cm}^{-1}$  but more than 60% of  $E_s=0.00325\text{ cm}^{-1}$ . The analysis performed demonstrates that theoretical modeling of the ZFS tensor  $\hat{D}_s$  as a function of the tensor interactions between three triplet sites in a six electron-spin cluster is appropriate for precise estimations of the parameter  $D_s$  but it is too crude to estimate small values of the parameter  $E_s$ .

### E. Assignments of the powder EPR spectra of triplet and quintet nitrenes

In order to completely describe the experimental spectrum in Fig. 3, we analyzed the EPR peaks of triplet mononitrenes 6 and 7 as well as of quintet dinitrenes 8 and 9. The experimental and computer simulated EPR spectra of triplet mononitrenes 6 ( $D_{t1}=1.005\text{ cm}^{-1}$ ,  $E_{t1}=0.0035\text{ cm}^{-1}$ ) and 7 ( $D_{t2}=1.021\text{ cm}^{-1}$ ,  $E_{t2}=0.0035\text{ cm}^{-1}$ ) are shown in Fig. 7. Both nitrenes displayed in EPR spectra the  $x_2$ - and  $y_2$  transitions due to nonvanishing values of  $E_t$ . The parameters  $D_{t1}$  and  $D_{t2}$  determined from spectral simulations were well correlated with DFT calculated spin densities (Fig. 1) on the nitrene units of triplet mononitrenes 6 ( $\rho(6)=1.5928$ ) and 7 ( $\rho(7)=1.6176$ ). Thus, for instance, the ratio  $D_{t1}/D_{t2}=0.984$  almost coincided with the ratio  $\rho(7)/\rho(6)=0.985$ . Again, the change in spin densities on the nitrene units of triplet mononitrenes 6 and 7 by 0.015 changed the values of  $D_t$  by  $0.016\text{ cm}^{-1}$ . This showed that our estimation of the parameter  $\lambda$  in Sec. III D, using the theoretically predicted spin densities  $\rho_1$  and  $\rho_3$  on the  $\alpha$ - and  $\gamma$ -nitrene units of septet trinitrene 10, was quite correct.

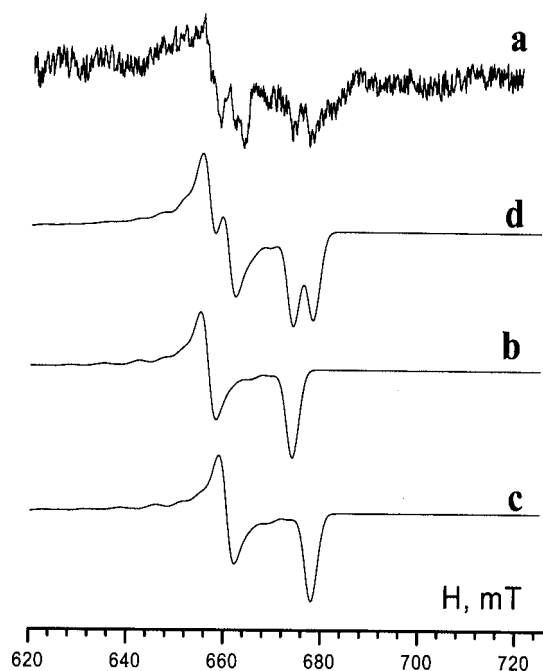


FIG. 7. (a) EPR spectrum of the photolyzed sample Ar/triazide 5 at 15 K. Simulated powder EPR spectra of (b) triplet mononitrene 6 with  $D_{11}=1.005\text{ cm}^{-1}$ ,  $E_{11}=0.0035\text{ cm}^{-1}$ , (c) triplet mononitrene 7 with  $D_{12}=1.021\text{ cm}^{-1}$ ,  $E_{12}=0.0035\text{ cm}^{-1}$ , and (d) simulated spectrum containing two triplet nitrenes 6 and 7 in the ratio 1:1.

According to statistical considerations, the probabilities of photochemical generation of triplet mononitrenes 6 and 7 from triazide 5 are equal to 0.67% and 0.33%, respectively. Meanwhile, the EPR transitions of these isomeric nitrenes in the experimental spectrum have nearly the same intensities, see Fig. 7. This suggests that the photolysis of triazide 5 in argon matrices with light at  $\lambda=337\text{ nm}$  occurs selectively, preferentially on the  $\gamma$ -azido group of this triazide. The same effect has earlier been observed during the photolysis of triazide 5 in frozen organic solutions at 77 K with light at  $\lambda=337\text{ nm}$ .<sup>21</sup> As shown in the quantum-chemical calculations of triazide 5,<sup>21</sup> its  $\gamma$ -azido group has the weakest N–N<sub>2</sub> bond that most easily dissociates during the photolysis.

Extensive EPR studies<sup>1,3,5,6,8</sup> have shown that most of aromatic quintet dinitrenes with *meta* orientations of the nitrene units on the aromatic ring display strong  $y_2$  transitions in the region of 290–310 mT. As a rule, these dinitrenes had  $\Theta=119^\circ\text{--}125^\circ$ . However, quintet pyridyl-2,6-dinitrenes with  $\Theta=114^\circ\text{--}115^\circ$  usually showed such transitions at 310–340 mT.<sup>6–8</sup> Based on these data, we assigned two intense EPR transitions at 297.2 and 318.5 mT (labeled as  $Q_1$  and  $Q_2$  in Fig. 3) to quintet dinitrenes 9 ( $\Theta=123.8^\circ$ , see Fig. 1) and 8 ( $\Theta=114.7^\circ$ , see Fig. 1), respectively. To achieve the best fit between the quintet ZFS parameters and experimental spectra, at least two EPR transitions in the spectrum of each quintet dinitrene were required to analyze. In our computer simulations, we used several EPR transitions of low intensity from the experimental spectrum that have not earlier been assigned to septet trinitrene 10. These EPR transitions in the experimental spectrum are marked as  $Q_1$  and  $Q_2$  in Fig. 3. The simulated spectra of quintet dinitrenes 8 ( $D_{q1}=0.2024\text{ cm}^{-1}$ ,  $E_{q1}=-0.0554\text{ cm}^{-1}$ ) and 9 ( $D_{q2}$

$=0.1970\text{ cm}^{-1}$ ,  $E_{q2}=-0.0421\text{ cm}^{-1}$ ) are shown in Fig. 3. The spectrum (c) for dinitrene 8 is described by the ratio  $|E_q/D_q|=0.27$  and typical for matrix powder EPR spectra of quintet dinitrenes with  $\Theta\approx 114^\circ$ .<sup>8</sup> The spectrum (d) for dinitrene 9 is described by the ratio  $|E_q/D_q|=0.21$  and much resembles the powder EPR spectra of quintet *meta*-phenylenedinitrenes with  $\Theta=122^\circ\text{--}124^\circ$ .<sup>5</sup>

#### IV. CONCLUSIONS

The high resolution 9 GHz EPR spectrum of a mixture of septet trinitrene 10, quintet dinitrenes 7 and 8, and triplet mononitrenes 6 and 7 has been recorded after the photolysis of triazide 5 in an argon matrix at 15 K. Owing to the high resolution of the experimental spectrum, the ZFS parameters of trinitrene 10 were determined with a high accuracy:  $D_s=-0.1019\pm 0.0004\text{ cm}^{-1}$  and  $E_s=0.003\,25\pm 0.000\,15\text{ cm}^{-1}$ . In the spectrum recorded, all EPR transitions of septet trinitrene 10 were, for the first time, unambiguously assigned based on the eigenfield calculations of the Zeeman energy levels.

The spectrum of septet trinitrene 10 represents a new type of EPR spectra of septet spin states with  $0.100\text{ cm}^{-1}<|D_s|<0.110\text{ cm}^{-1}$  and  $|E_s|>0.003\text{ cm}^{-1}$ . The nonvanishing parameter  $E_s$  of trinitrene 10 arises due to magnetic non-equivalence of three triplet centers in the molecule and is manifested in the appearance in the spectrum of characteristic doublet patterns corresponding to the separate  $x$  and  $y$  transitions. Septet spin states with  $|D_s|\approx 0.1\text{ cm}^{-1}$  display at very low magnetic fields two intense  $z$  transitions since the  $|3D_s|$  energy gap between levels  $W_{\pm 1}$  and  $W_{\pm 2}$  fits the quantum of microwave irradiation of EPR spectrometer. The analysis of the magnetic parameters shows that a scale of discrepancy between semiempirical calculations and experimental measurements of the fine-structure parameters  $D_s$  and  $E_s$  amounts to  $\sim 0.002\text{ cm}^{-1}$ . Semiempirical description of the fine-structure tensor for septet trinitrenes is appropriate for precise estimations of the parameters  $D_s$  but it is too crude to estimate small value of  $E_s$ .

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (Grant No. 07-03-00768).

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