# Molecular Structure and Magnetic Parameters of Septet 2,4,6-Trinitrenotoluene

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Received May 22, 2009
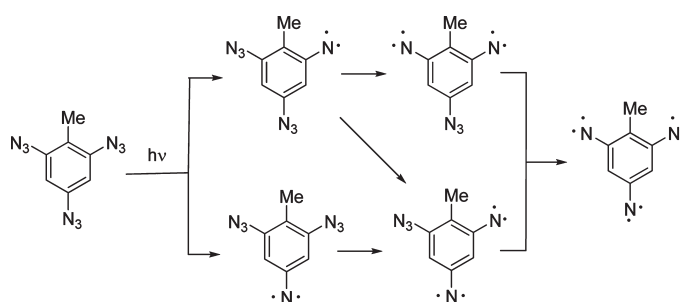
Septet 2,4,6-trinitrenotoluene is the major paramagnetic product formed during the photolysis of 2,4,6-triazidotoluene in cryogenic matrices. This trinitrene displays different electron paramagnetic resonance (EPR) spectra in solid argon and in 2-methyltetrahydrofuran (2MTHF) glass, corresponding to septet spin states with the zero-field splitting (ZFS) parameters $D_S = -0.0938$ cm^{-1}, $E_S = -0.0040$ cm^{-1} and $D_S = -0.0934$ cm^{-1}, $E_S = -0.0015$ cm^{-1}, respectively. Analysis of these parameters shows that the molecular and electronic structure of the septet trinitrene derived from the EPR spectrum in argon is in good agreement with the expectations from DFT calculations. The very small parameter E_S in 2MTHF glass is explained by significant changes of the spin densities on the three nitrene units due to interactions of the nitrogen atom with surrounding 2MTHF molecules.

Introduction

High-spin nitrenes are highly reactive intermediates formed during the photolysis or thermolysis of aromatic polyazides.[1,2] Due to the presence of several univalent nitrogen atoms attached to the aromatic ring, such nitrenes are very valence-deficient species and readily react with surrounding molecules or undergo rearrangements.[3] Therefore, all spectroscopic studies of these intermediates are carried out in cryogenic matrices such as solid argon[3−9] or 2MTHF glasses at cryogenic temperatures.[2,10−15] While matrix isolation of high-spin nitrenes requires that the

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(1) Brase, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188–5240.
(2) Nimura, S.; Yabe, A. In *Molecular Magnetism of Organic Molecules and Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 127−146 and references cited therein.
(3) Chapyshev, S. V.; Tomioka, H. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2075–2089.
(4) Chapyshev, S. V.; Kuhn, A.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **2000**, *122*, 1572–1579.
(5) Sato, T.; Narazaki, A.; Kawaguchi, Y.; Niino, H.; Bucher, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5206–5209.

(6) Sato, T.; Narazaki, A.; Kawaguchi, Y.; Niino, H.; Bucher, G.; Grote, D.; Wolff, J. J.; Wenk, H. H.; Sander, W. *J. Am. Chem. Soc.* **2004**, *126*, 7846–7852.
(7) Chapyshev, S. V.; Grote, D.; Finke, C.; Sander, W. *J. Org. Chem.* **2008**, *73*, 7045–7051.
(8) Misochko, E. Ya.; Akimov, A. V.; Chapyshev, S. V. *J. Chem. Phys.* **2008**, *128*, Article No. 124504.
(9) Misochko, E. Ya.; Akimov, A. V.; Chapyshev, S. V. *J. Chem. Phys.* **2008**, *129*, Article No. 174510.
(10) Wasserman, E.; Schueller, K.; Yager, W. A. *Chem. Phys. Lett.* **1968**, *2*, 259–260.
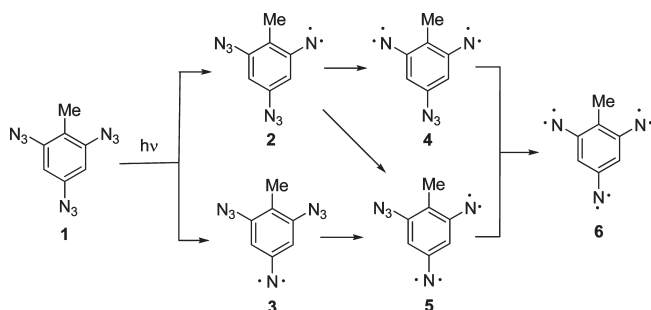(11) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547–5556.
(12) Ling, C.; Minato, M.; Lahti, P. M.; van Willegen, H. *J. Am. Chem. Soc.* **1992**, *114*, 9959–9969.
(13) Chapyshev, S. V.; Walton, R.; Sanborn, J. A.; Lahti, P. M. *J. Am. Chem. Soc.* **2000**, *122*, 1580–1588.
(14) Chapyshev, S. V.; Walton, R.; Serwinski, P. R.; Lahti, P. M. *J. Phys. Chem. A* **2004**, *108*, 6643–6649.
(15) Chapyshev, S. V.; Lahti, P. M. *J. Phys. Org. Chem.* **2006**, *19*, 637–641.

SCHEME 1. Photolysis of Triazide 1

precursor can be sublimed under high vacuum conditions, a prerequisite for the formation of organic glasses is the solubility of the precursor in a suitable solvent (e.g., 2MTHF). EPR spectra of matrix isolated nitrenes in general show higher resolution and less perturbation[6-9] than spectra recorded in organic glasses,[11-15] and thus allow more detailed insight into the electronic structure to be obtained. A further disadvantage of organic glasses is that nitrenes with high spin densities located at the nitrene centers are reactive toward solvent molecules such as 2MTHF even at low temperatures.[13,16,17] Previous studies have shown that for the primarily formed singlet aryl nitrenes the reaction with THF to form nitrene–THF ylides can compete with the intersystem crossing (ISC) to the triplet ground state.[18] Triplet nitrenes form weakly bound complexes with 2MTHF and similar solvents that might influence the EPR spectra. These interactions can be studied by comparison of the EPR spectra in organic glasses with that in solid argon.

Here we report on the synthesis and EPR spectroscopic characterization of septet trinitrene **6** in solid argon at 4 K and in 2MTHF glasses at 5.5 K (Scheme 1). The analysis of the EPR spectra gives insight into the electronic structure and solvent interactions of the trinitrene.

Results and Discussion

Theoretical Background. According to previous EPR studies,[6-17,19-22] the effective spin Hamiltonian of nitrenes with a total spin $S \geq 1$ can be represented by a sum of two terms,

$$\mathbf{H} = g\beta\mathbf{HS} + \mathbf{SDS} \qquad (1)$$

The first term describes the Zeeman interaction of the total electron spin angular momentum S with the applied magnetic field, and the second term describes anisotropic magnetic interactions between unpaired electrons in the molecule. The traceless tensor $\mathbf{D}$ is referred to as the zero-field tensor and described by two scalar ZFS parameters, D and E, characterizing the electronic structure and magnetic properties of high-spin molecules. The relationship between the electronic structure and the ZFS parameters of septet trinitrenes as well

(16) Nakai, T.; Sato, K.; Shiomi, D.; Takui, T.; Itoh, K.; Kozaki, M.; Okada, K. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 157–166.

(17) Chapyshev, S. V.; Walton, R.; Lahti, P. M. *Mendeleev Commun.* **2000**, *10*, 114–115.

(18) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054–5067.

(19) Weltner, W., Jr. *Magnetic Atoms and Molecules*; Dover Publications: New York, 1989.

(20) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251–1259.

(21) Oda, N.; Nakai, T.; Sato, K.; Shiomi, D.; Kozaki, M.; Okada, K.; Takui, T. *Mol. Cryst. Liq. Cryst.* **2002**, *376*, 501–506.

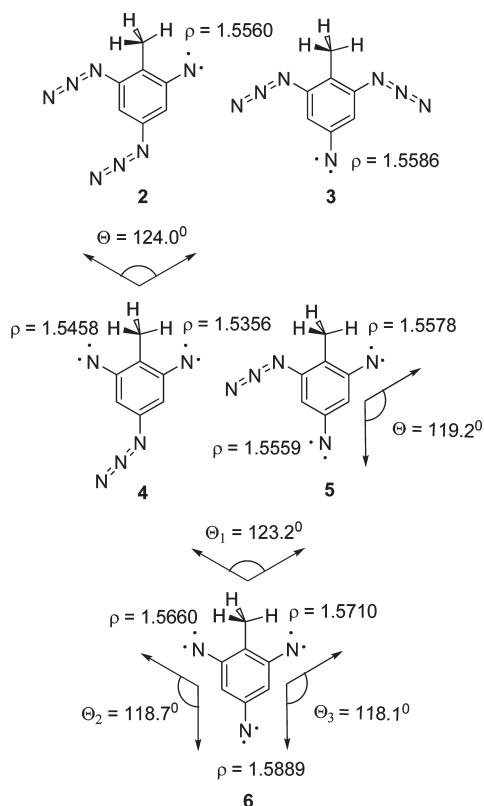(22) Chapyshev, S. V. *Russ. Chem. Bull.* **2006**, *55*, 1126–1131.

as the first-order EPR spectra of septet spin states are discussed in detail in the Supporting Information.

In septet trinitrenes, 15 types of spin–spin interactions between six unpaired electrons, occupying three in-plane "σ" orbitals and three out-off-plane π orbitals, can be distinguished.[10] The contribution of these interactions to the septet tensor $\mathbf{D_S}$ is expressed in the form of eq 2:

$$\mathbf{D_S} = \frac{1}{15}\sum_{i,j} D_{ij} \qquad (2)$$

The dominant terms D_{ij} arise from the interactions of electrons localized at the same univalent nitrogen atom ($D_{1\sigma1\pi} = D_{t1}$, $D_{2\sigma2\pi} = D_{t2}$, and $D_{3\sigma3\pi} = D_{t3}$).[10,20,21] The 12 other interactions contribute much less to the sum and can be expressed as $D_{ij} = D_{1\sigma2\sigma} + D_{1\sigma3\sigma} + D_{2\sigma3\sigma} + D_{1\pi2\pi} + D_{1\pi3\pi} + D_{2\pi3\pi} + D_{1\sigma2\pi} + D_{1\sigma3\pi} + D_{2\sigma3\pi} + D_{1\pi2\sigma} + D_{1\pi3\sigma} + D_{2\pi3\sigma}$, where $i \neq j$. Thus, eq 2 transforms into:

$$\mathbf{D_S} = 1/15(\mathbf{D_{t1}} + \mathbf{D_{t2}} + \mathbf{D_{t3}}) + 1/15\mathbf{D_{ij}} \qquad (3)$$
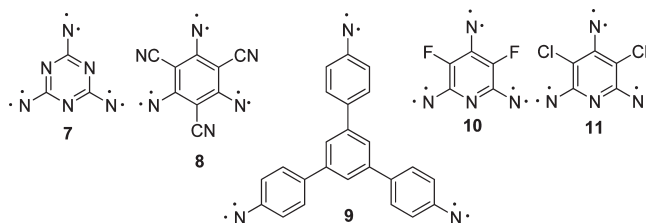
In a simple case, when a septet molecule shows D_{3h} point symmetry (the three nitrene units are magnetically equivalent and all three angles Θ between the C–N bonds are 120°) and the second term in eq 3 is negligibly small, eq 3 results in $D_S = -D_t/10$ and $E_S = 0$. An example of such molecules is the matrix-isolated septet trinitene **7** with $D_t = 1.461$ cm^{-1}, $D_S = 0.123$ cm^{-1}, $E_S = 0$ cm^{-1}, and $1/15D_{ij} = 0.023$ cm^{-1}.[6]

The magnetic parameters of two other D_{3h} symmetrical septet trinitrenes **8** ($|D_S| = 0.0548$ cm^{-1}, $E_S = 0$ cm^{-1})[10] and **9** ($D_S = -0.0912$ cm^{-1}, $E_S = -0.0039$ cm^{-1})[21] were reported in the literature. The unusually small D_S of trinitrene **8** and the large E_S of trinitrene **9** are in disagreement with the analysis given above and we thus suggest to re-evaluate the original spectra.

In the case of the C_{2v} symmetrical septet trinitrenes having two symmetrical nitrene units with $D_{t1} = D_{t2} = D_t$ and the angle Θ between their C–N bonds, and a third nitrene unit with $D_{t3} = D_t(1 + \lambda)$, where $\lambda = (\rho_3 - \rho_1)/\rho_1$, the solution of eq 3 yields:

$$D_S = -D_t(1 + \lambda/3)/10 \qquad (4)$$

$$E_S = D_t[4\cos^2(\Theta/2) - 1 + \lambda]/30 \qquad (5)$$

In this case the ratio E_s/D_s is a function of both the angle Θ and the parameter λ:

$$|E_S/D_S| \approx 1/3|\sqrt{3}\Delta\Theta + \lambda| \qquad (6)$$

where $\Delta\theta = (2\pi/3 - \Theta)$ and $|\Delta\Theta| \ll 1$.[9] Typical examples for such septet molecules are the trinitrenes **10** ($D_S = -0.1018$ cm^{-1}, $E_S = 0.0037$ cm^{-1})[7] and **11** ($D_S = -0.1019$ cm^{-1}, $E_S = 0.00325$ cm^{-1})[9] for which $1/15D_{ij} < 0.003$ cm^{-1}.

SCHEME 2. Selected Data from DFT Calculations on Nitrenes **2**−**6**

FIGURE 1. EPR spectra: (a) after 5 min and (b) after 23 min of UV irradiation of triazide **1** in the argon matrix at 4 K. The signals of triplet quintet and septet nitrenes are marked as T, Q, and S, respectively.

The comparison of E_S/D_S derived from experimental EPR spectra with that derived from calculations with eq 6 opens the way to explore the weak interactions between electron-deficient septet trinitrenes and organic electron-donating molecules. So far, only for trinitrene **11** have the magnetic parameters in both solid argon ($D_S = -0.1019$ cm^{-1}, $E_S = 0.00325$ cm^{-1}, $|E_S/D_S| = 0.032$)[9] and 2MTHF glass ($D_S = -0.1000$ cm^{-1}, $E_S = 0.0005$ cm^{-1}, $|E_S/D_S| = 0.005$) been determined.[13] To obtain more convincing data on the influence of 2MTHF solvent molecules on the electronic structure of septet trinitrenes, the trinitrenes should have relatively low spin density at the nitrene units to reduce their reactivity. According to the analysis of Wasserman et al.[10] the best candidates for such studies are derivatives of septet 1,3,5-trinitrenobenzenes.

DFT Calculations. The photolysis of triazide **1** should lead to the formation of triplet nitrenes **2** and **3**, quintet dinitrenes **4** and **5**, and septet trinitrene **6** (Scheme 1). Selected data of DFT calculations at the UB3LYP/6-311+G** level of theory are presented in Scheme 2.

The similar spin densities at the nitrene units of triplet nitrenes **2** and **3** suggest that their X_2Y_2-transitions in the 690−700 mT region might completely overlap to give only one signal in the EPR spectra. Typical triplet aryl nitrenes show D_T values in the range of 0.99−1.05 cm^{-1}.[3,22] Since the dipolar angles Θ of quintet dinitrenes **4** and **5** are equal to 124.0° and 119.2°, their E_Q values should be in the ranges of 0.035−0.040 and 0.040−0.042 cm^{-1}, respectively.[22] Quintet dinitrenes with such E_Q values usually display their strongest Y_2-transitions in the 300−310 mT region with D_Q between 0.196 and 0.210 cm^{-1}.[3,22] The two nitrene units in positions

2 and 6 of the trinitrene benzene ring can be considered as magnetically equivalent with $\rho = 1.57$. The third nitrene unit with $\rho = 1.59$ differs from the other two by $\lambda = 0.0127$. Since the dipolar angle Θ_1 of septet trinitrene **6** is equal to 123.2°, its E_S value should be between -0.003 and -0.004 cm^{-1}.[9] In this sense the septet trinitrene **6** represents a new type of C_{2v} symmetrical septet molecule with $\Theta_1 > 120°$, $\lambda > 0$, and $E_S < 0$. Due to relatively low spin densities at the nitrene units the D_S value of this trinitrene should be less than 0.1 cm^{-1}.

Photolysis in Solid Argon. Irradiation ($\lambda > 305$ nm) of triazide **1**, matrix-isolated in solid argon at 4 K, led to an EPR spectrum consisting of a superposition of EPR lines of triplet nitrenes **2** and **3**, quintet dinitrenes **4** and **5**, and septet trinitrene **6** (Figure 1a). The most intense EPR transitions appear at 6.9, 45.6, 151, 201, and 214 (doublet), 252 and 258 (doublet), 301, 308, 320, and 344 (doublet), and 431, 454, and 699 mT. The high resolution of this EPR spectrum allowed us to measure the resonance fields with an accuracy of ±0.4 mT. Prolonged irradiation results in the decrease of the three EPR lines at 301, 308, and 699 mT (Figure 1b). On the basis of these observations and data of our previous studies[7−9,22] we assign the two EPR lines at 301 and 308 mT to the Y_2-transitions of quintet dinitrenes **4** and **5**, and the line at 699 mT to the X_2Y_2-transitions of triplet nitrenes **2** and **3**. The other intense EPR lines represent a typical EPR spectrum of a septet trinitrene with $|D_S| \approx 0.1$ and a nonzero parameter E_S.[7,9]

Photolysis in 2MTHF Glass. Irradiation ($\lambda > 305$ nm) of triazide **1** in frozen 2MTHF solutions at 5.5 K leads to the appearance of EPR transitions of triplet nitrenes **2** and **3** at 698 mT, quintet dinitrenes **4** and **5** at 300 and 303 mT, and septet trinitrene **6** with intense lines at 8.2, 41, 151, 204, 252, 325, 441, 476, 504, and 644 mT (Figure 2). The EPR lines were broader compared to that recorded in argon matrices, and therefore in 2MTHF glass the resonance fields could only be determined with an accuracy of ±0.55 mT.

The strong signals of septet trinitrene **6** reveal its high kinetic stability in 2MTHF glass. In contrast, septet trinitrene **11** shows only several weak EPR transitions in the 150−280 mT region,[13] and septet trinitrenes **7** and **10** with
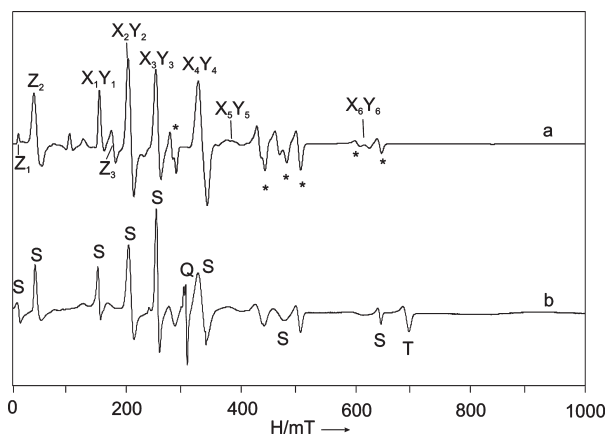
FIGURE 2. Comparison of experimental and simulated EPR spectra: (a) simulated spectrum of trinitrene **6** with $S = 3$, $D_S = -0.0934$ cm^{-1}, and $E_S = -0.0015$ cm^{-1}; (b) experimental spectrum (microwave frequency 9.47763 GHz) after 7 min of UV irradiation of triazide **1** in the 2MTHF glass at 5.5 K. The signals of triplet, quintet, and septet nitrenes are marked as T, Q, and S, respectively.

very high spin densities at the nitrene units could not be detected in 2MTHF by EPR spectroscopy.[13,16]

Zero-Field Splitting Parameters of the Nitrenes. For trinitrene **6** in solid argon seven transitions at 6.9, 45.6, 151, 201, 214, 252, and 258 mT were found and in the 2MTHF glass six transitions at 6.2, 40.9, 151, 204, 252, and 325 mT.

Optimized spectra were obtained with $D_S = -0.0938$ cm^{-1} and $E_S = -0.0040$ cm^{-1} in argon (Figure 3) and with $D_S = -0.0934$ cm^{-1} and $E_S = -0.0015$ cm^{-1} in 2MTHF (Figure 2). The signs of the parameters D_S and E_S were assigned based on semiempirical calculations of the septet ZFS tensor $\boldsymbol{D_S}$ for three interacting triplet nitrene units (see Figure 2 in the Supporting Information). The spectral simulations were performed without taking into account the Boltzmann factor. Since at low magnetic field strength ($H < 500$ mT) the energy gap between the highest and the lowest levels is less than kT, the relative intensities of EPR transitions at $T = 4$ K do not depend on the sign of D_S. However, the Boltzmann factor can affect the relative intensities of the two EPR transitions of the septet trinitrene at 590 and 650 mT where the energy gap between the highest and lowest levels is about kT. Simulations of these transitions for $D_S > 0$ and $D_S < 0$ at $T = 4$ K are presented in the Supporting Information. According to these simulations the septet trinitrene shows a negative parameter D_S.

The rms deviations (see teh Experimental Section) were determined to $R(\text{min}) = 0.67$ and 1.28 mT in argon and 2MTHF, respectively. An analysis of the experimental errors of D_S and E_S demonstrates that the difference between $|E_S (\text{argon})|$ and $|E_S(\text{glass})|$ substantially exceeds the experimental errors and is thus physically significant. Both parameters D_S and E_S decrease in the organic glass compared to the argon matrix.

The eigenfield spectral simulations (Figure 3) proved that the other paramagnetic species formed during the photolysis of triazide **1** in solid argon are triplet nitrenes **2** and **3** ($D_T = +1.020$ cm^{-1} and $E_T = 0$), quintet dinitrenes **4** ($S = 2$, $D_Q = +0.205$ cm^{-1}, $E_Q = -0.035$ cm^{-1}), and **5** ($S = 2$, $D_Q = +0.201$ cm^{-1}, $E_Q = -0.041$ cm^{-1}). In 2MTHF glass, triplet nitrenes **2** and **3** have $D_T = +0.998$ cm^{-1} and $E_T = 0$.
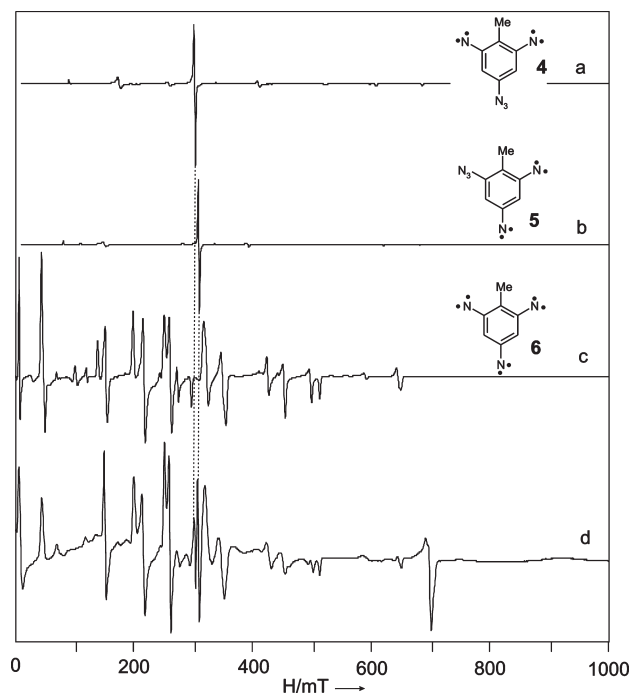

FIGURE 3. Comparison of experimental and simulated EPR spectra: (a) simulated spectrum of dinitrene **3** with $S = 2$, $D_Q = 0.205$ cm^{-1}, $E_Q = -0.035$ cm^{-1}; (b) simulated spectrum of dinitrene **4** with $S = 2$, $D_Q = 0.201$ cm^{-1}, $E_Q = -0.041$ cm^{-1}; (c) simulated spectrum of trinitrene **6** with $S = 3$, $D_S = -0.0938$ cm^{-1}, $E_S = -0.0040$ cm^{-1}; (d) experimental spectrum (microwave frequency 9.59482 GHz) after 5 min of UV irradiation of triazide **1** in solid argon at 4 K; the signal at 6985 G is assigned to triplet nitrenes **2** and **3** with $S = 1$, $D_T = 1.020$ cm^{-1}, and $E_T = 0$.

The assignment of signs of D_Q and E_Q of quintet dinitrenes **4** and **5** is based on our previous semiempirical calculations of the quintet ZFS tensor $\boldsymbol{D_Q}$ for two interacting triplet nitrene units.[8]

The ZFS parameters measured for nitrenes **2−5** are in good agreement with DFT calculations (Scheme 2). Triplet nitrenes **2** and **3** exhibit the same value for D_T due to the nearly equal spin density on the nitrene units. The EPR spectra of quintet dinitrenes **4** and **5** are typical for quintet *m*-phenylenedinitrenes with $\Theta = 118-124°$.[3,11,12,22,23] Quintet dinitrene **5** has a 5° smaller dipolar angle Θ than **4**, which results in a slightly larger ratio $|E_Q/D_Q|$. In quintet molecules of this type the Z-axis of the tensor $\boldsymbol{D_Q}$ lies in the molecular plane and is directed perpendicular to the molecular axis C_{2v}, and the X-axis is perpendicular to the molecular plane.[8] Both perpendicular eigenvalues X and Y of the tensor $\boldsymbol{D_Q}$ are negative and much smaller than Z in magnitude. Since $|Z| > |X| > |Y|$ at $\Theta > 109°$, the parameters $E_Q = (X - Y)/2$ of these quintet molecules are negative.[8]

Assignment of Signals in the EPR Spectra of Septet Trinitrene. To perform a complete assignment of all observable lines in the powder EPR spectrum of septet trinitrene **6** isolated in solid argon, the Zeeman energy levels for the canonical orientations ($\boldsymbol{H} \| \boldsymbol{X}$, $\boldsymbol{H} \| \boldsymbol{Y}$, $\boldsymbol{H} \| \boldsymbol{Z}$) were calculated based on the exact numerical solution of the spin Hamiltonian (1) for $S = 3$, $g = 2.0023$, $D_S = -0.0938$ cm^{-1}, and $E_S = -0.0040$ cm^{-1} (Figure 4).

(23) Fukuzawa, T. A.; Sato, K.; Ichimura, A. S.; Kinoshita, T.; Takui, T.; Itoh, K.; Lahti, P. M. *Mol. Cryst. Liq. Cryst.* **1996**, *278*, 253–260.
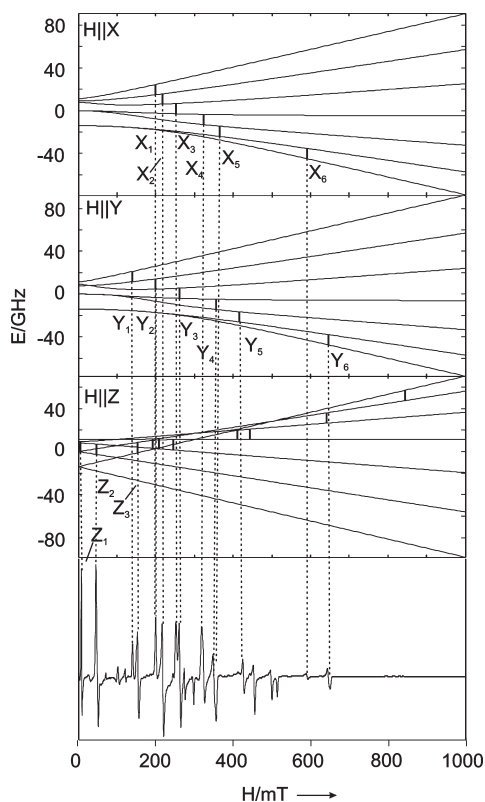
FIGURE 4. Zeeman energy levels and calculated transitions of septet trinitrene **6**.

Trinitrene **6** shows seven energy levels at zero field, as required by theory.[19] Since the parameter $|D_S|$ is much larger than $|E_S|$, the gaps between the energy levels are approximately equal to D_S, $3D_S$, and $5D_S$. One of these gaps, $|3D_S|$ with 0.29 cm^{-1}, is nearly equal to the quantum of the microwave irradiation ($h\nu_0 \approx 0.33$ cm^{-1}), therefore several intense transitions for the Z-components at very low magnetic fields become allowed. In the EPR spectra of septet trinitrenes **8** and **9** with $|D_S| = 0.1018-0.1019$ cm^{-1} and $|E_S| = 0.0033-0.0037$ cm^{-1} two such Z-transitions have been observed in the 3−20 mT region.[7,9] Because septet trinitrene **6** shows a somewhat smaller parameter D_S, its EPR spectrum displays three strong Z-transitions at 6.9, 45.6, and 151 mT (marked as Z_1, Z_2, and Z_3 in Figure 4). The Zeeman energy level diagram also shows that all six couples of perpendicular components (X_i and Y_i) are well resolved in the experimental spectrum, although some of them (X_1, Y_1, X_5, Y_5, X_6, and Y_6) are very weak.

The Zeeman energy level diagram calculated for septet trinitrene **6** with $g = 2.0023$, $D_S = -0.0934$ cm^{-1}, and $E_S = -0.0015$ cm^{-1} suggests that the strong EPR lines at 151, 204, 252, and 325 mT correspond to X_1Y_1-, X_2Y_2-, X_3Y_3-, and X_4Y_4-transitions, respectively (Figure 2). The remaining X_5Y_5- and X_6Y_6-transitions were identified as very weak and broad lines at 350 and 604 mT. In contrast to the EPR spectrum recorded in argon matrices, the EPR spectrum of trinitrene **6** in glasses displays only one strong Z_2-transition at 41 mT and two very weak Z_1- and Z_3-transitions at 6 and 160 mT.

In addition to Z-, X-, and Y-transitions, the powder EPR spectra of septet trinitrene **6** displayed many weak absorptions in the 259−300, 440−504, and 644−651 mT regions

(marked with asterisks in Figure 2), produced by trinitrene molecules with off-axis stationary angles in the principal axis frame of the fine-structure tensor $\boldsymbol{D}_S$. The appearance of such extra lines in the powder EPR spectra of septet molecules with $D_S \approx 0.1$ cm^{-1} has been discussed in detail earlier,[7,9,19] including illustrations of the calculated angular dependences of the resonance magnetic field for all allowed transitions.[7]

Fine-Structure and Molecular Parameters of Septet Trinitrene. According to eq 6, the fine-structure parameters D_S and E_S of septet trinitrene **6** are functions of the dipolar angle Θ_1 and the parameter λ. Using $\lambda = 0.0127$ (estimated from DFT calculations) and the ratio $|E_S/D_S|$ measured from the experimental EPR spectra, we calculate with eq 6 that the angle Θ_1 in **6** isolated in solid argon or 2MTHF glasses should be equal to 123.8° and 121.2°, respectively. The first value fits well Θ_1 predicted from the DFT calculations (123.2°), thus suggesting that the molecular structure and electronic properties of **6** in solid argon and in the gas phase are almost identical. On the other hand, the very small angle Θ_1 derived from EPR measurements of **6** in 2MTHF glass indicates significant changes in the electronic properties of this species, presumably due to interactions of the nitrene units with the 2MTHF molecules. Such interactions may affect the spin densities on the nitrene units of trinitrene **6**, increasing the parameter λ. Thus, the solution of eq 6 for $\Theta_1 = 123.2°$ and $|E_S/D_S|$ measured in 2MTHF glasses gives $\lambda = 0.0486$, which corresponds to trinitrene **6** with spin densities on the nitrene units equal to $\rho_1 = \rho_2$ and $\rho_3 = 1.0486\rho_1$. The lower parameter D_T of triplet nitrenes **2** and **3** in 2MTHF glass suggests that spin densities on the nitrene units are reduced due to interactions of nitrenes with 2MTHF. This effect is more pronounced for the nitrene units in positions 2 and 6 of trinitrene **6**, which is reflected in the large parameter λ. Similar effects were earlier observed for triplet 2,4-diazido-3,5-dichloropyridyl-6-nitrene that showed $D_T = 1.005$ cm^{-1}, $E_T = 0.0035$ cm^{-1} in argon[9] and $D_T = 0.999$ cm^{-1}, $E_T = 0.003$ cm^{-1} in 2MTHF glass[13] as well as for septet trinitrene **11** with $D_S = -0.1019$ cm^{-1}, $E_S = 0.00325$ cm^{-1} in argon[9] and $D_S = -0.1000$ cm^{-1}, $E_S = 0.0005$ cm^{-1} in 2MTHF glass.[13]

The formation of complexes between high-spin nitrenes and 2MTHF should also be taken into account in UV−vis studies of these species. Recent studies[3,24] have shown that some quintet dinitrenes in 2MTHF glass display strong electronic absorptions in the 600−700 nm region. However, according to extensive quantum-chemical studies,[25] the longest wavelength absorption of quintet dinitrenes should be below 450 nm. Similarly, many triplet nitrenes in 2MTHF glass show broad absorptions in the 500−570 nm region,[3,24,26] although calculations[27] predict the longest wavelength absorption at 420−450 nm. A possible explanation for these red shifts found in 2MTHF solutions of triplet, quintet, and septet oligonitrenes could be the formation of noncovalently bound complexes between the nitrenes and 2MTHF.

(24) Chapyshev, S. V. *Mendeleev Commun.* **2002**, *12*, 168–170.

(25) Sugisaki, K.; Toyota, K.; Sato, K.; Shiomi, D.; Takui, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2257–2260.

(26) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 6317–6329.

(27) Gritsan, N. P.; Zhu, Z.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 1202–1207.
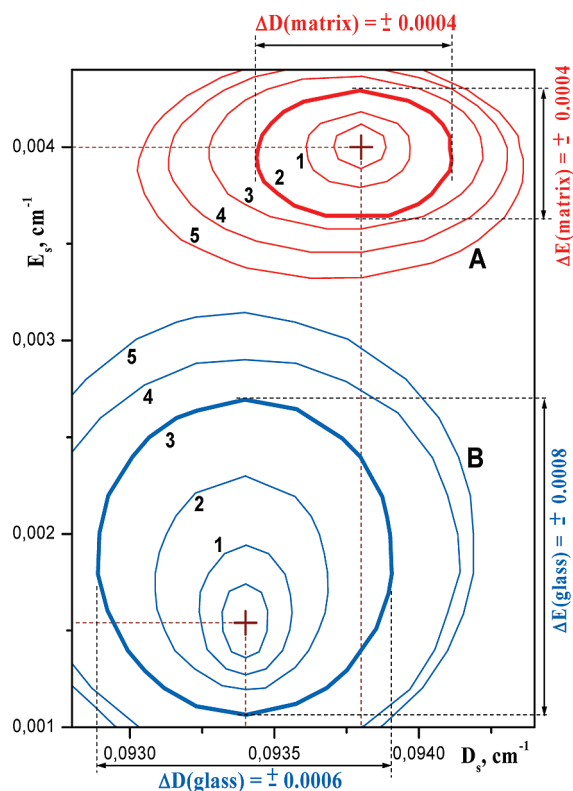
FIGURE 5. Contour plots of the functional R for EPR spectra recorded in solid argon (A, red: R_{min} = 0.67 mT, R_1 = 0.75 mT, R_2 = 0.9 mT, R_3 = 1.6 mT, R_4 = 2 mT, R_5 = 2.2 mT) and in 2MTHF glass (B, blue: R_{min} = 1.28 mT, R_1 = 1.35 mT, R_2 = 1.5 mT, R_3 = 1.7 mT, R_4 = 2 mT, R_5 = 2.6 mT).

The fine-structure parameters of trinitrene **6** provide important information regarding dipole−dipole interactions between the three nitrene units attached to the 1,3,5-benzenetriyl core. The energy of these interactions E_{ij} can be estimated from eq 7:

$$E_{ij} = D_S(\text{experiment}) + (D_t + \lambda/3)/10 \qquad (7)$$

For triplet nitrenes **2** and **3** D_T is 1.02 cm^{-1}, and the spin densities at the nitrene units are $\rho \approx 1.56$. In septet trinitrene **6** the nitrene units in positions 2 and 6 show $\rho \approx 1.57$, which corresponds to $D_t = 1.02 \times (1.57/1.56)$ cm^{-1} = 1.0265 cm^{-1}. With $\lambda = 0.0127$ and $D_t = 1.0265$ cm^{-1} we obtain for **6** from eq 7 $E_{ij} = 0.009$ cm^{-1}, which is about 10% of its D_S value. Previous studies have shown that E_{ij} of septet trinitrene **7** reaches about 18% of its D_S value.[6] This shows that the dipole−dipole interactions between the nitrene units at the 1,3,5-benzenetriyl core are weaker than those at the 2,4,6-triazinetriyl core. This is explained by a more efficient delocalization of the p_y unpaired electrons from the nitrene units in the benzene ring. On the other hand, due to this delocalization septet trinitrenobenzenes are rather stable in 2MTHF glasses and available for spectroscopic studies.

Conclusions

Septet 2,4,6-trinitrenotoluene **6** is the major paramagnetic product with a septet spin state formed during the photolysis of 2,4,6-triazidotoluene **1** in cryogenic matrices. This trinitrene displays remarkably different EPR spectra in solid argon (D_S = −0.0938 cm^{-1}, E_S = −0.0040 cm^{-1}) and 2MT-HF glass (D_S = −0.0934 cm^{-1}, E_S = −0.0015 cm^{-1}). In argon matrices the powder X-band EPR spectra show three strong *Z*-transitions in the 40−300 mT region and six couples of well-resolved *X*- and *Y*-transitions, whereas in 2MTHF glasses six unresolved *X*,*Y*-transitions in the 150−700 mT region are observed. The fine-structure parameters measured in argon matrices fit well the geometry parameters and spin densities at the nitrene units predicted by DFT calculations for the septet trinitrene **6**. The very small parameter E_S found for **6** in 2MTHF glass indicates significant changes in the spin densities at its nitrene units. Presumably, this is caused by specific interactions of these units with surrounding 2MTHF molecules. Compared to the very strong interactions of singlet nitrenes with THF resulting in the formation of ylides,[18] the paramagnetic nitrene units of **6** interact only weakly with the 2MTHF molecules, resulting in some redistribution of spin density without formation of new chemical bonds. The analysis of the magnetic parameters of septet trinitrene **6** shows that the energy of dipole−dipole interactions between three nitrene units attached to the 1,3,5-benzenetriyl core is about 0.009 cm^{-1} or 10% of the D_S value.

Experimental Section

Synthesis. 2,4,6-Triaminotoluene trihydrochloride was synthesized by the reduction of 2,4,6-trinitrotoluene according to the literature procedure.[28]

2,4,6-Triazidotoluene (1). 2,4,6-Triaminotoluene trihydrochloride (2.77 g, 10 mmol) was dissolved in 150 mL of 20% HCl and cooled to 0 °C. Sodium nitrite (3.1 g, 35 mmol), dissolved in 20 mL of H$_2$O, was added within 15 min, while the temperature of the solution was kept below 5 °C. Foaming was controlled by the addition of a few drops of diethyl ether. After 20 min of stirring at 0 °C, a solution of 2.93 g (35 mmol) of sodium azide was added slowly and the solution was stirred subsequently for an additional 30 min. After warming to room temperature, it was poured onto 250 g of ice and extracted twice with 200 mL of diethyl ether. The organic phase was extracted twice with 200 mL of a diluted NaHCO$_3$ solution and the procedure was repeated with saturated NaH-CO$_3$ solution. The organic phase was dried over Na$_2$SO$_4$ and the solvent was removed in vacuum. The solid residue was recrystallized from a hexane−benzene mixture to yield 900 mg (4.2 mmol, 42%) of 2,4,6-triazidotoluene as a bright yellow solid. Mp 103−104 °C dec; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.93 (c, 3H), 6.48 (c, 2H); ^{13}C NMR (CDCl$_3$) δ 10.0 (CH$_3$), 103.8 (C-3,5), 117.2 (C-1), 138.4 (C-4), 140.3 (C-2,6); IR (microcrystalline film) ν/cm^{-1} (%) 2961 (15), 2924 (13), 2854 (8), 2108 (100), 1580 (25), 1571 (42), 1560 (37), 1490 (30), 1419 (30), 1339 (15), 1266 (88), 1102 (38), 1019 (40), 961 (25), 815 (55), 702 (25), 590 (13), 532 (33); UV−vis (MeOH) λ_{max}, nm (log ε) 318 (3.24), 308 (3.32), 245 (4.30), 212 (3.87); MS (*m/z*, %) 215 (13), 187 (10), 104 (8), 77 (15), 66 (73), 63 (22), 52 (100), 51 (33), 39 (68). Anal. Calcd for C$_7$H$_5$N$_9$ (215.17): C 39.07, H 2.34, N 58.59. Found: C 39.32, H 2.44, N 58.24.

EPR Measurements and Analysis. X-band EPR spectra were recorded with a Bruker-Elexsys E500 EPR spectrometer with an ER077R magnet (75 mm gap between pole faces), an ER047 XG-T microwave bridge, and an ER4102ST resonator with a TE$_{102}$ cavity. The experimental technique for matrix isolation used in this study was similar to that described earlier.[7]

(28) Shevelev, S. A.; Shakhnes, A. K.; Ugrak, B. I.; Vorob'ev, S. S. *Synth. Commun.* **2001**, *31*, 2557−2561.

Solid argon matrices doped with triazide **1** were prepared by vacuum codeposition of two separate molecular beams (Ar and triazide **1** vapor) on the tip of an oxygen-free high-conductivity copper rod (75 mm length, 3 mm diameter) cooled at 4.2 K. The vapor of **1** was produced by an oven heating the polycrystalline **1** to 80 °C. 2-Metyltetrahydrofuran (2MTHF) glasses doped with triazide **1** were prepared by cooling a 4 mm o.d. quartz sample tube containing a degassed solution of **1** in 2MTHF (triazide concentration of ca. 10^{-4} M) in the cavity of the EPR spectrometer to 5.5 K. The matrix-isolated samples were irradiated with a high-pressure mercury lamp, using a filter passing the light at $\lambda > 305$ nm, and spectra were recorded at various irradiation times.

The computer simulations of EPR spectra were performed by using the EasySpin program package (version 2.7.0).[29] The simulations were performed by using a matrix diagonalization method for $S = 1$, 2, or 3, using the parameters $\nu = 9.60923$ (argon) or 9.47763 GHz (2MTHF glass), $g = 2.0023$, and line widths $\Delta H = 5$ mT for $S = 1$, 3 mT for $S = 2$, and 2.5 mT for $S = 3$, respectively. The EasySpin program package was also used for the eigenfield calculations of the Zeeman energy levels for canonical orientations of the tenzor $\boldsymbol{D}$ (**H**∥**X**, **H**∥**Y**, **H**∥**Z**) and for calculating the angular dependencies of resonance fields on rotating the tensor $\boldsymbol{D}$ by angle Θ in two planes ($\phi = 0$ and $\phi = \pi/2$, where Θ and ϕ are the Euler angles).

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, $H_k(\text{exp})$:

$$R = \sqrt{\frac{1}{n}\sum_{k}^{n}\left(H_k(\text{calcd}) - H_k(\text{exptl})\right)^2} \qquad (5)$$

where n represents the number of selected transitions.

To estimate the accuracy of the measurements of D_S and E_S, the rms deviations R were calculated by varying the ZFS parameters close to their optimum values (Figure 5). Rms deviations of $R = 0.9$ and 1.7 mT were chosen as crucial for the spectra in solid argon and in glass, respectively, if at least one of the tested lines showed a deviation $|H_{\text{calcd}} - H_{\text{exptl}}|$ exceeding the line width. This treatment gave the experimental errors D_S, $E_S \leq \pm 0.0004$ cm^{-1} for solid argon and $E_S \leq \pm 0.0006$, $D_S \leq \pm 0.0008$ cm^{-1} for 2MTHF glasses. The minimization of the functional R was also used for determination of the true g-factor value. The minimum value of R was found for $g = 2.0023 \pm 0.001$.

Computational Methods. All density functional theory (DFT) calculations were performed with the Gaussian 98 program package.[30] The geometries of the molecules were optimized by using the B3LYP method[31] in combination with the 6-311+G** basis set. The nature of the stationary points was assessed by means of vibrational frequency analysis.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of triazide **1**, mathematic description of interactions of three triplet tensors in septet molecules, and tables with Z-matrices of nitrenes **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

(29) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.

(30) Fisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman J. R.; Zakrzewski, V. G.; Montgomery J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Stain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonazalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonazalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc., Pittsburgh, PA, 1998.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.